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U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Analytical Methods for Safeguards and Accountability Measurements of Special Nuclear Materials

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Analytical Methods for Safeguards and Accountability Measurements of Special Nuclear Materials

Proceedings from American Nuclear Society
Topical Meeting held May 15-17, 1978
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ABSTRACT

This book contains proceedings of the American Nuclear Society's (co-sponsored by the National Bureau of Standards) topical meeting entitled, "Analytical Methods for Safeguards and Accountability Measurements of Special Nuclear Materials." The meeting was held in Williamsburg, Virginia, on May 15-17, 1978. The two objectives of the meeting were to discuss the latest techniques for chemical analysis of special nuclear materials and to strengthen lines of communication among scientists working in this field.

The presentations deal with advanced analytical chemistry techniques such as x-ray spectrometry for elemental content, neutron interrogation and gamma ray techniques for isotopic content, mathematical correlation models, and wet chemistry methods for elemental content. Examples of remote systems for handling highly radioactive samples for analysis are given. Progress is being made on the problems associated with obtaining high precision and accuracy for analysis of special nuclear materials while at the same time maintaining short turn around time and reduced possibility of diversion. Various approaches are described which emphasize computer-controlled operating systems with built-in safeguards and quality assurance programs. Current trends in the fuel cycle, along with future approaches to control and accountability of special nuclear materials, are discussed.

KEYWORDS: Nuclear safeguards; accountability; x-ray; gamma-ray; analysis; special nuclear materials; neutron

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The Chemical and Isotopic Analysis of Uranium, Plutonium and Thorium in Nuclear Fuel Materials

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ABSTRACT

The New Brunswick Laboratory (NBL) has developed or modified and used highly precise and accurate methods for the determination of uranium, plutonium and thorium content and isotopic abundances in a wide variety of nuclear fuel cycle materials in support of nuclear safeguards programs. The dissolution, separation and subsequent precise chemical analysis of these materials with an accuracy of 0.1% or less is achieved using gravimetric, titrimetric, spectrophotometric and coulometric techniques. Isotopic abundance measurements on uranium and plutonium are accurately measured with a relative limit of error (95% confidence limit) of approximately 20 to 0.007% for the isotope weight range of 0.001 to 97 weight percent using thermal ionization mass spectrometers. Other methods such as isotope dilution mass spectrometry, fluorimetry and radiochemical analysis are used where the uranium and plutonium sample content is in the microgram range. Many of the analytical methods used at NBL are in various stages of automation or mechanization to provide greater efficiency and productivity at existing levels of accuracy and precision. Quality assurance programs employing unknown control standards for the analysis of nuclear materials are used at NBL to maintain a high level of reliability.

KEYWORDS: Chemical analysis; isotopic analysis; plutonium assay; uranium assay; thorium assay; dissolution; chemical separations; automation; quality assurance programs

INTRODUCTION

During its history, the New Brunswick Laboratory (NBL) has developed or modified and used highly precise and accurate methods for the determination of uranium, plutonium and thorium content and isotopic abundances in a wide variety of nuclear fuel cycle materials. Currently, these capabilities have been used to provide comprehensive analytical chemistry support for the Department of Energy (DOE) and the Nuclear Regulatory Commission (NRC) nuclear safeguards programs.

NBL in its role as the USA Safeguards Laboratory receives nuclear materials for analysis not only from domestic sources (DOE contractors and NRC licensees) but from the international community via the International Atomic Energy Agency (IAEA). The laboratory receives a complete spectrum of sample types ranging from product quality uranium, plutonium and thorium metals, their alloys (binary, ternary or more complex), oxides (prepared over a range of temperatures, or unsintered), carbides, nitrides and others, to complex scrap materials. This latter category, consisting of fuel element rejects, process residues, or wastes, contain a broad range of matrices and have usually undergone treatments which make them difficult to dissolve under ordinary conditions. The challenge to the New Brunswick Laboratory is to accurately measure the uranium, plutonium or thorium content and isotopic abundances in these widely diverse materials and to complete these measurements in a timely manner.

The dissolution, separation and subsequent precise chemical analysis of these materials with an accuracy of 0.1% or less, is achieved using gravimetric, titrimetric, spectrophotometric and coulometric techniques. Isotopic abundance measurements on uranium and plutonium are accurately measured with a relative limit of error (95% confidence limit) of approximately 20 to 0.007% for the isotope weight range of 0.001 to 97 weight percent using thermal ionization mass spectrometers. Other methods such as isotope dilution mass spectrometry, fluorimetry and radiochemical analysis are used where the uranium and plutonium sample content is in the microgram range.

Because rapid turnaround times are required for the analytical results from these analyses, NBL has employed automated or mechanized equipment to accelerate productivity without sacrificing reliability.

SAMPLE DISSOLUTION

The variety of sample types received at NBL for analysis require flexible dissolution schemes such as those summarized in Tables I, II and III. For many years, these techniques have been the most useful in preparing samples suitable for subsequent measurement. No one method has been found to be successful under all circumstances especially when many sample types, regardless of their generic classification, contain unknown constituents which complicate or even defeat their proposed dissolution treatment. In many instances, the analyst resorts to a combination of these techniques. Currently, lithium-based fluxes for the fusion of uranium samples[1] and an adaptation of the Los Alamos Scientific Laboratory low-pressure dissolution technique for plutonium materials[2] are being evaluated. The general philosophy at NBL is to completely dissolve all solid samples to produce a clear, residue-free solution. Sample solutions received with sediment require a separation and dissolution of this residue followed by recombination to produce a homogeneous solution prior to sampling. The same logic applies to any multiphase sample. Any organic material in a sample must be destroyed and the sample reconstituted prior to analysis. Solid waste or ash samples must be homogenized and split prior to analysis or the entire sample must be dissolved. It is also required that, for highest accuracy, all sample solutions be made up by weight and that appropriate weighed aliquants be taken for analysis. Proper sample dissolution is the basis for the reliable measurement of the element of interest in the material.

SAMPLE ASSAY

Since samples received at NBL are usually of complex or unknown composition, the measurement method must be insensitive to interferences or must employ techniques to remove interfering impurities. NBL uses both approaches: (1) a modification of the Davies and Gray titrimetric method which is highly specific for the determination of uranium in the presence of most impurities, (2) a subsequent modification of this method using a tributyl phophate extraction/titration system for uranium which eliminates the few remaining interferences and (3) a system incorporating an ion exchange separation of impurities followed by the controlled potential coulometric determination of plutonium. Methods for thorium usually require a separation using precipitation or solvent extraction techniques prior to the determination of thorium.

a. Determination of Uranium

The method originally proposed by Davies and Gray is based on the titration of uranium (IV) with potassium dichromate in phosphoric acid media.[3] The NBL-modified method[4,5] is as follows: A HNO_3, $HClO_4$ or H_2SO_4 solution containing up to 150mg U in a 15-ml volume, or less, is treated with the following reagents and swirled after each addition: 5ml of 1.5$\underline{M}$ sulfamic acid, 40ml of H_3PO_4 (containing 2 drops of 2% $K_2Cr_2O_7$), 5ml of 1$\underline{M}$ $FeSO_4$ (10% H_2SO_4 solution), 10ml of oxidant (8M HNO_3/0.1$\underline{M}$ sulfamic acid/0.4% ammonium molybdate) after 30 seconds wait, 100ml of water after 3 minutes wait, and 125mg of solid vanadyl sulfate dihydrate. A magnetic stirring bar, a platinum wire indicator electrode and a calomel reference electrode is inserted into the beaker, and the solution, with stirring, is titrated immediately with 0.03$\underline{N}$ potassium dichromate to a potential of 590mv. The amount of uranium titrated is measured by the quantity of dichromate used to reach the end point.

The potential interferences associated with this method have been examined in great detail. Every element in the periodic table, with certain obvious exceptions, has been experimentally tested as a potential interferent. An element is considered an interferent if its presence in a concentration of 15% or less of the uranium present introduces an analysis error greater than 0.1% relative. Figure 1 summarizes the results of these studies at NBL. Note that few elements interfere and most of the interferences are removed by sample treatment. The remaining interfering elements can be removed by a separation described below. High alpha activity equivalent to $\leq 1\%$ ^{232}U does not interfere. The sample treatments which remove interferences are summarized in Table IV.

During the course of these interference studies, the existence of a nearly universal method for eliminating interfering elements from samples was developed.[6] The method involves converting the sample to a solution 4-5 N in nitric acid and extracting the uranium with 30% tributyl phosphate in carbon tetrachloride. The presence of diverse ions, chloride, sulfate, perchlorate in reasonable amounts does not adversely affect the extraction. Large amounts of $Al(NO_3)_3$, $NaNO_3$ or NaCl also can be tolerated. The only interfering elements not effectively removed by the extraction are iodine, technetium and gold. The CCl_4-TBP phase from the extraction may subsequently be titrated like an aqueous sample with the same high precision and accuracy.

Under routine conditions, uranium can be measured without bias using the NBL titrimetric method to a precision of 0.08% relative standard deviation (RSD) for >50mg U samples, to 0.15% RSD for 15-50mg U samples and to 0.25% RSD for samples containing <15mg U.

As indicated previously, the need to increase productivity so as to report analytical results in a timely manner prompted the mechanization and automation of the uranium titration method. Four generations of autotitrators have evolved at NBL. The last two are currently in operation at the laboratory. One system simply automates the manual titration although the standard potassium dichromate titrant addition is measured gravimetrically[7] instead of volumetrically. Studies have shown that this system can provide unbiased results with a precision of < 0.1% RSD, can process 36 determinations in an 8-hour day and is unaffected by room temperature changes of several degrees. The daily sample output is limited by the turntable which has a capacity for only 12 samples and must be reloaded manually. The second operating system, however, is based on the internal electrogeneration of vanadate ion, V(V), which in essence is the titrant[8], and can accommodate up to 44 samples and standards in a single loading. The system is controlled by a minicomputer with an internal quality control program and fault condition program to provide high reliability by preventing incorrect measurements. This autotitrator, developed in collaboration with the Lawrence Livermore Laboratory[9], can on a continuous basis compute and print the uranium content of each sample, including control standard, which it has measured. Current studies indicate that in the 40mg U sample range, accurate results can be achieved with an RSD of 0.1%.

b. Determination of Plutonium

To date, no measurement system for plutonium has been developed which has the specificity that the NBL titrimetric method has for uranium. The presence of iron, chromium, manganese, vanadium, Pu(VI) or complexing ions in the generally accepted potentiometric, amperometric or controlled-potential coulometric methods for plutonium requires corrections, separations or adjustments for these potential interferences. In order to eliminate known as well as unsuspected interferences (including organic material and salts from sample fusion treatments) NBL policy is to purify plutonium in all samples received using an ion exchange procedure prior to assay by controlled-potential coulometry. The basic procedure for this system is as follows[10]: An aliquot containing about 10mg Pu in 1N HNO_3 is reduced to the Pu(III) oxidation state with excess Fe(II) and the solution is then adjusted to 8N HNO_3 which produces Pu(IV) and oxidizes the excess Fe(II). The sample is passed through an anion exchange column (Dowex-1, X-2, nitrate-form resin), impurities are washed through with 8N HNO_3 and the purified plutonium is eluted with 0.35N HCl-0.01N HF solution. After fuming with H_2SO_4, the plutonium is determined by an improved rapid controlled-potential coulometric method[11] using a working gold electrode in 1N HNO_3-0.02M NH_2SO_3H media. The plutonium is reduced to Pu(III) and then oxidized to Pu(IV), blank corrections are applied, and the total quantity of plutonium is calculated using an electrical calibration factor.

Routinely, 6-12mg Pu samples can be assayed without bias with a precision of 0.06% RSD using this system. Additional data using NBS SRM 949e plutonium metal and SRM 944 plutonium sulfate tetrahydrate standards in 135 determinations over a period of one year have verified this performance, Table V.

The need for automating plutonium analysis concurrently with uranium analysis has been recognized and the mechanization of the NBL plutonium analysis system has been underway for several years. An apparatus (Autosep)[12] has been developed in which groups of ten plutonium samples are automatically separated from impurities according to the manual ion exchange method previously described. The purified plutonium is subsequently processed through an apparatus (Autocoulometer)[13] designed to automatically and continuously analyze two groups of 50 samples (total 100 samples) by the NBL controlled-potential coulometric method. A 5-fold increase in sample throughput is anticipated with this automated system while retaining an accuracy and precision of $<0.1\%$.

c. Determination of Thorium

NBL uses the classic gravimetric technique whereby an excess of saturated oxalic acid is added to a boiling solution containing at least 200mg Th. The solution is allowed to digest overnight, the precipitate is filtered and then ignited at 1100°C to constant weight. A precision of $<0.1\%$ is obtained; results can tend to be slightly biased probably due to the precipitation of certain oxalates if metallic ions are present in large amounts. In some instances a prior precipitation of the hydroxide with fresh NH_4OH is necessary to remove interferences such as fusion salts. An alternative titrimetric method using ethylenediamine tetraacetic acid (EDTA), has been used in which a solution buffered at pH 2.5 and containing about 100mg Th is titrated with 0.01M EDTA solution (standardized against copper) to a xylenol orange indicator end point. A comparison with the gravimetric method gave an RSD of 0.08% without significant bias. A third method utilizing spectrophotometry consists of mixing 0.1% Thorin solution (2- [2-

hydroxy-3,6-disulfo-1-naphthylazo] benzenearsonic acid) with a solution containing 0.5 to 2mg Th. After dilution and pH adjustment to 0.8 ± 0.1, the absorbance is read at 545nm. Unbiased results with a precision of 5-10% are usually obtained. However, since so many interfering elements usually are present in the sample, a preliminary separation of thorium is required.

d. Other Methods

Samples containing small amounts of uranium at the 0.05 to 2.5mg level can best be determined by fluorimetry.[14] The procedure consists of the following: Sample solutions are aliquoted into centrifuge tubes, the R_2O_3 group is precipitated using a solution of saturated ammonia gas, the supernantant is decanted, the precipitate is dissolved with nitric acid and the R_2O_3 group is reprecipitated. The precipitate is dissolved with nitric acid, magnesium nitrate hexahydrate is added and dissolved. The uranium is extracted with ethyl acetate, one milliliter of the extact is pipetted onto a gold dish, the dish is ignited and fused with a sodium fluoride/sodium-potassium carbonate flux. The fluorescence is measured with a fluorimeter and the uranium content is determined from a calibration curve prepared from standards processed in exactly the same manner as for samples. Unbiased results with a precision of < 10% RSD have been obtained.

Another method for the analysis of small amounts of sample, namely, the isotope dilution mass spectrometric technique, has been used at NBL for the determination of microgram amounts of plutonium and uranium in dissolver-type solutions[15] in which the uranium to plutonium ratio is typically 200 to 1. In this procedure, samples containing about 10 μg Pu and 2mg U are spiked with known amounts of ^{242}Pu and ^{233}U tracers, equilibrated physically and chemically, and the uranium and plutonium fractions are separated by a version of the anion exchange method described for plutonium assay. Each fraction is analyzed by mass spectrometry and the plutonium and uranium content in the sample is calculated. Experience at NBL has shown this method to be unbiased with a precision of about 0.5% RSD, although data under optimum conditions have been obtained with a precision of 0.2%. This method is presently being evaluated in long-term studies to more accurately define its reliability.

ISOTOPIC ABUNDANCE MEASUREMENTS

The isotopic composition of uranium and plutonium samples is routinely determined using thermal ionization mass spectrometry. In general, only high purity uranium and plutonium can be reliably analyzed with the thermal ionization technique. Impurities, especially alkali elements, tend to produce unstable emission and may alter the observed ratios in an unpredictable manner. Furthermore, in the case of plutonium analysis, the sample must be free of ^{238}U and ^{241}Am to avoid interference in the ^{238}Pu and ^{241}Pu measurements. Hence, in the majority of cases, the uranium and plutonium must be separated by an appropriate procedure.

a. Uranium

Uranium is separated from impurities for measurement by mass spectrometry by precipitation as the hydroxide with NH_4OH followed by dissolution in HNO_3 and subsequent extraction of the uranium into diethyl ether. Where thorium is present, the hydroxide precipitate is dissolved in 8 M HCl and passed through an anion exchange column (Dowex-1, X8, chloride-form resin). The column is washed with 8 M HCl to remove thorium, and the uranium is eluted with 0.1N HNO_3. The separated uranium is further purified by the ether extraction method described above.

The mass spectrometry method is applicable to the determination of the isotopic composition of uranium with sample sizes in the range of about 20-30 μg U.[16] Analyses are made with either a 12" radius 60° sector or a 12" radius 90° sector mass spectrometer equipped with a triple-filament thermal ionization source, Faraday cup ion collector, programmable calculator data acquisition system and an NBL-designed vacuum lock. Isotope ratios as low as 0.02 are measured routinely with a precision of 0.2% at the 95% confidence level. The basic method consists of loading the purified uranium onto a disposable triple-filament holder ("bead" or "hat") and inserting it into the ion source assembly of the mass spectrometer. The isotope ratio technique is used to determine the relative abundances of the uranium isotopes. The ^{235}U peak is used as the reference peak and the ^{238}U, ^{236}U and ^{234}U peaks are measured relative to it. Magnetic peak switching under calculator control is used to bring the ^{235}U peak and the isotope being measured alternately onto the collector slit. The ion currents are amplified with a vibrating-reed electrometer and measured with a digital voltmeter and variable gain amplifier interfaced to the calculator. The individual isotope ratios, relative standard deviations, and the weight percent abundances are computed and printed out by the calculator. Since the ^{235}U isotope is usually the major isotope, sufficient peak sets to yield 15 238/235 ratios and three 234/235 and 236/235 ratios each are taken. Since thermal ionization mass spectrometry is not an absolute measurement technique, all sample data are corrected from the analysis of NBS SRM U-005 through U-970 isotopic standards under the same controlled conditions as for samples. About 10 samples (including standards) can be run daily using the vacuum lock to reduce sample change time. Typical precision over the entire isotopic weight percent range is shown in Table VI.

b. Plutonium

Plutonium is separated from impurities for mass spectrometric measurement by anion exchange using a miniaturized version of the technique previously described for plutonium assay. Where large amounts of uranium are present in the original sample (PuO_2UO_2 material, for example) the ^{238}Pu content is often determined by alpha spectrometry on a separate fraction, or a two-stage ion exchange separation is performed. (Even traces of ^{238}U in the Pu fraction give apparent high ^{238}Pu values especially when the latter isotope is only abundant to < 0.1%). Occasionally, traces of neptunium as ^{237}Np may be found in the plutonium fraction since neptunium has similar characteristics in this separation procedure. The mass spectrometry method is applicable to the determination of the isotopic composition of plutonium with sample sizes in the range of about 0.5 to 5 μg Pu.[17] These relatively large sample sizes are used not because of instrumental limitations, but rather to minimize environmental and reagent contamination in the sample preparation. Analyses are made with a 12" radius 90° sector tandem mass spectrometer equipped similar to the uranium instruments but utilizing an integrating ratiometer in the data acquisition system. As with uranium, isotope ratios down to 0.02 can be measured with a precision of 0.2% at the 95% confidence level. The basic operating method is similar to the uranium procedure. In determining the relative abundances of the plutonium isotopes, the ^{239}Pu peak is used as the reference peak and the ^{238}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu peaks are measured relative to it. Accelerating voltage switching under calculator control is used to bring the ^{239}Pu peak and the isotope being measured alternately onto the collector cup. The ion currents are amplified with a vibrating-reed electrometer and measured with an integrating ratiometer interfaced to the calculator. Data computations are performed similar to the uranium manipulations. Since the normal isotopic distribution, in decreasing abundance, is ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{238}Pu, sufficient peak sets to yield 22 240/239 ratios, 18 241/239 ratios, 14 242/239 and 238/239 ratios each are taken. Plutonium data are corrected using NBS uranium isotopic standards and the validity of these corrections are verified using the NBS SRM 946, 947 and 948 plutonium isotopic standards. About six samples and standards can be run daily. Typical precision over the plutonium isotopic weight range is shown in Table VII.

QUALITY ASSURANCE PROGRAMS

In order to assure reliable measurements, analytical laboratories incorporate measurement control systems into their sample analysis schemes. The NBL Quality Assurance Program[18] is based on the use of unknown standards to monitor the performance of the analyst. The analyst uses the procedure shown in Figure 2 to implement the program. He enters the value found for the measurement of an unknown standard into a computer terminal and receives an evaluation of his performance as "in control" or "out of control." ("Out of control" responses require remedial action to identify and resolve the discrepancy). In order to maintain the integrity of the system, no corrections or changes may be made once a result is entered into the computer. The computer is also programmed to automatically update the analyst's control limits. Current control limits (90% confidence level) for uranium are: < 15mg U, 0.5%; 15-50mg U, 0.30%; > 50mg U, 0.20%; and for plutonium are: 6-12mg Pu, 0.18%. All analysts must be certified before routinely analyzing samples by demonstrating their proficiency within the accepted control limits.

SAMPLE ANALYSIS AND THE REAL WORLD

Most of the methods previously described have been used successfully at NBL for many years. All methods whether new or old have been thoroughly tested and certified to be highly reliable on a great variety of sample material. However, regardless of the proven superiority of these methods of analysis, NBL, as well as most analytical laboratories, has been faced with the enigma of applying highly accurate techniques to inadequately sampled material. Shipper-receiver differences may result, in many instances, not so much from differences in laboratory capability, techniques, or methods, but from the failure of both parties to analyze exactly the same sample. Many samples received at NBL are grossly heterogeneous and it is quite evident that the "average" sample is far from representative. The work of homogenizing this type of sample after receipt by calcining, blending or reconstituting, or alternatively, by using the entire sample to avoid processing, can be a lengthy and tedious procedure. Moreover, the subsequent precise analysis of the processed sample gives results that have little meaning when related to the larger material source from which it was taken. Not only must adequate sampling and sampling plans be addressed but necessary attention should be paid to the proper packaging and handling of samples so that both the shipper and receiver are analyzing the same material. For example, the problem of shipper-receiver differences for hygroscopic low-fired PuO_2 has existed for more than 10 years and only now are efforts being made to standardize fundamental sampling, packaging and handling conditions.

The New Brunswick Laboratory perceives as its mission not only the performance of high quality chemical and isotopic analysis of nuclear materials but also the identification and resolution of analysis-related problems in order to provide meaningful support to the USA Safeguards Program.

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TABLE I. DISSOLUTION OF URANIUM MATERIALS

Materials	Treatment
, UO_3, U_3O_8, UF_4	Dissolve in HNO_3.[a]
$)_2$ powders and ellets, ammonium iuranate, wastes, $)_2$-ThO_2, etc.	Dissolve in HNO_3, filter, fuse residue in $NaHSO_4$ or Na_2CO_3, combine solutions.[a]
re concentrates	Dissolve in HNO_3, fume sample aliquants with H_2SO_4 and HF.
TGR fuel beads: SiC-coated, pyrolytic arbon-coated, Th carbide)	1. Ignite to remove carbon, fuse with Na_2CO_3, dissolve cake and fume with H_2SO_4 and HF to remove silica. Precipitate U with NH_4OH to remove excess fusion salts, dissolve residue in HNO_3.[a] 2. Ignite to remove carbon, treat with Cl_2 at 900°C to decompose SiC, ignite as in 1, dissolve as with UO_2-ThO_2.
C, UC_2	Ignite, dissolve in HNO_3, fuse any residue.[a]
-Al, U-Si, UO_2-SS	Dissolve in HCl-HNO_3, fume with $HClO_4$, filter. Volatilize silica with HF, fuse remaining residue with Na_2CO_3.[b]
issium alloy issium dross	Dissolve in HCl-HNO_3; treat residue with NaOCl and NaOH, acidify with HCl, combine solutions.[b] (Residue from dross requires fusion with NaOH).
sh samples	Fuse with Na_2CO_3-$NaNO_3$ (5:1) and/or $NaHSO_4$, dissolve cake in HNO_3-$HClO_4$, volatilize silica with HF, fume with $HClO_4$.[a]
JO_2-ZrO_2-Nb-Zr, JO_2-BeO	Dissolve in HNO_3-HF.[a,b] (Large quantities of Nb may be removed by precipitation with SO_2).
Dissolver solutions, rganic solutions, wastes	Homogenize and reconstitute multiphase mixtures where necessary. Destroy organics with hot H_2SO_4-HNO_3.[a]
U-Zr	Dissolve in HF.[a,b]

NOTES: [a] Fume sample aliquants with H_2SO_4

[b] Fume sample aliquants with $HClO_4$

TABLE II. DISSOLUTION OF PLUTONIUM MATERIALS

Material	Treatment
Pu, Pu-Al, Pu-Ga	6 $\underline{N}$ HCl or 18 $\underline{N}$ H_2SO_4
U-Pu-Mo	3 $\underline{N}$ HCl - 8 $\underline{N}$ HNO_3 - 0.1 $\underline{N}$ HF
PuO_2, PuO_2-UO_2	8 $\underline{N}$ HNO_3 - 0.1 $\underline{N}$ HF, or fuse in $NaHSO_4$
PuO_2, fired $> 800^\circ C$	Fuse in $NaHSO_4$, or 8 $\underline{N}$ HNO_3 - 0.1 $\underline{N}$ HF (extended heating)
(U-Pu)C	Ignite; 8 $\underline{N}$ HNO_3 - 0.1 $\underline{N}$ HF, or fuse in $NaHSO_4$
"Calcined ash"	Leach in 8 $\underline{N}$ HNO_3 - 0.1 $\underline{N}$ HF, fuse residue in $NaHSO_4$, or fuse in $NaHSO_4$
"Brick residues" : (Al_2O_3, MgO, CaO, Fe_2O_3, SiO_2)	Fuse in $NaHSO_4$, dissolve in 2-8 $\underline{N}$ HNO_3, fuse residue in Na_2CO_3
"Grinder sludge" : (SiC)	Fuse in $NaHSO_4$

TABLE III. DISSOLUTION OF THORIUM MATERIALS

Material	Treatment
Metal	8-16$\underline{M}$ HNO_3 + 4% HF, or 6$\underline{N}$ HCl (F^- present).
Silica-base ores (thorite, monazite)	$NaHF_2$ fusion, or hot concentrated H_2SO_4 (losses occur).
ThO_2, low-fired ($< 600^\circ C$)	8-16$\underline{M}$ HNO_3 (F^- present).
ThO_2, high-fired ($> 600^\circ C$)	16$\underline{M}$ HNO_3 + 0.03$\underline{M}$ HF with extended digestion ($\leq$ 3 days) or $NaHSO_4$ or $Na_2S_2O_7$ fusion, or $HClO_4$ (F^- present) fuming.
UO_2-ThO_2	See Table 1.

TABLE IV. SAMPLE TREATMENTS WHICH REMOVE INTERFERENCES TO THE NBL TITRIMETRIC MEASUREMENT OF URANIUM

Element	Treatment
Mo, Tc, Ru, Os, Cl, Br, large excesses of F	Fume sample aliquant in 3-5ml $HClO_4$ and/or H_2SO_4
I	Add bromine water, evaporate, fume in $HClO_4$ or H_2SO_4
As, Sb, Sn	Add small amount of $K_2Cr_2O_7$ to sample aliquant prior to Fe(II) reduction step
V, Mn, Mo, Ru, Pd, Ag, Os, Ir, Pt, Hg, As, Sn, Sb, Cl, Br	TBP Extraction in CCl_4[a]
10% Au	Reduce to metal and separate

Note: All of the interfering elements are listed in this table.

[a] Kerosene interferes causing results low by 20-40% and cannot be used as a solvent for TBP in this application. Cyclohexane is a satisfactory substitute for CCl_4.

TABLE V. DETERMINATION OF PLUTONIUM USING RAPID CONTROLLED POTENTIAL COULOMETRY

Preparation	Standard Type	No. of aliquots[a]	Mean Recovery, %	RSD, %
A	949e	5	99.96	0.07
B	949e	11	100.03	0.06
C	949e	11	99.99	0.06
D	949e	9	99.99	0.03
E	944	5	100.02	0.05
F	944	17	100.01	0.07
G	944	39	100.01	0.06
H	944	11	99.98	0.05
I	944	7	100.03	0.04
J	944	18	100.02	0.05
K	944	2	100.00	0.01
Total		135	100.01	0.06

[a] 6-12mg Pu aliquots.

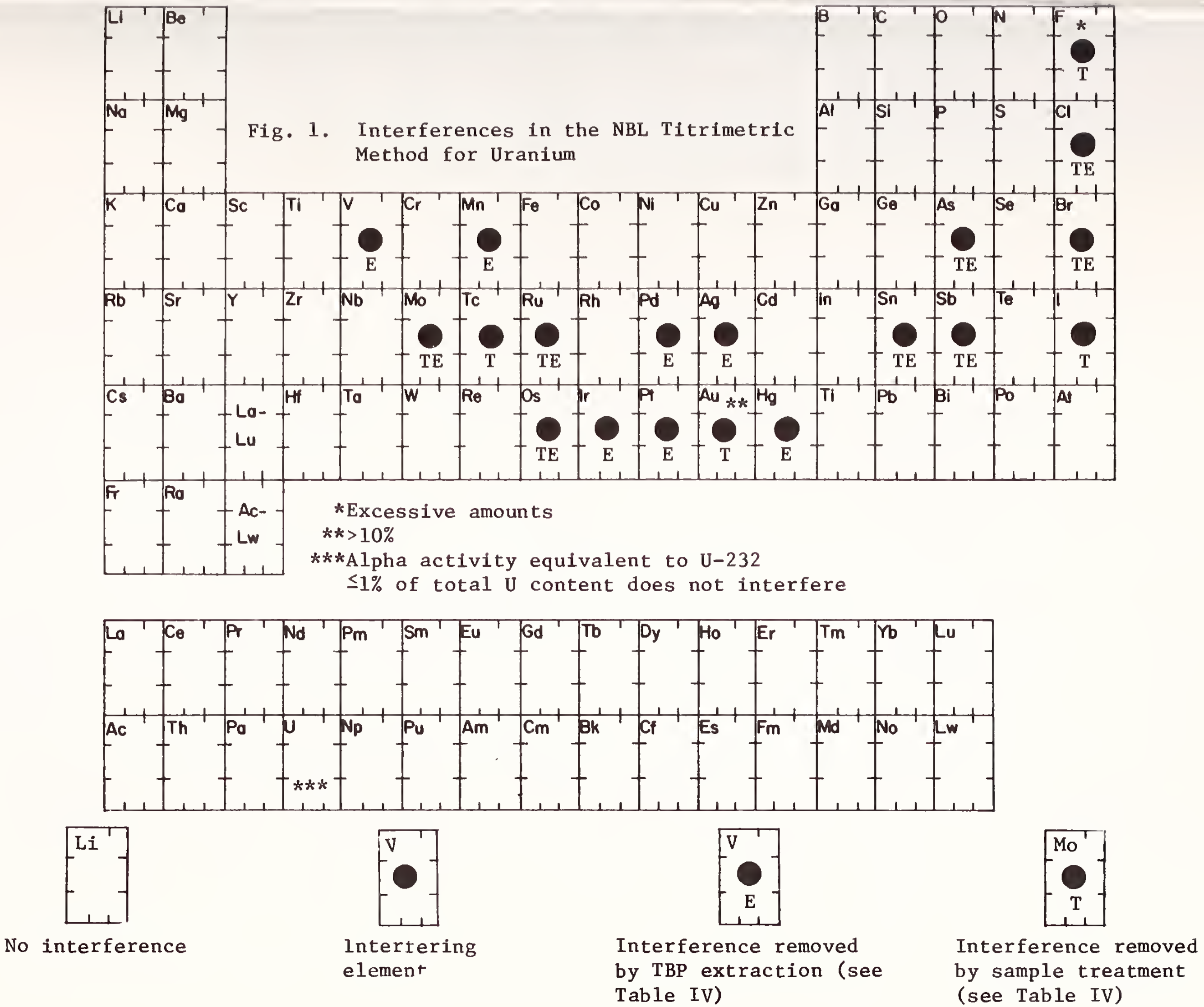
TABLE VI. RELATIVE LIMIT OF ERROR FOR URANIUM ISOTOPIC ANALYSIS
(95% Confidence Limits)

Wt.% ^{235}U	L.E., %
0.5-0.7	0.4
0.7-1.0	0.3
1.0-1.5	0.25
1.5-10	0.20
10-15	0.18
15-20	0.16
20-25	0.14
25-30	0.13
35-40	0.12
40-45	0.11
45-50	0.10
50-55	0.09
55-60	0.08
60-65	0.07
65-69	0.06
69-73	0.05
73-79	0.04
79-85	0.03
85-88	0.025
88-90	0.020
90-91.5	0.015
91.5-93	0.013
93-94	0.011
94-95	0.010
95-96	0.009
96-97	0.008
>97	0.007

TABLE VII. RELATIVE LIMITS OF ERROR FOR PLUTONIUM ISOTOPIC ANALYSIS (95% Confidence Limits)

Wt.% Pu	L.E., %
0.001-0.01	20.0
0.01-0.03	10.0
0.03-0.05	5.0
0.05-0.1	2.0
0.1-0.5	1.0
0.5-1	0.5
1-5	0.2
5-10	0.18
10-15	0.16
15-20	0.14
20-25	0.12
-	-
65-70	0.04
70-75	0.035
75-80	0.03
80-85	0.025
85-90	0.02
90-95	0.015
> 95	0.01

Fig. 1. Interferences in the NBL Titrimetric Method for Uranium



*Excessive amounts

**>10%

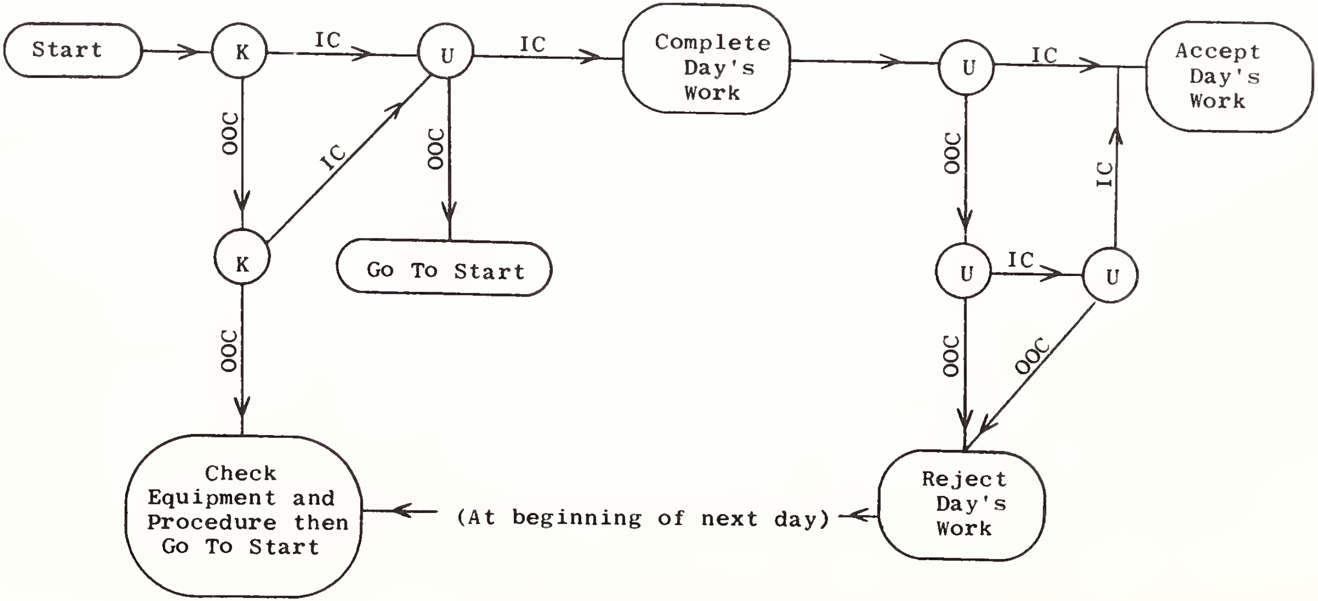
***Alpha activity equivalent to U-232 ≤1% of total U content does not interfere

No interference

Interfering element

Interference removed by TBP extraction (see Table IV)

Interference removed by sample treatment (see Table IV)



K - Known Standard
U - Unknown Standard
IC - In Control
OOC - Out of Control

FIGURE 2.. FLOW CHART OF CONTROL STANDARDS PROCEDURE

Analytical Methods and Laboratories for Safeguards and Accountability: Present and Future

by

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ABSTRACT

Accountability for special nuclear materials at ORNL requires a number of different analyses depending upon the kind and source of the material. The determination of uranium and plutonium in highly radioactive reactor fuel dissolver solutions must be performed remotely in hot cells or in glove boxes after a separation of the heavy elements from the bulk of the fission products. These determinations can be made by several different chemical techniques or radioactive solutions may be measured simultaneously and accurately by isotope dilution mass spectrometry.

Measurements where accuracy is essential are subject to a quality assurance program for all phases of the operation: equipment, standards, sampling, aliquoting, documentation and reporting.

Special material samples are stored either in hot cells or in glove boxes for analyses. The analytical laboratories are in zones that are not readily accessible to unauthorized personnel.

Future safeguards analytical laboratories will operate under the premise that if samples always remain in the hot-cell and glove-box systems, diversion of material will be difficult. Analytical procedures will be highly automated to minimize the need for human sample handling, and sample storage and retrieval will be under computer control.

Hot cells and glove boxes must and will be designed to optimize automated operations. Thus, they will have a very different appearance from hot cells of today.

Analytical techniques not previously used for automated radioactive operations must be adopted. Spark-source mass spectrometers are already being converted for hot cell use. Thus, there will be many opportunities for new and innovative approaches to chemical and radiochemical techniques in the years to come.

KEYWORDS: Accountability; analyses; remote; plutonium; safeguards; uranium

An Automated X-ray Spectrometer for Mixed Oxide Pellets

by

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ABSTRACT

This paper discusses the development of an energy dispersive x-ray (EDX) spectrometer for the rapid, automated, close-coupled analysis of solid mixed plutonium-uranium oxide fuel pellets. Reasons are given for the system design, which is intended to give a relative precision (RSD) of ± 0.2% in a total analysis time of two minutes. The principal problems in an EDX system are in maximizing the plutonium count rates.

KEYWORDS: X-ray spectrometer, energy dispersion, nuclear fuel assay, in-line, automation, faster counting.

INTRODUCTION

The Hanford Engineering Development Laboratory has a major responsibility for the deve opment of fuels for the breeder reactor program. The cost of fuel fabrication represents major portion of the total fuel-cycle costs for power reactors. Therefore, the earlier i the fabrication process that analytical measurements can be obtained the greater will be their effect on the quality of the product. To verify the quality of the finished oxide fuel pellets, chemical analyses are currently performed days or weeks after an entire fabrication run has been completed. This is too late to affect control of the process during any current production run.

Consequently, we are developing a close-coupled technique for rapid fuel pellet analys in order to improve fabrication quality control and to decrease or eliminate costly produ tion reruns. We say close-coupled, rather than in-line, because our present concept is t have the x-ray spectrometer with its own glove box close to, but not in, the production line. Samples from more than one location in the process can be transported pneumaticall into the analytical glove box and back again to the production line in an atmosphere of nitrogen.

The x-ray fluorescence method has been shown to be feasible by a number of people. Som of them are E.A. Hakkila at Los Alamos[1], by Von Baeckmann at Karlsruhe, West Germany[2], W. L. Pickles (the chairman of this meeting) and J. L. Cate, Jr. at Lawrence Livermore Laboratory[3], and by M. C. Lambert at Hanford[4], analyzing uranium and plutonium in solutio.

[1] E. A. Hakkila, R. G. Hurley, and G. R. Waterbury, Appl. Spectrosc. 22, 434-7(1968).

[2] A. von Baeckmann, Anal. Chim. Acta 47, 431-8 (1969).

[3] W. L. Pickles and J. L. Cate, Jr., Advances In X-ray Analysis (Plenum Press, New York 1974), Vol. 17, Page 337.

[4] M. C. Lambert, "X-ray Spectrographic Determination of Potassium, Uranium, and Thorium in Pyrochemical Samples", HW-65801 (1960).

nizlein, Gerding, and Steindler at Argonne National Laboratory[5] made a comprehensive dy of x-ray fluorescence with various forms of the solid mixed oxides. Their work icated great possibilities for the analysis of pressed pellets, but not for bulk mixed ders. We plan to achieve even better precision and faster analyses of solid fuel pellets.

Our primary goal is to develop an x-ray spectrometric method for the rapid determination the plutonium and uranium contents of finished fuel pellets immediately after they come m the sintering furnace. We may also analyze the mixed powder many hours earlier in the duction process. Powder samples will likely be pressed into a green slug before analysis order to achieve higher and more uniform density. Since the fuel pellets will be fabri-ed from high-exposure plutonium with its increased radioactivity, the spectrometer must capable of automated remote operation. A secondary goal is to achieve sufficient pre-ion for the analyses to be useful to the Safeguards program by providing an accurate entory control at one or more locations in the fabrication process.

One of the difficulties in making the analysis both rapid and precise and also in auto-ing the sample handling is the small size of the pellets. Current fuel pellets are only mm long and 4.95 mm in diameter.

The state of the art for commercial x-ray spectrometers in early 1975 was the basis of st of our decisions when we drew up the specifications. Since no commercial spectrometer ıld meet our requirements without some design work and modifications we received only ree bids that were responsive. The most practical bid was a combined one from Kevex rporation and Tracor-Northern, Inc. The bids were received in May 1976, our negotiations d discussions about design requirements were completed by late summer, and we began ceiving portions of the system in May 1977.

Figure 1 shows the nearly complete spectrometer before it was attached to the end of a ove box. It is an energy dispersive solid state spectrometer. Kevex did the custom orication and assembled all the instrumentation. At the left is a Siemens model 805 ray generator, selected in part because it could be automatically controlled by a computer. day there are other generators that can also be computer controlled. Next to the genera-r are two cabinets containing 31-liter liquid nitrogen dewars. Two lithium-drifted silicon tectors and the x-ray source are housed in the metal box above the cryostats. This small tal housing was temporarily used in place of a glove box. The inside of this box will seen in Figure 2.

To the right of the detector compartment is a Tracor-Northern TN-11 control and process-g system which includes a 32,000 word memory minicomputer and a dual floppy disc drive. e cabinet to the right of that contains a Kevex 5100 microprocessor system. Next is a Cwriter and the last unit on the far right is a Kevex 5100C four-color display and key-ard terminal. Kevex had no minicomputer system at the time we purchased the equipment, we specified a TN-11 control and data processing system from Tracor-Northern. Although ere were other similar data processing systems available we chose the TN-11 because of e abundance of good software available from Tracor-Northern, and because of our prior owledge of the Flextran language used by the TN-11 plus the fact that we will have to ite most of the control programs.

Figure 2 shows two detector tubes pointing upward toward the sample position. An x-ray be comes in from the left side. Right above that is a 6-position filter turrent, and hind that is a 6-position secondary target turret. The sample pellet can be excited ither by the x-ray tube directly or by selectable secondary radiation. Figure 3 shows the me housing as seen from the rear, showing it bolted to the end of the glove box. We will ome back to these pictures later. But now the question is: Why did we design the system ike this?

CHOICE OF ENERGY VERSUS WAVELENGTH DISPERSION

We had had more than twenty years experience with wavelength dispersive x-ray fluorescence WDX), but very little first hand experience with energy dispersive (EDX) equipment at the ime we were setting the specifications. It seemed to us that the EDX system had sufficient esolution for this application and offered a great deal in simplicity in that a single mall detector could simultaneously collect data from two or more peaks and two or more ackgrounds. If the working end of the instrument were to be put inside the glove box an DX system would take up much less space. Furthermore, since an EDX system utilizes no oniometer it would be much simpler to automate.

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[5] J. G. Schnizlein, T. J. Gerding, and M. J. Steindler, "Application of X-ray Fluorescence to On-Line Analysis of Plutonium in Mixed-Oxide FBR Fuels", ANL-8004 (1974).

A wavelength dispersive system would lose the advantage of its higher count rate capability if four or more sequential measurements were to be made with a single goniometer. O the other hand four or more separate mechanical goniometers and detector systems, which would permit simultaneous counting of the plutonium and uranium $L_{\alpha 1}$ lines and backgrounds, would crowd the glove box, require frequent tuning and calibration of the individual spectrometer systems, require more frequent use of standards, and require much more attention from the operator.

Consequently, we chose to use the American-created solid-state detector and are trying to push the energy dispersive technique to its current maximum capability.

CHOICE OF $L_{\alpha 1}$ VERSUS $K_{\alpha 1}$ FLOURESCENCE

We were next faced with the choice of using plutonium and uranium $L_{\alpha 1}$ fluorescence at about 14 keV or their $K_{\alpha 1}$ fluorescence at 104 keV. Using the Pu $L_{\alpha 1}$ line doesn't allow analysis of as deep a layer in the pellet as we would like to sample. Attenuation calculati show that only 10% of the Pu $L_{\alpha 1}$ fluorescence escapes from a depth of 28 μm from a pellet consisting of 25% PuO_2 and 75% of UO_2; 20% of the fluorescence escapes from a depth of 20 and 50% from a depth of only 8.5 μm. Thus the effective depth of analysis is less than 20 However, that was thought to be sufficient depth of analysis for two reasons. For one, th oxide powders are ground to about a 10 micron size; hence there should be no significant particle size effect. For another, the pellets will come directly from the sintering furnace in a reasonably inert atmosphere. Even if measurable surface oxidation were to occur it would not alter the plutonium to uranium ratio. Furthermore, use of the low energy L-lines for analysis greatly simplified design and construction of the glove box, sample manipulator, and parts of the spectrometer, since only 3.0 mm of stainless steel provides 12 half-thickness of shielding, giving an attenuation factor of 4000 for 40 KV x-rays.

Use of the $K_{\alpha 1}$ lines would result in an analysis depth about 52 times greater, which would be good. However, to excite this high energy fluorescence would require an x-ray tu to be operated at about 150 KV. This would mandate the use of a radiography-type generato instead of the highly stabilized laboratory generator. It would also require some heavy shielding, e.g., 6.4 mm thickness of lead plus 6.4 mm of stainless steel, to protect perso from a 150 KV source plus the secondary Pb K_{α} fluorescence. Finally, it would not be possible to utilize secondary radiation, nor even effective filtering. As a consequence there would be a sloping x-ray background of large magnitude under the analytical peaks resulting in some loss of precision. Therefore, we decided to use the L-spectral lines of plutonium and uranium.

CHOICE OF HIGH POWER VERSUS LOW POWER X-RAY TUBE

The recently developed low power (10 to 50 watts), air-cooled x-ray tubes, with self-filtering transmission targets and end window design, are very appealing from the point of view of space requirements. The extremely stable power supply is only a single chassis, requiring no extra floor space. Since these tubes have no heated filament wire, they can be pulsed on and off with extreme rapidity by simply deflecting the internal electron beam When the amplifier senses the beginning of a count it turns off the x-rays and they remain off until the ADC is no longer busy processing the signal. This decreases the amount of signal pile-up significantly and permits a higher count rate. Using one of these pulsed tubes recently in our general laboratory spectrometer, which has only one detector, we wer able to analyze Pu-U fuel pellets with a relative precision (RSD) of ± 0.4% in two real minutes per pellet.

However, we thought 50 watts was not enough power and chose a 3000 watt x-ray tube to permit the use of selectable secondary targets, which produce a minimum of x-ray backgroun and permit the most efficient excitation of plutonium. The reserve of power also allows spacing enough between the sample and detector to keep all of the instrument outside the glove box. This greatly simplifies any maintenance or modification work. The geometry still turned out to be fairly tight. Distance from the sample to the detector crystal in our present system is only 4.7 cm.

Figure 4 shows the sample manipulator pulled back away from the beryllium window inside the glove box. The pellet rotator is oriented for an end view of a pellet. The housing has X, Y, Z vernier adjustments and the open side toward the operator has an interlocked lead-glass window for shielding. The open end of the sample housing fits inside a framewo shown on the end plate in Figure 4. This prevents x-ray leakage and yet allows the sample sing to be moved up or down or sideways. The x-ray source and detector compartment on outside, see Fig. 3, bolts to studs on a stainless steel plate, the connection being le gas tight by means of a large O-ring.

The end plate of the glove box contains two 125 μm (5 mil) beryllium windows one inch in ameter. The 5 mm space between the two windows is slightly pressurized and gauged so that leak in either window will set off an alarm. The housing for the x-ray source serves as secondary containment vessel if both windows should ever break. The two windows to-her absorb less than 2% of the plutonium and uranium fluorescence. The sample manipul-or housing inside the glove box and the x-ray tube and detector housing on the outside of glove box are both interlocked to the end plate so that they must be in contact with end plate. As a result, x-ray leakage is barely measurable.

PARTICLE SIZE EFFECT AND ORIENTATION OF SOLID PELLETS

Since 50% of the plutonium and uranium fluorescence originates at depths less than 9 μm om the surface of a solid mixed oxide fuel pellet and since the average particle size of e oxide powders, before pressing and sintering, is about 10 or 11 microns, there is the ssibility for a slight particle size effect.

We analyzed the cross sectional ends of several fuel pellets on our general laboratory ectrometer by measuring the Pu/(U+Pu) ratio, then repeating this after rotating the pellet , 90, and 135 degrees. The maximum relative variation in the ratios was 0.56% whereas e precision of reproducibility of these ratios under the same conditions was ± 0.34%. The mber of data was insufficient to give statistically positive results but there appeared be a very slight variation in Pu/U ratios with changes in orientation of the pellets.

Consequently, a sample manipulator was designed so that it could present the pellet r either an end view or a side view analysis and rotate it at variable speeds. An end ew orientation presents an analysis area of 19 mm^2. The rotated side view presents the tire perimeter for about 85% of the length of the pellet and allows analysis of about 80 ^{2} and this is the way we plan to look at the pellets.

The final version of the sampling device has not been designed yet. It will be completely tomated, have two or more standards ready for calibration checks at programmed intervals, d pick up samples from an incoming line or boat, then return them after their analysis.

CHOICE OF EXCITING X-RAYS

The selection of the excitation source is important for optimizing the analysis of fuel ellets. One of the chief parameters is the separation between the exciting x-rays and the $_{III}$ absorption edge of plutonium. Figure 5 shows the energy values of uranium and plutonium $_1$ fluorescence, the absorption curves of uranium and plutonium, and the energies of the aracteristic K_{α_1} radiation from a number of exciting target materials. In fuel containing 5% plutonium dioxide and 75% uranium dioxide the precision for the plutonium measurement s the controlling precision. Ideally, the exciting radiation must exceed the energy of he plutonium L_{III} absorption edge, but be as close to it as possible in order to be highly bsorbed. Thus technetium K_{α_1} radiation would produce the greatest plutonium L_{α_1} fluores-ence yield. We obtained some technetium metal, since quite a bit of it was separated at anford, but it is not a practical target material as it emits 2.9 meV beta particles. The ext heavier metals are ruthenium, rhodium, palladium, and silver. We have been using a hodium secondary target for much of our early work. Recently we added a ruthenium target hich we pressed from 80-mesh pure ruthenium particles, producing a surface in appearance ike a shiny continuous metal sheet. Since we have no ruthenium foil we use a 0.025 zir-onium foil to filter out the continuum.

Figure 6 shows the 50 KV exciting spectrum from 0 to 40 keV as scattered by polyethylene. t includes the K_{α_1} and K_{β_1} peaks, their incoherently scattered Compton peaks, and the remmstrahlung with various degrees of filtering. We filter out much of the continuum. pectra from the other targets are similar to that from rhodium with the peaks displaced lightly to lower or higher energies.

Figure 7 shows the relative strengths of the rhodium peaks and the Compton peaks when cattered from matrices of different densities. The huge Compton peak is scattered from olyethylene. The rhodium K_{α_1} and Compton peaks are about the same size when the sample atrix is aluminum. The Compton scattering decreases considerably as the matrix is changed o heavier and heavier matrices, such as titanium, zirconium, and lead. There is almost o Compton scattering from uranium and plutonium. The oxygen content of fuel pellets, how-ever, creates a small Compton peak. But there is still ample separation between the plutonium $_{\alpha_1}$ peak and the Compton peak from any of the possible secondary targets to allow for a good background measurement.

In Table I the last two columns show the relative plutonium fluorescence intensities and the plutonium fraction of the total plutonium and uranium counts obtained, including interpolated values in parentheses, for the secondary targets we have been discussing. It is seen that for a given power input a ruthenium exciting source produces the highest plutoniu count rate of the practicable sources.

Figure 8 shows a typical fluorescence spectrum from a mixed plutonium-uranium oxide fuel pellet in a titanium holder and excited by a rhodium x-ray target. The two prominent peaks near the center are the L_{α_1} peaks of uranium and plutonium. Uranium has an L_{β_1} line that could be measured, but plutonium has no other useful L-line as its L_{β_2} peak is completely overlapped by uranium L_{β_1} and the plutonium L_{β_1} fluorescence is not efficiently excited by any of the targets from technetium to silver. Consequently, only the L_{α_1} peaks of each element are measured in the analysis.

INSTRUMENTAL METHODS OF INCREASING THE PU COUNT RATE

The principal limitation of an energy-dispersive system in this application is a badly restricted count rate. The voltage signals from each x-ray photon are shaped and stretched out in order to achieve good energy resolution, so they pass through the amplifier relative slowly. There are only two peaks in the sample spectrum (see Figure 8) that we want to integrate and measure. But all of the rest of the peaks must also be absorbed by the detector, and the signals from the entire spectrum from 0 to 40 keV must pass through the preamplifier and the amplifier before any part of that spectrum can be discarded. The L_{α_1} peaks of uranium and plutonium together contain only about 37% of the total counts that must get through the amplifier.

Optimizing the Exciting Radiation

One method of increasing the plutonium count rate is to optimize the choice of exciting radiation, as was discussed in the preceding topic. For a pellet containing 33% as much plutonium as uranium, a ruthenium secondary target yields a plutonium peak 39% as big as the uranium peak and raises the total uranium plus plutonium L_{α_1} counts to 37% of the total spectrum.

Dual Detectors

A second method is the use of multiple detectors. A second detector, complete with amplifier and ADC were added to the spectrometer in order to double the count rate by summing together the counts coming from both detector systems. Dual detectors looking at the sample pellet from different directions will also aid in averaging out the slight particle size effects.

Fast ADC and Direct Memory Access

In a third attempt to increase the count rate we have provided an alternative route for the signal through a very fast Tracor-Northern 200 MHz ADC. From here, instead of going through any microprocessors or terminal boards, the signal will go directly to the computer memory in four microseconds via a direct memory access (DMA) interface. However, as long as the amplifier is the major bottleneck there will be little improvement in count rate by use of direct memory access.

We plan to make two more changes that should increase the plutonium count rate by an additional factor of about four.

Monochromators to Isolate Pu and U Peaks

Molecular Data Corporation in Cleveland has developed a new kind of x-ray monochromator which is very compact, utilizing a cylinder about one inch in diameter and several inches long, which does not require a mechanical goniometer and, by using curved focusing crystal does not attenuate the x-ray beam nearly as much as conventional crystal monochromators do. These cylindrical monochromators can be designed to permit transmission of only the desired portion of the spectrum and to discard the unwanted counts before they get to the detector and amplifier. As a result, the exciting power can then be increased and the count rate in the two analytical peaks can be more than doubled without increasing the load on the amplifier.

These cylindrical monochromators work well with a point source such as the target insid an x-ray tube. It is not yet known how well they can function with a larger diffuse source such as a secondary target. But we will know by August. Molecular Data, under contract to the Hanford Engineering Laboratory, is currently experimenting with an x-ray source milar to ours to find out how well these monochromators will perform in the energy range thorium, uranium, and plutonium L_{α_1} lines with either a secondary target or with direct citation from a rhodium target x-ray tube.

Fast Amplifiers

The last modification will be to use faster amplifiers. Before the end of this year a w kind of integrating amplifier will become available. It does not stretch the signal d can process counts in less than half the time needed by today's amplifiers, and the esolution is said to be at least as good. Faster amplifiers may necessitate the use of irect memory access. We shall find out.

If all of these techniques work out successfully we may achieve an eight-to ten-fold ncrease in plutonium and uranium count rates over our starting rate with a 1977 commercial pectrometer. This means that a half million counts for plutonium could be accumulated in 0 to 70 live seconds and a relative precision (RSD) of ± 0.15% could be obtained for the lutonium counts in two real minutes per pellet, including the time to change pellets. opefully the overall analytical precision could be held to an RSD of ± 0.20%. The accumu- ative average for 100 to 200 analyses per shift should provide an extremely accurate lutonium inventory.

REDUNDANCY AND DOWN TIME

Figure 9 shows the entire x-ray spectrometer and glove box system as it was first ompletely assembled the last week of 1977. It can be seen that there are two floppy isc drives and two minicomputers. We did not plan instrument redundancy when we started rocurement, but we have acquired a considerable amount of it.

In the first place, we added a second detector system in order to double the count rate. onsequently, if one of the detector systems should fail we could still carry on the pellet nalyses at reduced speed. At the time we purchased this equipment Kevex had no computer ut used a number of microprocessors controlled manually from the keyboard of the color isplay terminal. Therefore, we purchased a Tracor-Northern TN-11 system, which we were amiliar with, in order to be able to program and control the entire operation automatically. t the time we were to receive our spectrometer Kevex introduced their model 6100 processor hich includes a DEC LSI-11 minicomputer and a dual floppy disc drive, and they have ranslated most of their programs utilized by the microprocessors into FORTRAN for disc ormatting. We exchanged a number of minor components and for an additional small relative ncrease in cost we were able to add the necessary interfacing and the new 6100 processor. he second floppy disc drive was included because that was expected to have the highest robability of failure.

Now we will be able to operate the entire system using either one of the disc drives ith either one of the minicomputers. Even if both computers should be down we still have he microprocessors that can be manually controlled from a keyboard. In most cases of omponent failure this redundancy should prevent appreciable down time. At present the two inicomputers use different languages. However, we have a FORTRAN compiler and a DEC RT-11 perating system in the Tracor-Northern part of the system and eventually we will convert all our programs to a single language and format.

PRESENT CAPABILITIES AND FUTURE PLANS

There is considerable development work yet to be done, including the design of a completely automatic sample manipulator. When that and the programming are completed it will be possible to control the entire system either locally or from a remote panel board. One or the other minicomputer will automatically control the water flow and the x-ray generator, choose one of several standards or sample pellets and control the sampling device, accomplish both energy calibrations and analytical calibrations when called for, measure the radioactive background periodically and calculate a cumulative average for correction purpose, acquire the analytical fluorescence data, calculate deconvolutions and matrix corrections, integrate the corrected peak areas, calculate percent plutonium and percent uranium, feed in the pellet weight, isotopic compositions, and oxygen-to-metal ratio obtained from other close-coupled stations and calculate the percentages of plutonium and uranium oxides and also calculate the absolute weights of plutonium and uranium, and finally store the desired information on a disc and communicate the results to the master control center.

If desired, the spectrometer may also periodically analyze a pellet for about 15 of the impurity elements of interest by counting for a longer period of time. In a matrix this dense these would include only those impurities heavier than chlorine and that have specification limits of 200 ppm or more. It would be possible to have a second x-ray source and detector system in another glove box analyzing the oxide powders as soon as they are mixe both for plutonium and uranium composition and for some of the impurities. This could be controlled by the same minicomputer that is controlling analyses of the sintered pellets

We plan for the next year or so to analyze every vendor fuel pellet selected for chara erization before it is subsequently dissolved and assayed by amperimetric titration. Thi will provide a firm fix on the calibration accuracy and also a comparison of the x-ray t layer analyses with the complete dissolution and accountability determinations. We will know then whether the pellets are as homogeneous as we think they are.

By August we should have experimental data for the cylindrical monochromators. During the following year we may be redesigning the x-ray source and detector compartment to make room for the monochromators. This would entail changing to direct excitation by th x-ray tube, but the monochromators would remove essentially all of the background. We a plan to incorporate faster amplifiers to permit faster counting and better precision. We must also complete all the programming, design a completely automatic sampling device, work out the bugs in the automatic equipment, and train some operators.

In its final design the automated x-ray spectrometer will be used in support of fuel fabrication in the high performance fuel laboratory to be built as part of the Hanford Engineering Development Laboratory.

Should the mixed oxide fuel pellets be changed in the future to carbide or nitride fuels this would have absolutely no effect on the spectrometer system except to require new calibration coefficients.

If the fuel material should be changed to recycled Th-232/U-233 fuel, which will cont a small amount of U-232 and decay daughters of Tl-208 and Bi-212 which emit gamma radiat in the energy range 0.51 to 2.6 meV, the increased shielding needed would require a redes of the detector housing, the glove box and the sampler. The calculated flux of this hig energy radiation is too great to permit use of Dr. Pickle's arrangment of two rate meter one to measure total counts and the other to measure the high energy counts. In this ca the detector would not have sufficient time to recover between high energy photons. It fairly certain that crystal monochromators would be necessary to sufficiently reduce the intensity of high energy radiation reaching the detector. This would not only lengthen the distance between sample and detector, thus decreasing the x-ray intensity, but it wo cause a further large loss of x-ray intensity by insertion of the monochromators. Thus analyzing times would be appreciably lengthened and precision decreased as compared to t analysis of uranium and plutonium oxide fuels.

Figure 1. X-ray Spectrometer System Before Attaching to Glove Box

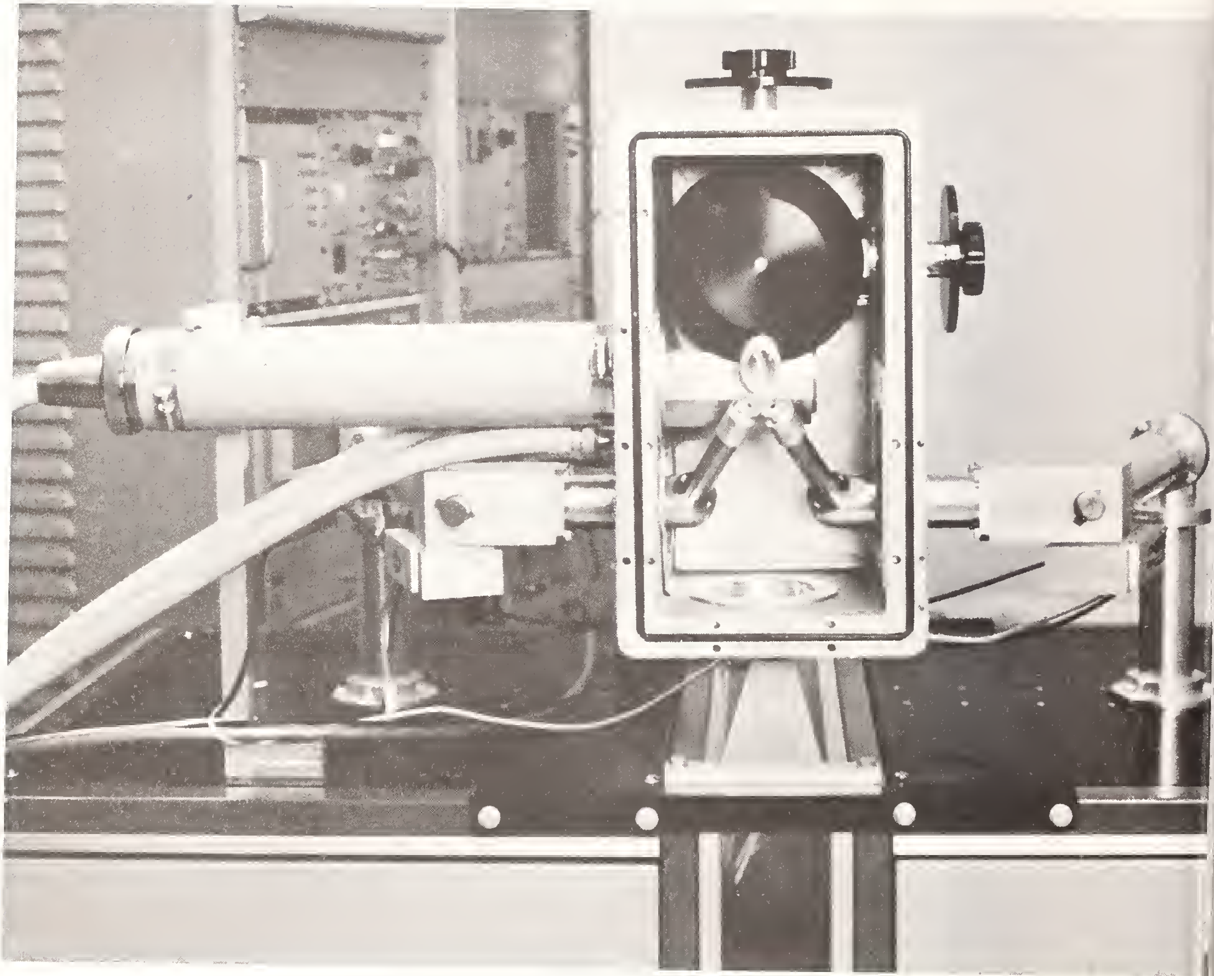

Figure 2. Inside of the Detector and X-ray Source Compartment

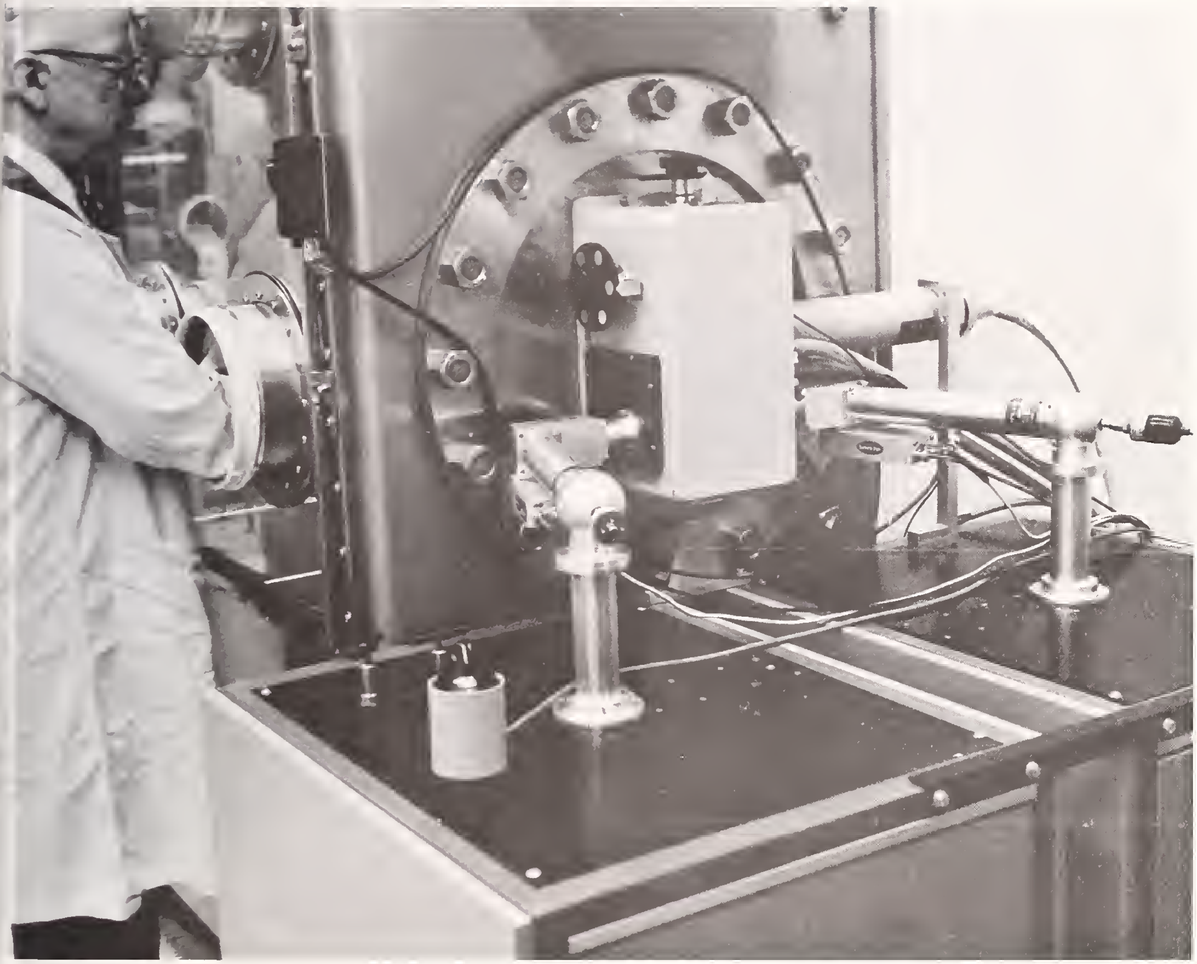

Figure 3. Detector and Source Compartment Bolted to the Glove Box

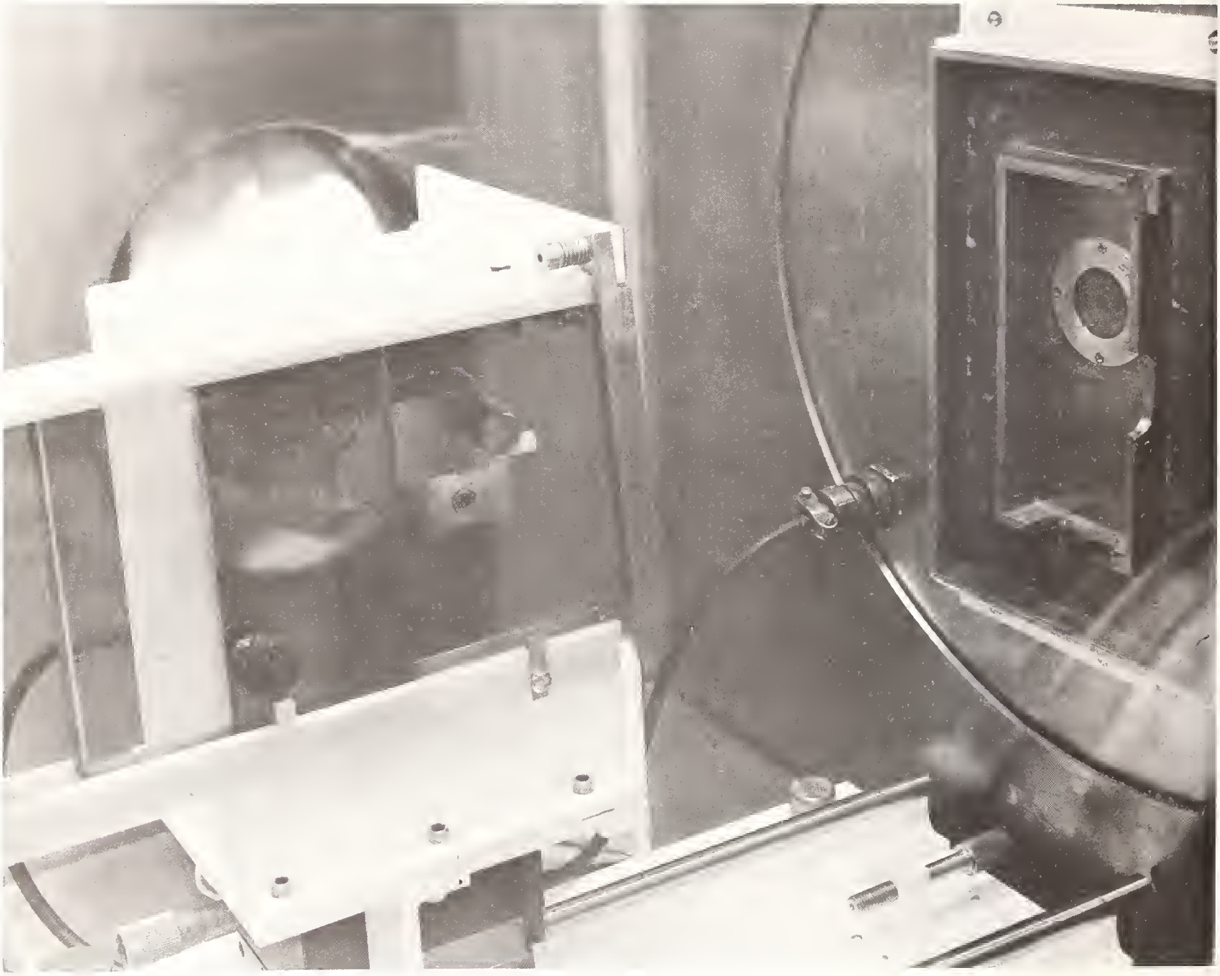

Figure 4. Sample Compartment Separated from End Plate Inside Glove Box

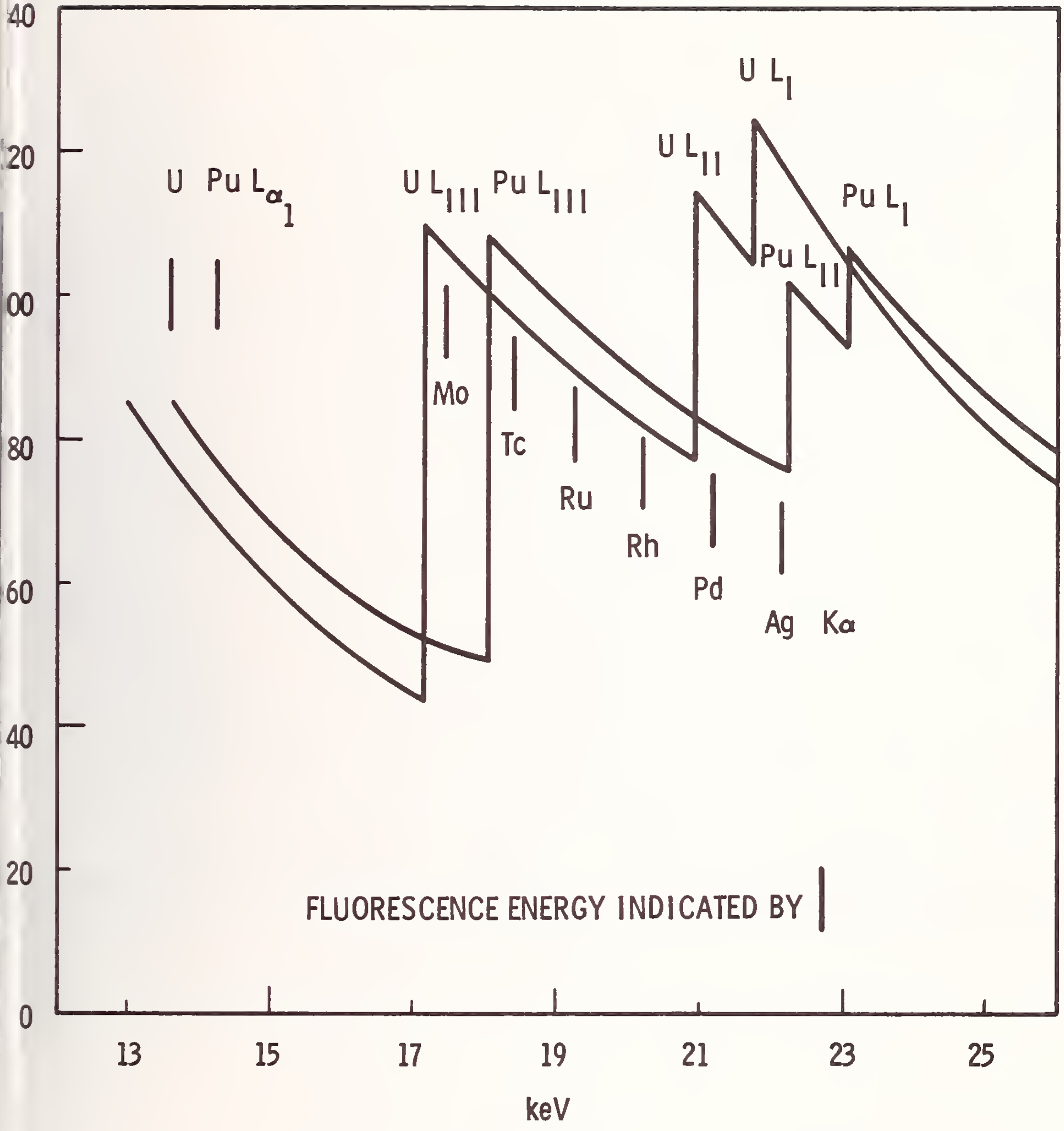

Figure 5. Uranium and Plutonium Absorption Curves

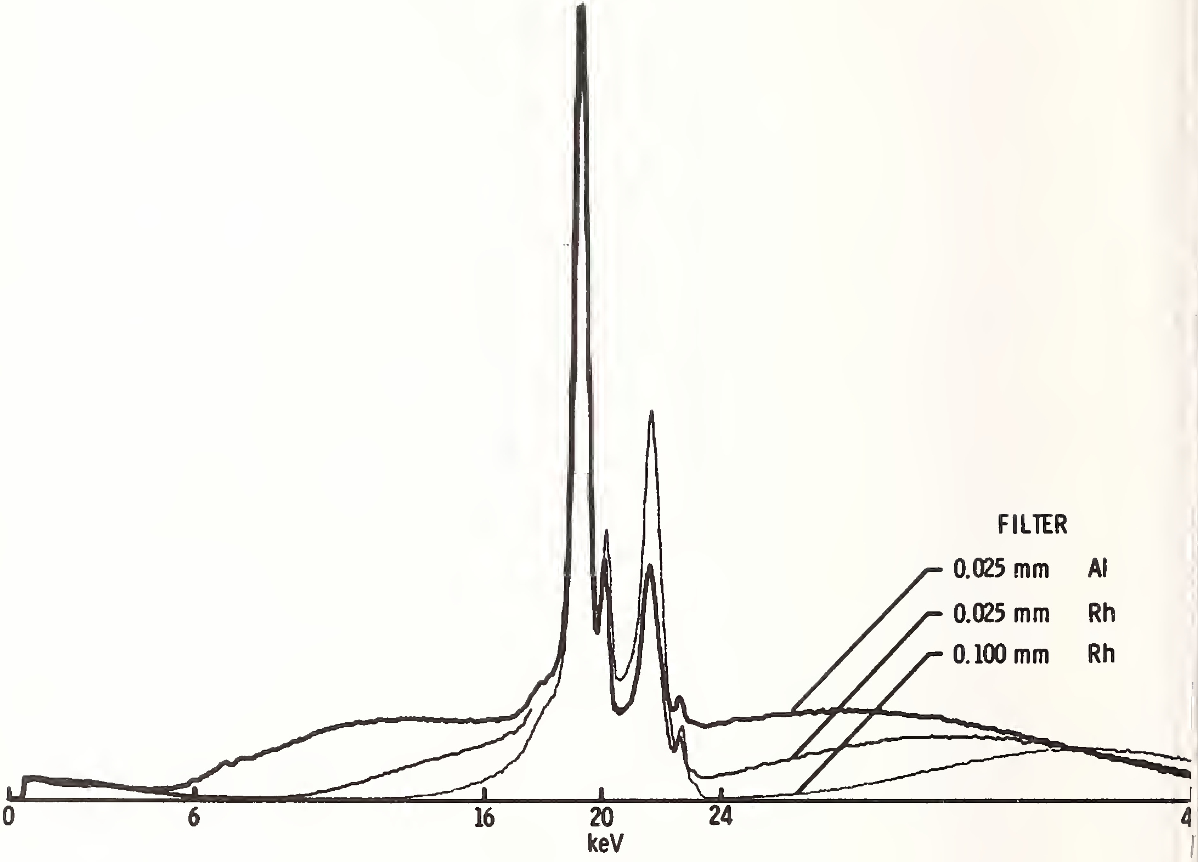

Figure 6. Rhodium Exciting Spectra (50KV) Scattered from Polyethylene

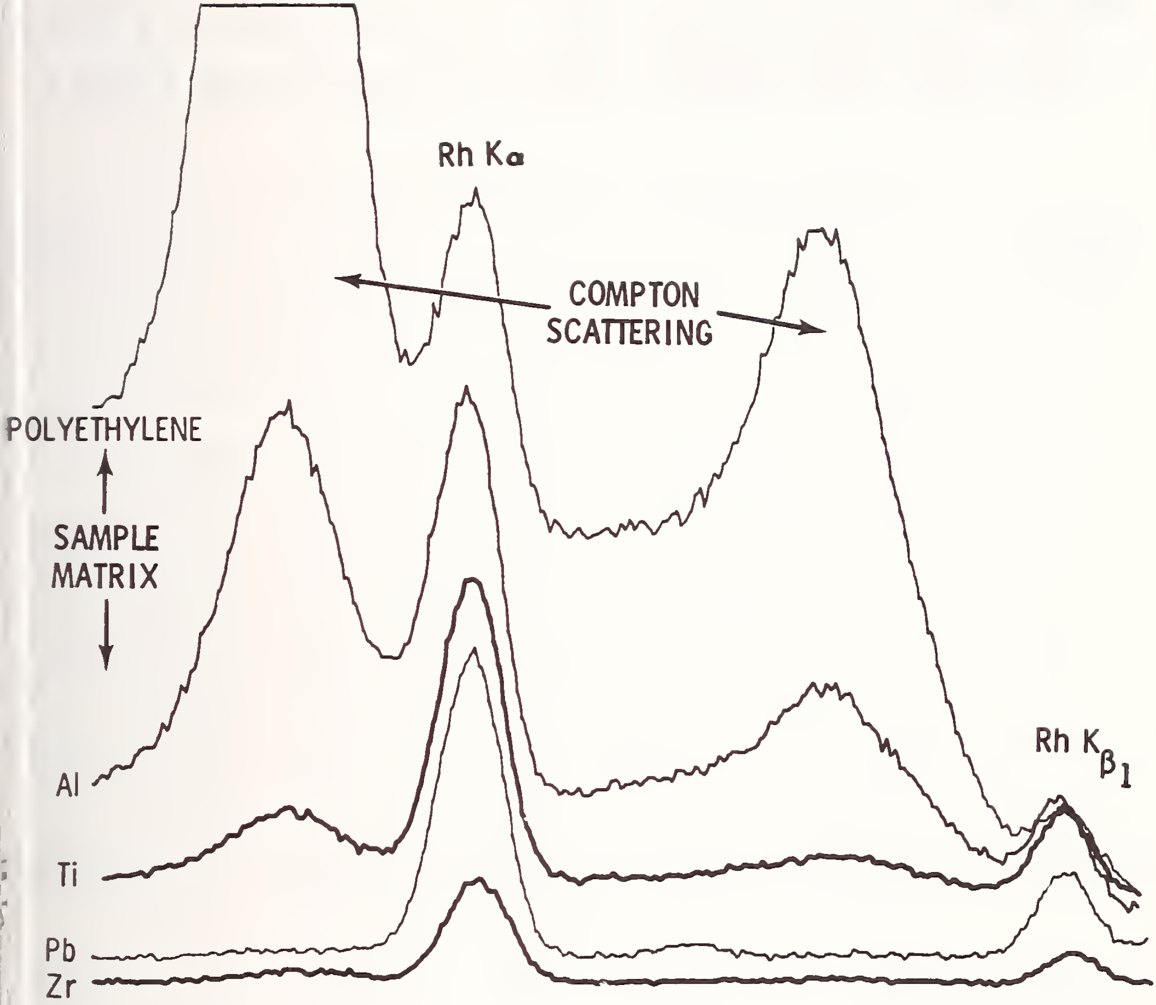

Figure 7. Rhodium L X-rays Scattered from Different Matrices

TABLE I

FLUORESCENCE YIELD VS SEPARATION BETWEEN EXCITATION ENERGY AND ABSORPTION EDGES

EXCITA: TARGET	SEPARATION, keV		NET PEAK AREAS, KC		RATIO
	X-U L_{III}	X-Pu L_{III}	U L_{α_1}	Pu L_{α_1}	Pu / (U +
Mo	0.32	-	1400	220	0.136
Tc	1.25	0.34	1400	600	(0.30)
Ru	2.12	1.21	1400	563	0.287
Rh	3.05	2.14	1400	528	0.274
Pd	4.02	3.11	1400	494	0.261
Ag	5.00	4.09	1400	461	0.248

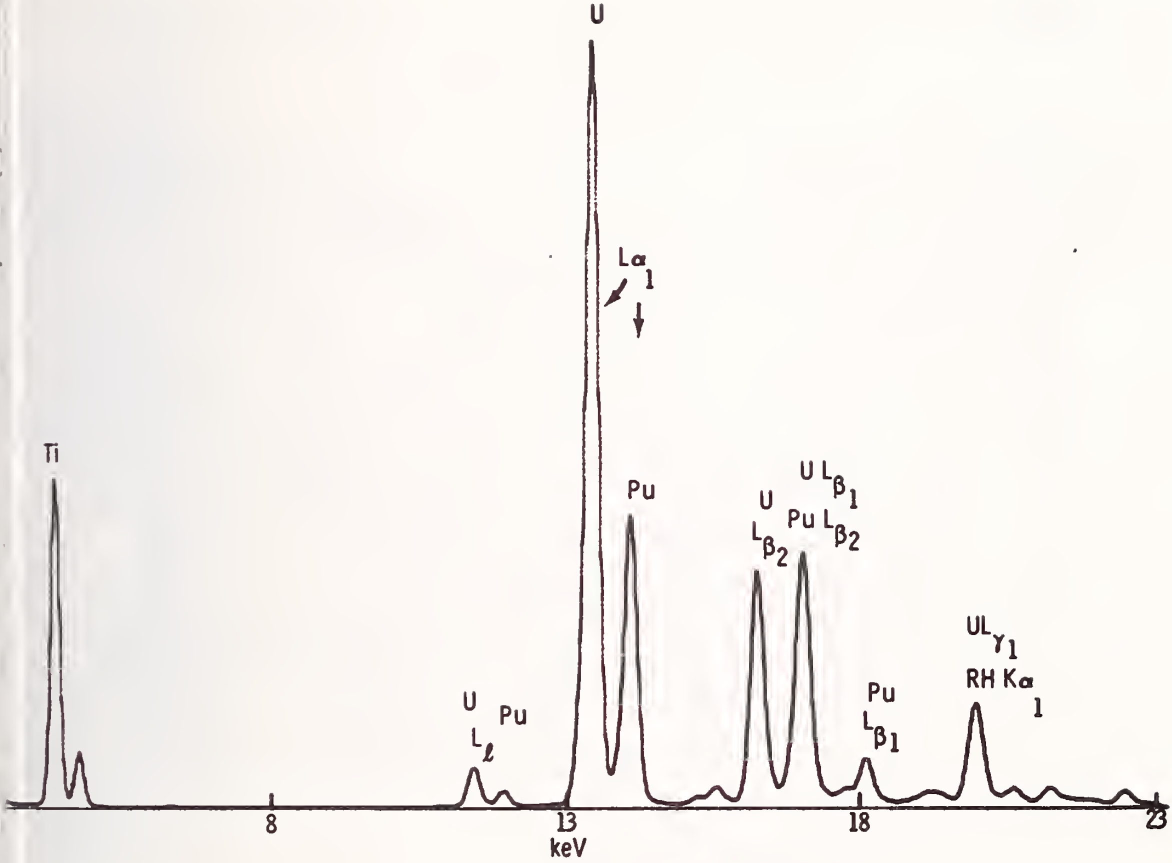

Figure 8. L-Fluorescence Spectrum from a PuO_2 UO_2 Fuel Pellet

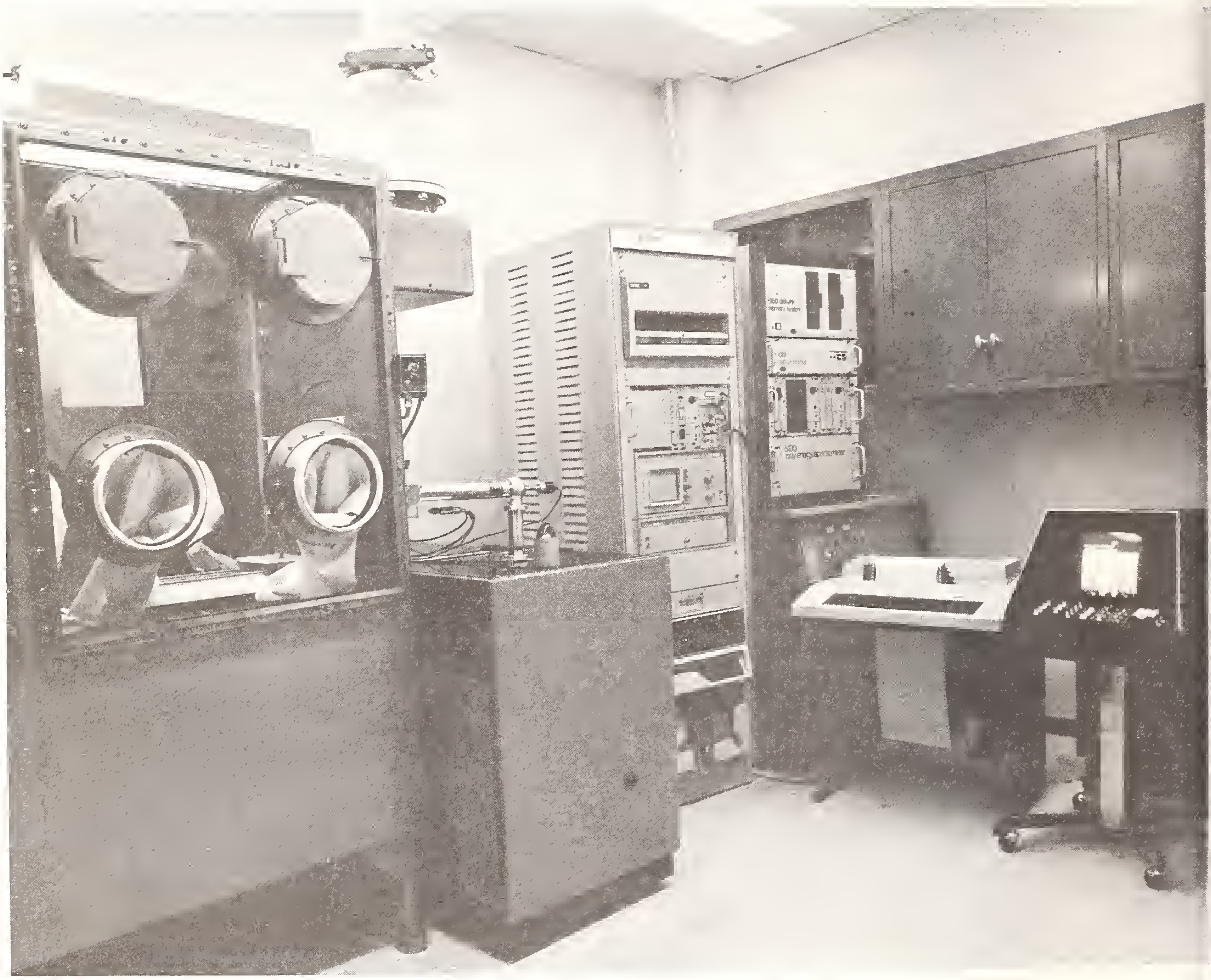

Figure 9. Complete X-ray Spectrometer System

Mechanisms for Assuring Accurate Measurement of Nuclear Materials

by

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ABSTRACT

A review of the procedures available to provide assurance of meaningful measurements of nuclear materials is presented. These procedures include the use of reference data, document or written standards, reference materials and instrument calibration services. Examples are given that demonstrate the determination of measurement uncertainty relative to nationally accepted standards. A clear case is made for the necessity of building a nuclear materials measurement system on a firm foundation of accuracy.

KEYWORDS: Nuclear safeguards; measurements; standards

INTRODUCTION

The determination of the amount of fissionable materials in nuclear fuel cycle ities is a goal of both our domestic safeguards program and the international ar safeguards activities as well. Although measurements play a key role in these ities, we have not fully developed and utilized all the standardization procedures able to insure accurate and compatible measurement results. Accuracy, in addition ecision in the measurement of nuclear materials for accountability purposes, is ly a necessity if one is to achieve meaningful results. However, measurements made cessive accuracy levels are overly expensive financially and can be technically iting. Therefore, the limits to measurement uncertainty, or in simple terms, the acy of the measurements should not be grossly in excess of the level that is sufficient et the end purpose.

ACHIEVING ACCURATE MEASUREMENTS

Accurate and compatible measurements on a national and international scale have been ved utilizing several different means. For example, the measurement of mass for rcial transactions takes place smoothly since weights traceable through NBS to the 's primary standard are readily available to verify commercial scales. This assures tibility over both time and geographical location. Time measurements also enjoy an lent reputation for accuracy and compatibility. Time measurements, made both by the nal Bureau of Standards (NBS) and the Naval Observatory, using an NBS-developed atomic reference method, are constantly compared and coordinated with other countries' time rements. The results are then disseminated via radio broadcast. Since users accept radio signals as their reference point, compatibility is achieved. Over the years, e accuracy requirements for the measurements became more and more demanding, NBS was d to develop increasingly more sophisticated reference measurement methods. The d can now be determined to better than 1 part in 10 million, which is comparable to 1 second in 370,000 years.

Many other measurement systems draw on somewhat similar mechanisms to achieve uniform, ate results. For example, measurements for steel production, clinical chemistry health the production of radiopharmaceuticals, and environmental monitoring all relate to a nally recognized system of standards provided jointly by NBS and others.

STANDARDIZATION FOR NUCLEAR SAFEGUARDS MEASUREMENTS

As the nuclear safeguards measurement system increased in sophistication and as la numbers of research, instrumentation, regulatory and production organizations entered t system, both domestically and internationally, the need for effective standardization h increased. In order to help meet this need, NBS has recently embarked on a broad standardization program for nuclear safeguards measurements. The NBS effort is supported b the Nuclear Regulatory Commission (NRC) and the Department of Energy (DOE). The undertaking is focussed on providing standardization for all of the measurements used for material accountability purposes to all of the parties making the measurements. Commer facilities, NRC regulators, government facilities, DOE inspectors, the International At Energy Agency (IAEA) and other countries all need, in general, to use an accurate, consistent set of standards to make the system work effectively. Of course, in many ca these same standards will serve for production quality control, environmental monitorin and buyer-seller equity in trade.

I should emphasize that NBS, as in many other measurement areas, is drawing upon t expertise and technology developed by other organizations. We will also develop cooper tive efforts with other organizations such as New Brunswick Laboratory (NBL) and Los Al Scientific Laboratory (LASL), that have already made substantial contributions to the standards effort. NBS is also strongly supporting the nuclear safeguards-related standards-writing efforts of the American Society for Testing and Materials (ASTM), the American National Standards Institute (ANSI) and the Institute for Nuclear Materials Management (INMM).

The NBS program is addressing standardization of measurements in areas that inclu bulk quantities (mass, volume, flow, pressure, density), destructive chemical and isot analysis, and passive and active non-destructive assay (NDA) techniques. The statisti aspects of materials accountability and sampling are also an important aspect of the e NBS is not aiming to develop field methods of measurement; our job is that of providin calibration methodology and data, standard reference materials (SRM's), calibration services and where need be, developing reference measurement methods for characterizin transfer standards and field methods.

NBS is also strongly committed to the concept of voluntary measurement assurance programs that allow participants to assess their measurement results relative to natio standards. These efforts also provide a two-way dialogue between the participants and standards laboratory. The participant is given, where requested, guidance on how to improve measurement results and the standards laboratory gets valuable feedback on the effectiveness of the standards-type services that they provide. Weaknesses in methodo and instrumentation can also become apparent in measurement assurance programs. New Brunswick Laboratory's Safeguards Analytical Evaluation (SALE) program is a good example of an effective Measurement Assurance Program (MAP) for chemical analysis. NB a cooperative project underway to develop a MAP for mass determination of large (up to 17,000 kg) UF_6 cylinders. Plans to help initiate additional measurement assurance pro for volume and various NDA techniques are also being formulated.

NDA REFERENCE MATERIALS

The NBS philosophy of how to provide for standardization of NDA measurements can be summarized by discussing the three areas of NBS activity in the NDA area. In the f area, NBS is developing and certifying a small, select number of primary NDA SRM's for materials that are in widespread use in one or more nuclear fuel cycles. An example i this area will be discussed shortly.

In the second area, we are developing reference measurement methods for the chara terization of both NBS reference materials and "custom made" reference materials produ by production and other types of facilities. These reference methods, which will most likely be costly and involve very large, expensive apparatus, will in general, not be suitable for use as field methods. However, they could be used as an independent meas ment method to help validate field methods. Possible reference methods include: resonance neutron radiography currently under development at NBS using either large li ctor-produced neutrons, Van de Graaff genereated 500 kev neutrons for interrogation oto-nuclear reactions using large linac-produced gamma rays to include fission and etecting delayed neutrons.

n the third area, NBS is developing calibration techniques for NDA. Included in this re our activities to assist voluntary standards-writing organizations in developing n consensus standards for NDA measurements. We also plan on trying to develop ed calibration techniques that might, in part, be based on nuclear data or radio- ty reference materials and calculation methods. Of course, the hardest problem that to be addressed is how to detect and correct the mismatch between a reference material unknown sample, especially in inhomogeneous materials.

would now like to describe a few ongoing projects at NBS that illustrate our approach andardization of NDA methods. In the first example, NBS and the European Atomic Community (EURATOM)'s Ispra Laboratory agreed to try to develop and certify a series enriched U_3O_8 Standard Reference Materials (SRM's) for gamma spectrometry. The Laboratory, with approval and guidance from the European Safeguards Research and pment Association (ESARDA) obtained the participation and support of several other om labs, while in the U.S., NBL and LASL agreed to join NBS in the effort. The IAEA also provide an observer at key steps in the process. The result will be NBS-certi- and distributed SRM's for the U.S., European Commission-certified and distributed for the European Community and IAEA-certified SRM's for use by IAEA inspectors. SRM's will be the first truly nationally and internationally-certified NDA SRM's.

The SRM's, which will be in the form of an infinite thickness for the emitted gamma will be extensively characterized by chemistry and NDA. They should be useful in alibration of gamma-based NDA methods used for the measurement of U_3O_8, UO_2, and UF_6. priate how-to-use documentation will be provided with the SRM's. Upon completion of low enriched U_3O_8 materials, NBS will most likely undertake (hopefully in a joint t), a series of high enriched U_3O_8 SRM's for calibrating NDA instruments.

The next NBS project I would like to discuss concerns the development and certifica- of plutonium heat source Standard Reference Materials to be used in the assay of nium by calorimetry. The first step in this project was completed about a year ago support by Mound Laboratory. The task involved a comparison of Mound heat flow imetry results with NBS calorimetry results obtained by Ditmars[1] with an ice imeter. Agreement between the two independent calorimetry methods was quite good. In urrent phase of thw work at NBS, heat flow calorimeter and associated constant rature baths are being set up and intercompared with the ice calorimeter. This or well characterized heat flow calorimeters will then be used to measure and certify nium heat source reference materials. Details of the certification program have not een completely developed.

These NDA activities are in agreement, in part, with the recommendations of a recent Advisory Group on Physical Standards for NDA. The group recommended that the IAEA the help of member countries), certify a very limited series of primary NDA reference ials. These reference materials should be very well characterized by both chemistry DA measurements and will be applicable in a wide number of fuel cycle facilities. materials recommended include uranium metal, plutonium metal and plutonium oxide (all a range of isotopic compositions).

In addition, the IAEA Advisory Committee recommended that "custom made" calibration ials for unique fuel cycle applications could usually be best made at the facility haracterized and certified via independent NDA measurements. In some cases,

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d A. Ditmars, "Measurement of Average Total Decay Power of Two Plutonium Heat Sources Bunsen Ice Calorimeter," International Journal of Applied Radiation and Isotopes, , Vol. 27, pp. 469-490.

destructive chemical and isotopic analysis would also be needed. NBS does not plan, in general, to provide this type of SRM. However, as discussed earlier, we do have an extensive effort to develop reference NDA characterization methods for reference materi

CHEMICAL AND ISOTOPIC REFERENCE MATERIALS

I would now like to discuss our efforts to develop and cerify additional SRM's for destructive chemical and isotopic analysis. New SRM's that are planned or underway inc a high purity, thorium metal assay SRM, a Pu-244 mass spectrometry spike SRM, a U-233 m spectrometry spike SRM, a series of UF_6 isotopic SRM's for gas mass spectrometry and ion-resin beads loaded with U and Pu for mass spectrometry. In addition, the isotopic composition of three existing NBS plutonium isotopic SRM's have been remeasured and new certificates will be issued. The new certificates will permit individual users to calculate, on a day-to-day basis, the decay of the individual isotopes and the build-up other elements due to this decay. Future plans also provide for the existing NBS pluto isotopic SRM's to be certified by assuming that plutonium exhibits similar behavior to uranium on evaporation from the filament of a mass spectrometer.

Many of these SRM's for chemical and isotopic analysis will be cooperative undertakings; for example, Oak Ridge National Laboratory will supply materials, LASL will pr purification and initial characterization and NBL will provide space and support in the plutonium-handling lab for a NBS plutonium chemistry lab to work on plutonium SRM's.

One of the most important facts built into most NBS SRM's is a known level of accu The certification of the SRM's that were just described will be established by either the following (in order of preference):

1. Use a reference method of analysis run independently by two or more analysts (at least one of whom is at NBS).

2. Use two or more reliable independent methods (at NBS).

In the first case, a reference method (according to the NBS definition) is a meth of known or proven accuracy, and its use assures the accuracy of the determination if personal bias is eliminated. This is why the measurements must be made, if possible, two or more analysts. An example of a reference method is the isotopic analysis of uranium by isotopic dilution mass spectrometry.

The second way to certify an NBS SRM, used when a reference method (or absolute m is not available, consists of using two or more independent methods. Each of these independent methods must have estimated systematic biases that are small relative to t accuracy goal set for certification. An example of this route to certification is ill trated by the recently completed replacement uranium oxide SRM for uranium assay. Thi material was certified through a coopeartive effort with NBL. NBS obtained assay resu by coulometry and NBS and NBL obtained assay results by the NBL-developed Davies Gray method. Agreement between the two methods was quite good.

CONCLUSION

The rapid advances in measurement methods, the need for increased and demonstrate accuracy for safeguards purposes and the worldwide expansion of nuclear fuel cycle facilities have all increased the need for NBS to strengthen its nuclear materials standardization activities. The NBS program outlined is in response to this demand. program is interactive by design and is drawing and building on the expertise and tec developed by the entire field.

Design of a Cf-252 Neutron Assay System for Evaluation at the Savannah River Plant Fuel Fabrication Facility

by

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ABSTRACT

A nondestructive assay (NDA) unit will be evaluated at the Savannah River Plant (SRP) reactor fuel fabrication facility for measurement of a range of highly enriched uranium materials. The unit employs cyclic neutron interrogation with a Cf-252 neutron source followed by delayed-neutron counting to assay the U-235 content of fuel alloys with up to 2.4 kg U-235 per item in addition to scrap and waste with a lower U-235 content. The accuracy goal for the majority of the measurements is 1-3%.

KEYWORDS: Nondestructive assay, enriched uranium, neutron interrogation, Cf-252, U-235, delayed neutrons

INTRODUCTION

Test and Evaluation Program

As part of the Nuclear Safeguards Program at the Los Alamos Scientific Laboratory ASL) several nondestructive assay (NDA) instruments are being evaluated or will be valuated in production facilities for monitoring the transfer and inventories of special aclear material (SNM). Use of NDA instruments should provide the capability for more imely accountability than is possible with destructive analysis methods alone.

In one of these test and evaluation programs a "Cf-252 Shuffler"[1] will be installed at ne Savannah River Plant (SRP) reactor fuel fabrication facility. LASL has been responsible or the design and construction of the unit within the constraints of the routine material andling procedures at SRP, available floor space, and expected degree of operator profiiency. SRP will provide calibration standards corresponding to their material types and ersonnel to operate the unit. LASL and SRP will share in documenting the results of the est and evaluation program.

Principle of Operation

The "Shuffler" measures the U-235 content of the SRP samples by counting the delayed eutrons produced by irradiating the sample with a Cf-252 spontaneous fission neutron ource. The mechanical design of the "Shuffler" unit is shown schematically in Fig. 1. ne unit consists of a source storage position and a sample interrogation-and-counting ell. A motor is used to cyclically transfer the Cf-252 source between the shielded torage position and the sample irradiation position. In order to achieve a mechanically imple system requiring few control features for assays, the SRP unit was designed to proide a uniform response throughout the range of sample heights using only one interrogation

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I. O. Menlove and T. W. Crane, "A Cf-252 Based Nondestructive Assay System for Fissile aterial," to be published in Nuclear Instruments and Methods.

position. In contrast, the first laboratory prototype "Shuffler" used an elevator to position the sample within its assay chamber, and two positions were selected by the operator to obtain a uniform interrogation.

The assay begins with a background count with the sample in the interrogation well and the Cf-252 source in its shielded storage position. Upon completing the background count, the assay proceeds with neutron activation of the sample by transferring the source to the irradiation position. Delayed-neutron counting follows after the source is transferred back to its storage position. A cyclic sequence of irradiation and delayed-neutron counting continues until a sufficient amount of data has been accumulated or the maximum time limit is reached. The final step in the assay is the calculation of the U-235 content of the sample. The assay value is then available to the operator and the SRP accountancy system.

SRP Materials

The primary material being handled at the SRP reactor fuel fabrication facility is highly enriched uranium (up to 93% U-235). The uranium is alloyed with aluminum and then fabricated into fuel elements. The materials to be assayed by the Shuffler include 1) pure scrap from machining and other parts of the process that may be returned directly to production melts, 2) contaminated scrap and various products from the SRP scrap recovery process, 3) contaminated scrap not recoverable at SRP that is shipped to Oak Ridge for processing, and 4) waste materials without significant U-235 content that are sent to the SRP burial ground.

The materials to be assayed will be packaged in steel cylinders (177.8 mm ID and 304.8 mm high). Standardizing the container size enables the assay to be accomplished more simply with less chance of a container being improperly positioned within the sample assay well. Large items requiring assay will be cut or broken up until they fit into the standard container.

Material Flow and Measurement Points

In the fabrication of fuel elements of highly enriched U-Al alloy, more than 50% of all alloy cast is recycled as scrap. About 90% of this scrap is suitable for direct recycling into the casting process. This material is relatively clean with its composition accurately known from process records. The remaining 10% of the scrap requires additional processing before recycling. Most of this scrap is processed and recovered at SRP. The low-level uranium waste product of the SRP recovery process is presently assayed with a gamma-ray NDA system. The items without significant uranium content are sent to the burial ground.

About one per cent of all the U-Al scrap is not suitable for recovery at SRP and includes floor sweepings, crucible pieces from the casting operations, and air filters. If the U-235 content is below that which is feasible to recover, the scrap is sent to the burial ground. Scrap requiring reprocessing is packaged and shipped to Oak Ridge for recovery. The "Shuffler" will measure most of these items before shipment.

SHUFFLER DESIGN FOR SRP

Neutronics Calculations

Some of the items to be measured by the "Shuffler" could contain as much as 2.4 kg of U-235. With this amount of uranium self-shielding can be significant, especially for thermal neutrons. In order to reduce self-shielding effects, the assay chamber is lined with boral (B_4C) and cadmium to remove low-energy and thermal neutrons while maintaining a penetrating (energetic) neutron flux. Ideally the interrogating neutrons should have energies above several keV so that the resonance and thermal region is avoided and the fission cross section is reasonably independent of the neutron energy. However, to limit biasing contributions through fissions of the isotopes U-234, U-236, and U-238, the interrogation neutron energies should be below where their fission cross sections are appreciable, typically between about a half and one MeV.

The Cf-252 source neutrons have a fission spectrum with the average neutron energy being about 2.35 MeV.[2] To reduce the contribution from the nonfissile isotopes, the Cf-25

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[2] Reactor Physics Constants, ANL-5800 (July 1963):

eutrons are moderated. A series of Monte Carlo studies was made using the LASL MCN code[3] ɔ compare the relative effectiveness of various moderating materials for producing a enetrating interrogation with the least amount of fissioning of the U-234, U-236, and -238 isotopes. Iron (steel) proved to be the most satisfactory choice for meeting the bove criteria when the additional factors of cost, availability, fabrication, and safety ere considered. Neglecting the practical considerations, beryllium was the best choice or lowering the contribution from isotopes other than U-235 and tungsten gave the most enetrating spectrum. Neglecting cost and machinability considerations, nickel is lightly preferred over steel.

A diagram of the assay chamber is shown in Fig. 2. This view is an enlargement of art of Fig. 1 with the material types noted. The moderating/reflecting material is rimarily steel although some nickel is used between the source and the assay chamber. The ungsten piece surrounding the source at the interrogation position is primarily for ersonnel gamma-ray shielding. The voids in the moderating assembly improve the uniformity f the interrogation over the sample length.

The effects of self-shielding are partially compensated for by multiplication within ne sample. For changes in the diameter of the alloy castings the effects of self-nielding and multiplication are nearly compensating. The data in Table I illustrate the ffect; the smaller diameter item gives a higher induced-fission rate per gram because of ess self-shielding but a lower delayed-neutron counting efficiency due to the lower ultiplication. The relative response given in Table I is the product of the fission rate nd the counting efficiency. The uniformity of the response for differing diameters is xcellent and thus variations in the diameter of the ingots will not require a set of tandards or correction factors based upon a separate measurement of the diameter.

TABLE I
Data from the Monte-Carlo simulations of the Shuffler designed for SRP. The quantity in parentheses is the 1-σ uncertainty in the last digit given.

Diameter (cm)	Relative fission rate/ g Uranium[a]	Relative Councint Efficiency[b]	Relative Response
14.00	1.106(19)	0.988(13)	1.004(23)
15.90	1.004(17)	0.992(14)	0.996(22)
17.78	0.980(16)	1.019(14)	0.999(21)

[a] Isotopic composition: ^{234}U-1.2%, ^{235}U-70.0%, ^{236}U-18.9%, ^{238}U-9.9%

[b] Counting efficiency for delayed neutrons including multiplication effects

For cast ingots the mass is proportional to the height, resulting in the low-mass amples being somewhat pancake shaped and the high-mass samples being tall cylinders. This hange in the sample geometry with mass affects the response of the system. For the low-ass samples (pancake shaped) the response per gram rises because the neutrons can interro-ate the sample more readily due to the increased surface-to-volume ratio. On the other and, the response per gram for the largest samples tends to increase slightly because of ultiplication. To compensate for both effects, the neutron-tailoring assembly (see Fig. 2) as designed so the interrogating neutron flux would be slightly lower at the top and ottom of the assay chamber. The flux depression was selected to cancel the increased esponse of short samples at the bottom of the assay chamber and to offset the multiplica-ion present in the heavy samples. Figure 3 shows the relative response of the system ased on Monte Carlo calculations of the interrogation and delayed-neutron counting fficiency. The data displayed indicate a linear esponse to within the accuracy of the alculation (± 3%, 1 σ).

E. D. Cashwell, J. R. Neergaard, W. M. Taylor, and G. D. Turner, "MCN: A Neutron Monte Carlo Code," Los Alamos Scientific Laboratory report LA-4751 (January 1972).

Small variations from linearity could be included in the calibration function or in a correction factor. If the correction factor approach is used, then a measure of the sample height can be obtained from the ratio of delayed neutrons detected by the bottom counters to the number of delayed neutrons detected by the side counters. This ratio decreases as the sample height increases because the fraction of the delayed neutrons detected by the side counters increases.

The accuracy of the measurements can be further improved by either correction factors or internal consistency checks based upon additional data available at the time of assay. Changes in the interrogation neutron flux, such as additional moderation or absorption in the sample that affect the fission rate, are monitored by placing small neutron detectors inside the assay chamber directly viewing the sample. Additional data to be obtained include the sample mass measured by calibrated precision load cells located in the assay chamber.

System Electronics

The electronics package contains the neutron detector power supplies, pulse amplifiers and a microcomputer that records the data and controls the measurement sequence including the source transfer, sample rotation, and load cell weighing. The detector preamplifiers are built into the high-voltage junction boxes attached to the neutron detectors. This location for the preamplifiers was chosen to minimize the noise pickup and thus improve th reliability. The remainder of the electronics except for the interlocks and a control console is contained in a temperature/humidity-controlled rack located just outside of the sample assay room. The electronics are located outside of the assay room to avoid the possibility of contamination. Should an item fail inside the assay room, it will be replaced and the failed component will be disposed of.

A hardcopy output stating the NDA measurement of the U-235 content and its measuremen uncertainty as well as the total mass of the sample is given for each assay. This information is also available to the operator on a large-format video display screen visible through a window in the assay room. A floppy disk storage unit provides a complete archival record for each assay. The detailed data stored on the disk file includes the detector's counts from the He-3 neutron detectors and the flux monitors, temperature, line voltage, time of day and date, the load-cell data, and the sample identification.

System Software

The "Shuffler" software is being developed using Fortran IV rather than machine-dependent assembly language. The software system will then be transferable to most standard computers with a minimum of modifications. The Fortran coding will also facilitate the use of sophisticated algorithms for calibration and calculation of the U-235 mas from the sample measurement.

The microcomputer will be programmed so that the details of the assay will be completely handled by the computer. The operator needs only to enter the sample identification number and even this step could be eliminated if an automatic label reader is adde to the system. The computer controls the assay sequence and performs all calculations an implements the correction factors based upon information obtained during the assay. Once the assay is complete, the data is recorded as noted earlier and the computer informs the operator that the system is ready to assay another sample. If a sample does not assay consistent with the standards, the operator is informed and the inconsistency is recorded for later study. The computer will also inform the operator of minor problems such as neglecting to put the sample in the assay chamber or leaving the assay chamber door open.

Standards and Calibration

During the initial phase of the test and evaluation of the "Shuffler" at SRP, the system will be calibrated with test samples. These items will span the range of uranium loading and be carefully prepared following a predetermined procedure. Once all the tes samples have been analyzed by the "Shuffler," some of them will have their total uranium content and isotopic composition precisely measured by destructive analysis. As the tes and evaluation proceeds, actual scrap and waste materials produced at SRP will be destructively analyzed after having been measured. Any biases will be fully investigate Eventually as experience is gained with the "Shuffler," a complete set of standards and calibration procedure will be developed.

SUMMARY

The "Cf-252 Shuffler," a nondestructive assay (NDA) instrument, will be tested and aluated for the measurement of highly enriched uranium at the SRP reactor fuel fabrica-on facility. The method of neutron interrogation with delayed-neutron detection is lieved to be the most practical solution for NDA of the enriched uranium materials found SRP. Pending a successful evaluation at SRP, the "Shuffler" unit will be used to nitor the transfer of uranium alloys within the plant and to establish an assay value for ste materials going to either disposal areas or recovery operations.

ACKNOWLEDGMENTS

We would like to thank Dr. S. C. T. McDowell and Dr. S. Baloga, Division of Safeguards d Security, Department of Energy, and Dr. R. B. Walton, LASL, for their efforts to itiate and coordinate this test and evaluation program.

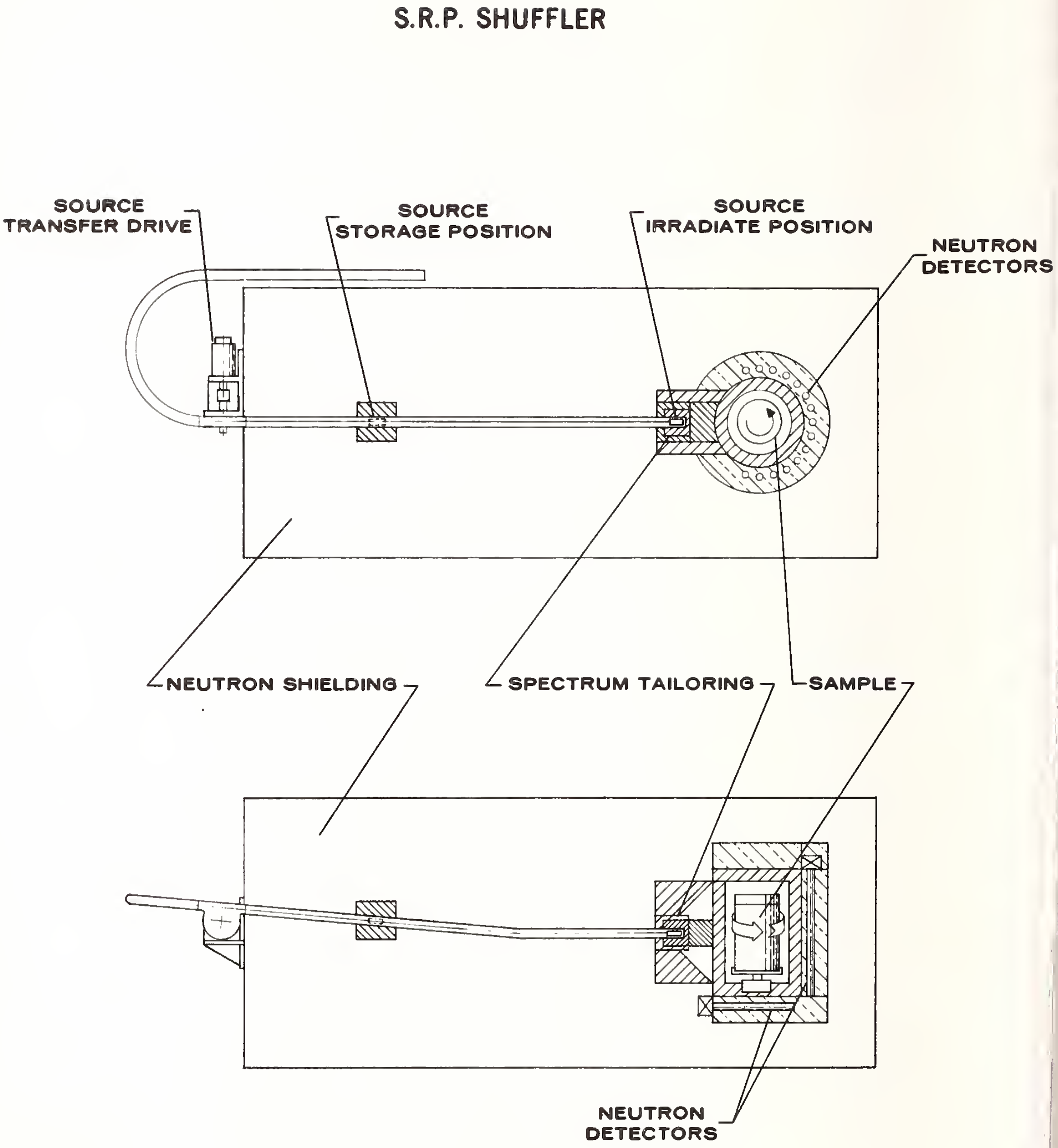

Figure 1. Schematic Diagram of the "Shuffler" Assay System for the Savannah River Plant. A Sample is Shown in the Interrogation-Counting Well.

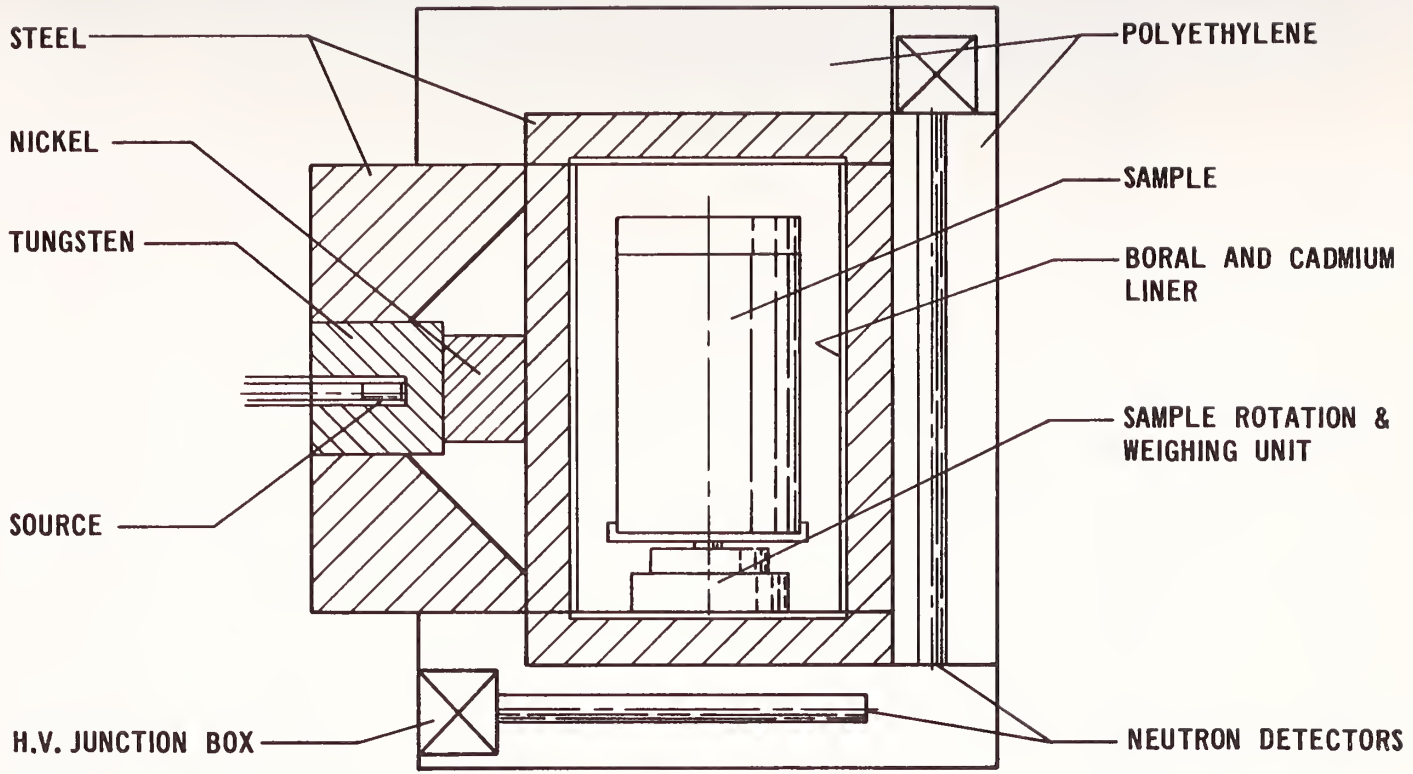

Figure 2. Schematic Diagram of the Interrogation-Counting Well

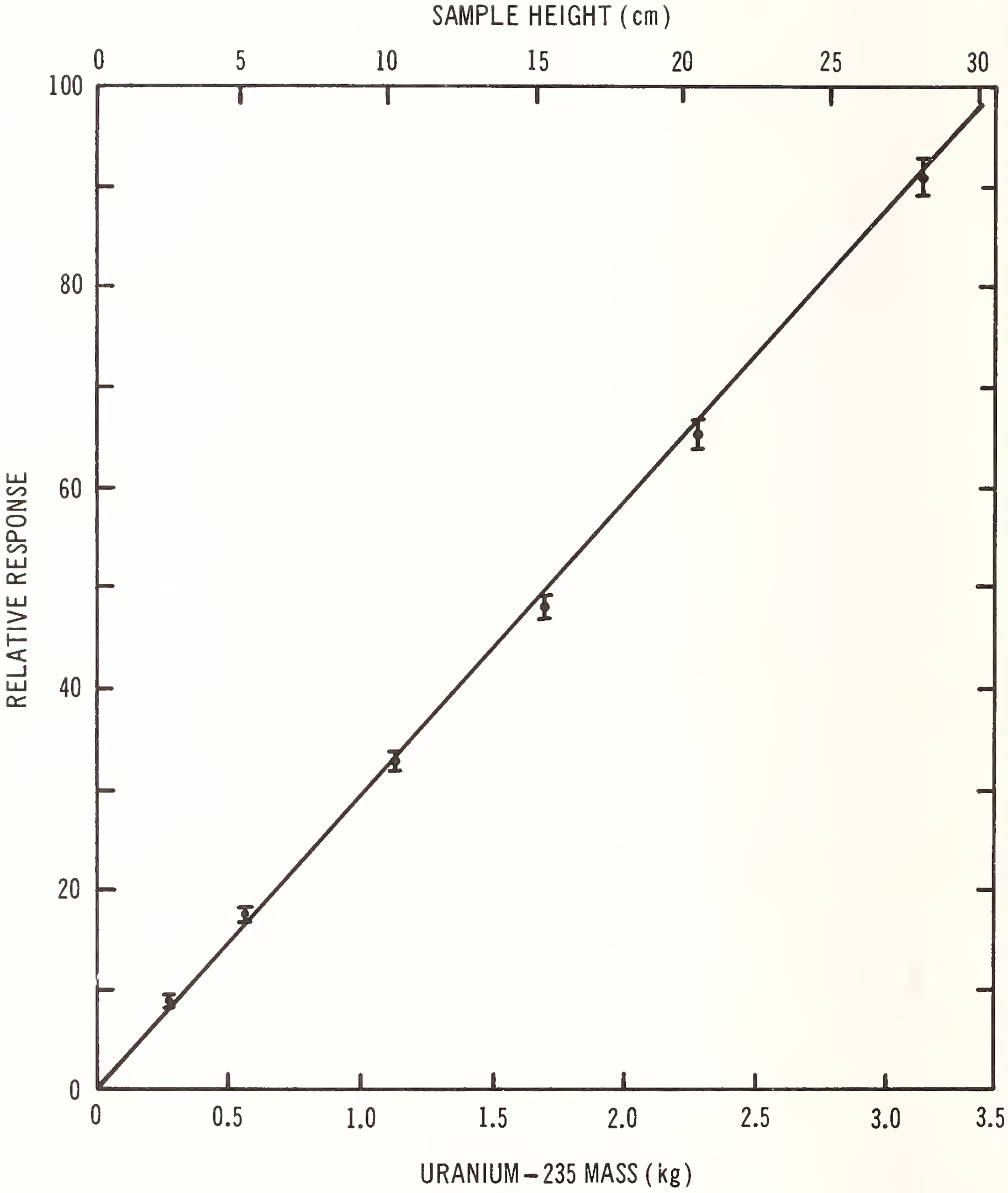

Figure 3. Delayed-Neutron Response as a Function of the U-235 Mass and Corresponding Sample Height.

Gamma Spectrometric Methods for Measuring Plutonium[*]

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ABSTRACT

Nondestructive analyses of plutonium can be made by detecting and measuring the gamma rays emitted by a sample. Although qualitative and semiquantitative assays can be performed with relative ease, only recently have methods been developed, using computer analysis techniques, that provide quantitative results. This paper reviews some new techniques developed for measuring plutonium. The features of plutonium gamma-ray spectra are reviewed and some of the computer methods used for spectrum analysis are discussed. The discussion includes a description of a powerful computer method of unfolding complex peak multiplets that uses the standard linear least-squares techniques of data analysis. This computer method is based on the generation of response profiles for the isotopes composing a plutonium sample and requires a description of the peak positions, relative intensities, and line shapes. The principles that plutonium isotopic measurements are based on are also developed, followed by illustrations of the measurement procedures as applied to the quantitative analysis of plutonium liquid and solid samples.

KEYWORDS: Plutonium analysis; gamma-ray analysis; computer analysis; plutonium safeguards.

INTRODUCTION

The accountability and safeguarding of plutonium as a special nuclear material ntinues to be an important issue. Material balance and control require that an accurate ventory be kept wherever plutonium is processed or handled. As a result, it is necessary have methods for accurately measuring plutonium in its various forms. Not only must the tal elemental amount be determined, but the amounts of the individual isotopes from mass 8 to 242 must usually also be measured. An assay of ^{241}Am is also frequently of interest.

The procedures for making these measurements have traditionally involved a combination two or more destructive chemical methods. Although these procedures have become highly curate and will undoubtedly continue to be a mainstay of the analytical laboratory, they ve the disadvantages of requiring considerable time and effort and of being difficult to plement in-line. For these reasons, nondestructive methods have been sought that might ovide a more timely and more automated analysis.

We have been developing techniques for nondestructive analysis methods using passive ounting techniques by detecting and analyzing gamma rays emitted by or transmitted through plutonium sample. In the following discussions, we will develop some of the bases for hese analyses, described some applications, and present typical results we have obtained.

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[*] Work performed under the auspices of the U.S. Department of Energy by the Lawrence ivermore Laboratory under contract number W-7405-Eng-48.

PLUTONIUM SPECTRA

Measurement Considerations

Taken with a germanium detector, the spectra of plutonium samples are very complex as Fig. 1 shows. All of the isotopes except ^{242}Pu make detectable contributions to the spectrum, but to varying extents and at different energies. The gamma-ray energies and absolute emission rates have been carefully studied and published in previous reports.[1- From a review of these data, one can deduce several important characteristics that are useful for spectral analysis:

- ^{239}Pu exhibits significantly intense peaks over the energy region from 50 to 800 keV.
- The ^{238}Pu and ^{240}Pu isotopes emit relatively few gamma rays, with the most inter ones being of low energy.
- Only about seven or eight energy regions (see Fig. 1) exhibit contribution from more than one isotope.[3,4]
- The energy spacing in some of these regions is such that the peaks overlap seve

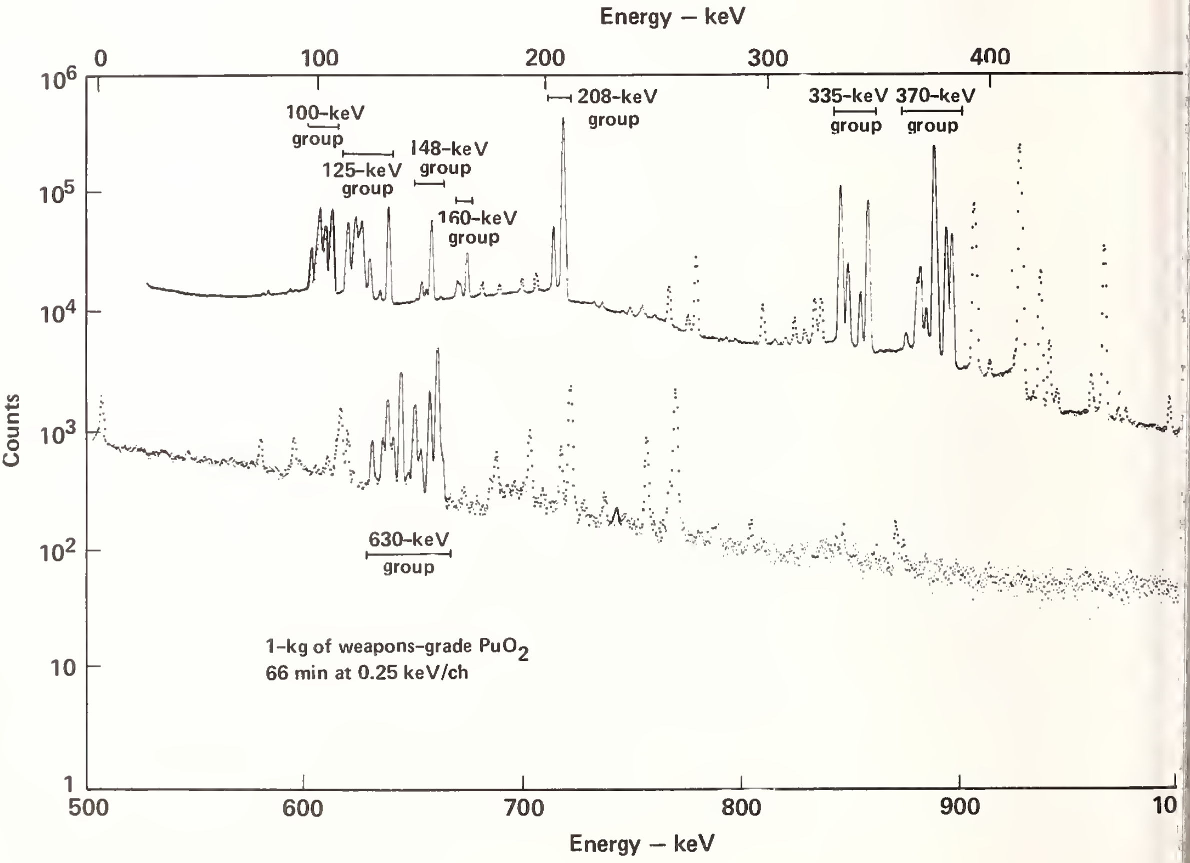

Fig. 1. A typical spectrum of aged plutonium. The intensified peak regions contain contributions from more than one isotope.

These characteristics obviously present some problems for spectrometric analysis. e analyzing them further, we note that gamma-spectrometric analyses are also dependent e physical characteristics of the sample, such as:

- Physical/chemical form (e.g. solution vs solid)
- Age of the material since chemical processing
- Concentration of the plutonium in the sample
- Homogeneity of the sample
- Elements or isotopes contained in the sample
- Isotopic grade of the plutonium

The combination of these physical factors with the gamma-emission characteristics of plutonium isotopes makes it impossible to have a single method or technique that can be to analyze all sample types. Instead, one must tailor the method to the type of urement. For this reason, it is important to establish a foundation of basic data and analysis methodology that, when properly developed and understood, can be modified and according to the prevailing circumstances.

Spectral Analysis Techniques

Although the plutonium gamma-ray spectra are quite complex, some of the isotopes it single, well-resolved peaks. The amount X_k of such an isotope in a sample can be mined by integrating to find the net area of a given peak, A_j, and dividing by the ing efficiency $\varepsilon_{j,k}$. That is

$$X_k = A_j/\varepsilon_{j,k}, \tag{1}$$

e

$A_j = \sum(y_i - b_i)$,

y_i = counts in channel i,

b_i = background counts in channel i.

ore than one gamma ray of a given isotope or if more than one isotope contributes to same peak, a more generalized expression can be written as follows

$$A_j = \sum_{k=1}^{m} \sum_{j=1}^{n} \varepsilon_{j,k}\, X_k \,. \tag{2}$$

As long as the equations do not form an ill-conditioned set, they can readily be ed by the method of linear least squares.

Some of the plutonium isotopes, however, can only be determined from spectral regions happen to be quite complex. To resolve the overlapping peak multiplets in these ons, we must first have a description of the peak shape. Although the peaks in anium-detector spectra are principally Gaussian in shape, some tailing does occur, icularly on the low-energy side. Therefore, the algorithms that we have formulated to the data in a peak region, such as shown in Fig. 2, usually include a central Gaussian onent, a background continuum, a short-term tailing and sometimes a longer-term tailing.

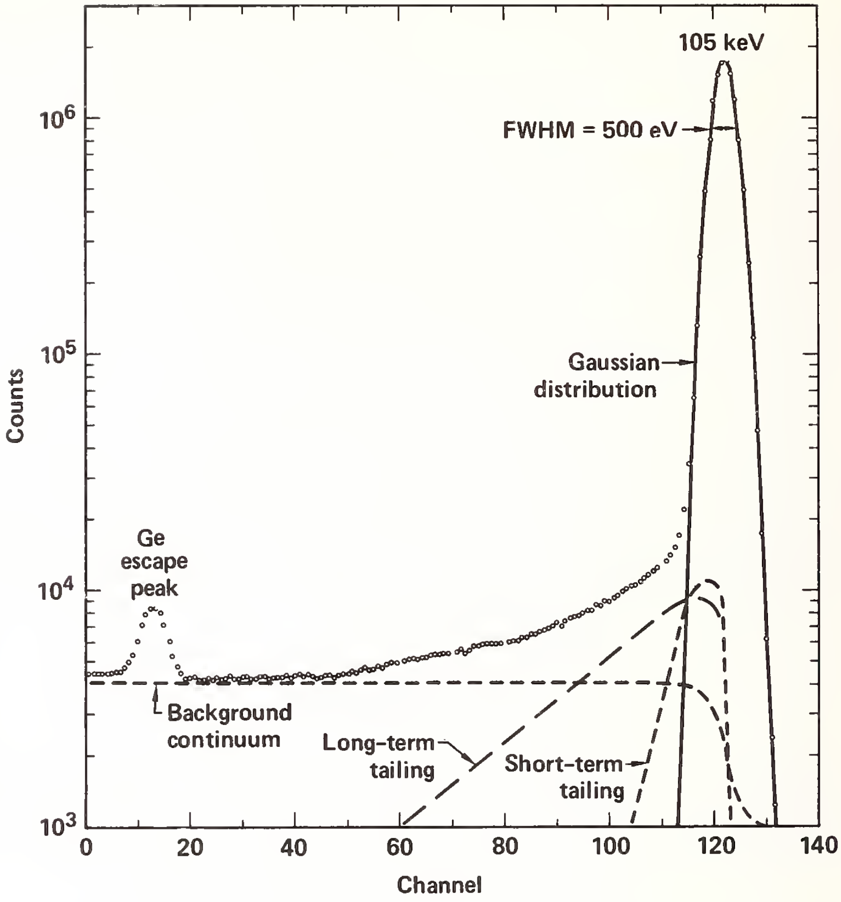

Fig. 2. Gamma-ray peak shape showing the Gaussian and tailing portions of the response.

We have found that after subtraction of the background continuum, the following algorithm adequately describes the component elements of a peak:

$$y_i = y^0 \exp\,[\alpha(x_i - x^0)^2] + T(x_i), \tag{3}$$

where

y_i = net counts in x_i,

y^0 = peak height at the peak position x^0,

α = peak-width parameter,

and

$T(x_i)$ = tailing function.

The tailing function is given by:

$$T(x) = [A \exp\,(Bx) + C \exp\,(Dx)]\,[1 - \exp\,(0.4\alpha x^2)]\delta \quad , \tag{4}$$

where A exp (Bx) accounts for the short-term tailing and C exp (Dx) accounts for the lon term tailing. Also, A and C are tailing-amplitude parameters, B and D give the slope of the tailing, and $x = x_i - x^0$. The final term involving α reduces the effect of T(x) to at the peak position, and δ, which has a value of 1 or 0, removes the effect of T(x) positive values of x.

Although Eq. (3) is useful for describing gamma-ray peak shapes, it does not quately describe the observed distribution of K-series x rays associated with the heavy ents.[5] Because of the short lifetime of K-shell vacancies, the Lorentzian energy dis- ution of the emitted x rays has a FWHM of about 100 eV. When this distribution is con- ted with the instrumental dispersion, the resulting peak shape, as shown in Fig. 3, is stantially different from that of an equivalent-energy gamma ray.

The data values, Y_i, in an overlapping peak multiplet can be considered to be a linear ition of the appropriate contribution from each peak j so that

$$Y_i = \sum_{j=1}^{n} y_{j,i} = \sum_{j=1}^{n} y_j^0 \cdot f(x_i, \text{ shape parameters}). \tag{5}$$

Techniques have been developed for characterizing many of the shape parameters used the above algorithms.[6] However, these techniques were first used in generalized computer grams, which usually also assume that the peak positions x^0 and the peak amplitudes y^0 always unknown and therefore must be considered as free, rather than fixed, parameters. se codes must therefore treat Eq. (5) as a set of nonlinear equations and resort to some rative method to solve them for the unknown parameters.

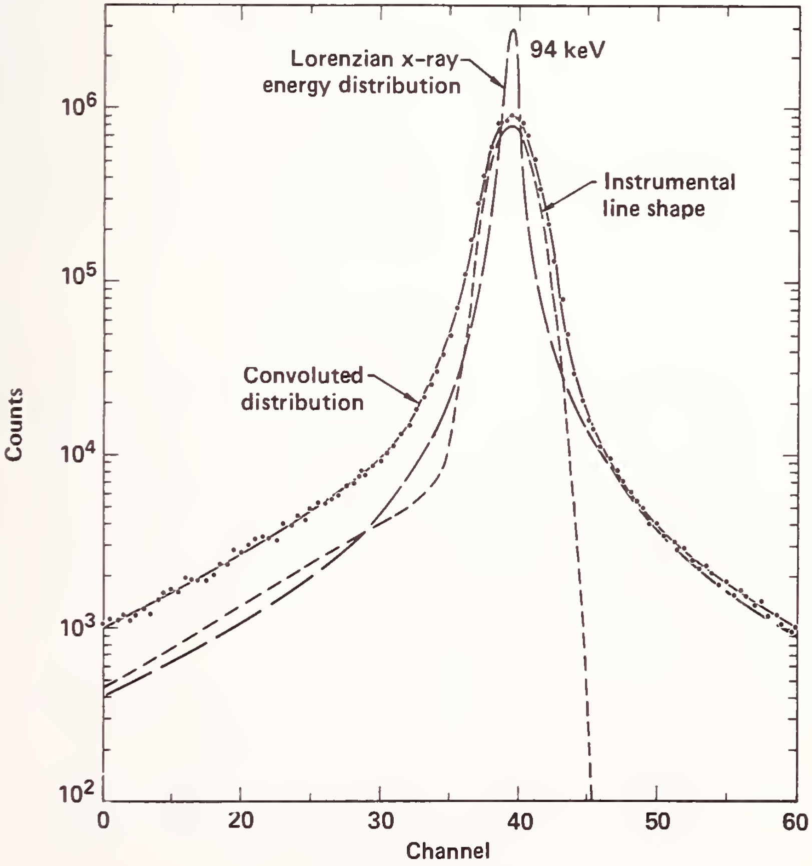

Fig. 3. Detail showing the convolution of the intrinsic x-ray distribution with the instrumental line shape.

However, for a spectrum resulting from a pure plutonium sample, both the exact ga ray energies and the relative intensities can be predetermined for each of the isotopes interest using tables that report the gamma emissions of plutonium and its daughter products.[3] Therefore, once an energy scaling has been established, it is possible to c late the exact position x^0 where each of the peaks is expected to appear in a spectrum. This means that all of the parameters in the exponentials of Eqs. (3) and (4) can be pr determined and therefore held fixed in the fitting process. The resulting set of equat expressed by Eq. (5) then become linear in form and can be solved by a standard least-squares method.

The number of free parameters can be further reduced by realizing that many of th peaks in a complex grouping might belong to the same isotope. Therefore, the relative intensities y_j^0 for each isotopic component k in the group can be predetermined and the composite spectrum profile can be expressed by:

$$Y_i = \sum_{k=1}^{m} \sum_{j=1}^{n} y_{i,j,k} \; . \qquad (6$$

This means that component response spectra can be generated from known peak positions a relative intensities, thereby reducing the number of unknown parameters to the number o isotopic components. This procedure is illustrated in Figs. 4 and 5. Figure 4 shows t 94- to 104-keV response spectrum that can be generated from the gamma and x-ray peaks resulting from the ^{239}Pu component. Response profiles can be similarly calculated for of the isotopes that contribute to this region, as shown in Fig. 5. When these spectra properly normalized, they can be fitted by linear least squares to the observed composi spectrum to yield the amounts of the component they represent.

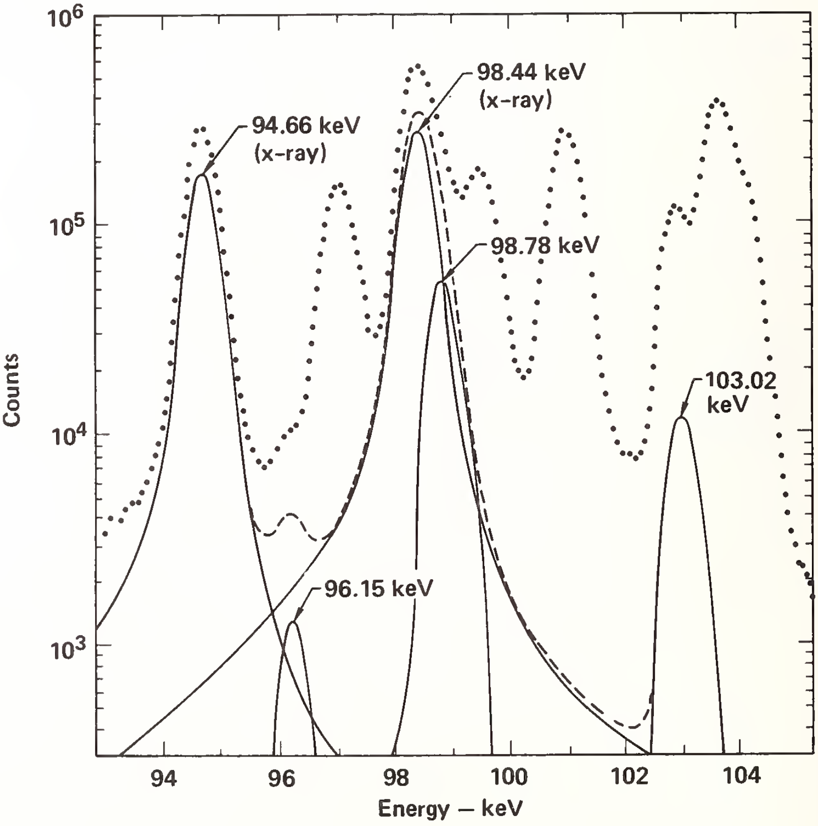

Fig. 4. The response spectrum of ^{239}Pu in the 94- to 104-keV region. This spectrum can be calculated from known energies and intensities of the five x rays and gamma rays contributing to this region.

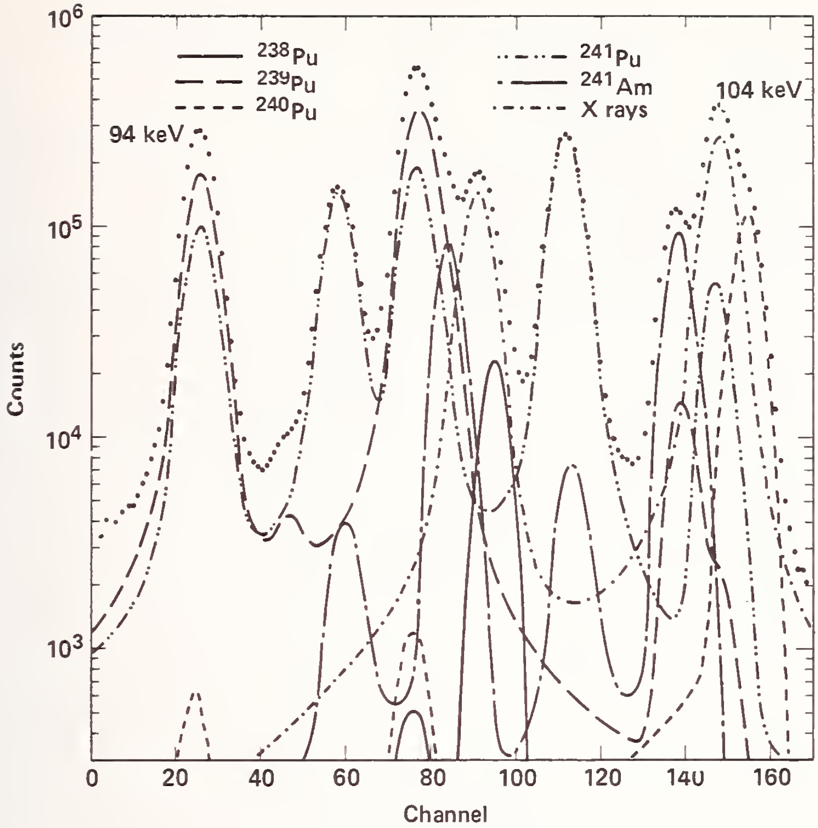

Fig. 5. The 94- to 104-keV region showing the response spectra of the six plutonium isotopes contributing to this region. Each isotope is represented by one or more radiations, as illustrated in Fig. 4.

One additional feature should be noted here. Equations corresponding to integrated
le peaks, as expressed in Eq. (2), can be added to the set of equations expressed by
(6), provided the equations are appropriately normalized and weighted. Figure 6 illus-
es the constitution of a matrix of coefficients for such a mixed set of equations.

A complete and quantitative measurement of the isotopes requires that the efficiency
ficients and normalization factors be carefully calibrated. Frequently, however, it is
necessary to determine the ratios of the plutonium isotopes. Such ratios can be easily
ulated without extensive calibrations, provided that for each pair of isotopes two or
gamma rays of similar energy, but arising from the different isotopes, can be found and
rately measured. For example, the isotopic ratio A/B can be given by:

$$A/B = \frac{I_1\ t_A}{\varepsilon_1\ P_1}\left(\frac{I_2\ t_B}{\varepsilon_2\ P_2}\right)^{-1} = \frac{I_1}{I_2}\,\frac{\varepsilon_2}{\varepsilon_1}\,\frac{P_2}{P_1}\,\frac{t_A}{t_B}\ , \qquad (7)$$

e

I_1, I_2 = peak intensities of the gamma rays arising from isotopes A and B, respectively,

ε_1, ε_2 = counting efficiencies for the respective gamma rays,

P_1, P_2 = the gamma yields or branching probabilities of the respective gamma rays,

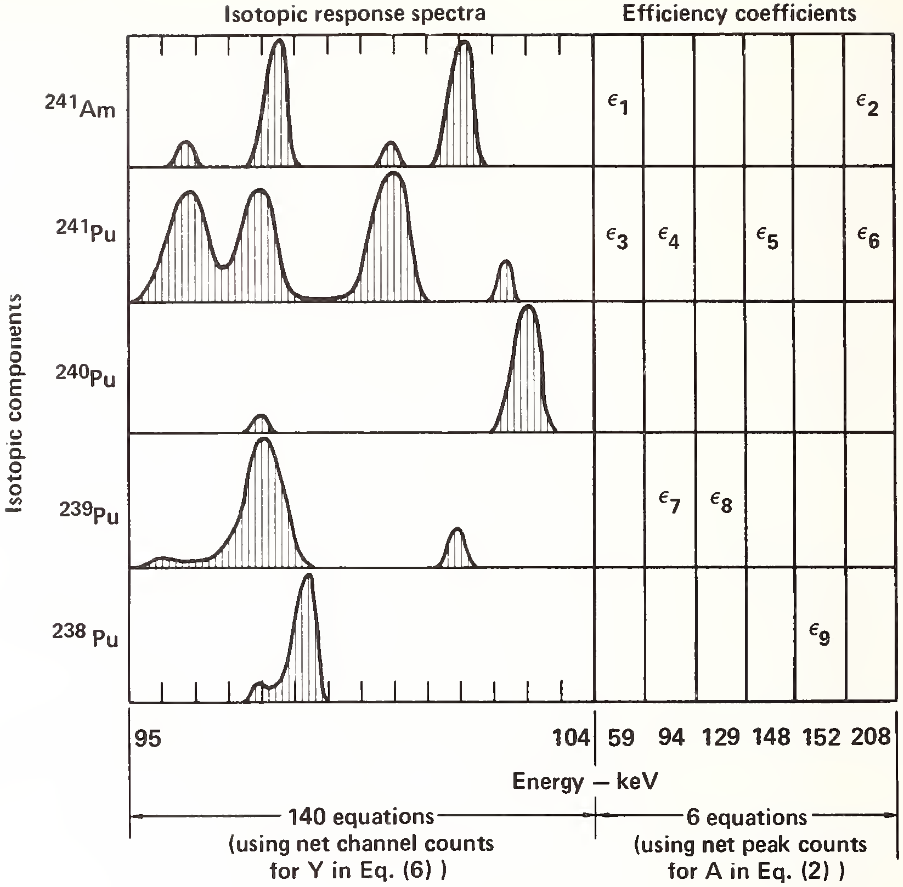

Fig. 6. Illustration of a heterogeneous set of equations to be solved for unknown isotopic abundances. Some of the equations are set equal to the net peak counts while others are equated to the net channel counts.

and

t_A, t_B = the respective half-lives for A and B.

Although it might not be possible to obtain accurate values of ε_i and P_i individual it is possible to obtain accurate ratios over a small energy range. The half-lives are well known, and therefore the accuracy of the calculated isotopic ratio is largely limite by the precision with which the peak intensities I_i can be measured.

Isotopic ratios can be calculated from a grouping of resolved peaks by multiplying $\varepsilon_{j,k}$ in Eq. (2) by $P_{j,k}$. A program called RATIO was written to calculate isotopic ratios using data from the 94- to 104-keV region. This program first computes response spectra each of the isotopic unknowns using peak-shape information, library branching intensities the detector-efficiency curve, and some estimated physical characteristics of the sample its containment. Because the efficiency ratios $(\varepsilon_i/\varepsilon_1)$ can only be estimated, an additio parameter is allowed to be free. The coefficients of this unknown are simply the channel counts Y_i multiplied by the channel value. When this profile is included in the fitting process, the effects of small residual efficiency disparities are effectively removed. T effects of this process are shown in Fig. 7.

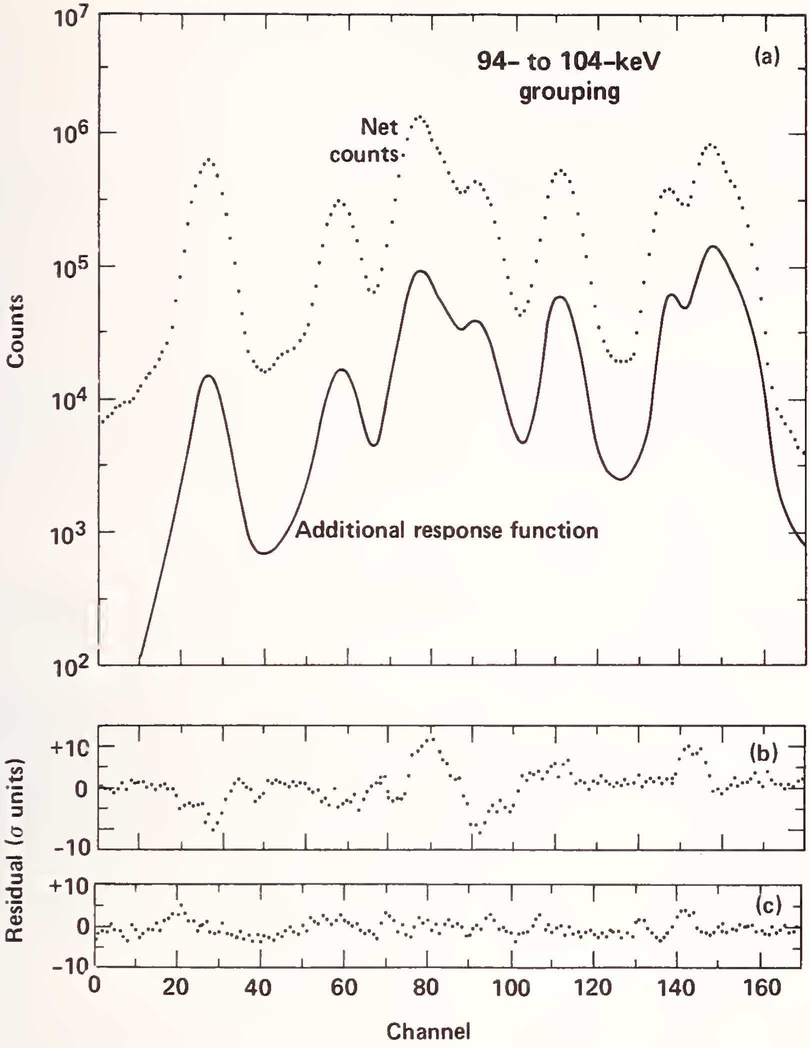

Fig. 7. Using the additional response function (a) in the fitting process lowers the residual efficiency disparities. Part (b) shows the residual spectrum without the additional function; (c) shows the residual spectrum when the additional function is included.

There are about eight peak groupings from which isotopic information can be obtained. se have been studied in some detail using computer simulation techniques.[4] Because most he groupings do not contain peaks from all the plutonium isotopes, it is useful to ine several groups so that all of the ratios can be accurately established. To do this, tart by modifying Eq. (2) so that it takes the following form:

$$A_j = \sum_{k=1}^{m} \sum_{j=1}^{n} P_{j,k} E_\ell X_k , \tag{8}$$

re E_ℓ = counting efficiency for the group.

To obtain the isotopic ratios with respect to one component, we can write Eq. (8) a

$$\frac{A_j}{E_\ell X_1} = \sum_{j=1}^{n} P_{i,j} + \sum_{k=2}^{m} \sum_{j=1}^{n} P_{j,k} \left(\frac{X_k}{X_1}\right) . \qquad (9)$$

If we let $R_k = X_k/X_1$ and generalize the above equation using s different peak groupings, obtain

$$\sum_{j=1}^{n} P_{j,1} = \sum_{\ell=1}^{s} \frac{A_j}{E_\ell} X_1 - \sum_{k=2}^{m} \sum_{j=1}^{n} P_{j,k} R_k . \qquad (10$$

From this equation, we see that one additional degree of freedom is required for e new grouping that is added. The set of equations can be put partially or totally into a response-spectrum format, as discussed earlier, rather than in the peak-area form shown Eqs. (8)-(10).

APPLICATION AND RESULTS OF THESE TECHNIQUES

As we have indicated, the application and expected results of gamma spectrometric methods cannot be divorced from a consideration of the physical and chemical characteris of the sample. A first convenient division is to consider plutonium to be either in a solution or in a solid.

Plutonium in Solution

Plutonium in solution form is handled in many places and will be the principal for in reprocessing facilities. The design of counting cells and the method of counting and spectral analysis depends on such factors as time since chemical processing occurred, th concentration of the solution, the isotopic grade, and the presence of foreign activitie Recently processed solutions containing ^{238}Pu, ^{239}Pu. ^{240}Pu, and ^{241}Pu exhibit intense p at low energies. As a result, relatively short counting periods (10-20 min) can provide accurate results. Some typical results are shown in Table I.

Solutions that have aged several days since chemical purification rapidly grow in content and therefore require a different procedure of spectral analysis. The computer analysis program is somewhat more complex, and a longer counting period is generally required. Typical analysis results for such samples are also shown in Table I.

Table I. Precision of plutonium isotopic-ratio measurements by gamma-ray spectrometry f reactor-grade plutonium solutions.

Isotope	Abundance, wt%	Precision (1σ), %[a] Recently separated solution	Aged Solution
^{238}Pu	0.230	0.46	0.44
^{239}Pu	76.06	0.07	0.07
^{240}Pu	19.09	0.26	0.26
^{241}Pu	2.98	0.45	0.23
^{241}Am	~0.17	—	0.38

[a] Values obtained from ten or more replicate analyses.

Solution isotopic analyses of weapons-grade plutonium samples are continuously made the Savannah River Plant and at Lawrence Livermore Laboratory by counting 10-ml portions a special counting vial. Also, we have performed several experiments at the Allied eral Nuclear Services plant[8,9] to demonstrate the feasibility of using gamma spectrometric hods for in-line measurement. A dual-cell system, schematically represented in Fig. 8, designed to permit both direct counting of the gamma rays emitted by the isotopes in ution and a total plutonium-concentration measurement. The latter is performed by erving the differential attenuation of two transmitted gamma rays, one on either side of K-shell absorption edge of plutonium. Figure 9 shows an assembly of the experimental aratus that is now being tested. Although the experiments are not yet completed, the liminary results are encouraging.[7,9]

Plutonium in Solids

The analysis of plutonium in solid samples by gamma spectrometry presents additional ficulties. Some problems here are controlling or defining the counting geometry, severe f-attenuation of the gamma rays by the sample, and potential sample inhomogeneity.

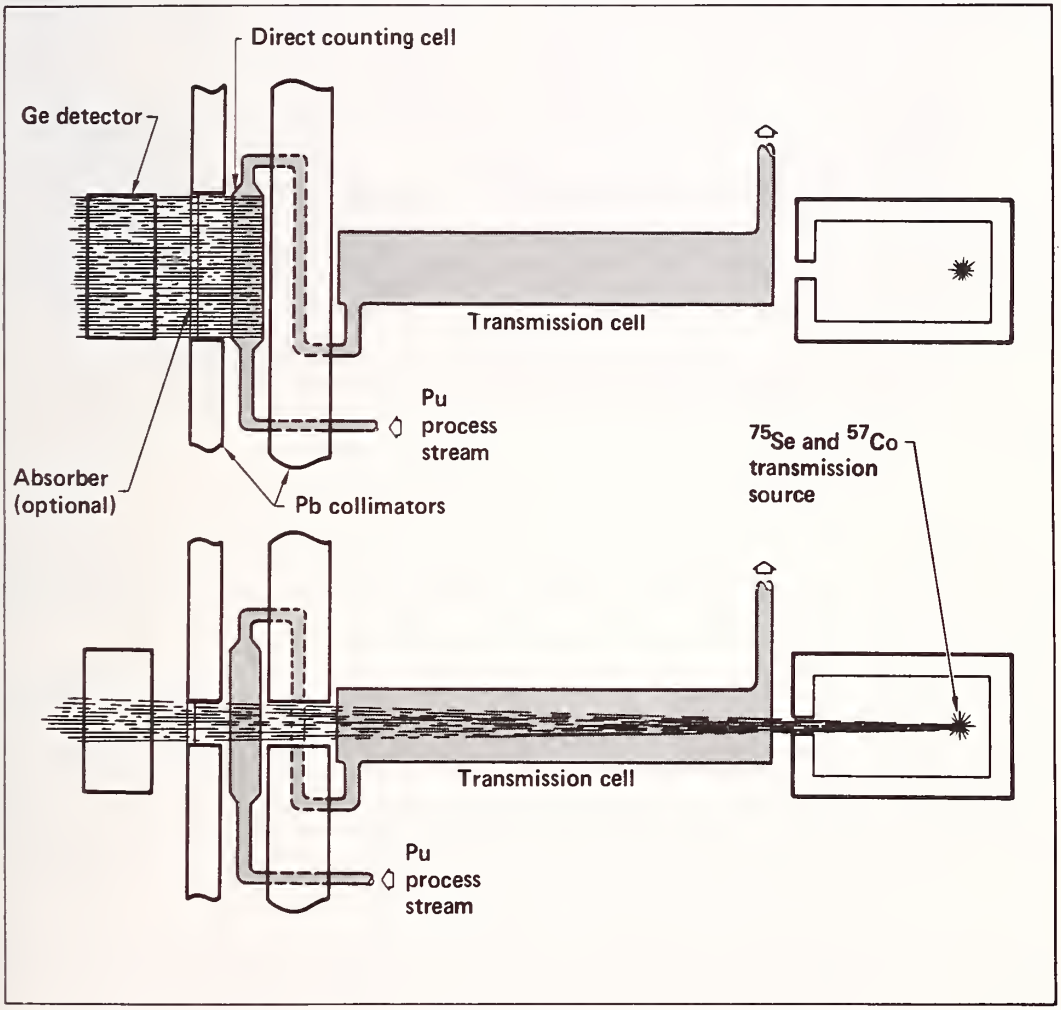

Fig. 8. Schematic drawing of the experimental arrangement used in a gamma-ray absorptimeter. In the top drawing, the Ge detector records only the natural radioactive gamma rays emitted by the plutonium solution from the thin front cell; this data yields the plutonium isotopic distribution. In the bottom, the Ge detector records predominantly the highly collimated ^{75}Se and ^{57}Co gamma rays that pass through the solution in the long transmission cell; this data is used to determine the plutonium concentration.

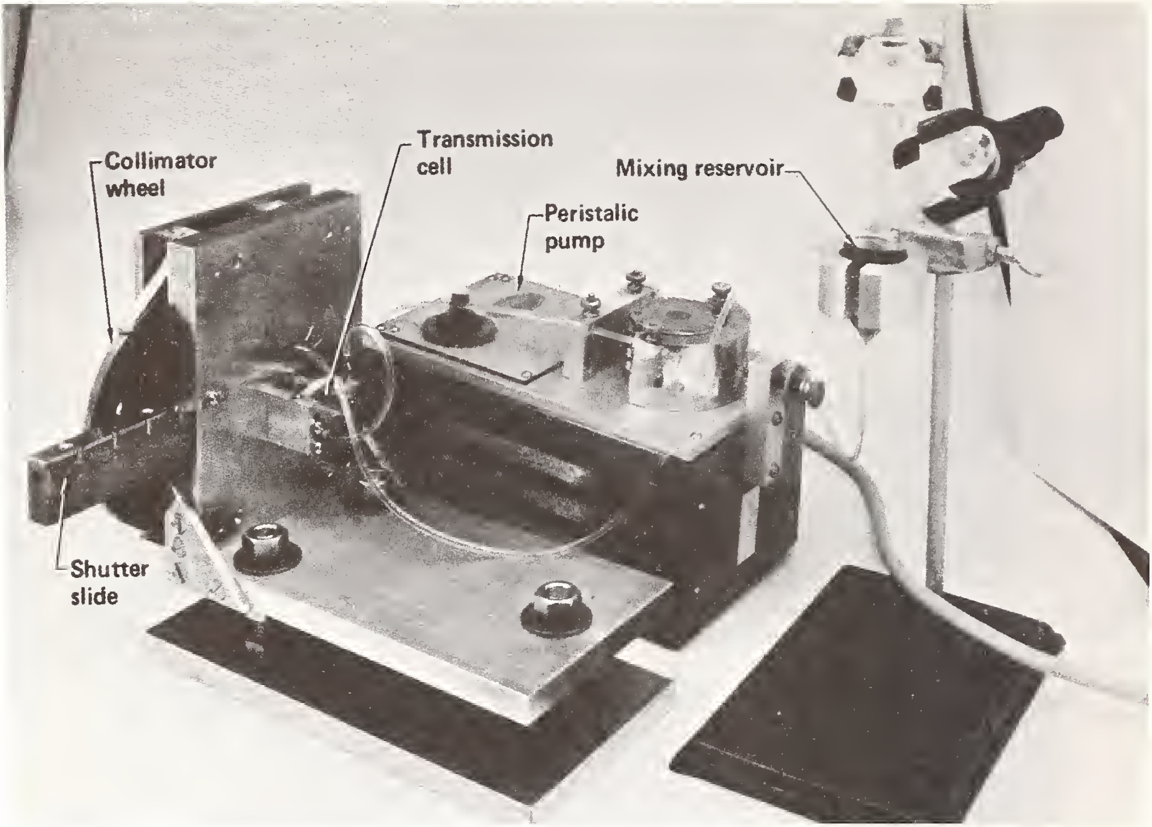

Fig. 9. Photograph of experimental set-up illustrated by Fig. 8. The set-up simulates in-line measurement of plutonium streams. The arrangement is designed to accommodate both a direct measurement of the solution and a K-edge differential-attenuation measurement. The transmission source is not in place.

One analysis method that overcomes most of these problems combines gamma-ray spectrometry with calorimetry. The former provides isotopic-ratio data and the latter measures total power production of the sample. Because both measurements are nondestructive, quantitative analyses can be made without breaching the containment of the sample.

This method has been implemented at Lawrence Livermore Laboratory for the routine assay of 1- to 2-kg lots of plutonium oxide whose isotopic content is about 93% ^{239}Pu. We obtain the low-energy gamma spectrum by rotating the container in front of a small, 1-cm^3 high-resolution germanium detector, as shown in Fig. 10. We use the program RATIO, mentioned earlier, to calculate the isotopic ratios from data found in the 94- to 104-keV region of the spectrum (see Fig. 5). The program generates component response spectra for ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am, for alpha-induced plutonium x rays, and for small efficiency disparities over the region being fitted (see Fig. 7).

Table II compares results produced by RATIO with mass-spectrometry results. Although counting periods of several hundred minutes are generally used, reasonably good precisions can be attained with much shorter counting periods, as Table III indicates.

The procedure, used in RATIO, of analyzing only the 94- to 104-keV group is adequate for weapons-grade samples, where the ^{239}Pu content is high. To obtain sufficiently accurat isotopic ratios for reactor-grade materials, we will have to expand the program, using Eq. (10), so that more groups will be simultaneously considered. We might also need a two-detector system. We will still need a small but very high-resolution detector for the 94- to 104-keV region, but we will also need a larger, more efficient detector to obtain a sufficient counting rate in the 300- to 400-keV region.

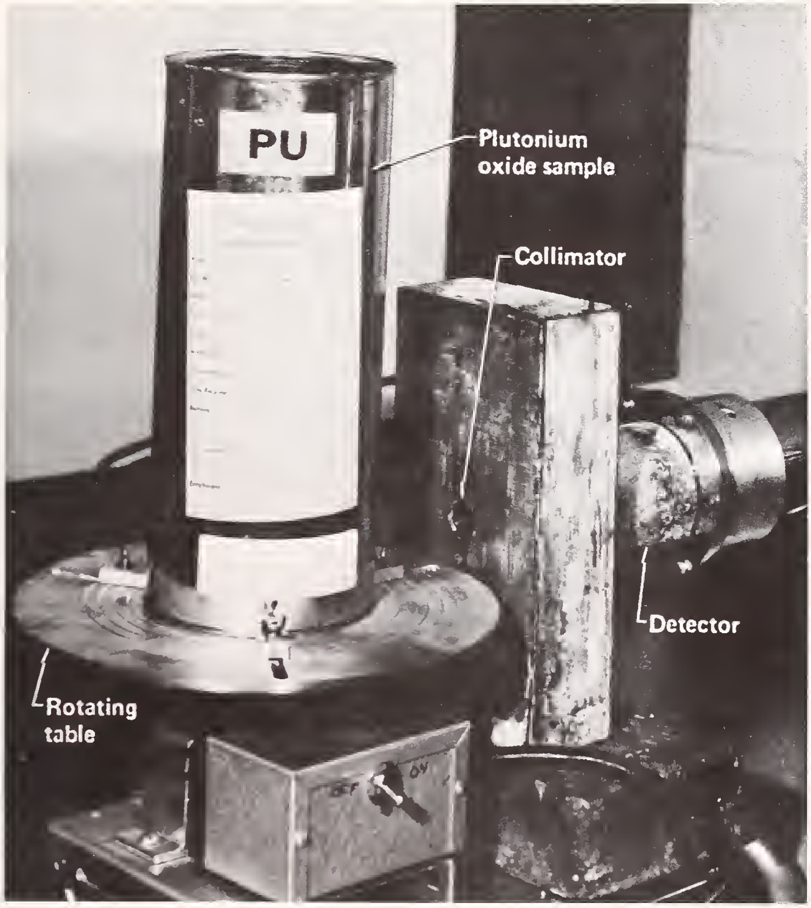

Fig. 10. Simple arrangement for measuring the plutonium isotopic ratios of plutonium-oxide samples.

Table II. Standard deviation between gamma-spectrometry isotopic-ratio results and mass spectrometry results.

Isotope	Approximate abundance, wt%	Relative standard deviation, %	
		Solutions[a]	Solids[b]
^{238}Pu	0.01	2.5	2.5
^{239}Pu	93.5	0.03	0.03
^{240}Pu	6.0	0.33	0.62
^{241}Pu	0.5	0.88	1.3
^{241}Am	0.01-0.2	2.7	4.0

[a] Comparison of 24 analyses.

[b] Comparison of 7 analyses.

Table III. Precision of plutonium isotopic-ratio measurements using the RATIO program for analyzing weapons-grade plutonium oxide.

Isotope	Abundance, wt%	Precision (1σ), %,[a] for various counting perio			
		4 min	40 min	120 min	600 mi
^{238}Pu	0.01	5.1	3.0	2.0	0.7
^{239}Pu	93.7	0.17	0.05	0.03	0.013
^{240}Pu	5.8	2.3	0.9	0.5	0.2
^{241}Pu	0.44	1.2	0.6	0.2	0.1
^{241}Am	0.1	2.5	0.9	0.4	0.4

[a] Values obtained from ten or more replicate analyses.

CONCLUSIONS

We have established a good foundation of basic spectrometric data for the gamma emissions and decay properties of the plutonium isotopes and their attendant daughter products. We have also made progress in developing techniques and algorithms for analyzing the spectral data and in forming a methodology that allows the analysis programs to be tailored to the type of sample and measurement that is to be made. Although additional developmenta work will be required, we are now at a point where gamma spectrometric techniques can be used for the routine measurement of plutonium in several forms.

FOOTNOTES

[1] R. Gunnink and R. J. Morrow, Gamma-Ray Energies and Absolute Branching Intensities for ^{238,239,240,241}Pu and ^{241}Am, Lawrence Livermore Laboratory, Rept. UCRL-51087 (1971).

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Rapid Nondestructive Plutonium Isotopic Analysis*

by

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ABSTRACT

Methods for plutonium isotopic measurements have been evaluated for nuclear safeguards inventory verification. A mobile, real-time, nondestructive assay, gamma-ray spectrometric measurement system has been assembled, moved and operated at several nuclear storage facilities to perform rapid, real-time plutonium isotopic measurements on Pu metal, Pu nitrate and Pu oxide.

KEYWORDS: Nondestructive analysis (NDA); plutonium isotopes; gamma-ray spectrometry; x-ray spectrometry

INTRODUCTION

At Battelle, Pacific Northwest Laboratories methods for performing plutonium isotopic measurements have been evaluated for use in verifying nuclear material safeguards inventories. Since effective verification requires the on-site analysis of a significant fraction of the total inventory in a relatively short time period, rapid analytical methods are necessary. Methods of calculating plutonium isotopes by gamma-ray and x-ray spectrometry have been reported by several investigators,[1-6] but these methods have previously been used primarily for the nondestructive analysis (NDA) of laboratory nuclear material samples in which analysis times could be long and precise results were required. Nuclear material inspectors need to make equivalent measurements at nuclear storage facilities but are limited by time and the large number of items to be measured. To meet this need, plutonium isotopic measurements could be used along with other NDA measurements, such as neutron counting and gross weight, to verify the nuclear material content of items selected by the inspectors. These measurements need to be made at the nuclear material storage facility since it is impractical to move large quantities of nuclear material to the laboratory to make verification measurements. This paper describes rapid plutonium isotopic measurement techniques using gamma-ray and x-ray spectrometry that can be used for on-site nuclear inventory verification.

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EQUIPMENT DESCRIPTION

high-resolution gamma-ray spectrometer interfaced to a minicomputer was used for experiments. The spectrometer is part of a mobile, real-time nondestructive assay system, which with data processing and data storage equipment, is mounted in a lly constructed vehicle. The nuclear material detection equipment is transported in hicle and is then moved into the nuclear material vault area to perform the measure- while the data processing and storage equipment, a multichannel analyzer and analog- ital converted (ADC), remain in the vehicle. Interfaced to the computer, the analyzer controlled remotely from a portable terminal located in the nuclear material storage ith the detector. This system has been described in other reports.[7]

he measurements were made with a planar germanium detector with a 500 mm^2 active area mm thick and a resolution of 560 eV for 122 keV gamma-rays. For some of the measure- the detector was operated 70 m away from a multichannel analyzer and ADC, and the onal cable between the ADC and detector amplifier reduced the resolution at 122 keV eV. This resolution loss did not significantly interfere with the plutonium isotopic ements. The detector was operated with a gain of 0.075 keV/channel and the count rate pt at 5000 counts per sec or less. The low-energy detector response was reduced by g absorbers consisting of 0.02 cm of copper and 0.15 cm of cadmium between the tor and the sample.

coaxial germanium detector 43 mm long with a resolution of 980 eV at 122 keV was used asure the higher energy gamma-ray spectrum. When this detector was operated with 50 m ole between the ADC and detector amplifier, the 122 keV resolution dropped from 960 eV 30 eV.

The computer system located in the mobile vehicle consists of a PDP-11, 32K word ter, dual RK05 disk drives, terminal and electrostatic printer. The system is also faced with the NDA equipment. Gunnink developed the data analysis technique we ted to evaluate for rapid plutonium analysis.[8-10] Originally, the computer code for ata analysis was written in Fortran II to run on a 12-bit, 28K word minicomputer faced to a disk storage device. For these measurements, it was modified to run on the 1 16-bit, 32K word computer using Fortran IV and the RT-11 operating system supplied gital Equipment Corporation (DEC). The Fortran language and system library routine ied by DEC were used for all program modifications. Since dual disk drives were able on our system, we had ample disk storage for the operating system, programs, tor calculation data, raw spectral data and calculated results.

Two of Gunnink's data analysis methods were evaluated.[11,12] The first method generates ponse function for each of the components of the 94 to 104 keV peak multiple from nium, americium and alpha-induced x-rays. The response functions are fit by a least- es method and the plutonium isotopic composition is calculated. This method requires the sample matrix and material between sample and the detector be well known.

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The second method calculates the plutonium isotopics from ratios of selected adjacent gamma-ray peak areas. The computer code developed by Gunnink will calculate selected peak areas and unfold selected peak multiples by describing the fundamental peak shapes. If the ratios listed in Table I are measured and the mass fraction of ^{238}Pu + ^{239}Pu + ^{240}Pu + ^{241}Pu = 1, the four equations with four unknowns can be solved to yield the plutonium isotopic abundance. The computer code to automatically calculate the selected peak areas and plutonium isotopic ratios and reduce these to plutonium isotopic abundance has been written.

TABLE I. Peak Pairs Used for Pu Isotopic Calculations from Gamma-ray Spectra

Nuclide Ratio	Gamma Energies (keV)	Factors to Convert Peak Area-ratios to Atom Ratios
^{238}Pu/^{241}Pu	152.8/148.6	1.183
^{239}Pu/^{241}Pu	208.0/203.5	1585.
^{240}Pu/^{241}Pu	160.3/164.6	50.7

The computer time required to run either program is from 2 to 4 minutes, depending on how many iterations are required for the least squares fit to converge to the desired precision.

EXPERIMENTS

Several investigators have reported branching intensities and gamma-ray energies fo ^{237}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{241}Am.[13] Since ^{242}Pu has no gamma-rays associated with its decay, it cannot be measured by gamma-ray spectrometry. Table I lists the plut isotopic ratios and the gamma-ray energies of the peaks used in the isotopic calculation Table I also lists the factors used to convert the peak area ratios to plutonium atom ratios. These factors are the gamma-ray intensity ratio divided by the ratio of the nuclide decay constants. This method of plutonium isotopic computation was suggested by Parker and Reilly,[14] but the gamma-ray intensities and decay constants are from the work by Gunnink.[15]

Tables II through X summarize the various experiments performed to compare the plutonium isotopic computation methods. The National Bureau of Standards (NBS) SRM-946 plutonium standard was counted 9 times for 200 seconds and the plutonium isotopic abunda was calculated from the 100 keV spectral region and by the gamma-ray peak pair method (Table II). The large uncertainty in the ^{240}Pu estimate is caused by the ^{241}Pu interfer at 160 keV peak. The gamma-ray branching intensity ratio for the 159.9/164.6 keV peaks from ^{241}Pu is 0.1488.[16] Since the 160.28 keV ^{240}Pu peak cannot be resolved from the 159 ^{241}Pu peak, the 164.6 keV ^{241}Pu peak area must be used to correct the 160 keV peak area for the ^{241}Pu interference. For the NBS SRM-946 4.17% ^{241}Pu standard, about 70% of the peak at 160 keV is due to the ^{241}Pu interference in the ^{240}Pu measurement. The high standard deviation of 2.39 for the ^{240}Pu estimate reflects the uncertainty in the 160.28 ^{240}Pu area estimate.

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TABLE II. NDA Plutonium Isotopics of NBS SRM-946 Derived from Gamma-ray Peak Pair Ratios

	Weight Percent			
200-Second Count	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu
1	0.239	84.56	10.68	4.06
2	0.217	87.86	7.39	3.97
3	0.230	88.69	6.44	4.07
4	0.209	83.80	11.24	4.08
5	0.229	89.10	5.83	4.28
6	0.231	85.18	9.90	4.12
7	0.262	81.76	12.56	4.84
8	0.236	83.88	11.26	4.05
9	0.239	84.46	10.68	4.06
Mean	0.232	85.49	9.55	4.17
Std. Dev.	0.015	2.50	2.39	0.26
NBS Value	0.246	83.05	12.11	4.02
Difference	0.014	-2.44	2.56	-0.15
% Difference	5.6	-2.9	21.	-3.7

TABLE III. NDA Plutonium Isotopics of NBS SRM-946 Derived from 100 keV X-ray and Gamma-ray Spectral Region

	Weight Percent			
200-Second Count	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu
1	0.275	83.55	12.21	3.97
2	0.258	83.44	12.36	3.94
3	0.229	84.58	11.38	3.81
4	0.253	84.29	11.60	3.86
5	0.236	84.78	11.17	3.81
6	0.250	85.49	10.57	3.69
7	0.233	83.95	12.06	3.76
8	0.253	83.57	12.12	4.06
9	0.236	84.75	11.25	3.76
Mean	0.247	84.27	11.63	3.85
Std. Dev.	0.015	0.70	0.60	0.12
NBS Value	0.246	83.05	12.11	4.02
Difference	-0.001	-1.22	0.48	0.17
% Difference	-0.4	-1.5	4.	4.2

TABLE IV. NDA Plutonium Isotopics of NBS SRM-948 Derived from Gamma-ray Peak Pair Ratios

	Weight Percent			
200-Second Count	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu
1	0.011	92.29	7.19	0.473
2	0.010	91.81	7.66	0.484
3	0.013	92.51	6.98	0.463
4	0.009	92.63	6.85	0.476
Mean	0.011	92.31	7.17	0.474
Std. Dev.	0.002	0.36	0.36	0.007
NBS Value	0.011	91.54	7.94	0.472
Difference	0.0	-0.77	0.77	-0.002
% Difference	0.	-0.8	9.7	-0.4

TABLE V. NDA Plutonium Isotopics of NBS SRM-948 Derived from 100 keV X-ray and Gamma-ray Spectral Region

200-Second Count	Weight Percent ^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu
1	0.0194	92.24	7.30	0.442
2	0.0106	91.92	7.62	0.456
3	0.0227	92.05	7.47	0.456
4	0.0104	91.95	7.59	0.450
Mean	0.0158	92.04	7.50	0.451
Std. Dev.	0.0062	0.14	0.15	0.007
NBS Value	0.011	91.45	7.94	0.472
Difference	-0.0048	-0.5	0.44	0.021
% Difference	-44.	-0.5	5.5	4.4

TABLE VI. NDA Plutonium Isotopics of NBS SRM-948 Derived From 100 keV X-ray and Gamma-ray Spectral Region as Function of Counting Time

Counting Time (Sec)	Weight Percent ^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu
30	0.013 ± 0.003	92.75 ± 0.56	6.80 ± 0.56	0.437 ± 0.02
60	0.026 ± 0.002	92.73 ± 0.37	6.80 ± 0.39	0.446 ± 0.01
200	0.010 ± 0.001	91.95 ± 0.18	7.59 ± 0.19	0.450 ± 0.00
500	0.013 ± 0.001	91.89 ± 0.12	7.64 ± 0.11	0.451 ± 0.00
1000	0.016 ± 0.001	91.47 ± 0.14	8.05 ± 0.14	0.464 ± 0.00
NBS Value	0.011	91.54	7.94	0.472

TABLE VII. Comparison of Facility and NDA Plutonium Isotopics for 34.4 Grams of PuO_2 Derived From Gamma-ray Peak Pair Ratios

Counting Time (Sec)	Weight Percent ^{239}Pu	^{240}Pu	^{241}Pu
60	90.5 ± 1.2	8.8 ± 1.2	0.63 ± 0.012
100	92.8 ± 0.7	6.5 ± 0.7	0.63 ± 0.009
300	91.8 ± 0.4	7.6 ± 0.4	0.62 ± 0.005
Facility Value	91.5	7.9	0.59

TABLE VIII. Comparison of Facility and NDA Plutonium Isotopics for 66 Grams of PuO_2 Derived From Gamma-ray Peak Pair Ratios

Counting Time (Sec)	Weight Percent ^{239}Pu	^{240}Pu	^{241}Pu
60	89.5 ± 1.9	8.4 ± 1.9	1.9 ± 0.07
100	87.8 ± 1.5	10.1 ± 1.5	1.9 ± 0.05
300	87.0 ± 1.2	10.8 ± 1.2	2.0 ± 0.04
Facility Value	86.3	11.8	1.7

TABLE IX. Comparison of Facility and NDA Plutonium Isotopics for Plutonium Metal Derived From Gamma-ray Peak Pair Ratios Counting for 200 Seconds

^{239}Pu Weight Percent			^{240}Pu Weight Percent			^{241}Pu Weight Percent		
Facility	NDA	Difference	Facility	NDA	Difference	Facility	NDA	Difference
73.2	75.2 ± 2.9	-2.0	22.6	20.4 ± 2.9	2.2	3.05	3.34 ± 0.2	-0.29
80.6	81.4 ± 2.7	-0.8	17.1	16.2 ± 2.7	0.9	1.85	1.94 ± 0.11	-0.09
85.5	87.3 ± 2.4	-1.8	12.1	10.5 ± 2.4	1.6	1.98	1.92 ± 0.11	0.06
91.6	94.8 ± 1.7	-3.2	7.6	4.5 ± 1.7	3.1	0.66	0.64 ± 0.03	0.02

TABLE X. Comparison of Facility and NDA Plutonium Isotopics for Plutonium Nitrate Derived from Gamma-ray Peak Pair Ratios Counting for 1000 Seconds

^{239}Pu Weight Percent			^{240}Pu Weight Percent			^{241}Pu Weight Percent		
Facility	NDA	Difference	Facility	NDA	Difference	Facility	NDA	Difference
87.2	85.7 ± 2.2	1.5	11.1	12.8 ± 2.2	-1.7	1.5	1.3 ± 0.1	0.2
90.8	90.5 ± 0.7	0.3	8.3	8.8 ± 0.7	-0.4	0.80	0.66 ± 0.02	0.14
90.8	91.0 ± 0.7	-0.2	8.3	8.3 ± 0.7	0.0	0.80	0.65 ± 0.02	0.15

Table III summarizes the plutonium isotopic abundance derived from the 100 keV spectral ons. In each case the counting time was 200 seconds and the low energy detector response reduced by the addition of 0.02 cm copper and 0.15 cm cadmium absorbers between the detec- and the sample. The difference between the NDA and NBS values for all four of the onium isotopes is less than two times the standard deviation of the nine observations.

Tables IV and V summarize the plutonium isotopic abundances calculated for the NBS 948 standard, Table IV by the peak area ratio method and Table V by the 100 keV method. e the ^{241}Pu abundance was 0.472%, the 160 keV peak area is subject to less interference the ^{241}Pu. Lower uncertainty and better NDA-NBS agreement for the ^{240}Pu estimate was rved for the measurement of NBS SRM-948 than for the measurement of NBS SRM-946.

The high count rate of the 100 keV spectral region suggests that counting periods even ter than 200 sec could be used to obtain plutonium isotopic information. Table VI lists calculated isotopic abundances as a function of analysis time from 30 sec to 1000 sec. shorter counting period results appear to be biased low for the ^{240}Pu and ^{241}Pu estimates high for the ^{239}Pu and ^{238}Pu estimates.

Two larger PuO_2 samples were analyzed by the peak area ratio method. Table VII ares the facility value with the NDA value as a function of counting time for a 34.4 g le of PuO_2. Table VIII summarizes the same comparison for a 66 g PuO_2 sample. Four onium metal samples of about 200 g were measured by the peak area ratio method. Table ompares the facility and NDA plutonium isotopic abundances calculated from a 200 sec t. Three 2 kg plutonium nitrate samples were analyzed by the peak area ratio method. e X compares the facility and the NDA results. A coaxial germanium detector was used these measurements. The side-pointing 41 mm diameter by 43 mm-long detector has a olution of 980 eV for 122 keV gamma-rays and 1.93 keV for 1332 keV gamma-rays.

The errors reported in Table VII through X are at the 1σ level and are derived from the st squares fit of the peak shape parameters. The agreement between the facility and NDA ues for the plutonium oxide and nitrate measurements is better than 2σ. Most of the ults agree within 1σ. These results were very encouraging and showed that a wide variety aterials could be measured at the storage facility and in a short analysis period.

CONCLUSIONS

The results to date indicate that the plutonium isotopic measurements can be performe by gamma-ray and x-ray spectrometry in counting periods as short as 200 sec. Because of the high count rate of the 100 keV spectral region, the plutonium isotopics could be obtained in even shorter counting periods, but the sample matrix, sample container and other material between the sample and the detector must be known to make use of this regio Most nuclear material in a storage facility is packaged in several metal containers, plast bags and bottles and facility records do not always show the complete packaging history. This limits the usefulness of the 100 keV spectral region.

The higher energy adjacent gamma-rays peak areas used to calculate the plutonium isotopes by the peak pair ratio method are less affected by sample matrix and packaging. The ^{241}Pu concentration limits the precision in measuring the ^{240}Pu 160 keV peak in short counting periods. The 642.41 keV ^{240}Pu gamma-ray peak has been used to estimate the ^{240}Pu concentration.[17] No ^{241}Pu gamma-ray peak is adjacent to the 642.48 keV ^{240}Pu gamma-ray peak, so detector efficiency and sample attenuation factors would have to be considered to measure the ^{240}Pu/^{241}Pu ratio by using the 642.48 keV peak. The decreased detection efficiency for the higher energy gamma-rays also limits the detected counts at 642 keV in short counting periods. Use of the 642.48 keV gamma-ray with the present detector systems needs to be evaluated.

These plutonium isotopic measurements have been made at several nuclear material stor age facilities. The analytical results from these measurements are available to the inspe tor in less than 5 minutes and the isotopic results can be used along with other NDA measurements to make real-time decisions about the contents of selected plutonium samples. Thus, if necessary, the inspector could require additional samples to be analyzed or some samples to be reanalyzed, based on the real-time data analysis this system provides.

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Non-Destructive Assay of Leached Hulls in a Nuclear Fuel Reprocessing Plant

by

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ABSTRACT

In a nuclear fuel reprocessing plant, the spent light water reactor fuel elements are chopped into approximately 2-4 inch lengths and the irradiated fuel dissolved from the Zircaloy hulls in a nitric acid dissolver solution. From the dissolver, the empty hulls are transferred batchwise to a leached hull monitor to be assayed for undissolved uranium and plutonium. After the assay, the hulls may be recycled back to the nitric solution for continued dissolution or disposed of as solid nuclear waste using the assay results to provide accountability data for special nuclear material content.

The hull monitor at the Barnwell Nuclear Fuel Plant (BNFP) will be a remotely controlled, fully automated system designed to quantitatively assay leached hulls for undissolved uranium and plutonium. The hull monitor will assay the hulls from one metric ton of fuel per dissolver basket with the design goal of detecting 0.1% undissolved fuel and yet remain within the framework of the BNFP materials flow, i.e., handle five hull baskets per day.

The non-destructive assay will be accomplished using a computer-based gamma-ray pulse height analysis system employing a 5x5 inch NaI(Tl) scintillation detector. The intense radiations from the fission product isotopes and the activation product isotopes produced in the reactor prevent direct assay of the undissolved fuel left in the hulls. The measurement will be made indirectly by demonstrating a correlation between the amount of ^{144}Ce undissolved and the remaining uranium. The isotope ^{144}Ce is a direct fission product with high (6%) cumulative yield. The daughter isotope ^{144}Pr has a gamma ray at 2.18 MeV well above other predominant radiations in the spectrum from the major interferences ^{60}Co, ^{58}Co, ^{95}Zr(^{95}Nb), ^{137}Cs and ^{106}Ru(^{106}Rh).

Segmented scanning operation of the hull monitor is accomplished by rotation and vertical transversal of the hulls container past the detector station. Proper collimation and absorbers are required to maximize the ^{144}Ce(^{144}Pr) to background ratio. A basket indexer is provided which monitors the scanning rate and ensures repositioning.

The leached hull monitor system will be interfaced to a computer-based multichannel analyzer for ease of operation and data handling. A calibration basket has been fabricated to accomodate radioactive sources and inactive Zircaloy hulls. Experiments to be performed with the hull monitor using this basket will simulate operation prior to plant startup. The system, calibration, geometry and hull attenuation, spectral interferences, quantitative limits of assay, and the role of the hull monitor in nuclear materials accountability will be discussed.

KEYWORDS: Design of experiments; leached hull monitor; non-destructive assay; evaluation, calibration

INTRODUCTION

The Leached Hull Monitor (LHM) was built by Intelcom Rad Tech for the Barnwell Nuclear Fuel Plant and has been described by Gozani.[1] Its purpose is to detect the presence of undissolved fuel in chopped hulls of irradiated fuel elements after leaching with nitric acid The assay can be used to determine any shipper-receiver differences as well as for accountability of special nuclear materials. For a reprocessing plant with a capacity of 1500 metri tons of spent fuel per year throughput, the leached hull monitor would detect and account fo approximately 4-5 kg of undissolved uranium per day. The position that has been applied to the BNFP states that a quantity of fuel remaining in the leached hulls exceeding 0.1% of th input must be detected and accounted for. This corresponds to approximately 1 kg of uraniu in each basket of hulls (about 650 kg of hulls are associated with one metric ton of fuel).

The hull monitoring system involves passive gamma-ray techniques to scan the dissolver basket for ^{144}Ce(^{144}Pr), a fission product isotope produced at a 6% cumulative fission yiel The daughter isotope ^{144}Pr has a 2.186 MeV gamma ray which is relatively free of spectral interferences. The ratio of ^{144}Ce to uranium in the dissolver solution, determined by laboratory analysis is used to calculate the amount of undissolved fuel remaining in the leache hulls.

DESCRIPTION

The hull monitor is an attempt to develop an improved non-destructive assay method fo measuring the undissolved fuel remaining in a basket of hulls from a chop-leach type nuclea fuel reprocessing plant. It has evolved into a specialized and sophisticated system as potential problems became apparent. Because of the extremely high radiation environment, th detector, absorbers, and collimator are located in a sealed maintenance gallery. The electronics, data acquisition and analysis system, and remote controls are located in the analytical laboratory, a cable run of about 650 feet. The detector, absorber filters, and th collimator are mounted on carts that can be independently moved to a position of optimum geometry. The carts ride on rails bolted to the sides of the maintenance gallery. The detector can be placed a maximum of 12.5 feet from the hull basket. A schematic of the LHM shown in Figure 1.

To optimize the detector for highest efficiency at 2.186 MeV, a 5-inch by 5-inch NaI(scintillation detector was chosen. The 2.186 MeV gamma ray is only 0.74% abundant in the decay of ^{144}Pr, and, therefore, maximum sensitivity is required. With this detector appro imately 82% photointeraction of the gamma ray occurs. The mean stopping distance of the gamma ray in NaI is 1.75 in. or at 35% total depth of the crystal. The NaI(Tl) detector displays excellent intrinsic efficiency for the 2.186 MeV gamma ray. A 4% full-width at half maximum resolution is observed for the 2.186 MeV peak using this detector.

The filter assembly is located between the collimator and the detector. It is cart-mounted and remotely controlled for ease of operation. The purpose of the filter assembly is to optimize the ^{144}Ce to background ratio. Three lead filters (1-inch, 2-inch, and 4-in thickness) can be remotely placed between the detector and the radiation source. Because different burnup and decay times of the fuel assemblies to be reprocessed, it may be necessary to change the thickness of the absorbers to minimize the intensity of low energy radi tions and yet maintain reasonable yield for the high energy gamma ray. A pneumatic contro system with electric solenoid switches was designed and installed on the filter cart assemb to position the filters in the beam line. The hull monitor cannot be approached once fuel assembly assay has begun due to the high radiation background. In fact, the entire hull monitor system was designed under the criterion that maintenance and calibration would occ only during plant shutdown or two weeks out each year.

The collimator is a three-foot long bored lead cylinder with a 3-inch diameter collimating hole. There is a 3-foot by 3-inch by 0.180-inch wall copper sleeve down the center of the bore to minimize X-ray and secondary radiation originating from the gamma-ray interaction with the lead. The hull monitor is separated from the hull basket by a 16-inch wal

igh density concrete that has a 24-inch wide by 6-inch high window. This window has been
d with lead brick to produce a 4-inch by 6-inch hole to further collimate the the gamma
ations. The collimator, concrete wall and the lead-lined window allows the detector to
s on a relatively small portion of the hull basket as it is rotated and lifted past the
ow.

The hull basket receives the hulls from the shear equipment and is lowered into the
olver solution. After dissolution of the fuel from the chopped hulls, the basket is
ed, allowed to drain, and lowered onto the hull monitor table. The table is rotated and
ed vertically while scanning is accomplished. The hull basket is approximately 3 feet
iameter and 7 feet high, and capable of holding the hulls from one metric ton of fuel.
e is a basket positioning transducer that permits repositioning of the basket for further
y of localized lumps of undissolved fuel. This basket indexing mechanism was installed
ne drive axle gear and is interfaced to the data acquisition system. The transducer
es as a monitor device for the consistency of the scanning rate and provides the capa-
ty of repositioning the basket for futher study of irregular scans.

The electronics and the data acquisition system are located in the laboratory where
erature and humidity control can be closely maintained. The electronic system was de-
ed to take advantage of pulse pile-up rejection techniques. The leached hull monitor
acquisition and analysis system (LHM-DAS) is a 16K PDP 11/05 computer with input/output
mass storage devices. The LHM-DAS will be interfaced to the materials accountability
uter for permanent record storage and status alert for plant operators. The system can
rogrammed to locate hot spots and apply appropriate correction factors. The system was
loped to automatically interpret data and calculate the quantity of undissolved fuel with
mum operator intervention.

HULL MONITOR CALIBRATION

Specific calibration tests of the leached hull monitor detection system will be performed
ng the cold checkout period for performance evaluation of BNFP. The calibration tests
he LHM will require a number of radioactive sources to duplicate the fission products
induced activity in the cladding, end pieces, and spacers present in the leached hull
et during a normal basket scan. The sources will represent several concentrations of
ion products and cladding activity corresponding to 0.1% - 0.001% undissolved uranium
remaining with the Zircaloy hulls. Unirradiated Zircaloy hulls will be placed in the
bration basket along with the radioactive sources using remote handling techniques.
blishment of the relationships between spectral data and radial position of the sources
ecessary in order to determine the average mass of Zircaloy hulls between the source
the detector. Attenuation correction factors can be determined. Isotopes with possible
rference potential can be placed in the calibration basket in the same ratio found in
hulls to determine limits of assay.

The calibration basket is a stainless steel drum that will simulate the dissolver basket.
is designed to hold calibration sources in thin tubes running vertically in the basket.
tubes are located at varying distances from the center of the basket so that different
ix combinations of hulls and sources can be obtained. The calibration basket is filled
unirradiated Zircaloy hulls and the sources placed into the source tubes.

A small calibration check source of ^{144}Ce(^{144}Pr) is located on the detector cart that
be remotely moved into position directly in front of the detector. The check source
l be used to verify the performance of the electronics and the detector response to
Ce(^{144}Pr) between calibrations with the calibration basket. It will be used to monitor
ector efficiency and amplifier gain shifts. The assay system is also equipped with a
ser to monitor the detector preamplifier electronics.

Cladding and dissolver residue studies give some indication of the environment and
ntitative limits of assay expected for the leached hull monitor.[2,3] Gamma activity can
ginate from several sources when scanning the basket of hulls and an understanding of
ir associations with the cladding will minimize the error for the total assay.

During the dissolution cycle, insoluble residue is formed which would be expected to
nsfer out of the dissolver with the dissolver solution. Approximately 0.2 - 0.3 weight

percent of the irradiated UO$_2$ in light water reactor fuel is insoluble. The cladding can become coated with a thin film of this residue during dissolution in HNO$_3$ that is not necessarily associated with undissolved fuel. Filtration and/or centrifugation of the dissolv solution will collect a substantial black deposit with a weight of 0.05% to 0.3% of the tot weight of the UO$_2$ depending on the type fuel and the amount of burnup; the lower the burnu the less residue is present. The dominant fission products are ^{103}Ru, ^{106}Ru(^{106}Rh), ^{140}Ba(^{140}La) ^{95}Zr(^{95}Nb), ^{137}Cs, ^{134}Cs, ^{141}Ce and ^{144}Ce(^{144}Pr) with the ruthenium isotopes accounting for as much as 40% by weight. Very small amounts of uranium can be detected in the residue. The residue also contains Cs, Ce, Cm, and Pu activities in approximately the same ratio to uranium as in the fuel and therefore can be associated with undissolved fuel

The residue is extremely radioactive due to the fission product ruthenium. This will require special attention because of the possible spectral interference with the ^{144}Ce(^{144} peak and its heat generating properties. Temperature gradients can cause performance variations in the detector.

Gamma activity associated with the cladding is the result of the recoil of the fissio products of nuclear reactions ejected from the fuel into the cladding as well as induced activity in the cladding. The fission products have a much greater recoil energy than the transuranium elements. Thus the relative fraction of fission products trapped in the cladding would be much greater than the transuranium elements. Approximately 0.1% of the tota fission product inventory is found associated with the cladding. The fraction of transuranic elements associated with the cladding is 0.001 - 0.002% of the total present.[2] These contamination levels will then contribute a minimum base or background in the hull assay and will vary according to total burnup time and location in the fuel assembly. The recoi of ^{144}Ce into the cladding is approximately 0.09% of the total in the fuel and unrelated t the amount of plutonium or uranium left undissolved.

Another potential problem in the non-destructive assay technique of leached hulls is the intense gamma activities of ^{60}Co due to the activation of the end pieces and spacers in the fuel assembly. The Zircaloy is a relatively pure alloy which contains very little cobalt. Unfortunately, activation products in the core hardware greatly diminish the spectral sensitivity and selectivity of the ^{144}Pr peak. These end pieces and spacers contain up to six hundred times more cobalt as in the Zircaloy. Cobalt activation in the miscellaneous components could produce from 100 to 400 times the ^{60}Co activity observed in th cladding alone. The ^{144}Ce(^{144}Pr) peak at 2.186 MeV is well above that for ^{60}Co; however, 400 fold addition of ^{60}Co to the spectrum makes the ^{144}Pr peak limits difficult to define. This interference limits the quantitative capabilities of the monitor to perhaps 1-2% of the total fission product inventory. It is anticipated that the electronic pulse pile-up rejection system will make the spectral sensitivity to ^{144}Pr acceptable. Figure 2 is a spectrum taken of check sources of ^{60}Co and ^{144}Ce(^{144}Pr) in a gross activity ratio of 375 to 1. This system is capable of maintaining approximately 4% resolution with only 9-12% system dead time.

These tests are indicative of the environments and quantitative limits expected of th hull monitor. The spectral interference of ^{106}Ru(^{106}Rh) as a dissolver residue, the recoi of fission products into the cladding not associated with the undissolved uranium, and th intense induced activity of the cladding hardware will be some of the limiting factors to the system. Time also becomes a limiting factor for the sensitivity of the leached hull monitor as the spent fuel waits to be reprocessed. The decay of the ^{144}Ce(^{144}Pr) (half life 285 days) causes the ratio of ^{144}Ce to longer lived fission products to increase. It is estimated that spent fuel older than seven years can not be assayed using the ^{144}Pr 2.185 MeV gamma ray to quantify the amount of undissolved uranium or plutonium left in th hulls. In that case, another gamma ray relatively free from spectral interference may be chosen or an alternate method used to determine the amount of undissolved uranium.

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FIGURE 1

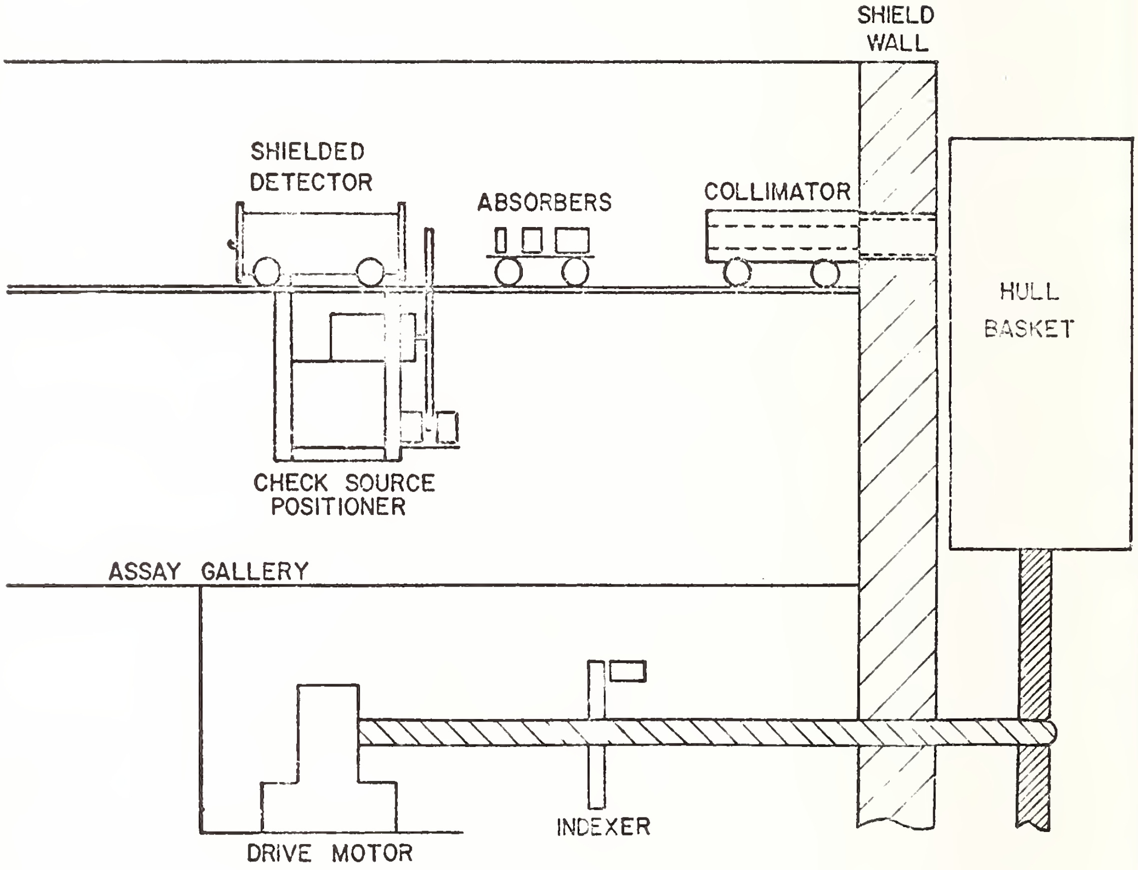
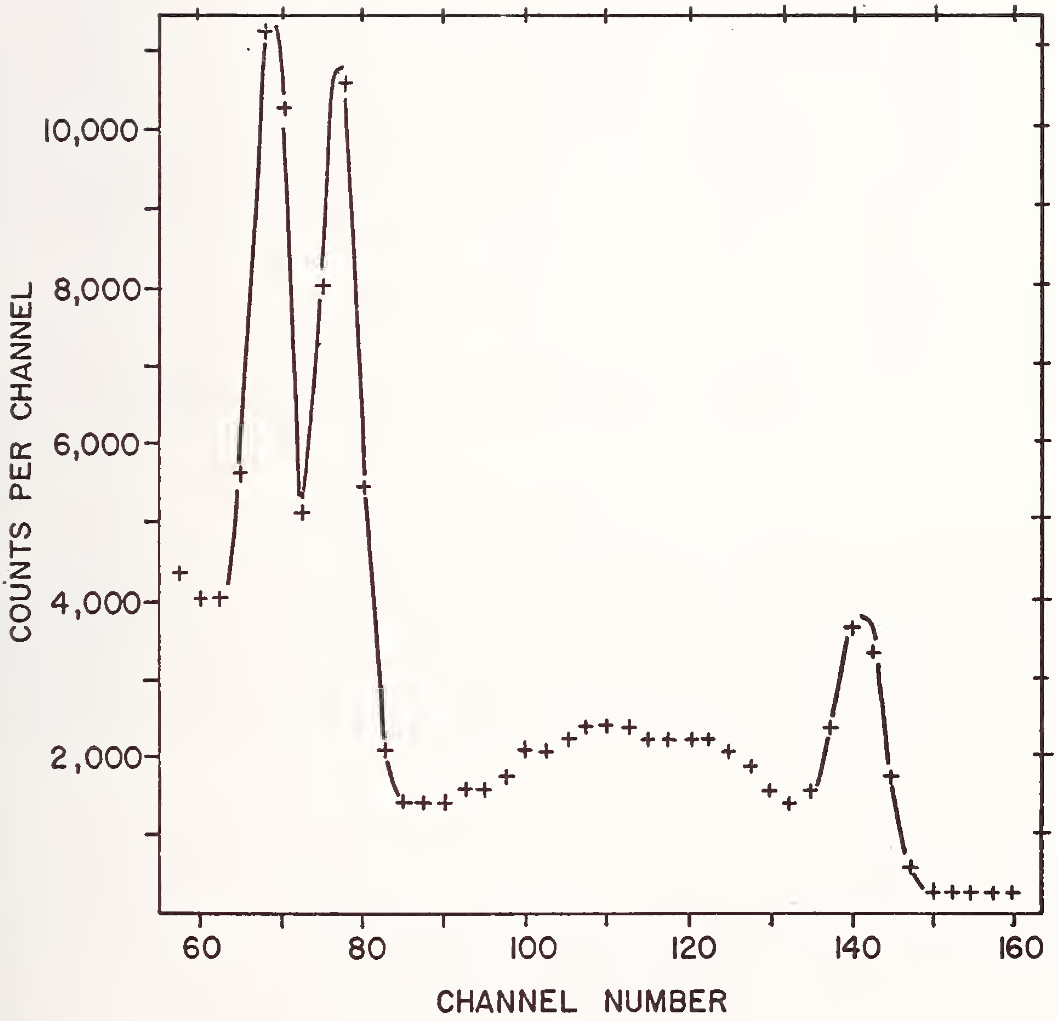

SHIELD WALL
SHIELDED DETECTOR
ABSORBERS
COLLIMATOR
HULL BASKET
CHECK SOURCE POSITIONER
ASSAY GALLERY
INDEXER
DRIVE MOTOR

FIGURE 2


COUNTS PER CHANNEL
10,000
8,000
6,000
4,000
2,000
60
80
100
120
140
160
CHANNEL NUMBER

Safeguards and Nonproliferation

by

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ABSTRACT

U. S. nonproliferation objectives cannot be achieved without the development and implementation of modern safeguards systems that are timely, sensitive and perhaps most important, inspectable by the International Atomic Energy Agency. In the nonproliferation context, the purpose of safeguards is to deter or reveal national intentions to obtain nuclear weapons capability by providing the time required to enact international sanctions. The Department of Energy is developing safeguards concepts and systems based on minimizing the opportunity for diversion and maximizing the probability of timely detection to allow for the necessary communication and control actions. The current U. S. nonproliferation policy can afford the time to make available practical, active safeguards for assuring the world that nuclear materials are being used only for peaceful purposes.

KEYWORDS: Safeguards and nonproliferation, active and passive fuel cycle safeguards concepts, integrated safeguards systems.

INTRODUCTION

The most critical issue facing the international nuclear community today is nonproliferation. The term nonproliferation can be simply defined as the prevention of weapons capability in a non-weapons state. For nuclear power to be considered a viable option for meeting future energy requirements, questions of proliferation, safeguards and waste management must be resolved. The U. S. and general world agreement on a delay in large scale commercial reprocessing and recycle does, however, allow some time to address the proliferation and safeguards issues in a meaningful and systematic fashion. Waste management, I will leave as the subject for another paper at another time.

Nonproliferation objectives cannot be achieved without the development and application of modern safeguards systems that are timely, sensitive, and perhaps most important, inspectable by the International Atomic Energy Agency. While other major considerations are also involved, including such things as types of fuel cycles, coordinated sanctions, and declared national intent, it is only through the implementation of timely, reliable safeguards systems and adequate inspection technology and procedures that we can be assured strategic quantities of weapons material have not been diverted from nuclear facilities. In the nonproliferation context, the purpose of safeguards is to deter or reveal national intentions to obtain nuclear weapons capability by providing the time required for abortive international actions to be taken.

The U. S. Department of Energy has instituted a variety of programs to establish nonproliferation criteria and develop fuel cycle technologies and safeguards systems consistent with these criteria. This year the Department of Energy Nonproliferation ternative Systems Assessment Program will have completed a review of literally scores alternatives to the existing LWR uranium-plutonium fuel cycle. At that time those chnically feasible and economically practical fuel cycles which may offer superior nproliferation features will be identified and considered for possible development ward commercialization objectives.

In a larger context, some forty nations are currently participating in the ternational Fuel Cycle Evaluation Committee which has a similar two year charter examine alternatives to plutonium reprocessing and recycle and establish relative nproliferation features. U. S. support for this activity is provided by the DOE SAP program and direct participation in the various INFCE working groups, including put of the U. S. technical information needed to allow in-depth consideration of the ternatives.

In support of the U. S. nonproliferation efforts, the Department of Energy feguards and Security program is currently developing safeguards concepts, technologies, and integrated systems that can be applied to any of the future fuel cycles. addition, methodologies have been developed and are being utilized in selected ternatives to quantitatively determine the inherent detection timeliness and sensivity features of those fuel cycles. These results will be compared with our studies the LWR fuel cycle and the conclusions submitted to the NASAP and INFCE programs.

SAFEGUARDS AND NONPROLIFERATION

Regardless of the detailed form of the future domestic commercial and international el cycles, we believe that certain safeguards considerations are inherent to profeeration resistance. The most critical area of the current fuel cycles is the postactor segment including reprocessing, conversion and fuel refabrication. Whether the ture fuel cycle is based on coprecipitated plutonium, thorium or spiked recycle el materials, safeguarding the back end of the fuel cycle will still place its eatest demand on the technological capabilities available to be used in that area.

The selection of future fuel cycles on the basis of nonproliferation criteria ll depend, to an extent, on the passive safeguards features inherent to those fuel cles and the active measures that can be additionally made available to achieve equate levels of safeguards effectiveness. Passive safeguards features that differ om one fuel cycle to another include levels of biologically hazardous constitutents, emical and physical form, and the complexity of processing required to convert el cycle material to weapons usable form. The Civex fuel cycle and its variants, r example, possess the passive safeguards feature of biologically hazardous, relatively attractive fuel cycle materials, since recycled fissile material is never completely parated from fission-product contaminants.

Although minimizing the attractiveness of nuclear material in future fuel cycles is desirable feature, the choice of proliferation-resistant fuel cycles for domestic and ternational energy production will undoubtedly be tempered by environmental, economic, d political considerations. Fuel cycles with potentially high environmental risks, ch as high radioactivity levels and possible criticality accidents, are not likely be acceptable as nuclear energy options. As an additional nonproliferation tool believe that active safeguards measures such as continuous material monitoring and asurement, surveillance, and automatic process controls, can be added to the passive atures.

We believe that the technologically and economically feasible, and environmentally ceptable fuel cycles of the future will require active safeguards systems to supplent the inherent, passive safeguards features. Because of this belief, our developental program is structured to culminate in integrated safeguards systems capable of al-time control and continuous process monitoring.

To satisfy the demands of proliferation resistance, fuel cycle safeguards must be based on continuous monitoring of nuclear material from the reactor through reproces ing, refabrication and back to the reactor. Only by continuous monitoring can uncontrolled build-up or diversion of weapons material be prevented. In our view, the principal safeguards element for continuously monitoring irradiated and refabricated fuel assemblies is containment, surveillance, and inspector verification of shipment and reception. Since these fuel assemblies are either highly radioactive or denatured to low enriched levels, the technology, systems, and institutional arrangements for the safeguards are currently available. Whether the fuel cycle is uranium/plutonium, uranium/thorium, or any of the alternatives, this portion of the fuel cycle can be safeguarded by today's methods.

Continuous monitoring of nuclear material during reprocessing, chemical conversio and fuel refabrication is substantially more difficult. During these processing operations, the form and concentration of nuclear material becomes relatively more attractive as a diversion target. In the nonproliferation context, the principal safeguards elements are the active measures: continuous process monitoring, surveillan and real-time accounting. As the nuclear material form and concentration become more attractive, increasingly stringent safeguards are required, that is, better measurements, tighter administrative control, and more timely detection and detailed process monitoring. The ability to monitor the movement of nuclear material by active safeguards measures during these processing operations, may well decide the fate of many of the currently proposed alternative fuel cycles.

SAFEGUARDS AND SECURITY PROGRAM

Our safeguards concepts and systems are based on a "mini-max" principle: minimizing the opportunity for diversion and maximizing the probability of timely detection to allow for the necessary communication and control actions. The ability to continuously monitor and control nuclear material during processing in accordance with this principle is the final goal of our research and development program. It is believed that all fuel cycles must inherently be affected, if not governed, by the adoption of these active safeguards measures.

Of key importance to the nuclear energy option is the cost-effectiveness of futur safeguards systems. In all of our efforts, effectiveness must be measured against design, implementation and operational costs. There can be no doubt, however, that a modern, automated safeguards system substantially increases a plant operator's ability to monitor and optimize the efficiency of his processing operation. Cost effectiveness is the corollary to our "mini-max" principle of safeguards system design

The SS plan for developing integrated safeguards systems consistent with national proliferation objectives is composed of three phases:

- Generic conceptual design;
- Technology and subsystem development testing and evaluation; and
- Integrated safeguards system design testing and evaluation.

The generic conceptual design for safeguarding a particular facility or alternati fuel cycle represents a preliminary scoping, definition and analysis of the safeguards problems. The generic conceptual design establishes basic engineering design criteria and considerations for the incorporation of effective safeguards, and outlines preliminary material control and accounting and physical protection systems. In additio these studies identify available and reasonably projected safeguards technology and those subsystems requiring further research and development. In direct support of U. S. nonproliferation objectives, we are currently adapting our generic safeguards concepts to the alternative fuel cycles under DOE technology development programs. This effort will address all aspects of the fuel cycles including reprocessing,

fabrication, multi-national fuel centers, denatured and biologically hazardous
clear material forms and concepts for international inspection. Generic studies
two alternatives, coprecipitation and uranium-thorium will be completed this year.

The technology and subsystem development phase of our program includes the
velopment of nuclear material measurement methods and instrumentation, process
nitoring and control modules and subsystems, data management and analysis method-
ogy, and physical protection, surveillance, containment subsystems. Individual
bsystem development projects, such as specific measurement instrumentation, culminate
rigorous, well-defined test and evaluation programs in operating nuclear facilities.
the development of nuclear material measurement methods, we have reached the stage
ere reliable, prototype instrumentation can be engineered and installed in the
ocessing lines of today's nuclear facilities. Examples of recently developed proto-
pe instrumentation include the absorption-edge densitometer and californium-252
uffler to be discussed later during this conference. These technological develop-
nts are the individual building blocks for the improvements at existing facilities
d for the integrated safeguards systems of the future.

Recently, the joint project between the U. S., and Japan, with participation
France and the IAEA has been agreed upon to test advanced safeguards instrumenta-
on and methods at the Tokai-Mura reprocessing facility in Japan. Thirteen tasks
ve been established, inclusively covering surveillance and containment at the
orage pond to measurement and monitoring systems at the product end of the facility.
though complete evaluation results will not be available until the end of calendar
ar 1979, this joint effort is expected to produce results that will be available
r INFCE considerations.

The third phase of safeguards system development in our program is the integrated
stem design testing and evaluation. Our goal for integrated safeguards system
velopment is to achieve real-time accounting supplemented by continuous process
nitoring in accordance with the "mini-max" principle and its corollary, cost-
fectiveness. In this phase, we assemble the basic components developed under Phase 2
nto a cost-effective system and test the entire system under operating conditions
a nuclear facility. Based on detailed engineering designs, safeguards systems
odeling and simulation are used to establish safeguards system effectiveness, relative
ost-effectiveness of alternative systems and in the case of alternative fuel cycles,
stablish a quantitative comparison of effectiveness, cost, and inspectability with
xisting LWR fuel cycles.

These efforts have culminated in the implementation of advanced material control
nd accounting systems at several Department of Energy facilities. Real-time material
ontrol and accounting is currently beginning test and evaluation at the plutonium
rocessing and recovery facility, TA-55 at Los Alamos, and the Y-12 facility at Oak
idge. Similar systems based on this concept are in the planning stages for other
acilities. We are also beginning to test an advanced process monitoring system at
he Idaho Chemical Processing Plant that will enable continuous monitoring of bulk
aterial flow throughout a reprocessing facility.

CONCLUSIONS

The fuel cycle safeguards concepts, technology, and advanced, integrated systems
nder our development programs are emerging as factors that will shape the future of
he nuclear energy option.

The deferral of domestic reprocessing and recycle and the associated U. S. policy initiatives in the international nuclear community can afford us time to make available practical active safeguards for assuring the world that nuclear materials are being used only for peaceful purposes. This is the goal underlying today's conference.

Decision Analysis for Dynamic Accounting of Nuclear Material

by

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ABSTRACT

Effective materials accounting for special nuclear material in modern fuel cycle facilities will depend heavily on sophisticated data-analysis techniques. Decision analysis, which combines elements of estimation theory, decision theory, and systems analysis, is a framework well suited to the development and application of these techniques. Augmented by pattern-recognition tools such as the alarm-sequence chart, decision analysis can be used to reduce errors caused by subjective data evaluation and to condense large collections of data to a smaller set of more descriptive statistics. Application to data from a model plutonium nitrate-to-oxide conversion process illustrates the concepts.

KEYWORDS: Nuclear safeguards, materials accounting, decision analysis, CUSUM, Kalman filter, alarm-sequence chart, plutonium nitrate-to-oxide conversion

INTRODUCTION

aterials accounting for safeguarding special nuclear material (SNM) has two important
ts: (1) the collection of materials accounting data, and (2) the analysis of materials
nting data. The collection function is a broad, highly developed subject (e.g., see
1-5 and the references therein) that we will not pursue here; in this paper we are
rily concerned with the analysis of materials accounting data.

The data collection function is usually structured to facilitate performance of the
sis function, commonly by providing sufficient measurements of SNM within a facility
low the drawing of material balances around selected portions of the facility on a
nable time scale. The data, which are always corrupted by measurement errors, often
r as time sequences of material balances, one sequence from each part of the facility
hich material balances are drawn.

Therefore, the data-analysis function must operate on imperfect data that become avail-
sequentially in time. Its primary goals are (1) detection of the event(s) that SNM has
diverted, (2) estimation of the amounts diverted, and (3) determination of the signifi-
of the estimates. Furthermore, data analysis must search for evidence of diversion
may have occurred in any of several patterns.

These goals are ideal for statistical treatment using sequential, probabilistic tech-
s that have been developed for applications to communications and control systems.[6-9]
ion analysis[10,11] is a framework of such tools, and combines techniques from estimation
y and hypothesis testing, or decision theory, with systems analysis for treating com-
dynamic problems. The decision-analysis framework is general enough to allow a wide
in the level of sophistication in examining SNM accounting data, while providing
lines for the development and application of a variety of powerful methods.

THE DECISION PROBLEM

Let us suppose that over some time period we have acquired materials accounting data consisting of a set of in-process inventory measurements at discrete times and a set of material transfer measurements between those times. Let I(k) be the k^{th} inventory measur ment, and let T(k) be the measurement of the net transfers that occurred between the I(k) and I(k+1) inventory measurements. If the measurements were exact and there had been no diversion of SNM, then the continuity equation would be satisfied:

$$I(k+1) = I(k) + T(k) \quad .$$

However, we never have perfect measurements of bulk material, and SNM may or may not have been diverted, so that (1) should be rewritten as

$$I(k+1) = I(k) + T(k) - M(k+1) \quad ,$$

where M(k+1) is the imbalance in the continuity equation (1) at time k+1 caused by measu ment errors and diversion. We call M(k) the material balance value at time k, or the k^{t} material balance for short. Clearly, M(k) is a random variable, and the sequence $\{M(k),\ k = 2,3,\ldots\}$ is a stochastic process, about which we can make probabilistic statements if something is known of the nature of the measurement errors.

For convenience, denote the set of inventory measurements $\{I(k),\ k = 1,2,\ldots,N\}$, th set of net transfer measurements $\{T(k),\ k = 1,2,\ldots,N-1\}$, and the statistical informatio the measurement errors by the quantity Z(N). Then Z(N) contains all information availab for the N materials accounting intervals. Thus, the decision problem is to determine, b on observation of Z(N), whether the set $\{M(k+1),\ k = 1,2,\ldots,N-1\}$ (M^N for simplicity) co tains diversion.

The Likelihood Ratio

For any particular Z(N) that is observed, M^N may or may not have contained diversic Define the hypotheses

H: M^N does not contain diversion,

K: M^N does contain diversion.

Then the actual probability density function that governs Z(N) is determined by which o H, K is true; i.e.,

$$Z(N) \sim p[Z(N)|H] \text{ for H true,}$$

$$Z(N) \sim p[Z(N)|K] \text{ for K true,}$$

where ∿ means "has the density function." These two conditional density functions are called likelihood functions for the hypotheses H and K. The values of the likelihood f tions for a particular Z(N) are relative measures of the likelihood that Z(N) is govern one or the other density function, or in other words, that H is true or K is true.

The usual statistical test consists of forming the likelihood ratio,[6-9] L, and com ing it to a threshold:

$$\text{If } L[Z(N)] \triangleq \frac{p[Z(N)|K]}{p[Z(N)|H]} \begin{cases} < T, \text{ accept H,} \\ > T, \text{ accept K,} \end{cases}$$

where T is the threshold to be determined below. Roughly speaking, if Z(N) is "enough" likely to have occurred as a result of H being true than of K being true, then decide t is true; otherwise, decide that K is true.

Conversion to Sufficient Statistics

e likelihood functions are difficult to work with because they are joint density ns of many variables, in general. Under certain circumstances, which usually hold accounting, it is possible to condense the quantity Z(N) to a single number S(N) loss of information. The number S(N) is called a sufficient statistic[7] and is ent to knowledge of Z(N). If such a S(N) can be found, and if its density function calculated, then the likelihood ratio test (3) can be replaced by

$$\text{If } L[S(N)] = \frac{p[S(N)|K]}{p[S(N)|H]} \begin{cases} < T', \text{ accept } H, \\ > T', \text{ accept } K. \end{cases} \tag{4}$$

e density (i.e., likelihood) functions are univariate and, therefore, much more le mathematically. The hidden problem is to find a sufficient statistic that is cantly indicative of whether H or K is true.

Sequential Formulation

we have seen, the likelihood ratio test, (3) or (4), for a fixed number N of points s of comparing the likelihood ratio to a single threshold. However, in practical ons we seldom will know when the test should start or end. Therefore, we will want n the test at all possible starting points and let the test itself determine when it be terminated. This procedure also has the provident property of requiring fewer , on the average, than a fixed-sample-size test having the same characteristics.[8]

r the sequential likelihood ratio test, also called the sequential probability ratio SPRT,[8] there are three possible results at each decision time, rather than two:

$$\text{If } L[S(k)] \begin{cases} \leq T_0, \text{ accept } H, \\ \geq T_1, \text{ accept } K, \\ \text{otherwise, take another observation,} \end{cases} \tag{5}$$

SPRT is repeated for all possible starting points. The thresholds T_0 and T_1 can be rom the Neyman-Pearson criterion or by minimizing the Bayes risk,[7] but that may some information that is unavailable. The following approximation, devised by Wald, seful thresholds that can be shown to be conservative.

P_M and P_F be the desired (given) miss and false-alarm probabilities, respectively, SPRT. Then the thresholds are[7,8]

$$T_0 = \frac{P_M}{1 - P_F} \ ,$$
$$T_1 = \frac{1 - P_M}{P_F} \ . \tag{6}$$

bability of detecting diversion, related to $1-P_M$, is called the power or size of the $_F$ is called the significance or level of the test.

SOME SUFFICIENT STATISTICS

r any decision problem, there is a large number of sufficient statistics that may be ted, but some are more useful than others because of computational reasons, closer nship to physically meaningful quantities, or better discriminatory powers between hypotheses. Following are several statistics that have been effective in various tions.

The CUSUM Statistic

The CUSUM[1,12-16] (cumulative summation) of material balances is just the sum of the material balances over the time period of interest.

$$\mathrm{CUSUM}(k+1) = M(2) + M(3) + \ldots + M(k+1) \quad ,$$

where the M(i) are found from (2):

$$M(i+1) = -\,I(i+1) + I(i) + T(i) \quad , \qquad i = 1,2,\ldots,k \quad .$$

The CUSUM can also be written as

$$\mathrm{CUSUM}(k+1) = -\,I(k+1) + I(1) + \sum_{i=1}^{k} T(i) \quad ,$$

which emphasizes that the material balances are negatively correlated through the commo inventory measurement. For uncorrelated transfer measurements, the CUSUM variance is

$$VC(k+1) = VI(k+1) + VI(1) + \sum_{i=1}^{k} VT(i) \quad ,$$

where VI(·) and VT(·) are the inventory and transfer measurement error variances, respe tively In recursive form suitable for a SPRT, the cusum and its variance can be writt as

$$\mathrm{CUSUM}(k+1) = \mathrm{CUSUM}(k) - I(k+1) + I(k) + T(k)$$

$$VC(k+1) = VC(k) + VI(k+1) - VI(k) + VT(k) \quad .$$

The corresponding SPRT can be shown to reduce to

$$\text{If} \quad \frac{\mathrm{CUSUM}(k+1)}{\sqrt{VC(k+1)}} \begin{cases} \leq -\sqrt{2|\ln T_0|} & \text{, accept H,} \\ \geq +\sqrt{2|\ln T_1|} & \text{, accept K,} \\ \text{otherwise, take another observation.} \end{cases}$$

The CUSUM statistic is interesting because it is an estimate of the total amount of mi material during the period. However, the CUSUM is not a minimum-variance statistic un the variances of the material balance measurements are all equal, and unless the knowl of how the material balances combine inventory and transfer measurements is unimportan last condition would hold if the inventory were small or well measured compared to the fers.

The Two-State Kalman Filter Statistic

The two-state Kalman filter statistic[2,17-20] estimates the average amount of miss material per balance. It uses all available information from the continuity equation and from the statistics of the measurement errors. The two-state Kalman filter statis can be shown to be optimal in the sense that it is the minimum-variance, unbiased, lin estimate whenever the measurement error probability densities are symmetric about the means.[21]

The two-state Kalman filter yields estimates of both the inventory and the mater balance at each time. In recursive form, the equations are[21,22]

$$\hat{I}(k+1) = \hat{I}(k+1|k) + K_1 [I(k+1) - \hat{I}(k+1|k)] \quad ,$$
$$\hat{M}(k+1) = \hat{M}(k) + K_2 [I(k+1) - \hat{I}(k+1|k)] \quad , \tag{10}$$

$$\hat{I}(k+1|k) = \hat{I}(k) + T(k) - \hat{M}(k) \quad ,$$

1) and $\hat{M}(k+1)$ are the inventory and material balance estimates, respectively, at
based on all information through time k+1. The filter gains, K_1 and K_2, are given

$$K_1 = \frac{VIE(k+1)}{VI(k+1)} \quad ,$$
$$K_2 = \frac{VMIE(k+1)}{VI(k+1)} \quad , \tag{11}$$

E(k+1) and VMIE(k+1) are respectively the inventory estimate error variance and the
ce between the inventory and material balance estimate errors. They are given
ely by

$$VIE(k+1) = \frac{VIE(k+1|k)\ VI(k+1)}{VIE(k+1|k) + VI(k+1)} \quad ,$$
$$VMIE(k+1) = \frac{VMIE(k+1|k)\ VI(k+1)}{VIE(k+1|k) + VI(k+1)} \quad , \tag{12}$$

$$VIE(k+1|k) = VIE(k) - 2VMIE(k) + VME(k) + VI(k)$$
$$VMIE(k+1|k) = VMIE(k) - VME(k) \quad . \tag{13}$$

ance of the error of the material balance estimate at time k+1, VME(k+1), is

$$VME(k+1) = VME(k) - \frac{VMIE^2(k+1|k)}{VIE(k+1|k) + VI(k+1)} \quad . \tag{14}$$

rences 2 and 17-24 for more detail.

resulting SPRT is similar to that for the CUSUM, and reduces to

$$\text{If} \quad \frac{\hat{M}(k+1)}{\sqrt{VME(k+1)}} \begin{cases} \leq -\sqrt{2|\ln T_0|} & \text{, accept H,} \\ \geq +\sqrt{2|\ln T_1|} & \text{, accept K,} \\ \text{otherwise, take another observation.} & \end{cases} \tag{15}$$

Other Sufficient Statistics

sufficient statistics such as those just discussed are called parametric because
end upon knowledge of the statistics of the measurement errors. They also happen to
t when the measurement errors are Gaussian, a quite common but by no means all-
e situation. If the measurement error statistics are unknown or non-Gaussian, then
etric[25] sufficient statistics may give better test results. In addition, nonpara-
ests can provide independent support for the results of parametric tests even though
etric tests are generally less powerful than parametric ones under conditions for
e latter are designed.

The two most common nonparametric tests are the *sign* test and the *Wilcoxon* rank su test. The sufficient statistic for the sign test is the total number of positive materia balances. That for the Wilcoxon test is the sum of the ranks of the material balances. The rank of a material balance is its relative position index under a reordering of the material balances according to magnitude. Other, possibly more effective, nonparametric tests are being investigated. Further discussion of nonparametric tests is beyond the scope of this paper.

TEST APPLICATION

Procedure

As discussed above, we seldom will know beforehand when diversion has started or ho long it will last. Therefore, the decision tests must examine all possible, contiguous sequences of the available materials accounting data. That is, if at some time we have material balances, then there are N starting points for N possible sequences, all ending the N^{th}, or current, material balance, and the sequence lengths range from N to 1. Beca of the sequential application of the tests, sequences with ending points less than N hav already been tested; those with ending points greater than N will be done if the tests d not terminate before then.

Another procedure that helps in interpreting the results of tests is to do the test at several significance levels, or false-alarm probabilities. This is so because, in p tice, the test thresholds are never exactly met; thus, the true significance of the dat obscured. Several thresholds corresponding to different false-alarm probabilities give least a rough idea of the actual probability of a false alarm.

Displaying the Results

Of course, one of the results of most interest is the sufficient statistic. Commo practice is to plot the sufficient statistic, with symmetric error bars of length twice square root of its variance, vs the material balance number. The initial material bala and the total number of material balances are chosen arbitrarily, perhaps to correspond the shift or campaign structure of the process. For example, if balances are drawn hou and a day consists of three shifts, then the initial material balance might be chosen a the first of the day, and the total number of material balances might be 24, covering t shifts. Remember, however, that this choice is for display purposes only; the actual ing procedure selects all possible initial points and sequence lengths, and any suffic statistic may be displayed as seems appropriate.

The other important results are the outcomes of the tests, performed at the severa significance levels. A new tool, called the alarm-sequence chart,[1-3,12] has been deve to display these results in compact and readable form. To generate the alarm-sequence each sequence causing an alarm is assigned (1) a descriptor that classifies the alarm ing to its false-alarm probability, and (2) a pair of integers (r_1,r_2) that are, respe tively, the indexes of the initial and final material balance numbers in the sequence. alarm-sequence chart is a point plot of r_1 vs r_2 for each sequence that caused an alar with the significance range of each point indicated by the plotting symbol. One possi correspondence of plotting symbol to significance is given in Table I. The symbol T d

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* It is also possible to define (r_1,r_2) as the sequence length and the final material ance number of the sequence. The two definitions are equivalent.

TABLE I

ALARM CLASSIFICATION FOR THE ALARM-SEQUENCE CHART

Classification (Plotting Symbol)	False-Alarm Probability
A	10^{-2} to 5×10^{-3}
B	5×10^{-3} to 10^{-3}
C	10^{-3} to 5×10^{-4}
D	5×10^{-4} to 10^{-4}
E	10^{-4} to 10^{-5}
F	$< 10^{-5}$
T	~ 0.5

ences of such low significance that it would be fruitless to examine extensions of them; letter T indicates their termination points. It is always true that $r_1 \leq r_2$ so that all ols lie to the right of a 45° line through the origin. Examples of these charts are n in the section on results.

AN EXAMPLE

The Process

To illustrate the application of decision analysis, we present results from a study of erials accounting in a plutonium nitrate-to-oxide conversion facility.[3] The reference cess is based on plutonium (III)-oxalate precipitation; a simplified block diagram is n in Fig. 1. Nominal capacity is 116 kg of plutonium per day, processed in 2-kg ches. Some of the most important design parameters for the main process stream are given able II.

TABLE II

CONVERSION PROCESS DESIGN PARAMETERS

Function	Volume or Weight Per Batch	Concentration	Frequency
eceipt tank feed	200.0 L	30.0 g/L	1/0.41 h
alence adjust feed	66.67 L	30.0 g/L	1/0.41 h
recipitator feed	75.44 L	26.5 g/L	1/0.41 h
u oxalate boat to furnace	4.65 kg	0.422 kg/kg	1/0.41 h
u oxide to accountability	2.21 kg	0.882 kg/kg	1/0.41 h
u product to storage	2.18 kg	0.882 kg/kg	1/0.41 h
iltrate	154.9 L	66.4 mg/L	1/0.41 h
recipitator flush	109.2 L	4.6 g/L	3/day
urnace sweeping	0.85 kg	0.882 kg/kg	1/week
oat flush	34.4 L	2.9 g/L	10/day
ump station sweep	0.85 kg	0.882 kg/kg	2/day

The Materials Accounting System

Many different ways of drawing material balances for the conversion process can be ined. Based on the conversion study,[3] one strategy that works very well is to consider main process stream from the receipt tank to the product dump and assay station as one process. Thus, the transfers consist of feed into the receipt tank, product out of the and assay station, and recycle solids and liquids. All these transfers must be meas- d, and we must obtain an estimate of the in-process inventory. Table III gives the ired measurements and some possible measurement methods and associated uncertainties.

TABLE III

MATERIALS ACCOUNTING MEASUREMENTS FOR THE CONVERSION PROCESS

Measurement Point	Measurement Type*	Instrument Precision (%)	Calibration Error (%)
Receipt tank	Volume	0.2	0.1
	Concentration (by L-edge densitometry)	1	0.3
Wet boat (precipitator output)	Mass (by neutron well counter)	2	5
Precipitator holdup	Mass (by He-3 neutron counter)	2	--
Filtrate	Volume	0.2	0.1
	Concentration (by alpha monitor)	10	2
Precipitator flush	Volume	0.2	0.1
	Concentration (by L-edge densitometry)	1	0.3
Boat flush	Volume	0.2	0.1
	Concentration (by x-ray fluorescence)	1	0.3
Furnace sweep	Mass (by neutron well counter)	2	0.5
Dump station sweep	Mass (by neutron well counter)	2	0.5
Product cans	Mass (by neutron well counter, calorimeter, or gamma spectrometer	1	0.5

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[*] See References 1-3 for detailed discussions of measurement techniques.

Results

The techniques of decision analysis described earlier have been used to evaluate the diversion sensitivity of this materials accounting strategy and others. Part of the evaluation consists of examining test results, in the form of estimate (sufficient statistic) and alarm-sequence charts, for various time intervals. Examples of typical one-day charts for the CUSUM and two-state Kalman filter are shown in Figs. 2 and 4; the corresponding alarm-sequence charts are given in Figs. 3 and 5.[3] In the course of evaluation, many such sets o charts are examined so that the random effects of measurement errors and normal process variability can be assessed; that is, we perform a Monte Carlo study to estimate the sensitivity to diversion. In applying decision analysis to data from a facility operating under actual conditions, only one set of data will be available for making decisions, rather than the multiple data streams generated from a simulation. The decision-maker will have to extrapolate from historical information and from careful process and measurement analysis t ascertain his true diversion sensitivity.

The results of the evaluation are given in Table IV. By comparison, current regulatio require that the material balance uncertainty be less than 0.5% (2σ) of throughput for each two-month accounting period, which corresponds to 33 kg of plutonium for this process. Su large improvement in diversion sensitivity is possible through the combination of timely measurements with the powerful statistical methods of decision analysis.

TABLE IV

DIVERSION SENSITIVITY FOR THE CONVERSION PROCESS

Detection Time	Average Diversion Per Batch (kg Pu)	Total at Time of Detection (kg Pu)
1 batch (1.35 h)	0.13	0.13
1 day	0.03	0.63
1 week	0.01	1.24
1 month	0.005	2.65

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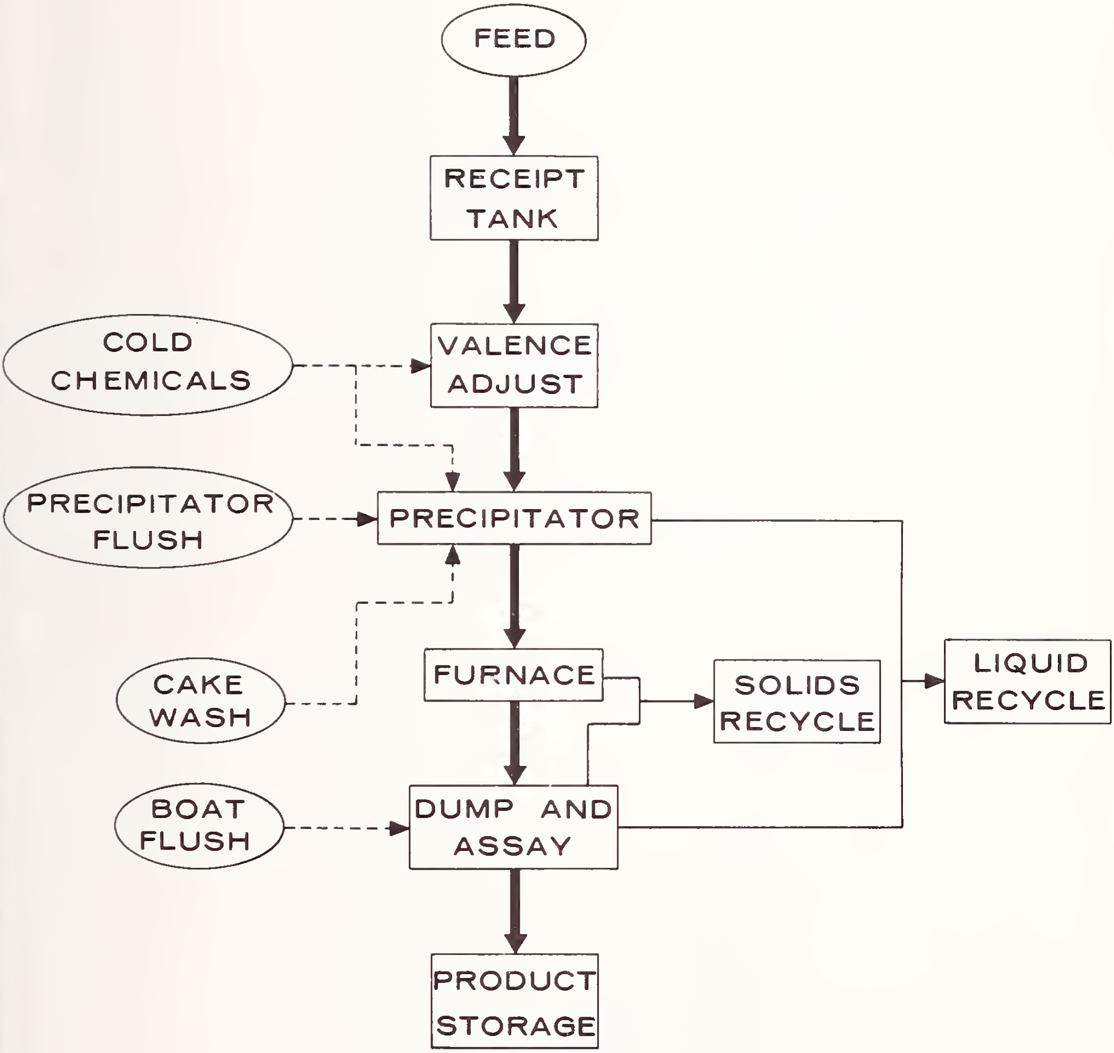

Fig. 1. Simplified block diagram of the plutonium nitrate-to-oxide conversion process.

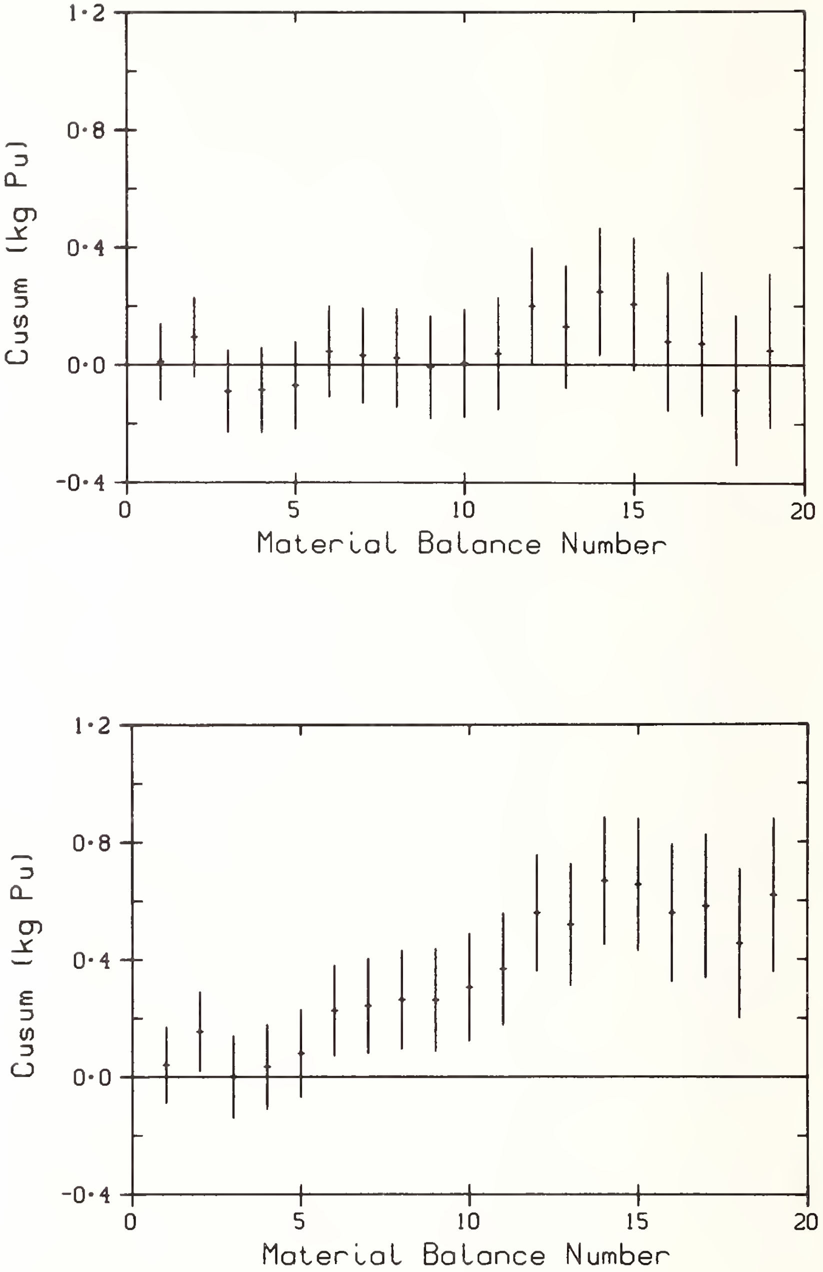

Fig. 2. CUSUM charts for one day with no diversion (upper), with diversion (lower).

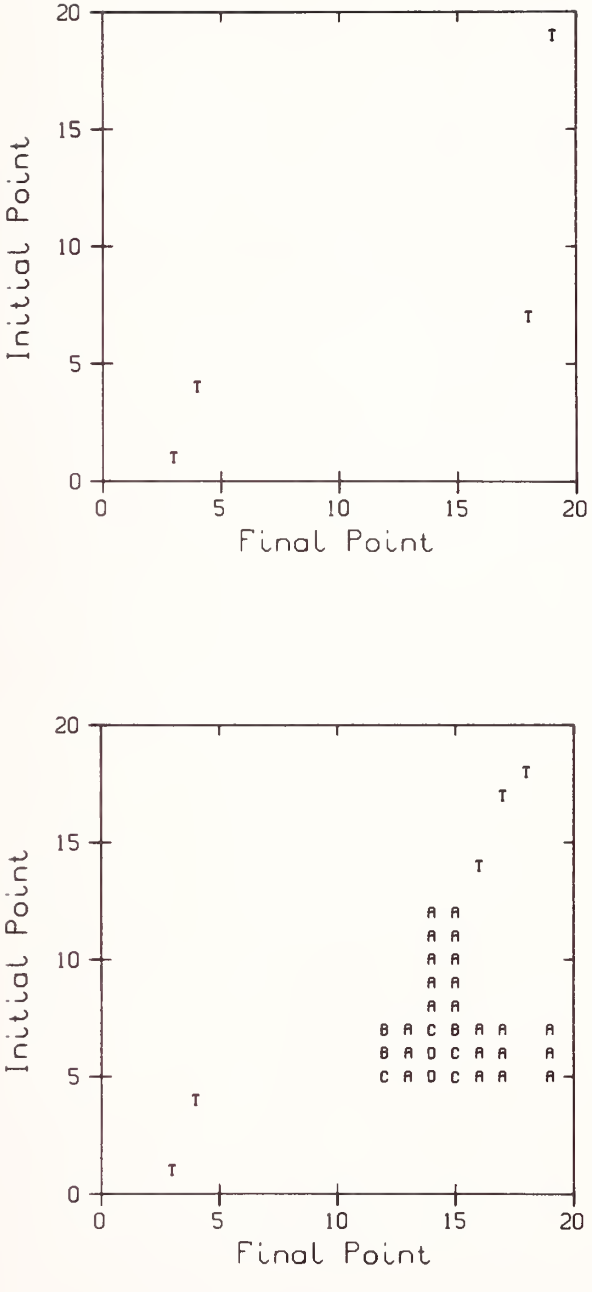

Fig. 3. Alarm-sequence charts for CUSUM: with no diversion (upper), with diversion (lower).

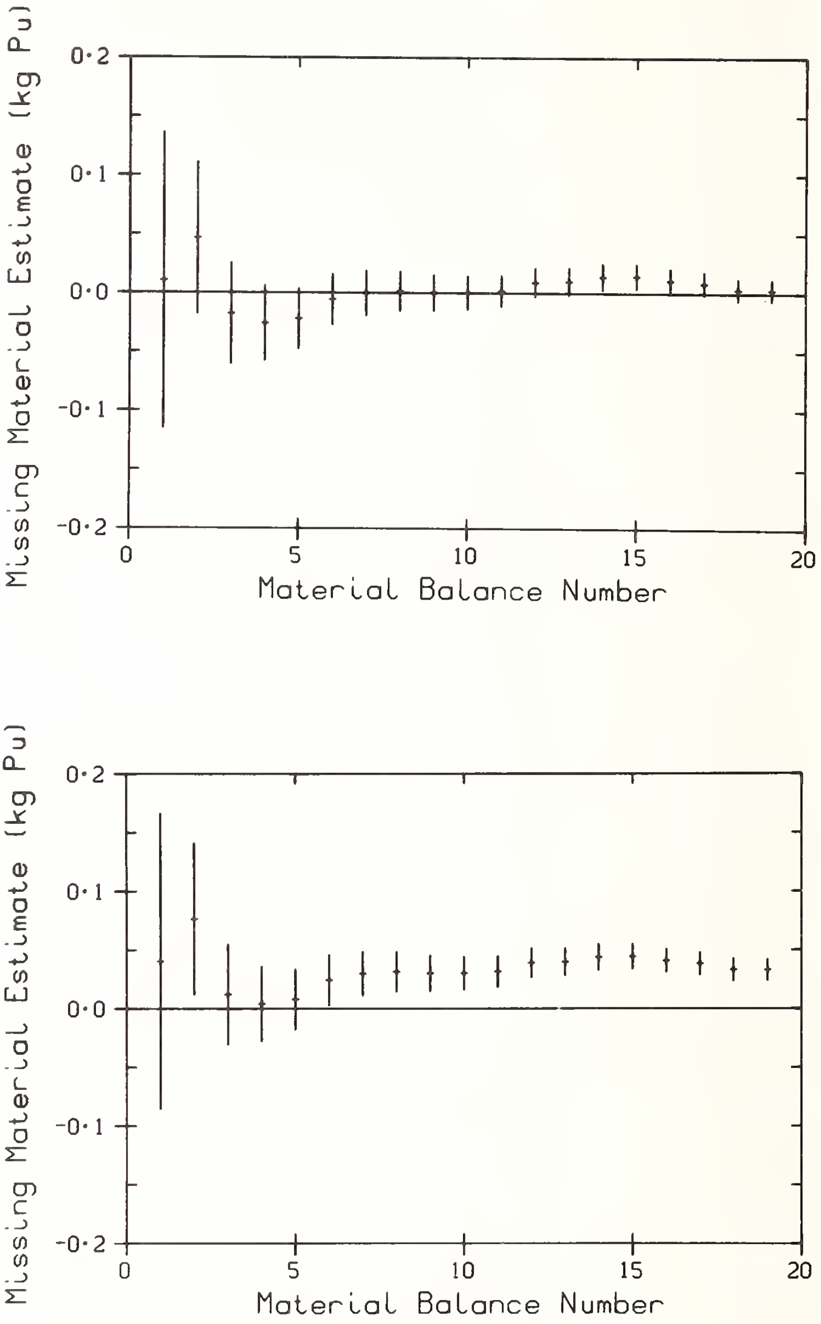

Fig. 4. Kalman filter estimates of average missing material for one day with no diversion (upper), with diversion (lower).

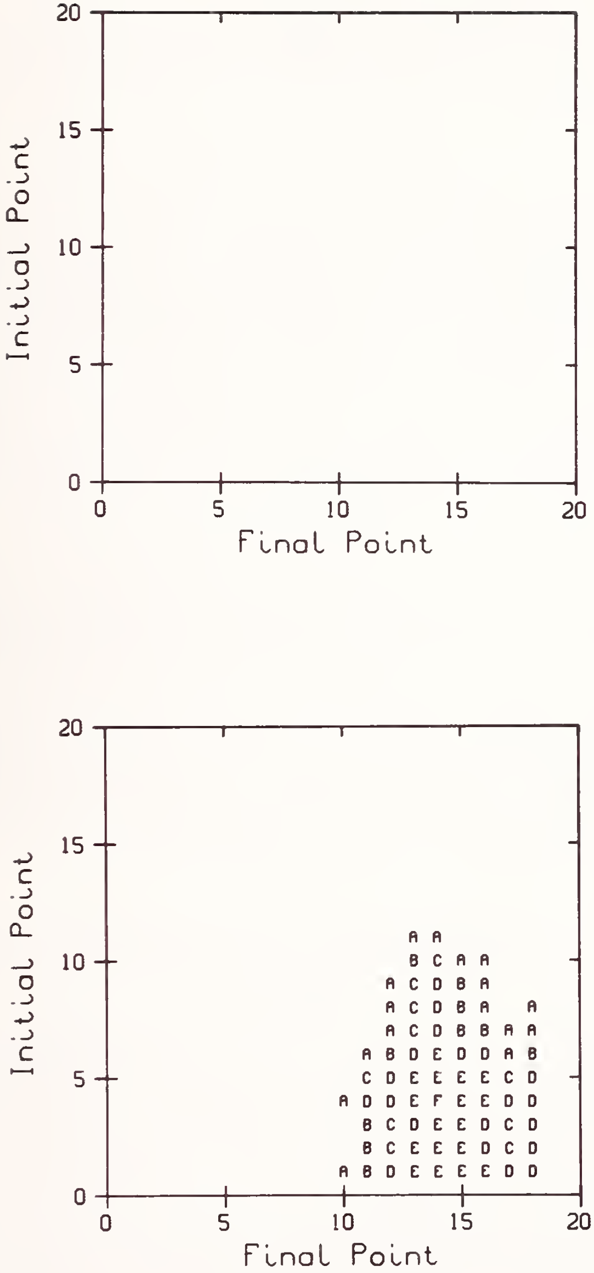

Fig. 5. Alarm-sequence charts for Kalman filter estimates: with no diversion (upper), with diversion (lower).

Analytical Chemistry Measurements Quality Control Program Using Computer Applications

by

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ABSTRACT

An Analytical Chemistry Measurements Quality Control Program assures the reliability of analytical measurements performed at the Barnwell Nuclear Fuel Plant. The program includes training, methods quality control, replicate samples and measurements, mass measurements, interlaboratory sample exchanges, and standards preparation. This program has been designed to meet the requirements of 10CFR70.57. Portions of the program have been automated by using a PDP 11/35 computer system to provide features which are not readily available in manual systems. These include such items as realtime measurement control, computer calculated bias and precision estimates, various surveillance applications, and evaluation of measurement system variables.

The efficiency of the computer system has been demonstrated in gathering and assimilating the results of over 1100 quality control samples during a recent cold chemical checkout campaign. These data were used to determine equations for predicting measurements reliability estimates; to evaluate measurement performance of the analysts, equipment, and measurement period; and to provide directions for chemistry methods modifications and additional training requirements. A procedure of replicate sampling and measuring provides random error estimates. The analytical chemistry measurement quality control activities during the campaign represented about 10% of the total analytical chemistry effort.

KEYWORDS: Assurance; measurement quality control; realtime quality control; reliability; replicates; standards

INTRODUCTION

This paper describes the Analytical Chemistry Measurements Quality Control Progr used at the Barnwell Nuclear Fuel Plant located in Barnwell, South Carolina. This pl was built to recover uranium and plutonium from spent light water reactor fuel. At capacity operation, the plant will daily process five metric tons of uranium and have over 200 samples taken, requiring 800 analytical determinations per day. Analytical vices Department personnel are responsible for these determinations, which are made f controlling plant processes, calibrating in-line monitors, and accounting for nuclear materials. The quality of these measurements is of utmost importance. Therefore, a surement quality control program has been designed to determine the reliability of th analytical measurements. The program helps identify faulty methods, equipment, analy techniques, reagents, and systems which require remedial attention.

A "Measurement Control Program for Special Nuclear Materials Control and Account (10CFR70.57) is required by the Nuclear Regulatory Commission. In addition to nuclea material measurements, the Barnwell program includes all routine measurements. The t program includes the following segments:

1. A procedure for training and testing the technicians.
2. A procedure for analytical chemistry methods quality control.
3. A procedure for replicate samples and measurements.

4. A procedure for mass measurements and balance quality control.
5. Participation in an interlaboratory sample exchange program.
6. The preparation of reagents and standards.

Large portions of segment two of the program have been automated by using the labora- computer system. The use of the computer system will be discussed in detail. Other nts of the program will be addressed briefly.

THE ANALYTICAL CHEMISTRY METHODS QUALITY CONTROL PROCEDURE

Presently some 25 analytical chemistry methods are included in this segment of our ty control program. Each method has a stated range for which the method is appli- . Standards are prepared to cover the range of each method. Usually several pairs andards are made up a couple of standard deviations apart to cover the range. These sed in the quality control program to test the various levels over the range. In most these standards are packaged in glass ampuls and flame sealed. Currently, the Stan- Laboratory has over 50,000 standards packaged in flame sealed ampuls for use in the ty control and training activities. The reference values for these standards are ietary and known only to the Standards Laboratory personnel.

Technicians are trained to use the analytical chemistry methods by analyzing a known standard until they become proficient with the method. Then they are required to ze nine unknown standards. If statistical evaluation of the results proves satisfac- the technician is qualified to use the method for the analyses of plant samples.

Routinely, each shift an analytical chemistry method is used, the analyst is required alyze a quality control standard. If this measurement is within the control limits he method, he is permitted to use the method for plant sample measurements. However, is out of control, the measurement system must be corrected before plant samples can alyzed.

To achieve this requirement, the laboratory computer system has been programmed to ol the quality of our analytical methods measurements. The computer monitors each atory method and will lock out the calculation program for a method if a standard ates the method is out of control. A description of this system is given.

Laboratory Computer System Description

The laboratory computer system as shown in Figure 1, consists of a PDP 11/35 CPU with of memory, multiple disk drives, dual magnetic tape transports, and various input/ t terminals (DECwriters and CRT terminals). One-fourth of the disk storage provides 5000 files for the quality control standards activities. Periodically, data from zed standards are transferred to magnetic tape for long term storage. Terminals are ed at strategic points in the laboratories, process control rooms, and the administra- building. Initially, only two laboratory instruments were interfaced directly to the m, a mass spectrometer and a multichannel analyzer. We are currently interfacing ces, densimeters, fluorophotometers, automatic titrators, and other laboratory instru- s.

The system is built around the RSTS/E (resource sharing-time sharing) operating sys- , version 6B, and utilizes a BASIC-PLUS language processor. All applications programs he individual analytical methods are written in a modular format using this powerful on of BASIC. This system has been operating successfully for two years. During this d we have experienced less than 1% unscheduled downtime.

The plant recently completed a 10-week cold run during which some 4300 samples were zed to produce 11,000 measurements. This system proved to be effective in handling 200 samples per day in addition to the quality control standards. During the run quality control standards (QCS) were analyzed. The quality control effort represented 10% of the total analytical effort.

Quality Control Standards

For an analyst to have assurance that a measurement system is working properly when using a manual measurement control system, he must analyze a bench standard having a kno value and plot the result on a control chart. There is a possibility the analyst's resu might be biased to fall within the control chart limits when the value is known. Therefo for management to obtain unbiased estimates of the measurement errors, standards with val unknown to the analyst must be measured in addition to the known bench standards. Actual measurement control is usually limited to administrative control and could be ignored by the analyst. In an automated system, only unknowns are required. The computer provides immediate evaluation of the analyst's result. If the computer indicates the measurement in control, the analyst may analyze process samples. If not, the computer locks out the method until corrective action is taken and an analyzed standard is in control. This sy tem provides realtime measurement quality control.

One of the objectives of the program is to determine each method's precision over i stated range. To do this, quality control standards are arranged in a sequence to cover the method's range.

The quality control chemist uses a computer program to rapidly log standards onto t disk and sequence them. This achieves the objective of covering the range of the method with an equal number of standards. Figure 2 illustrates how the computer prompts the ch ist for the information needed to generate an alternating scheme of standards in a seque He has an opportuntiy to approve input before it is stored. By alternating sublevel sam that are one or two standard deviations apart, the analyst never knows which subsample h has at the level being tested.

Upon final approval, the computer prints out a table similar to the one in Table I the data are stored on the QC disk. This printout is used in the laboratory as a guide labeling the ampuls containing the standard solutions.

After labeling, the ampuls are placed in a sample storage area. One standard is ar lyzed each shift a method is used. All levels of the method's range are tested by requi the analyst to take the lowest numbered standard from the available sequence and use a c stant aliquot size. It is analyzed according to the procedure in the method. Upon completion of the analysis, the analyst uses the computer to calculate his results. He in all of the data requested by the computer.

Figure 3 provides a sample of the dialogue between the analyst and computer. The analyst's input is underlined. He calls for the "DATA" program to calculate results of measurement. In this illustration, on line 14, the computer prompted "QC OR SPL?" and t analyst typed, "SPL". The computer responded "NO SAMPLE ANALYSIS UNTIL A QC STANDARD I RUN THIS SHIFT." The computer checks to see if an "in limits" standard has been analyz within the past nine hours. If not, the computer locks out that method until a standar analyzed that is in limits.

The calculated value is displayed for approval before being tested by the computer If the result appears questionable, the analyst can reject the calculation and enter new data. After approval, the result is compared with the reference value's acceptable ran The computer responds whether the measurement is within limits or not. What the analys does next depends upon the response. The three possible responses are shown in Figure A three standard deviation limit has been established as the out-of-control limit. Res between the two to three standard deviation limit are flagged with an asterisk. If two consecutive standards are flagged, the method may be going out of control and correctiv action is required. The analyst and his supervisor evaluate the situation and take the necessary action. In cases where they are unable to determine a cause for out-of-contr situation and cannot get the computer unlocked with the unknown standards, bench standa of known concentration have been logged into the computer. Known values provide the analyst with guidance as to the direction of his bias. Also, if there is a mismatch be tween the reference values in the computer and the actual values, these standards can b used to unlock the computer if the results are within the control limits.

Surveillance

Surveillance activities are performed by all personnel. Upon evaluation of a stan-
s analysis, the analyst is given a message to indicate the state of control of the
rement system and appropriate action is taken. In addition to the analyst, the super-
monitors the quality control results. Standards Laboratory personnel daily monitor
easurement activities of the laboratory. The computer is programmed to daily print
summary of all standards measurements made during the past 24 hours on a terminal.
uality control chemist exercises his surveillance responsibility by reviewing the
rements and initiating corrective action as needed.

Control activities can be checked at any time by a "QC STATUS" program. Analyzed
ards can be reviewed by method, acronym, standard number, or all methods. An example
e "QC STATUS" using the acronym subroutine to check a method is shown in Table II.
hemist specified status by the acronym 2U02 for a uranium fluorophotometric method.
2 denotes a specific instrument. The computer listed the stored quality control stan-
that have been analyzed on that instrument. The analysis, reference value, dif-
ce between the two, standard deviation, result of the evaluation ("IN" or "OUT"), num-
f standard deviations, plus the analyst's initials, crew, and date are given in the
s report.

This information was plotted on a control chart so measurement performance of the
d can easily be viewed. Figure 5 illustrates a control chart depicting the results
e "QC STATUS" sheet plus subsequent data. The control chart reveals a problem on the
f February. One of the reagents was contaminated. After it was replaced, the method
back in control and there were no further problems.

Quality Control Standard Data Evaluation

In addition to method performance surveillance, quality control data can be evaluated
thod, instrument, analyst, or time period. The results of these evaluations can be
ed to determine if there are any problems with the components of a measurement system.
III shows the evaluation of one analyst's measurements for the fluorophotometric
d. When all the data for a method are analyzed, the analyses are grouped according
eference value. The mean and standard deviation of the reported values at each sublevel
alculated. Equations are fitted to the data by regression. They are used to calculate
mates of the standard deviation and provide bias corrections. These equations are in-
ed into a program which generates bias correction tables and estimates of the standard
ations of various levels of the method. These reports are used by laboratory super-
s and Nuclear Materials Control personnel in evaluating measurement performance.

The equations are also included in the calculation programs for the appropriate analy-
l method. All measurements are bias corrected and reported with the standard deviation.
statistics provide reliability estimates for analytical measurements.

PROCEDURE FOR REPLICATE SAMPLES AND MEASUREMENTS OF NUCLEAR MATERIALS

Replicate measurements are required for all measurement methods used to generate data
nuclear materials control and accountability purposes. The replicate measurements are
to estimate the combined random error variance for sampling and analytical measure-
s. Sample points within the plant that are covered in the replicate measurement pro-
re include input, output, and inventory locations. There are two parts to this proce-
.

Replicate Sampling

Multiple samples are taken from accountability sample points. At least two samples
taken and measured using a density method to test for homogeneity. Analyzing duplicate
les provides assurance that the samples are representative of the nuclear materials in
vessel from which they were collected. Most of the sampling is performed in remote
ytical facilities equipped with master slave manipulators. The facility is divided
cells which are used for sampling and analytical measurement work. Needle block sam-
s are used to sample some 75 measurement points within the plant. Samples are analyzed

by a densimeter which has a remote head in one of the sample analytical cells. The instr ment readout panel is located outside the cell. This equipment is currently being interfaced with our computer system. After two samples have been analyzed, the results are tested to see if they fall within the predetermined limits set up for that point. If the do, the samples are accepted as homogeneous and further analyses are performed. If not, additional samples are taken until they satisfy the requirements for replicate samples.

Replicate Measurements

During a cold run using natural uranium, 20% of the samples were resubmitted for replicate measurements. They were randomly selected by the quality control chemist and sub mitted within 48 hours to different crews for analyses. These samples were distributed over the measurement period. The samples submitted for replicate measurements were codec as quality control samples from the measurement point from which they were taken. They were analyzed for nuclear material content, density, and acid concentration. The replica result was compared to the original result and if the difference between the results exceeded the limits for the measurement point, a third bottle was analyzed. All data were handled by our computer and stored for evaluation at a later date. Eventually, they were transferred to magnetic tape for long term storage. These data were used by Nuclear Materials Control personnel to estimate the random error associated with the sampling and analytical measuring activities of the measurement process. Figure 6 is an illustration a final report generated by the computer for one of the replicate samples submitted as quality control sample for a measurement point.

MASS AND BALANCE QUALITY CONTROL ACTIVITIES

The purpose of the mass and balance quality control segment of the program is to com with the requirements specified in 10CFR70.57 (b)(8)(i), (b)(12). Procedures are provid for measuring and documenting mass measurement reliability. They provide data for rando error estimates on weighing measurements. They are applicable to all mass standards and balances used for the measurement of nuclear materials.

OUTSIDE MEASUREMENT EVALUATION PROGRAMS

The Safeguards Analytical Laboratory Evaluation (SALE) Program administered by the United States Department of Energy's New Brunswick Laboratory is sponsored by the NRC an DOE. The goal of the program is to provide a means for laboratories to demonstrate thei continued proficiency in safeguards measurements of nuclear material by periodic interlaboratory measurements comparisons. The Barnwell laboratory participates in the SALE p gram for the following reasons:

1. To demonstrate our analytical measurement capabilities.
2. To provide outside surveillance of our nuclear material measurement processes.
3. To provide an independent evaluation of our measurement activities.
4. To compare our measurement ability with those of other participants in the prog

ANALYTICAL STANDARDS AND REAGENTS

All standards and reagents used in the laboratory are prepared by the Standards Sec tion. This minimizes the error introduced by having a large number of people making the own reagents and standards for analytical chemistry methods. For nuclear materials measu ments, standards are prepared having traceability to the National Bureau of Standards. Most of these standards are packaged in ampuls and flame sealed as mentioned earlier. R gents and standards preparations are documented and dated. If they are suspected when a measurement system goes out of control, this provides a means of checking them.

SUMMARY

This program has been developed to include proven measurement control techniques, innovations of modern technology, and requirements for good measurement reliability. Du periods of high measurement activity, the quality control activities represent 10% of th analytical effort. The computer system:

Permits the use of a minimum number of standards,
Allows physical control of the measurement process by locking methods out,
Handles large quantities of data using modern record handling techniques,
Permits readily available surveillance of the measurement process,
Provides in-depth evaluation of the various components of the measurement process,
Bias corrects the measurements and calculates the appropriate standard deviation.

ocedures for replicate samples and measurements provide random error estimates for ts of the measurement systems. The other segments of the program assure us that our ment activities are under control.

FIGURES AND TABLES

I. Computer printed table of quality control standard sequence.

II. Computer printed program for obtaining the status of analyzed quality control standards.

III. Computer printed evaluation for an analyst's quality control standard generated during the measurement period.

1. Schematic showing the components of the laboratory computer system.

2. Computer printout illustrating the login program for a sequence of quality control standards.

3. Computer printout illustrating the program for quality control standard data entry by an analyst.

4. Quality control standard flow diagram for various responses by the computer.

5. Method U-F-1-B quality control chart illustration of plotted data from Table II and subsequent data. Analyst's initials and standard's identification number are listed.

6. Illustration of computer printed final report of analytical measurements on a sample submitted as a quality control standard for replicate measurements.

Table I. Computer printed table of quality control standards sequence.

```
METHOD
QC STD # LEVEL SUB LEVEL REF VALUE SD
2U 501   1     1          1        .1
2U 502   1     2          1.2      .1
2U 503   2     1         13       1.3
2U 504   2     2         11.7     1.3
2U 505   3     1         56       2.5
2U 506   3     2         58.5     2.5
2U 507   4     1         98       4.0
2U 508   4     2         96       4.0
      .
      .
      .
      .
      .
      .
2U 561   1     2          1.1      .1
2U 562   2     2         11.7     1.3
2U 563   3     2         58.5     2.5
2U 564   4     2         96       4.0
DATA STORED
```

Table II. Computer printed program for obtaining the status of analyzed quality control standards.

```
QC STATUS

? ACRONYM = 2U02
                 (DENOTES INSTRUMENT)
2U02


STD #   REF    EXP    BIAS   SD    IN/OUT DEVIATION  C/A DATE

501      1.00   1.15   .15   .1     IN       1.5     E/JAL 27-JAN-78
502      1.1   1.05   -.05   .1     IN       -.5     A/CJA 31-JAN-78
503     13.0  15.8    2.8   1.3     IN       2.15    E/JAL 03-FEB-78
504     12.7   15.2   2.5   1.3     IN       1.92    B/LAK 06-FEB-78
505     56     62     6.0   2.5     IN       2.4     E/JAL 07-FEB-78
506     58.5   66.5   8.0   2.5     OUT      3.2     E/JAL 07-FEB-78
90005   30.0   36.0   6.0   1.5     OUT      4.0     E/JAL 07-FEB-78
90006   30.0   29.0   1.0   1.5     IN       -.33    E/JAL 07-FEB-78
```

Table III. Computer printed evaluation for an analyst's quality control standards generated during the measurement period.

```
ACRONYM = 2U02

KNOWN    REPORTED     BIAS    ANALYST    # OF STD DEV

 2.8       2.98        -.18    B/TMS        -.642
 2.8       2.65         .15    B/TMS         .535
  .24       .24        0       B/TMS        0
  .24       .18         .06    B/TMS        1.818
 2.8       2.74         .06    C/TMS         .214
16        14.64        1.36    B/TMS          .85
  .23       .29        -.06    B/TMS       -1.818
15.5      14.52         .98    B/TMS         .612
15.5      13.29        2.21    B/TMS        1.381
50        54.22       -4.22    B/TMS        -.843
  .23       .24        -.01    B/TMS        -.303
  .23     23.71      -23.48    B/TMS     -711.515 OVER 5 SD (POINT REJECTED)

ONE POINT AT K = 16 R = 14.64
ONE POINT AT K = 50 R = 54.22
 3 POINTS AT K = 2.8 MEAN = 2.79  STD DEV = .170587
 2 POINT AT K = .24 MEAN = .21  STD DEV = .424264E-1
 2 POINTS AT K = .23 MEAN = .265  STD DEV = .353553E-1
 2 POINTS AT K = 15.5 MEAN = 13.905  STD DEV = .869741

TOTAL NO. OF DATA POINTS = 11
TOTAL NO. OF LEVELS = 6

STANDARD DEVIATION EQUATION:
STD DEV = A*K^2+B*K+C    WHERE A = .00024, B = .05061, C = .02697

BIAS CORRECTION EQUATION:
CORRECTION = A*K^2+B*K+C    WHERE A = -.00181, B = .0732, C = -.0194
```

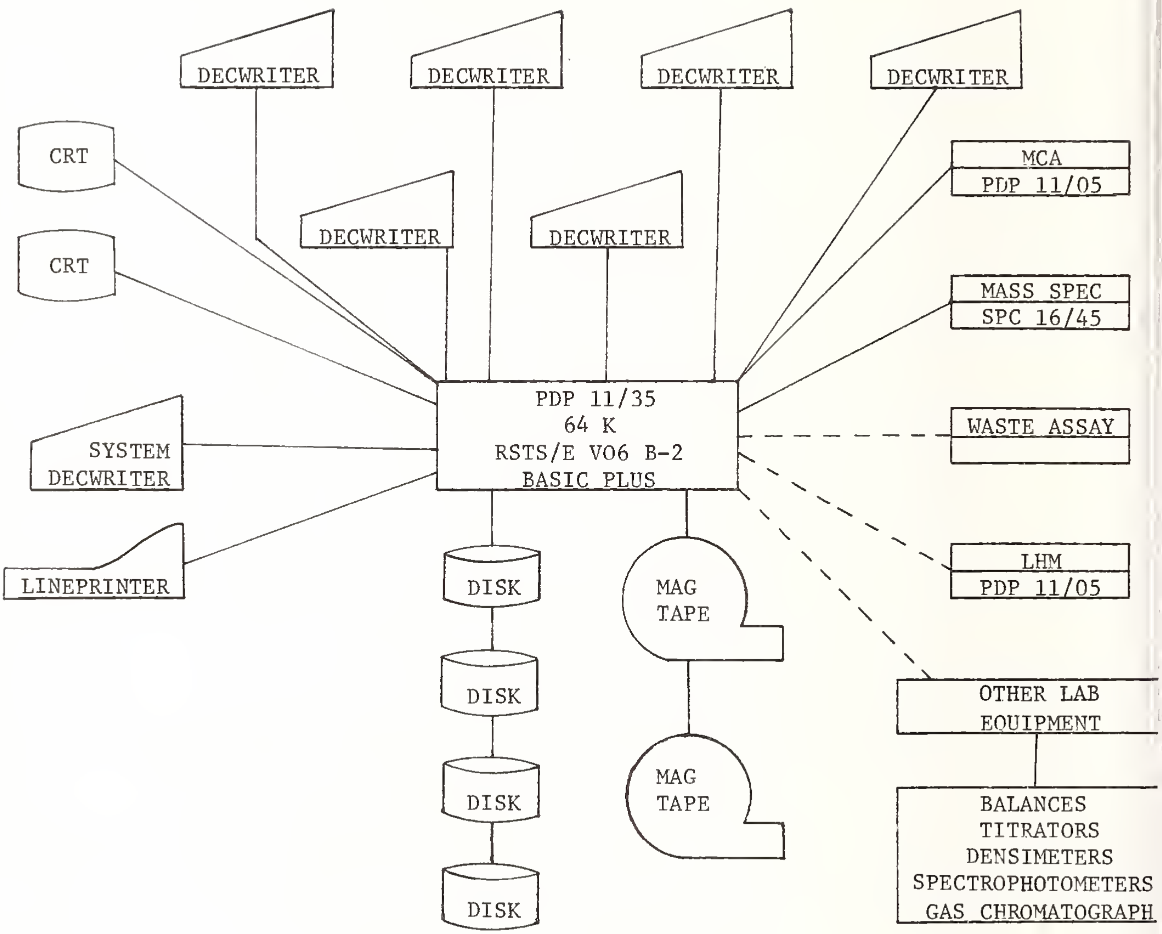


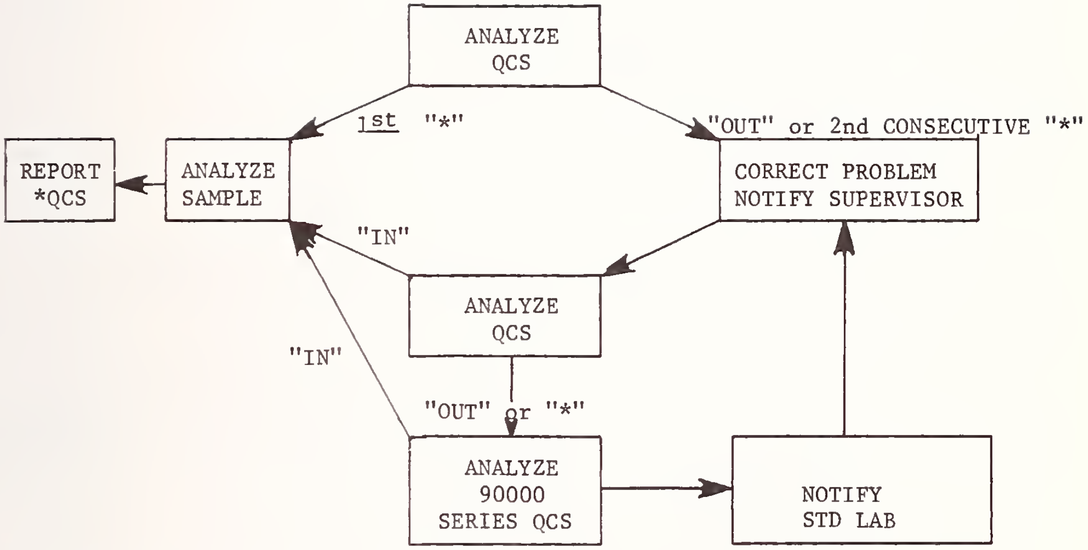
Figure 1. Schematic showing the components of the laboratory computer system.

```
QC LOG
ID? ####
03-FEB-78  11:02
? SEQUENCE
STORE DATA (Y OR N)? Y
METHOD OF ACRONYM (M OR A)? M
METHOD = U-F-1-B
UNITS = PPM
NUMBER OF LEVELS = 4
NUMBER OF STDS AT EACH LEVEL = 2
HOW MANY CYCLES = 2
INITIAL SEQUENCE NUMBER = 501
LEVEL 1
R1 = 1.0
R2 = 1.1
SD = .1
OK (Y OR N)? Y
LEVEL 2
R1 = 13
R2 = 11.7
SD = 1.3
OK (Y OR N)? Y
         .
         .
         .
         .
         .
         .
```

Figure 2. Computer printout illustrating the login program for a sequence of quality control standards.

```
DATA
03-FEB-78, 10:45
CREW/ANALYST = E/JAL
METHOD = U-F-1-B
WHICH INSTRUMENT
ENTER 1 FOR JA, 2 FOR ORNL (HCLA), 3 FOR ORNL (UF6)? 2
CALIBRATE (Y OR N)? N
LAST EQUATION COEFFICIENTS
ON 22-JUL-77 BY E/JMR
A = .644664
B = .859144
C = .179854E-3
CORR COEF = .999998
QC OR SPL? SPL
NO SPL ANALYSIS UNTIL A QC STANDARD IS RUN THIS SHIFT
QC OR SPL? QC
QC NUMBER? 2U00503
ENTER QC DATA:
03-FEB-78, 10:45
AQUEOUS SAMPLE (Y OR N)? Y
DILUTION (Y OR N)? N
SPL ALIQUOT (ML)? .5
MIBK VOL (ML)? 2
ORG ALIQ VOLUME (ML)? .1
INSTRUMENT READING? 421.5
CONC = 15.79 PPM
RESULTS OK (Y OR N)? Y
*RESULTS BETWEEN 2 and 3 SD
```

Figure 3. Computer printout illustrating the program for quality control standard data entry by analyst.



"IN", RESULT IS WITHIN THE ±2 STANDARD DEVIATION RANGE.

"*", RESULTS ARE WITHIN THE ±2-3 STANDARD DEVIATION RANGE.

"OUT", RESULTS EXCEED THE ±3 STANDARD DEVIATION LIMIT. THE METHOD IS STATISTICALLY OUT OF CONTROL AND CORRECTIVE ACTION IS REQUIRED.

Figure 4. Quality control standard flow diagram for various responses by the computer.

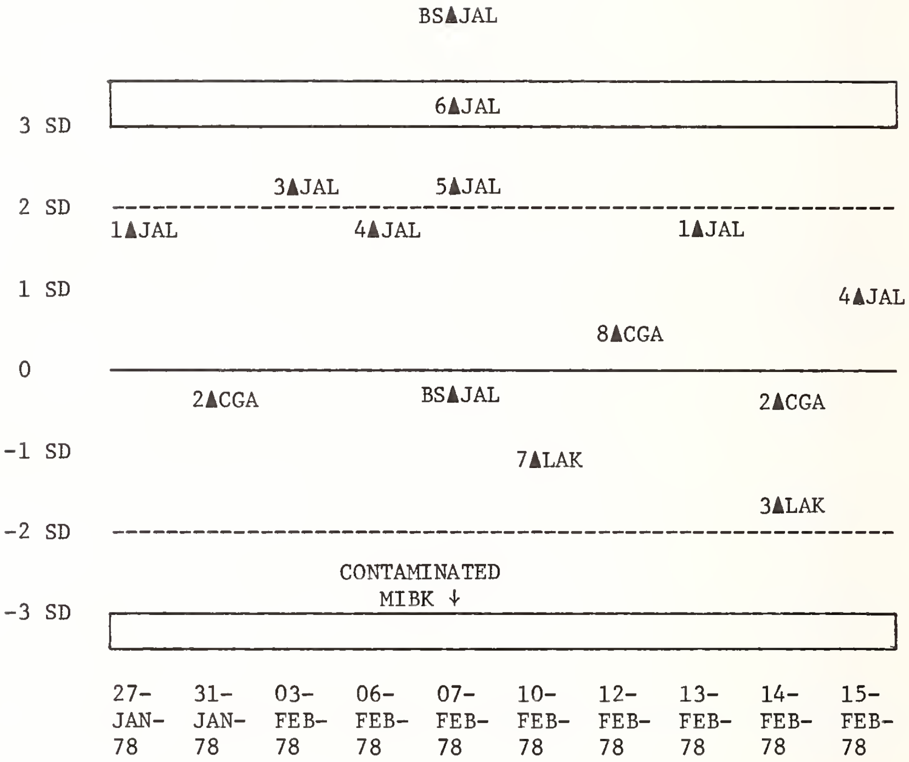


Figure 5. Method U-F-1-B quality control chart illustration of plotted data from Table II and subsequent data. Analyst's initials and standard's identification number are listed.

```
                                   FINAL REPORT
                                   SAMPLE 11157

                                Sample Point:  N-34

                                 Sample ID:  QC 32

                      REQUESTED BY                  APPROVED BY
                         AS/JPC                         JDS

                  LOG IN                        LOG OUT
                  15-SEP-77, 15:33              15-SEP-77, 23:10
                    SAMPLING DATE                 SAMPLING TIME
                    9-15-77                       15:33

                    COMMENT
U-VI REQUESTED AND RUN
SMALL AMOUNT OF SAMPLE DID NOT TITRATE ENOUGH

ANALYSIS  RESULT  UNITS     SD(ISIGMA) METHOD        ANALYST  DATE       TIME

U         0.5     G U/L     .03        U-VI-1-A      C/LAK    15-SEP-77  18:10
H+        3.623   N         .07        ACID-VP-1-B   C/LAK    15-SEP-77  20:06
DN        1.1222  G/ML      .0006
              AT 25 DEG C              DN-DM-1-A     C/LAK    15-SEP-77  20:20
```

Figure 6. Illustration of computer printed final report of analytical measurements on a sample submitted as a quality control standard for replicate measurements.

ACTINIDE DETERMINATION BY ROCKWELL HANFORD OPERATIONS' ANALYTICAL LABORATORIES

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ABSTRACT

A review of the procedures currently used by the Analytical Laboratories Department of Rockwell Hanford Operations for the determination of actinide composition. Methods used include extraction followed by alpha energy analysis, visible spectrophotometric, x-ray emission and x-ray diffraction techniques.

INTRODUCTION

Actinide analysis required of Rockwell Hanford Operations Analytical Laboratories Group is done on several different matrices.

The first matrix has a high nitrate concentration; the actinides being present in the hydrate metal nitrate form. The samples of this type are from the feed, waste and product streams of the PUREX chemical separations plant. Samples vary in amount of nitrate present (both as free acid and complexed with the metal ion), actinides present, and concentration ranges. Types include 397-445 g/l Th with 6×10^{-5} - 2×10^{-2} g/l ^{233}U; <0.05 g/l U with 3×10^{-3} g/l Np; 7 g/l U with only trace amounts of other actinides; 238-506 g/l U with 3×10^{-5} - 8×10^{-3} g/l Np; 10-26 g/l U with 5×10^{-2} g/l Np; 2×10^{-2} g/l Pu and 2×10^{-2} g/l Th; <.1 g/l U with 3×10^{-4} - 1×10^{-3} g/l Pu and others that have not been as well characterized as yet. These samples are analyzed predominantly for Th, U, Np and some Pu. X-ray emission analysis is used to characterized solutions with U and Th concentrations 2 g/l and greater. A visible spectrophotometric method is used for determining Th concentration in lower level solutions. An extraction/fluorimetric method is used to determine uranium at concentrations lower than 2 g/l. Extraction and alpha counting are used in the analysis of the isotopes ^{233}U and ^{237}Np. Extraction and alpha energy analysis (AEA) methods a used to analyze for Pu content.

The second matrix consists of wastes varying from a pH of 8 to solutions 8 <u>M</u> in hydroxide, the matrix having been adjusted to maintain the integrity of the steel tanks that the solutions are being stored in until appropriate long-term waste storage methods are developed. The samples of this type were the effluents from the bismuth phosphate, REDOX, PUREX and plutonium reclamation chemical separation plants. These samples consist of four types. 1) Sludge - The insoluble metal hydroxides formed from the neutralization with NaOH, containing iron and aluminum as major metallic components with manganese, magnesium, chromium, actinides and other miscellaneous metals as minor constituents. When analysis of this samp is required the sample is first centrifuged and the interstitial liquid removed. The soli are then washed with water several times to remove any water soluble components present. The solids are fused with KOH or $LiBO_2$ and then dissolved with HCl and water. 2) Tank Far - The water soluble constituents of the waste tanks. These samples are combinations of the constituents present in the following two sample types, found here in a more diluted form. 3) Salt Cake - The salt left when tank farm material is put through an evaporation process This consists mainly of the sodium salts of nitrate, carbonate, and aluminate with some sodium nitrite and other salts present in minor quantities. Actinides are present here as minor to trace components. When salt cake is analyzed it is first centrifuged to remove t interstitial liquid, the solids are then dissolved in water and heated. Any water insolubl solids that remain are fused with KOH, then dissolved using HCl and water. 4) Interstitia Liquid - The concentrated liquid left in the evaporation process. It contains dissolved sodium nitrates, aluminates and other salts in a high caustic solution. Trace levels tinides are found in these samples. These samples are analyzed for Pu and U content. traction/fluorimetric method is used for determining U concentration. Either an ex- ion/alpha counting or an extraction/alpha energy analysis method (AEA) is used to mine Pu content.

hird matrix consists of a wide variety of specimens from the plutonium processing plant. samples include plutonium nitrate solutions, oxide and metal. Scrap from engineering es, samples from hood and process areas, process stream samples, and solid waste samples ll a part of this sample type. These samples are analyzed for plutonium content both afeguards and accountability. Physical plant items, such as gloveboxes, hoods, ducts, pipes are also in this third sample type and are analzyed in situ and may be dismantled lutonium recovery. Amperometric and visible spectrophotometric methods are used for mining Pu content in the plutonium nitrate, oxide and metal samples. Alpha counting sed to determine Pu levels in process streams and waste samples. Non-destructive niques are used in the Pu determination of the rest of the items. It should be noted when the non-destructive techniques are used it is the item itself that is analyzed ost cases and not just a sample of that item.

g x-ray diffraction techniques the fourth matrix is analyzed for actinide composition. ganic powders and masses are analyzed to determine the presence of actinide compounds to identify the chemical forms of the compounds present.

EXTRACTION AND COUNTING METHODS

in Solutions of High Thorium Concentration

matrix for this sample type is that of high nitrate as described previously. The first of this procedure therefore is a calcination process using HCl to destroy the nitrate. uranium and thorium form nitrate complexes which extract into the organic phase. The ds left from the calcination are then dissolved with 9 M HCl and the uranium chloro lex is extracted into 5% TIOA (tri-iso-octylamine) in xylene. This accomplishes the extraction of uranium from thorium since thorium does not form anionic complexes with chloride ion. Refined separation is then further accomplished by stripping the uranium 0.1 M HNO_3. Although separation is complete at this point this solution corrodes the a discs used for counting the samples and gives erroneous results. To separate out mounting interferences the pH of the samples is adjusted to 3 and the uranium extracted 0.5 M TTA (thenoyl-tri-fluoroacetone) in xylene.

liquot of this extraction is then mounted on a one inch stainless steel alpha disc and orated to dryness on a "cold spot" heating stove or a wire heater. The disc is then ned to reduce self absoption and fix it to the disc. The sample is then counted on an a proportional counter (APC). Recovery on eight standards (5.046×10^7 dpm/l) run over eriod of two months showed a mean recovery of 93.5% with a standard deviation of 3.1% at 95% confidence level.

Np in High Level Beta-Gamma Samples

s method is seldom used in our laboratory at the present time, but is included for com- teness. The sample is adjusted so that the acid content is 4 M. Ferrous sulfamate and razine are used to reduce neptunium to the (IV) state. The actinides are extracted ng 10% (by volume) TIOA (tri-iso-octylamine) in xylene. The actinides are then stripped o 1 M HCl and ferrous sulfamate and hydroxylamine-hydrochloride added; the solution is n heated. At the end of this process neptunium is in the extractable (IV) state while tonium is in the inextractable (III) state; uranium is present in the inextractable (VI) te. The Np is then extracted into 0.5 M TTA (thenoyl-tri-fluoroacetone) in xylene. aliquot of this is mounted on an alpha disc, evaporated to dryness, fired and counted ng an alpha proportional counter (APC). No accuracy and precision data was available.

Np in Solutions of High Uranium Concentration

using this procedure the plutonium to neptunium ratio of the sample is in the range from to 10. The hydrogen ion concentration of the sample is first determined then hydroxylamine hydrochloride, ferrous sulfamate and deionized water are added. The hydrogen ion centration is then adjusted to 0.9 M using HNO_3 or NaOH. By these steps the neptunium i reduced from the (V) and (VI) states, in which it is most prevalent in aqueous solutions the (IV) state which is extractable. The plutonium is reduced to the (III) state which inextractable; the uranium is left in its inextractable (VI) state. The neptunium is th extracted into 0.5 M TTA (thenoyl-tri-fluoroacetone) leaving Pu (III), U (VI), Fe (III) sodium, aluminum and potassium ions which interfere with counting due to alpha absorptio The neptunium - TTA is then washed with .8 M HNO_3, mounted on an alpha disc, evaporated dryness, fired and counted by an APC.

In 1972 using seven pieces of data an average recovery of 88.3% was obtained with the pr cision of a single observation 29.8% at the 99% confidence level. Standard recoveries r lately have yielded only about 70% recovery.

Pu From Other Alpha Emitters and Fission Products

This procedure is the most commonly used of the two available for Pu analysis in our laboratory. The hydrogen ion concentration of the sample is first adjusted to 2-3 M, then ferric nitrate, hydroxylamine hydrochloride and aluminum nitrate are added. The solutio is then heated. The heat and acid are used to destroy any plutonium polymer present whi the aluminum nitrate ties up fluoride ion and the ferric ion and hydroxylamine reduce th Pu to the (III) state by the following mechanism:

$$NH_2OH_2^- + Fe^{+3} \xrightleftharpoons{\Delta} Fe^{+2} + H_2O + 2H^+ + \frac{1}{2} N_2 \uparrow$$

$$Pu(III, IV, VI) + Fe^{+2} \rightleftharpoons Fe^{+3} + Pu\ (III)$$

After cooling, the acidity of the sample is adjusted to 0.8 - 1.0 M. Sodium nitrite is t used to form nitrous acid which oxidizes the Pu to the extractable (IV) state. The plutonium is then extracted using 0.5 M TTA in xylene and an aliquot mounted on a one inch stainless steel alpha disc, dried, fired and counted on an APC.

If samples containing high ^{95}Zr-^{95}Nb are analyzed the mounts will have very high beta-ga activity which will lower the beta threshold of the APC down onto the alpha plateau resu in an alpha breadkown. If ^{95}Zr-^{95}Nb is present the Pu (III) is stripped into 8 M HNO_3. This strip will recover >99% of the Pu and ≈2% of the ^{95}Zr-^{95}Nb. An aliquot of this pha is then mounted , dried, fired and counted as described above. Iron (III) will also extract into the 0.5 M TTA in xylene and relatively large quantities (1 mg) can cause low results because of alpha absorption. Am (III) and Cm (III) do not extract, however Np,(will extract and its contribution to the alpha count is corrected through alpha energy analysis (AEA). An AEA is also run whenever the isotopic content is questionable since small amounts of relatively short lived isotopes, particularly ^{238}Pu, can make a fairly large difference in the sample alpha activity. Many of our samples are routinely report as activity (or count rate) per unit liquid volume, however, these results can be convert to grams using the appropriate isotopic correction factor. In most cases the concentrat of Pu in these fission product waste samples is relatively low and may be reported as 10 ^{239}Pu. Because of the small amount of shorter lived ^{240}Pu present in all Hanford waste results using this conversion method will always be biased high since average AEA detect have a resolution of 25 keV @ FWHM and thus cannot distinguish ^{240}Pu from ^{239}Pu. This b is likened to a "worst case" situation, and usually is not too big a problem. Small amo of ^{238}Pu can increase the alpha activity by orders of magnitude and result in a very hig bias (e.g 20 wt.% ^{240}Pu will increase the uncorrected answer about 1 ½ times, while an e alent amount of ^{238}Pu will increase it 56 times). If a result based on 100% ^{239}Pu is 0. or greater then an AEA is run and the results corrected for any ^{238}Pu present.

This method has been found to give, under controlled conditions, an accuracy of 95.9% ± at the 95% confidence level. As a check on the method a standard plutonium solution is routinely analyzed containing Pu in a matrix similar to the samples being run. For the month of Januray 1978 five standards were run giving an average recovery of 96.6% with a standard deviation of 8.2%. At the 95% confidence level the precision of a single observation is 22.6% with the precision of the average at 10.1%.

ium in Caustic Waste Sample

rocedure is a new one and still is undergoing refinement. The procedure now gives
bout 65% recovery for Pu, however since a tracer is used this helps reduce the problems
recovery causes. In order to do this analysis the concentration levels of the fol-
are needed in order to adjust the acid concentration: hydroxide, aluminate, carbonate
osphate. Carbonate and phosphate are neglected if they are known to be present in
rations considerably less than the OH^- and $Al(OH)_4^-$. A ^{236}Pu tracer is added to the
and allowed to equilibrate. The sample is then acidified with concentrated HNO_3 to
dity of 4-5 M. Urea is added and the sample is heated to destroy any nitrous acid
(nitrous acid will consume reducing agents used in later steps.) (An excess of urea
avoided as it will consume nitrite that is added later to oxidize Pu (III) to Pu
Ferric nitrate and hydroxylamine hydrochloride and heat are then used to reduce
) and (VI) to Pu (III); the heat will also destroy any polymer that may be present.
ium (V) will be reduced to Np(IV) and U and Am will be unaffected. After the solution
led sodium nitrite is added to oxidize the Pu (III) to Pu (IV). The Np (IV) is not
ed since the acid concentration is ≥ 4 M; Am remains in the (III) state. Pu (IV),
with any UO_2^{++} and Np (IV) is then extracted by adding an aliquot of 30% (by volume)
t-336 in xylene. Two batch contacts are made and then a scrub with 8 M nitric is done.
ueous phase can then be used in an americium determination.

n and some salts are then stripped from the organic using 10 M HCl. The organic then
dium carbonate and xylene added to it so that the Aliquot is diluted to 10% to assure
tative stripping of the actinides into the aqueous phase. Following a wash, concen-
HCl is added to destroy the carbonate. The solution is then evaporated to dryness
some sodium bisulfite has been added to prevent baking of the actinides on the vial
drying. After cooling, the electrolyte, sodium sulfate, is added and the pH adjusted
mmonium hydroxide until a pH of 2-2.3 is reached. A platinum electrode is then used
ctroplate the actinide onto an electropolished disc. Ammonium hydroxide is added just
to completion of the electroplating; this causes the hydrous oxide of the actinide to
fixed to the disc. The disc is rinsed with ethanol, dried and then counted on an APC
AEA methods. The ^{236}Pu spike recovery is then used to correct for any procedural
that have occured. Certain anions, such as sulfate, oxalate, phosphate and organic
ing agents may inhibit the extraction by complex formation, resulting in lowering of
ural recovery. However, since a ^{236}Pu spike is used and presumed to be in equilibrium
he sample these interferences can be corrected for.

s being continued on finding an adequate method for Am determination from the aqueous
obtained in this procedure after the extraction with 30% Aliquot-336 in xylene. As
s date the methods tested give only a 10% recovery when a ^{243}Am pike is used to check
ural recovery.

NON-DESTRUCTIVE ASSAY

metric

antity of plutonium in a package is determined by measuring the heat output of the
package and quantifying this amount using a standard. The isotopic distribution is
ined via a gamma scan since the heat output of the sample is dependent on the relative
s of isotopes present. The specific heat/isotope is then used with the isotopic dis-
ion and the heat output to determine grams of Pu. Current measurement error is esti-
to be ±.5 to 4.5% relative standard deviation depending on isotopic composition.

ounting[1]

amma detectors and associated electronics which record gamma radiation in the 375-450
egion are used to determine plutonium quantities. These systems are used in fixed
ions to determine Pu amounts in items such as half liter polyjars containing wet sludge.
systems are also used in a portable mode to determine quantities of Pu in such things
ilding pipes, ducts, hoods and gloveboxes. The plutonium content is determined by
rement of the ^{239}Pu gamma ray complex emitted at 414 KeV, correcting for compton
ering and background, and comparing to calibration standards. In situ measurements of
nium in several gloveboxes were found to give agreement within 16% with actual amounts
ered.

Plutonium Isotopic Analysis

Items analyzed on this system must meet the requirement of homogeneity throughout, sinc density of the item causes the low energy radiation to be absorbed so that the detector counts only the outer layer of sample facing it. The system uses a high resolution int sic germanium detector to collect a gamma spectrum covering the energy region from 20 k 420 keV. The spectrum is analyzed by computer. The computer analysis involves the construction of a relative counting efficiency curve for each item by comparing known bran ratios of various ^{239}Pu and ^{241}Pu peaks with their observed intensities and then normal calculated analytical peak areas. Actual isotopic ratios are calculated using closely spaced peak pairs with the subject isotope activity being compared to the activity of ^{2} or ^{241}Pu in a nearby peak.

Segemented Gamma Scan Assay

A Ge(Li) detector is used to measure the 414 keV gamma complex used to determine ^{239}Pu content in packages. This system is not used on items containing $\leq$ 1 gram Pu. The san is rotated at a constant speed during counting to reduce the effects of radial inhomoge within the item. Correction for variations in density are made by simultaneous measur of a ^{75}Se (400.7 keV) gamma transmission source mounted directly opposite the detector. A ^{133}Ba (356 keV) gamma source is mounted on the detector housing and is used for dead and pulse pile-up corrections. The item is scanned in individual vertical segments an the ^{239}Pu values are computed on a segment-by-segment basis using the appropriate calib tion factors and correction factors for density, dead time, and pulse pile-up. The sum the individual segment results gives the ^{239}Pu value for the package. This value is th used with the ^{240}Pu isotopic content estimate to calculate the total plutonium content. measurements on a 40 g Pu standard gave an average recovery of 100.15 ± 4.5%. For six measurements on a 160 g Pu standard an average recovery of 98.5 ± 1.45% was obtained.

AMPEROMETRIC METHOD

The amperometric titration method is used to determine the plutonium content in pluton nitrate solutions, plutonium oxide and plutonium metal. The first step in this method a fusion with sodium bisulfate for the oxide and metal samples. The samples are then solved in "Q" water to give a plutonium concentration of 5-12 mg/ml. The nitrate solu is diluted to give a similar amount. To the sample H_2SO_4 is added and the sample stir While the sample is stirring an excess of argenic oxide (AgO) is added to convert all (IV) to the Pu (VI) state. The excess argenic oxide is then removed by heating. A we excess of ferrous ammonium sulfate is then added to convert the Pu (VI) to Pu (IV). T excess ferrous ions are then back-titrated with potassium dichromate, using an amperom endpoint detection method. The plutonium content is then calculated from the amount o ferrous ions needed for complete oxidation of the plutonium. The estimated relative s dard deviation for the analysis of plutonium oxide is 0.1% with an average accuracy fo measurement of 100.03%

FLUORIMETRIC METHOD

This method is used for uranium analysis in concentrations less than 2.0 g/l, and has used periodically for many years. When free from quenching agents such as Cr^{+3}, Cr^{+6}, Fe^{+3}, Al^{+3}, Na^{+1}, Mn^{+2}, and HNO_3 in process solutions, an aliquot of the sample is mou directly on a platinum dish, dried, fused with NaF - LiF (98%-2%) and read on a calibr fluorimeter. If quenching agents are present the U (VI) is extracted into methyl isob ketone (hexone) from an aqueous solution heavily salted with ammonium nitrate or alumi nitrate. No accuracy and precision data was available.

VISIBLE SPECTROPHOTOMETRIC METHOD

Thorium

This method is used for determining Th concentration in samples with concentrations le than 2 g/l Th. The sample is first treated with HCl and sodium nitrite to convert all to the (IV) valence state. 10% TIOA (tri-iso-octylamine) in xylene is then used to ex Zr, Hf, U (IV), Pu (IV), and Np (IV) from the Th. These metals all form interfering c ns with the complexing agent. The extraction is done a minimum of two times and a third time if the Pu/Th ratio is greater than 500. An aliquot of the aqueous ning the Th) is then adjusted to an acidity of 5-9 M with con. HCl, and sulfamic ded to destroy any excess nitrite present. Arsenazo III, which is used for the ing agent, is sensitive to both oxidizing and reducing agents so it is necessary to that neither are present for the complexing process. An aliquot of 0.05% Arsenazo 8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis-[(azo-2) phenylarsonic acid]) mixed with the sample. The absorbance of the sample is then read against a reagent t 660-665 nm, and the sample absorbance used to calculate the Th concentration. A ecording double beam spectrophotometer is used for this determination. About 1 μg/ f solution may be detected by this method. The best working range is 2-20 μg/10 ml. lard is run with each batch of samples run through the method to check for recovery. ndards have been giving a 99 ± 7% recovery.

n^2

rk has been done on a spectrophotometric method for the determination of uranium when in concentrations less than 2 g/l using Br-PADAP [2-(5-bromo-2-pyridalazo)-5-dieth- phenol]. However, demand for this analysis is small so the final work has not been ed.

ium

ethod measures the concentration in g/l of Pu in aqueous samples or solutions of dis- metal. Hydroxylamine hydrochloride and heat are used to reduce the Pu to the (III) e state. The blue solution is cooled to room temperature and then diluted to volume. sorbance of the blue sample solution is measured at 565 nm relative to that of a blue filter on a double-beam spectrophotometer. The most accurate measurements are ed when the solution has a concentration between 11.0 and 11.5 g/l Pu. The precision s method has been reported as ± 0.6%, no accuracy data was available. This method is red to alpha counting techniques for plutonium process solution samples ≥100 g/l Pu.

X-RAY EMISSION ANALYSIS

m

m concentrations are determined annually on solutions in storage tanks as part of the SS Nuclear Material Inventory. Solutions with U concentrations 2 g/l or greater are ed using this method.

m concentration is determined in aqueous solutions using yttrium as an internal con- tandard. The internal control-standard is used to compensate for variations in vol- emperature, density and bubble formation in the liquid mounts. A constant amount is to all samples and calibration curve mounts to provide this correction. Calibration e using the linear relationship that exists between uranium concentration and the of uranium counts to yttrium counts. Two calibration curves are prepared covering two ent concentration ranges as Table I shows.

TABLE I

Curve	mg U Mounted	mg Y Mounted	U Concentration Range Covered
A	2 to 12	2	2 g/l to 60 g/l
B	20 to 77	20	25 g/l to solubility limit

Sample aliquots and yttrium aliquots are then chosen according to the concentration ran of the sample. The aliquots are pipetted into 5 ml volumetrics and then diluted to vol with 1 N HNO_3. Two aliquots of this mixture are then mounted in x-ray sample cups that covered with mylar. The samples are then counted on an energy dispersive x-ray emissi spectrometer using a molybdenum tube with molybdenum filter. The FWHM (full width half imum count) integration area is then used to determine the number of counts under each On our system we commonly use the areas 13.54 to 13.78 keV for U, and 14.38 to 15.12 ke Y. A linear regression analysis is then used with mg U as the abscissa and U/Y ratio ordinate. The concentration ranges of the two curves shown in Table I appear to be li over their ranges, however extrapolations of either curve outside it's stated range ha been found to give incorrect results. Results obtained on a standard using the low cu have given an average recovery of 96.8% ± 2.0%, while results obtained using the high have given an average recovery of 97.7% ± 1.4%.

Thorium

Because of fairly stringent accountability requirements for this group of samples this ique has been investigated quite extensively. When this x-ray method for determinatio Th concentration levels was first developed a dry mount was used, however a dry mount found to be more susceptable to error, had a higher detection limit and required a lon sample preparation time. Like the uranium method just described this one also utilize yttrium as an internal control-standard, and the sample mounts are prepared in the sam We use calibrated pipets and volumetrics in working with these samples although using calibrated volumetrics will show little effect on the standard recovery in 98 out of 1 samples. Whenever the same pipet can be used between samples, standards and calibrati curve mounts we do this as it simplifies the calculations. One pipet can be used to a yttrium to all of the vials, similarly one pipet can be used in mounting the samples, though here again small volume differences will have a negligable effect on recovery. our initial sample characterization we ran a full calibration curve covering a range o to 238 mg Th/5 ml with each set of sample mounts. However, since that time, we have f that it is only necessary to run a two point calibration curve because of the linear c tion range and the close concentration levels found in our samples. Samples are count the energy dispersive x-ray emission spectrometer using the molybdenum tube and filter the following peak integration areas; 12.88-13.12 keV for Th and 14.84-15.08 keV for Y have found it unnecessary to do a background subtraction; neglecting the background ha than a half a percent effect on the recovery obtained. When the calibration curve is an average recovery of 99.2% ± 1.1% at the 95% confidence level is obtained. With rec data obtained using the two point calibration curve we got an average recovery of 100. ± 0.54%, however this data was obtained on a much smaller number of data points than t for the calibration curve and so gives a misleading indication. We feel it does show, ever, that with our sample type we have obtained essentially as good of results with t point curve as with the full calibration curve, which reduces the amount of work neede calibration.

X-RAY DIFFRACTION ANALYSIS

As mentioned previously x-ray diffraction analysis is used in our laboratory as more o qualitative method than quantitative, however I mention it here because some of the te iques we use may be of use to others. Specifically I would like to mention some of th mounting techniques that have been developed that have greatly improved our results.

Oxide compounds of the actinides have a well-known tendency to creep and become easily borne. Because of these characteristics and our need to keep our x-ray instruments fr radioactive contamination we have developed a mount for use on a diffractometer that i minimum expousure to personnel preparing them, complete sample containment and essenti no background effects on the diffraction scan. When we receive our samples they have ready been ground to a fine powder state; using a transfer pipet, resin is added to th powder in the flask. This involves little personnel exposure since the flask can be s a block of shielding material and no close physical contact is necessary in using the A few drops of fixer are then added to the flask and the contents stirred using the tr pipet. Sample can be drawn up into the pipet as an aid to mixing and a check of it's pleteness. A sample mount is prepared by placing some mylar on a glass slide and coat it with releasing agent; a glass ring is then placed on the mylar. Previous mounts us elite rings for the mount but we have found that glass has a minimal background affect also allows you to see through the side of the mount to check and see that the sample cure is without air bubbles and other complications. The sample/resin mixture is then wn up into the pipet and pipetted into the glass ring. The sample is encased by the in in this process so there is no danger of it's becoming airborne. The pipet and sample are then disposed of as radioactive waste. The sample is allowed to dry, which takes ut 24 hours. When the sample is dry it is lifted off the mylar which is disposed of (we found this piece to have quite a bit of contamination on it.) We then wrap the mount ng two layers of Kapton X-ray Film (Spex Industries) which we have found to be the best n for x-ray diffraction use. The film is sealed at the back with tape. Depending on radioactive level of the sample we then use either our hands or long tweezers to place mount in the diffractometer. We have deliberately tried to break this mount by dropping and bumping into objects with it; as of yet we have been unable to do so, hence we feel mount is safe even if fairly roughly handled. If the wrap were removed from the sample smearable contamination could occur, however, this amount would be small and confined a small area; it is highly doubtful that any of the actinide could become air-borne. Aner advantage of this mount is that the sample surface is flush with the front of the ple mount so there is no need to worry about shift in d-spacings obtained. Using a nt prepared in this manner of α-SiO_2 no background effects were observable other than a ering of count rate as compared to a mount with a similar amount of the powder. We curtly use the glass ring/Kapton X-ray Film combination on all of the diffraction mounts lyzed in our laboratory. We use two glass rings cut so that one (or two if a radioactive ple is to be analyzed) layer of Spex wrap will fit between the rings giving a flush face. We have been unable to observe any background effects caused by this mounting hnique on any of the sample types that we use in our laboratory.

n diffraction scans are needed on very small quantities of radioactive sample we use an ay powder diffraction camera mount. This mounting technique was developed by combining hniques shared with us by Mr. P. L. Wallace of Lawrence Livermore Laboratory and Mr. M. C. hols of Sandia Laboratories. A very small amount of powder is placed on a glass slide a drop of rubber cement/benzene mixture is added. A second glass slide is used with a cular sliding motion to form the powder/glue mixture into a small ball. Because such a ll sample amount is used the radioactivity level is low enough that no remote manipulation necessary. A gel strip or rod moistened at one end is then used to pick up the ball and two are dropped into a glass capillary. The safest and easiest method to use in handling glass capillary is to insert it through a cork stopper into a test tube. The capillary ide the test tube is easier to hold, will not become contaminated and can still be seen. glass capillary is then sealed and used in the powder diffraction camera. We are intigating the possibility of using the rod/sample ball directly in a Gandolfi camera (here will use a glass rod with glue on the end to hold the ball.) Using this technique the m mounting, as well as the other operations will have to be performed in a hood.

samples are analyzed on the diffractometer and camera using standard techniques. We use opper tube on our diffraction instruments. We have two horizontal diffractometers, one which is set up on the medium focus so that a camera can be used simultaneously with it. other diffractometer we have set up with a Si(Li) detector and a single channel analyzer the fine beam focus. This instrument gives particularly good resolution for powder fraction studies, with it we can resolve the α-SiO_2 quintuplet found at 1.37-1.38 d-spac-.

SUMMARY

overview is given of the methods used for actinide characterization by the Analytical oratories Department of Rockwell Hanford Operations. Brief explanations are given of the enteen methods used in the analysis of widely different sample types containing the actdes in concentration levels ranging from just above background to the solubility limits.

ACKNOWLEDGMENTS

I am grateful to Chuck Clark and the chemists of the AL Department for their help in data collection and review. Gratitude must also be given to Wayne H. Sant who encouraged me to start and complete this project. Secretarial and editorial assistance was efficiently carried out by Linda A. Leemhuis.

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For more detail on a particular procedure, please contact the author.

X-ray Diffraction Sample Holder for Radioactive Samples or Samples that React with Air or Light

by

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ABSTRACT

A very versatile sample holder for an x-ray diffractometer will be described. It provides double containment while in operation on the diffractometer and triple containment while being transported from a hot cell or dry box to the diffractometer and back to a disposal area. This cell is suitable for fairly high alpha activity or mild beta-gamma activity. It is also good for materials that react with air or light. Either solid or liquid samples can be used.

KEYWORDS: X-ray diffraction, analysis of radioactive materials, transporting radioactive samples, handling radioactive materials

INTRODUCTION

We occasionally get requests for x-ray diffraction analysis of radioactive materials, t our equipment is located in a building that has no facilities for handling radioactive terials. Therefore, any such materials that we handle must be at least double contained.

FACILITIES FOR HANDLING SPECIAL SAMPLES

We have designed a sample cell that allows us to handle special samples where activity involved. An exploded view of the device is shown in Figure 1. It is made of stainless eel with thin plastic windows cemented in place.

Figure 1, Part 1, shows the cell in which the sample is placed. It is introduced rough the slot "B". The thin plastic windows, "A", allow the x-rays to be transmitted th very little loss. After the sample is introduced, usually in a hot cell or dry box, e cell is sealed with plastic tape. The sample cell can then be moved to another area d decontaminated. The sample cell is then inserted through slot "C" and seated in oove "D" in the base unit, Part 2. The slot and groove are machined for a slip fit as to hold the cell in proper alignment when it is placed on the diffractometer.

The containment unit, Part 3, is then inserted over the base unit and aligned by the ot "I" in the containment unit and pin "F" in the base unit so that the primary and ffracted x-ray beams pass through the plastic windows on the cell and containment unit. e assembly is locked together by means of the knurled screw "K". A thin plastic window ", "O" ring "E" in the base unit, and "O" ring "L" on the underside of the knurl screw " completely seal the assembly giving double containment to the sample. Since the ndow on the containment unit is thin, it could be punctured while in transit from the t cell or dry box to the diffractometer. To prevent this, a carrying unit, Part 4, ips over the containment unit and is sealed by the "O" ring "J". These two units are cked together by the knurled screw "P" that contains an "O" ring "D" on the underside

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perated for the U.S. Department of Energy by Union Carbide Corporation under contract -7405-eng-26. Research supported by the Office of Basic Energy Sciences.

to complete the seal. The threaded hole "N" does not go completely through the metal. This gives triple containment while the assembly is being transported from the hot cell or dry box to the diffractometer. A track "R" is machined into the shaft head of the diffractometer, Figure 2. A tight slip fit with the matching track "G" on the base unit and the stop pin "S" accurately position the sample on the diffractometer. After the assembly is placed on the diffractometer, the carrying unit is removed and the sample is examined to be sure no spillage has occurred. If not, the sample is then ready for analysis on our Philips x-ray diffraction equipment.

The signal to background ratio is improved considerably if the diffracted beam monochrometer is installed on the diffractometer. If much beta-gamma radiation is present, it would also help to install some additional shielding.

Since the samples can be loaded and sealed in a dry box containing an inert atmosphere, this assembly can be used for samples that react with oxygen or moisture in the air. If an opaque material is used for the cell windows, this same system can be used for samples that are affected by light. Slurried samples or liqud samples can also be used.

After the analysis is complete, the carrying unit is replaced and the complete assembly is removed from the diffractometer. It is then carried to a disposal area where the cell is removed, cleaned, and made ready for the next sample.

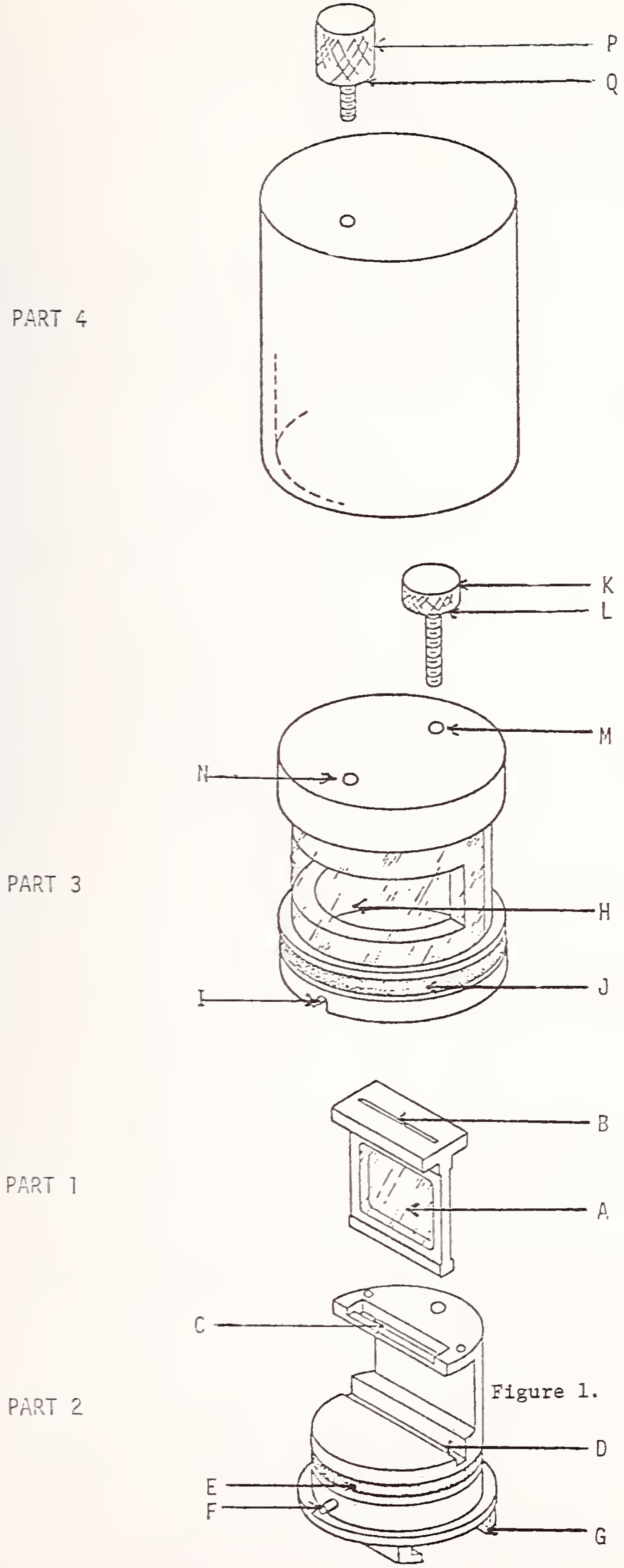

Figure 1. Exploded View of Cell Assembly

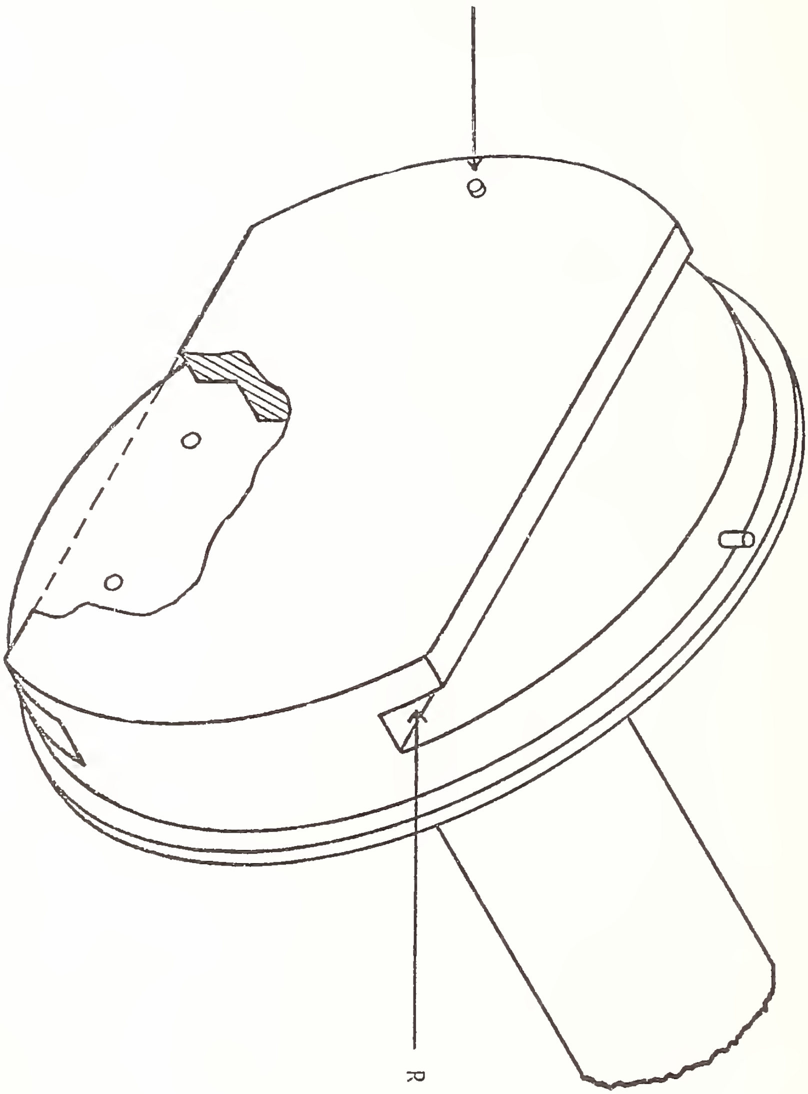

Figure 2. Modification to Diffractometer Shaft Head

Feasibility Study of a High-Precision XRF System for Analysis of Solutions and Slurries

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ABSTRACT

Wavelength dispersive X-ray fluorescence (XRF) is uniquely applicable to the analysis of dissolver solutions because of its high immunity to the intense gamma emissions of the solutions, its inherently high signal-to-noise (S/N) ratios, and its adaptability as an on-line, tamper-resistant, accurate analysis of both dilute and concentrated plutonium in dissolver solutions.

The taking of aliquots and transfer of samples would be eliminated by placing the system on-line. Sampling thereby would become total: during the progress of of the analysis the entire contents of the dissolver tank--or its logical equivalent, a large, thoroughly mixed fraction of its contents--would be circulated through the sample cell. Internal standards would be used for realization of the highest accuracy of analysis. The addition of standards would impose no complications to subsequent chemical processing.

The use of monochromatic exciting radiation would further improve the S/N ratio, and, by eliminating useless radiation, would reduce photochemically formed gas bubbles which perturb sample geometry. For rapid analysis a rotating target, high-power X-ray generator would be necessary.

Control and monitoring of the equipment, the analytical process, and data processing would be done by a minicomputer for error-free operation, and for prompt detection of all but the most sophisticated attempts at tampering with the analytical process.

The specifications of the system components have been conservatively estimated so that the r.m.s. variation of the entire system during a single determination would not exceed 0.20%. Counting statistics is considered separately because it is a function of fluorescent intensity, and therefore may be limited by available time for dilute solutions. For concentrated solutions with strong fluorescent emissions the total variation of a single determination could approach the 0.20% level. By using the usual strategy of repeated determinations, any arbitrary precision could be reached.

The performance specifications have been written with awareness of the capabilities and limits of modern technology. The capabilities are exploited and the limits are not strained. The conservative designs thus permitted will allow the construction of an XRF system of high reliability and advanced capability.

KEYWORDS: Nuclear safeguards; X-ray fluorescence analysis; rotating target X-ray tube; X-ray monochromator; X-ray liquid and slurry sample cell; high-precision, wavelength dispersive X-ray spectrometer; analysis of solutions and slurries

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INTRODUCTION

Safeguards needs for on-line, tamper-resistant, accurate analysis of both dilute and concentrated uranium and plutonium in dissolver solutions[1] have been documented. Wavelen dispersive XRF is uniquely applicable to the analysis of dissolver solutions because of i high immunity to the intense gamma emissions of the solutions, and because of its inheren high signal-to-noise (S/N) ratios. The use of monochromatic exciting radiation would fur improve the S/N ratio, and would largely eliminate photochemical gas formation which is a analytically detrimental effect of the usual white exciting radiation. Monochromatizatio does incur power losses, however, and for rapid, precise analysis, a very high power X-ra generator of the rotating variety would be necessary.

The taking of aliquots and transfer of samples for XRF analysis would be eliminated placing the system on-line, effected by installing the XRF sample cell in a recirculating loop with the dissolver tank. In this mode, sampling errors would be eliminated, because during the progress of the analysis the entire contents of the dissolver tank--or its log equivalent, a large, thoroughly mixed fraction of its contents--would be circulated throu the sample cell. In addition, undissolved material in the form of a slurry would be assa along with the dissolved material. Internal standards would be used for realization of t highest accuracy of analysis. The addition of suitably chosen standards would impose no complications to subsequent chemical processing.

Control and monitoring of the equipment and of the analytical process, and data proc sing, would be done by a minicomputer for error-free operation, and for prompt detection all but the most sophisticated attempts at tampering with the analytical process.

EQUIPMENT

The specifications of the individual components described in the following pages hav been conservatively estimated so that the r.m.s. variation of the entire system during a single determination would not exceed 0.20%, exclusive of counting statistics. The latte is considered separately because it is a function of fluorescent intensity, and therefore be limited by available time for dilute solutions. For concentrated solutions with stro fluorescent emissions the total variation of a single determination could approach the 0. level. By using the usual strategy of repeated determinations, any arbitrary precision c be reached.

An XRF system for on-line analysis of solutions and slurries is diagrammed in Figur The system consists of:

1. A high power, rotating target X-ray tube.

2. Monochromator for providing monochromatic exciting radiation.

3. Sample cell connected in a recirculating loop to the solution tank.

4. X-ray spectrometer.

5. Computer for controlling the data taking process.

Each of these components will be considered in detail.

X-Ray Tube

The X-ray tube must generate a well-monitored flux of characteristic radiation such after excitation of the sample and the passing of the fluorescent radiation through the of the X-ray spectrometer, count-rates sufficient to realize the desired analytical prec within reasonable times are attained. The X-ray power requirement has been estimated fr first principles for a typical Savannah River Plant accountability tank, which has a plu content of 0.4 g/liter--a dilute solution with severe analytical problems.

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[1] LA-6881, Vol. II, E. A. Hakkila et al., "Coordinated Safeguards for Materials Manageme a Fuel Reprocessing Plant," Sept. 1977.

An approximate calculation indicates that a generator of 60 kW electrical input should fect a complete analysis of this dissolver solution in 4 to 8 hours, the bulk of which time uld be spent in precisely measuring the X-ray emission of the very dilute plutonium. Only rotating target X-ray tube can absorb such high power input. Rotating target X-ray gener-ors, available only from foreign manufacturers, have proved power capabilities of up to 90 /, which is well in excess of the suggested 60 kW. Such machines have been used successfully research laboratories for many years. Unfortunately, they utilize obsolete high vacuum d power regulation technologies, and consequently do not have the long-term reliability and e X-ray generation stability necessary for use as a dependable, on-line, high-precision alytical tool.

A solution to one failure point, the high-speed rotating seal separating target from mosphere, has been demonstrated by the use of a Ferrofluidic rotating seal[2]. The use of is seal and dry, high vacuum pumps would yield a tube with dependable, long-term performance. e incorporation of a minicomputer to control and monitor the operating parameters of the be and power supply would permit operation by relatively unskilled technicians. Suitable, gh-wattage power supplies are readily available on the domestic market.

Monochromator

The use of monochromatic exciting radiation increases the signal-to-background ratio[3], d would substantially reduce the variations resulting from photochemically produced gas bbles in the sample. The use of monochromatic radiation also precisely defines the excitation conditions, and because the theory of interpreting fundamental parameter XRF data is ased on monochromatic excitation, improvement of analytical accuarcy would be realized.

The monochromator is essentially an X-ray spectrometer of limited angular range. For racticality it must yield maximum flux of selected X-rays, have mechanical and thermal tability, be convenient to adjust, be well-shielded, and have mechanical features that acilitate close coupling to the sample cell. The selected beam intensity is critically ependent upon the diffracting crystal. The best choices for this purpose are the bent raphite crystals produced by Union Carbide, which have exceptionally high diffracting powers. rovision for accurate monitoring of the monochromatic beam would be included since even the est regulated X-ray generators exhibit unaccountable intensity variations[4].

Sample Cell

The sample cell would be on-line, and designed to handle samples in solution, as slurried olids[5], or as mixtures of both. The elemental content of suspended solids, as well as that f the dissolver solution, would therefore be included in the analysis. The on-line feature as three important advantages: samples would not be removed from the recirculating system; n analysis continued over a sufficiently long time would effectively, or actually (depending n tank size), analyze the entire sample; and the completeness of mixing would be monitored y the XRF analysis. The latter two points are critical for a valid analysis.

The sample, of volume ranging from several tens of milliliters up to the entire contents of a holding tank, would be pumped continuously through the cell. Flow-through operation would prevent the buildup in the cell of photochemically produced gas bubbles which introduce analytical errors, and of course, is the only way to implement the use of the analytically superior large sample. Turbulence in the cell, necessary to ensure homogeneity of slurries, would be effected by an internal stirrer or static baffles. The window of the cell must have resistance to acid, abrasion and radiation, and have maximum transparency to X-rays. The best window material for X-rays, beryllium, does not have the necessary acid resistance, and would

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[2] W. Longley and R. Miller, "A Simple Rotating Anode Generator," Rev. Sci. Instrum. 46:1 (1975).

[3] Thomas C. Furnas and Robert R. L. Towns, "High Intensity Monochromatic X-Ray Excitation for Clinical Analysis," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 3-7, 1975.

[4] Dr. Thomas C. Furnas, personal caveat, 1975.

[5] C. R. Hudgens and G. Pish, "X-Ray Emission Analysis of Slurries," Developments in Applied Spectroscopy 5, 25 (1966).

have to be protected. Materials which would serve as protective barriers or as stand-alone windows must be evaluated. Among these are Mylar and cleaved natural mica, both of which ha been used as cell windows at Mound with good results.

The irradiation chamber in which the sample cell is contained also serves as the platf for the entrance slit to the spectrometer and as radiation shielding. For highly radioacti solutions, it must also incorporate sensors for the prompt detection of leaks. Upon detecti of the leak, fluid flow through the sample chamber would be stopped and the chamber sealed b means of gate valves.

Spectrometer

The spectrometer, a curved crystal (Johannson) type for simplicity of optics, must hav robustness, high-setting precision, and shielding against the highly radioactive background inherent in the materials analyzed. Its design would incorporate high-resolution encoders, precision stepping motors, and high-precision bearings, resulting in a reliable instrument advanced capability at reasonable cost. With an analyzing crystal of dispersion and diffra tion profile carefully matched to the setting precision of the spectrometer, interference-fr spectra would be realized.

The performance of the spectrometer is a function of: the analyzing crystal, which is primarily responsible for resolution and counting efficiency; and setting precision, which mainly affects counting precision. These two parameters are interdependent. The optimal values of resolution and setting precision are dictated by the closest lying energies expec in the X-ray spectrum. The following table (Table I) lists the X-ray lines of interest (analytical lines underlined), and their 2θ setting precision requirement on the spectromet

Table I

X-Ray Wavelengths of Elements in Dissolver Solutions

Element	Transition	Wavelength (Å)	2θ (Degrees)
Y	K-α1	0.82884	23.75
Cm	L-α1	0.8289	23.75
Rb	$K\beta_3$	0.82921	23.86
Y	K-α2	0.83305	23.88
Cm	L-α2	0.8411	24.11
Am	L-α2	0.860266	24.66
Pu	L-α1	0.86830	24.90
Sr	K-α1	0.87526	25.10
Sr	K-α2	0.87943	25.22
Np	L-α2	0.901045	25.85
U	L-α1	0.910639	26.13
Th	L-α1	0.95600	27.46
As	K-α1	1.17588	33.95
Se	K-α1	1.10477	31.84
Np	L_1	1.0428	30.01
Br	K-α1	1.03974	29.92
U	L_t	1.0347	29.77

Based on the requirement that the strontium K-α doublet be completely resolved, the di fracting half-widths ($W_{1/2}$) of commonly used orientations of LiF, silicon, and germanium, and the 2θ setting precisions (Δ2θ) required for attainment of 0.1% contribution to the counting precision for each have been calcuated. These are presented in Table II along wit the theoretical integral diffracting power (Eω/I) of each.

For 99% assurance of setting precision, the targeted precision should be about 1/3 Δ2 which for the most stringent case is about 0.0003°. These performance specifications are considerably higher than are found in commercial X-ray spectrometers, which have setting precisions of, at best, about 0.005°. Commercial X-ray spectrometers, however, are by no means modern. Without exception they use the design philosophy, materials, manufacturing processes, and angle setting techniques of the immediate post-World War II period. A spectrometer capable of meeting the high performance specifications of Table II would use

Table II

Diffracting Crystal Characteristics

Crystal	Orientation	$E\omega/I$	$W_{1/2}$	$\Delta 2\theta$
LiF	200	6.68	0.076°	0.0015°
LiF	400	0.67	0.16	0.006
LiF	220	2.35	0.12	0.0046
LiF	420	0.44	0.20	0.0076
Si	111	0.59	0.049	0.0009
Si	220	0.10	0.081	0.0015
Ge	111	0.19	0.047	0.0009
Ge	220	0.083	0.078	0.0015

ost dimensionally stable of high-strength materials and conservatively loaded precision bearngs, but, in particular, it would exploit the highest resolution angular encoders[6] and angle ositioners under continuous control of a microprocessor.

The X-ray gathering efficiency of the spectrometer is a function of its geometrical eficiency and its relationship to the sample, and to the reflectivity of the analyzing crystal. eometrical efficiency is determined by the radius of the spectromater, and the area and difraction profile of the crystal. For this study, a sample-spectrometer system with dimensions ear those of commercial instruments, using an 8 cm^2 LiF(220) crystal with a reflectivity of .56%, gives an overall efficiency of 2×10^{-6}.

In order to realize the projected system precision, the analyzing crystal must be thermotated. Appropriate temperature control depends upon the crystal and desired counting preision; for the above crystals to contribute 0.1% to the counting precision, the temperature luctuation would range from 0.1°C to 0.5°C.

The diffracting powers are calculated for ideally imperfect crystals (which give the ighest integrated intensities) without the attenuating temperature factor. "Ideal imperfecion" in crystals is a hypothetical case which is convenient for calculation of the order of eflecting powers of analyzing crystals. (The diffraction profiles of such crystals would be npracticably broad in any case.) Crystals with small to moderate imperfections, readily vailable from domestic sources, show smaller differences of reflecting powers, smaller osolute reflectivities, and narrower diffraction profiles. Since reflectivity is important n determining the time required for analyses, crystals should be individually selected with ne broadest permissible diffraction profiles for the task at hand.

With a spectrometer of the specified resolution, the only interferences would be incoerent, multiply scattered (Compton) fluorescent X-rays. Incoherent scattering causes a shift oward longer wavelengths of the scattered X-rays, and has the effect of introducing interering spectra. It is most intense when scattered from light elements, and is not negligible. alculation of the intensity of incoherent scattering is a complex process that is extremely ime-consuming on even a medium-sized computer. Fortunately, it can be adequately determined eforehand for all elements of interest by profiling any X-ray line of wavelength in the egion of interest.

Process Control Computer

In closed-loop operation, the computer monitors and controls all functions of the instruent. While taking data, it also inspects the data for consistency. In an XRF application, nis would involve a running statistical analysis of the incoming data. Data which did not onform to predetermined criteria would immediately be retaken. Situations that the computer ould not handle, such as equipment malfunction, would be called to the operator's attention or correction.

Itek Corp., Newton, Mass.

EFFECT OF GAMMA RADIATION ON COUNTING BACKGROUND

The background from gamma radiation with a well-shielded sample handling system can be expected to be acceptably low. The geometry of the sample chamber will reduce the radiant flux striking the diffracting crystal by a factor of 4 x 10^{-4}. The detector slit, which is out of the direct line of sight to the entrance slit, will pass mainly that radiation incoh ently scattered from the diffracting crystal--another 4 x 10^{-4} factor. The analyzing cryst would scatter, at most, about 0.1% of the incident high-energy radiation. Including the effect of the insensitivity of the detector to high-energy radiation, total attenuation of gamma radiation reaching the detector would be better than 10^{-10}. Loading of the pulse pr cessing electronics would thus be negligible, and the pulses, being of high energy, would b rejected by the energy discriminating (PHA) electronics.

XRF ANALYSIS OF PLUTONIUM AND URANIUM IN DISSOLVER SOLUTIONS

In analyzing for plutonium and uranium, the dissolver solution would be pumped contin ously through the fluorescent sample cell, and the analytical X-ray lines of the internal standards, plutonium and uranium, would be counted in sequence. Referring to the flow dia (Figure 2), steps 1 and 4, which are background determining steps, are predicated on the assumption that all elements would be excited by the brehmstrahlung and beta rays of the fission products. The importance of these steps depends upon the intensity of excitation the X-ray tube. Either or both may be eliminated if the ratio of internal excitation to e ternal X-ray induced excitation is sufficiently low.

Strontium and yttrium (see Table I) are logical choices for internal standards becaus their X-ray lines lie near those of plutonium and uranium, and because the addition of the elements would not perturb subsequent chemical processing. Both strontium and yttrium are present as fission products; hence, the necessity for step 2. Other, less desirable, elem for internal standards are bromine, selenium, and arsenic.

The availability of several elements for internal standards opens two options: 1) th u of more than one internal standard element, which may be necessary to achieve the targeted analytical accuracy; and 2) separate analyses of the contents of the dissolver and account ability tanks, using different sets of internal standards for the two samples.

An analysis by the fundamental parameter program of the Naval Research Laboratories (RL of the data from step 2 would, by itself, give an approximate analysis of the solution[7]. he data of step 5 analyzed by the NRL program with the inclusion of the internal standards da a, and corrected for the fission products strontium and yttrium, from step 2, would give the final analysis.

ERROR ANALYSIS AND SUMMARY OF PERFORMANCE

The standard deviation of a series of independent XRF analyses is dependent upon: a) the total count accumulated, and b) all other errors. A practical "proper minimization" woul be one in which categories (a) and (b) contribute equally to the variation. The first is a p rely mathematical entity. The second category includes mechanical and electronic factors, suc as: 1) counting variations due to setting error (including thermal expansion of components); 2) errors in measurement of intensity of the exciting beam; 3) drift in detector electron s; and 4) variations in the sample--compositional or geometrical. The proper minimization o each category is a necessary condition for attaining a desired analytical precision. Eac of the four factors in category (b) has been assigned a value of 0.1%, the rationale being t t the requisite setting precision is attainable, that electronic equipment matching this pr cision is readily available, and that the other variances can be made to attain this prec ion The summed effect of these variables would yield a variation of about 0.20%. This appara s variation justifies the accumulation of 2 - 2.5 x 10^{5} counts--much more would waste time-which, with appropriate background measurements (approximately equal time counts), would effect a precision of about 0.30% for a single determination of a major element, or, beca e

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[7] J. W. Criss, "HRLXRF, A Fortran Program for X-Ray Fluorescence Analysis," distributed by Computer Software Management and Information Center, Suite 112, Barrow Hall, Univ. of Ge gia Athens, Georgia 30702.

e relatively high contribution of background, 0.4 - 0.5% for a single determination of y low concentration element. With repeated determinations the variation diminishes in-ly with the square root of the number of determinations; therefore, time permitting, sion can be made to reach any arbitrary level.

With the dissolver solution from Savannah River Plant (0.4 g/liter of plutonium with 400 er uranium considered as the dominant absorber), the described system would yield about unts/sec for plutonium. About 80 minutes would thus be required to accumulate 2 x 10^5 s from this very dilute component. For the uranium and the internal standards, the time sary for the same total count would be 1-2 minutes per element. An estimated 4 to 5 would be required for a complete single-pass analysis of this dissolver solution.

For plutonium at 9 g/liter concentration (dissolver solution of Allied General Nuclear ces), about three minutes would be required for a 2 x 10^5 count accumulation. Require-of the Atlantic Richland Hanford Company could be met by a system of much more modest power--about 10% of that needed for Savannah River Plant or Allied General Nuclear. oth of these cases, the ultimate precision of the XRF system could be reached with te reasonable investment of time.

SAFEGUARDS IMPACT

This XRF system offers an alternative to other analytical techniques presently in use as several advantages over these techniques. X-ray fluorescence would be performed on- therefore the sampling error would be minimized since the sample size restriction is nated. On-line analysis would reduce the frequency of transporting highly radioactive es to an analytical facility. Reduction in the amount of handling also lessens the risk mpering with samples. There is no need to remove fission products when using this m, therefore uranium, plutonium and other actinides, if needed, could be determined ut lengthy chemical separations. Undissolved solids could be tolerated in sample ions, whereas they are intolerable with other techniques. Owing to the high per-nce components, a considerable improvement in precision over existing XRF systems be realized with this system.

Concealment of diversion of special nuclear materials would depend on success- falsifying an analysis. This could, in principle, be done by adding a carefully ited excess of standards, which would depress the plutonium assay by a calculated amount. checks between steps 2 and 5 (Figure 2) would impose limits on this strategem. A yet rigorous cross check would be realized by analyzing for a fission product not readily able, in particular technetium, which is present in levels comparable to the fission icts, strontium and yttrium.

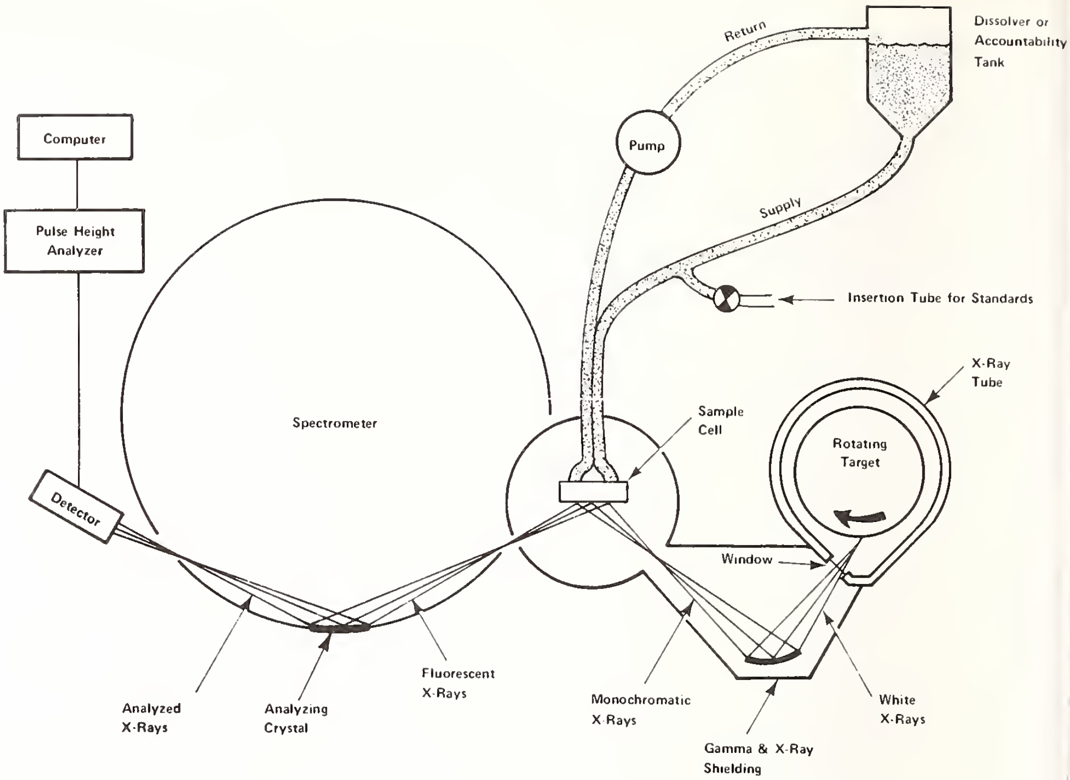

FIGURE 1 - On-Line X-Ray Fluorescence Analyzer.

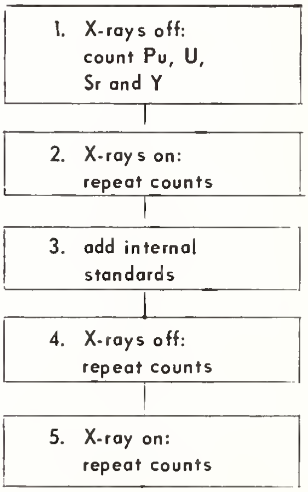

FIGURE 2 - XRF Analysis Procedure.

Establishing the Traceability of a Uranyl Nitrate Solution to a Standard Reference Material

by

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ABSTRACT

A uranyl nitrate solution for use as a Working Calibration and Test Material (WCTM) was characterized, using a statistically designed procedure[1] to document traceability to National Bureau of Standards Reference Material (SRM-960). A Reference Calibration and Test Material (RCTM) was prepared from SRM-960 uranium metal to approximate the acid and uranium concentration of the WCTM. This solution was used in the characterization procedure. Details of preparing, handling, and packaging these solutions are covered.

Two outside laboratories, each having measurement expertise using a different analytical method, were selected to measure both solutions according to the procedure for characterizing the WCTM. Two different methods were also used for the in-house characterization work. All analytical results were tested for statistical agreement before the WCTM concentration and limit of error values were calculated. A concentration value was determined with a relative limit of error (RLE) of approximately 0.03% which was better than the target RLE of 0.08%.

The use of this working material eliminates the expense of using SRMs to fulfill traceability requirements for uranium measurements on this type material. Several years' supply of uranyl nitrate solution with NBS traceability was produced. The cost of this material was less than 10% of an equal quantity of SRM-960 uranium metal.

KEYWORDS: Calibration; characterization; reference materials; traceability standards; and uranyl nitrate solution

INTRODUCTION

Uranyl nitrate solutions are essential for use as standards in the surveillance of
ytical methods, calibration of equipment and methods, and training and testing labora-
personnel. Because of these functions and the importance of uranium measurements for
ear materials accounting purposes, the standards must be of unquestionable quality and
ly traceable to a primary standard reference material.

Ideally, for a standard to be used as a working calibration and test material it
ld:

1. be stable over extended storage periods,
2. closely match the material routinely analyzed,
3. have an uncertainty consistent with its intended use,
4. be convenient to use, and
5. be economical.

S. Yamamura, et al, NUREG-0253, NRC-13, "Preparation of Working Calibration and Test
erials: Uranyl Nitrate Solution " (1977).

Uranyl nitrate solutions, for use as working calibration and test materials, havi uranium concentrations traceable to the National Bureau of Standards can be prepared i ways. They can be synthesized from well characterized starting materials of known int such as Standard Reference Materials, using NBS certified mass and volume standards fo solution measurements. Using this procedure, the integrity of the starting material i transferred to the standard, which can be used as either a reference or working calibr test material. The second way uranyl nitrate WCTMs can be prepared is by characterizi plant uranyl nitrate solution by two different methods of analysis. The NBS traceabil is established by calibrating the measurement systems used to characterize the WCTM wi reference standard while concurrently analyzing both solutions.

The cost of NBS SRMs prohibits their use where large quantities of working standa required for routine analytical measurement operations. Therefore, the second method used in preparing a large supply of uranyl nitrate WCTM. The overall cost of procurem preparation, and characterization was considerably less than the cost of preparing an quantity of the standard from SRM-960. By characterizing, the desired reliability was tained and NBS traceability was established.

PREPARATION OF CALIBRATION AND TEST MATERIALS

Two uranyl nitrate solutions were prepared as calibration and test materials as s in Figure 1. A large quantity of uranyl nitrate solution was prepared for characteriz and establishing traceability to the standard reference material. This quantity would the future needs for a working calibration and test material. After the specification the working standard had been determined, calculations were made to determine how much uranium and acid would be needed for the RCTM. Then a small quantity of uranyl nitrat solution was prepared for use as a reference standard to calibrate the measurement sys used in the characterization of the working standard.

Preparing the Working Calibration and Test Material

Approximately 80 liters of uranyl nitrate were obtained from a plant product tank used in the preparation of the working standard.

The solution was filtered to remove insolubles and the filtrate was transferred t large drum for mixing. The drum was covered and the solution thoroughly mixed by spar overnight to ensure homogeneity. Samples were analyzed for concentration of acid, ura and impurities. The results of these analyses were satisfactory. The solution was mi again and systematically transferred to four clean dry 27 liter poly bottles. The nec were sealed with a plastic film and closed with a screw cap to protect against evapora until the solutions were packaged.

Synthesizing the Reference Calibration and Test Material

The reference calibration and test material was prepared from NBS SRM-960 uranium metal to approximate the acid and uranium concentration of the WCTM. The metal was pi for approximately ten minutes in warm eight molar nitric acid to remove the surface o The pickled metal was rinsed with water and acetone and air dried. The required quant of metal was weighed several times alternately with NBS traceable Class S weights. Th metal was transferred to a precleaned Erlenmeyer flask fitted with a standard taper ai cooled condenser and reflux head. The metal was dissolved in eight molar nitric acid. dissolution was completed in 24 hours using low heat. The solution was cooled and qua tatively transferred to a calibrated bubble neck flask having a screw cap enclosure. acid concentration was adjusted before the solution was diluted to volume at the desi temperature. This solution was weighed several times on a double pan analytical bala using the double transposition weighing technique. The mean weights were determined corrected to the certified apparent masses of the Class S weights. The makeup value certainty error was propagated. Table I shows the actual data used and the calculati The reference values were also calculated on a volume basis.

PACKAGING THE CALIBRATION AND TEST MATERIALS

The prepared solutions were packaged in various sizes of borosilicate glass ampul e sealed the day after they were prepared. Specially fabricated 500 ml borosilicate ss ampuls were used for packaging large quantities of the WCTM for long term storage. large ampuls will be opened as needed and repackaged in smaller ampuls. The ampuls were leaned with hot four molar nitric acid, thoroughly rinsed and allowed to air dry prior se. Several 2, 5, 10, 20, and 50 ml ampuls were filled for the characterization work routine use.

A mechanical ampul filler was used to rapidly aliquot solution to the ampuls, which immediately flame sealed with a commercial ampul sealer to prevent evaporation. ial precautions were taken when transferring the solution from the large poly bottles he ampuls. Care was taken to prevent dripping solution in the ampul necks which could when the neck was sealed and affect the solution concentration.

The packaging provided 180 large ampuls containing about 130 grams of uranium which is valent to approximately five units of SRM-960 uranium metal. Many smaller ampuls were filled.

PROCEDURE FOR CHARACTERIZING WORKING CALIBRATION TEST MATERIALS

Two analytical chemistry methods known to provide precise and accurate results were to characterize the WCTM. They were a gravimetric uranium method based on the ignition ranium to U_3O_8 and the New Brunswick Laboratory's modification of the Davies and Gray imetric method.

Two independent laboratories, selected for their measurement expertise, were contracted nalyze the solutions. In-house characterization of the two solutions was also performed g two different analytical methods.

ANALYTICAL MEASUREMENTS

NUREG-0253 lists criteria covering the selection of the number of replicate analyses characterizing the working standard in section 5.3. The desired limit of error is ted to the end use of the WCTM and is a function of the accuracy and precision of the t material to which the WCTM applies. A relative limit of error (RLE) of less than $^1/_3$ he 0.25% RLE established for the plant material measurements was selected. The number amples analyzed determines if satisfactory measurement precisions are attained. In acterizing the WCTM by two methods, the limit of error is a function of the precisions he two analytical methods used.

A minimum of five replicates is recommended in the NUREG. On the basis of the Safe- ds Analytical Laboratory Evaluation Program Report of the "Average Within Lab Standard ation" for the two methods, nine replicate aliquots were selected for the titrimetric od and six were selected for the gravimetric method. These numbers should have given oximately equal estimates of the standard deviation of the means, but did not. The al precision estimates are shown on page 1 of Appendix I. The in-house measurement ision estimates were well known, therefore, six replicate aliquots were chosen the in-house characterization of the WCTM. An equal number of determinations were per- ed on both standards by each method.

Evaluation of the Analytical Measurements

The statistical tests given in NUREG-0253 were applied to the data to compare the con- ation analyses and establish an assigned value and limit of error for the working stan- . The statistical comparison of the results of the two methods was accomplished fol- ng this scheme:

1. The means and associated standard deviations were calculated for each data set.
2. The precisions of the results obtained by both methods for the WCTM and RCTM were compared.
3. The two WCTM means were bias corrected for the difference observed between the RCTM analyses and its makeup value.
4. The WCTM population means, obtained using the two methods, were tested for equality of means. The approximate variances and degrees of freedom were derived by error

propagation.

5. An assigned value and associated standard deviation for the WCTM was calculate weighting the bias corrected means for both methods.
6. The limit of error and relative limit of error were calculated for the WCTM an tested.
7. The 95% confidence interval was calculated.

The results of the outside laboratories analyses are given in Appendix I with the tistical treatments listed above. When the WCTM mean results of the two laboratories w tested using the t-test of equality of means, the difference in population means was si nificant.

Investigation revealed that Laboratory II's analyses of the WCTM had better precis than the historical precision of the laboratory. Therefore, a pooled standard deviatic was calculated from historical data and characterization data and used instead of the s dard deviation of the WCTM and RCTM results. This was permissible since precision data previously obtained for a method used for similar sample analyses can be pooled with current data to compute a better estimate of the standard deviation with a larger numbe degrees of freedom.

The results of the outside laboratories appeared to be positively biased from the up value and in-house analyses of the reference standard. However, no significant dif ence was observed between the laboratories' values for the working standard after corre for the difference between the observed values and the reference value of the RCTM. Tl results confirmed the in-house assigned value of the WCTM.

SECOND CHARACTERIZATION PROGRAM

The unexplained bias of the reference standard caused in-house concern that o analytical results may have been negatively biased, so in 1978 a new reference standar prepared for a second characterization of the working standard. Table II shows the ac data used in calculating the concentration and associated standard deviation values fo 1978 RCTM.

Several 500 ml ampuls of the WCTM were opened and six aliquots of each standard w analyzed by two methods as done previously. The analytical measurements and subsequen statistical treatment of this work are given in Appendix II.

These analyses confirmed the makeup value of the 1978 RCTM and the value previous assigned to the WCTM. The new assigned value of the WCTM was within the confidence in val established in the previous work.

Table III summarizes all of the analyses performed in the characterization effort The mean value of all the analyses of the WCTM is 219.20 ±0.03 mg U/g.

SUMMARY

Detailed instructions are given in the regulatory guide for the preparation and c acterization of a uranyl nitrate WCTM. However, some potential problems that could be encountered are not specifically addressed. For example, the particular problems that encountered with Laboratory II's very precise measurements and the apparent bias betwe the outside laboratories and in-house results, before they were corrected for, by usin techniques described in NUREG-0253.

Following the procedure, a uranyl nitrate WCTM can be prepared from a plant urany nitrate solution at a minimum cost, with NBS traceability, and within a predetermined of error.

FIGURES, TABLES AND APPENDICES

Table I.	1976 RCTM makeup value and associated standard deviation calculations.
Table II.	1978 RCTM makeup value and associated standard deviation calculations.

ble III. Characterization data summary generated by three different laboratories, using two different analytical chemistry methods, in two different years, while concurrently analyzing one of two different RCTM's. Each mean has been corrected for the apparent bias observed in the analysis of the RCTM.

gure 1. Preparation schemes for calibration and test materials.

pendix I. Statistical treatments of the WCTM characterization analyses from outside laboratories.

pendix II. Statistical treatments of the WCTM characterization analyses by the in-house laboratory.

Table I. 1976 RCTM makeup value and associated standard deviation calculations.

Symbol	Component	Mean Value g/g	Standard Deviation g/g
A =	assigned makeup value		
S_A =	associated standard deviation		
F =	purity of starting material	0.99975	0.000085
b =	air buoyancy	0.99992	0.0
W_1 =	weight of starting material	166.45221	0.00019
W_2 =	tare weight of the flask	176.695	0.034
W_3 =	gross weight of solution & flask	910.209	0.034
W_4 =	$W_3 - W_2$ = net weight of solution	733.513	0.048
S =	standard deviation		

$$A = \frac{(F)(b)(W_1)}{W_4}$$

$$S_A \approx \frac{1}{W_2} [b^2 \{F^2 (S_{W_1}{}^2) + (W_1)^2 S_F{}^2\} + A^2 (S_{W_2}{}^2 + S_{W_3}{}^2)]^{1/2}$$

$$A = \frac{(0.99975)(0.99992)(166.45221 \text{ g U})}{733.512 \text{ g}}$$

$$A = 0.226851 \text{ g U/g}$$

$$S_A \approx \frac{1}{733.512} [(0.99992)^2 \{(0.99975)^2 (0.00019)^2 + (166.4522)^2 (0.000085)^2\} + (0.226851)^2 \{(0.034)^2 + (0.034)^2\}]^{1/2}$$

$$S_A \approx 2.44 \times 10^{-5}$$

Final concentration = 226.851 ±0.024 mg U/g

Table II. 1978 RCTM makeup value and associated standard deviation calculations.

Symbol	Component	Mean Value g/g	Standard Deviation g/g
A =	assigned value		
S_A =	associated standard deviation		
F =	purity of NBS-960 metal	0.99975	0.000085
b =	air buoyancy correction	0.99992	0.0
W_1 =	weight of uranium metal	155.37830	0.00011
W_2 =	tare weight of flask	164.858	0.0083
W_3 =	gross weight of solution & flask	882.044	0.0132
W_4 =	$W_3 - W_2$ = net solution weight	717.186	0.0156
S =	standard deviation		

$$A = \frac{(F)(b)(W_1)}{W_4}$$

$$S_A \approx \frac{1}{W_2} [b^2 \{F^2 (S_{W_1})^2 + (S_{W_1})^2 (S_F^2)\} + A^2 (S_{W_2}{}^2 + S_{W_3})]^{1/2}$$

$$A = \frac{(0.99975)(0.99992)(155.378304 \text{ g U})}{717.186 \text{ g}} = 0.216578 \text{ g U/g}$$

$$S_A \approx \frac{1}{717.186} [(0.99992)^2 \{(0.99975)^2 (0.00011)^2 + (155.3783)^2 (0.000085)^2\} + (0.216578)^2 \{(0.013)^2 + (0.00826)^2\}]^{1/2}$$

$$S_A \approx 1.9 \times 10^{-5}$$

Final concentration = 216.578 ±0.019 mg U/g

Table III. Characterization data summary generated by three different laboratories, using two different analytical chemistry methods, in two different years, while concurrently analyzing one of two different RCTM's. Each mean has been corrected for the apparent bias observed in the analysis of the RCTM.

LABORATORY	METHOD	CORRECTED MEAN
IN-HOUSE - 76	GRAVIMETRIC	219.20
OUTSIDE #1		219.18
IN-HOUSE - 78		219.24
IN-HOUSE - 76a	NBL-MODIFIED D.G.	219.17
IN-HOUSE - 76b		219.20
OUTSIDE #2		219.26
IN-HOUSE - 78		219.18

THE AVERAGE OF THESE 7 MEANS IS 219.20 MG U/G SOLUTION.

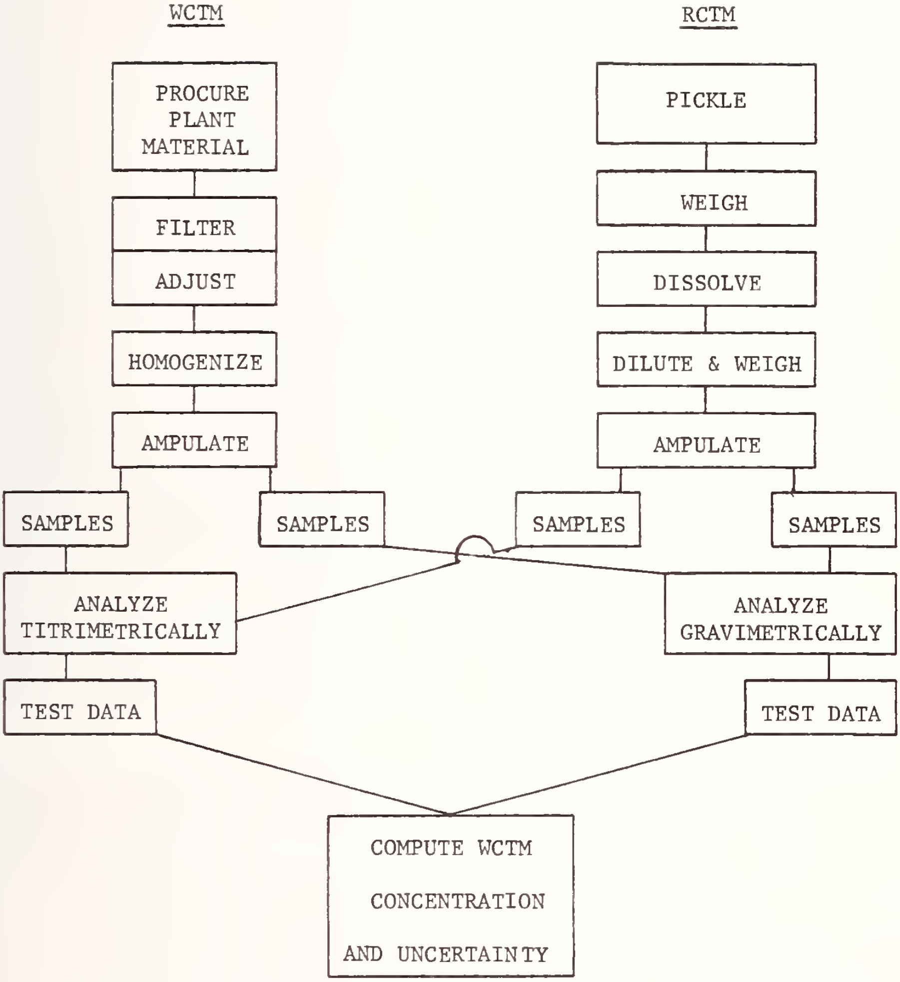

Figure 1. Preparation schemes for calibration and test materials.

APPENDIX I

STATISTICAL TREATMENTS OF THE WCTM CHARACTERIZATION ANALYSES

1. Data Collected in Confirmation Work From Outside Laboratories

The Mean (M) and Standard Deviation (S) of each set of results were calculated using t
following equations:

$$M = \frac{\sum X_i}{n}$$

$$S = \sqrt{\frac{\sum (X_i - M)^2}{n-1}}$$

n = number of samples in each set

Outside Laboratory I		Outside Laboratory II	
RCTM	WCTM	RCTM	WCTM
226.99	219.25	226.95	219.39
226.98	219.24	226.99	219.40
227.02	219.38	227.01	219.38
227.00	219.24	226.96	219.37
226.96	219.38	226.98	219.40
227.04	219.32	227.03	219.38
		226.98	219.39
		226.98	219.39
		227.01	219.40
M_1 = 226.99	M_2 = 219.31	M_3 = 226.99	M_4 = 219.39
S_1 = 0.030	S_2 = 0.063	S_3 = 0.025	S_4 = 0.011
RSD_1 = 0.013	RSD_2 = 0.029	RSD_3 = 0.011	RSD_4 = 0.005

2. F-Test of Precision

Calculated F ratios for both methods are compared to tabulated F values at the 95% confidence level.

Laboratory I

$$F = \frac{S_1^2}{S_2^2} = \frac{(0.030)^2}{(0.063)^2} = \underline{0.226} \qquad \frac{1}{F} = \underline{4.42}$$

$$F(1-\alpha/2,\ n_1-1,\ n_2-1) \quad \text{or} \quad F(0.975,5,5) = \underline{7.15} \qquad \frac{1}{F} = \underline{0.14}$$

Because 0.226 <7.15 and >0.140, the precisions are not different.

Laboratory II

$$F = \frac{S_3^2}{S_4^2} = \frac{(0.025)^2}{(0.011)^2} = \underline{5.6} \qquad \frac{1}{F} = \underline{0.178}$$

$$F(1-\alpha/2,\ n_1-1,\ n_2-1) \quad \text{or} \quad F(0.975,8,8) = \underline{4.43} \qquad \frac{1}{F} = \underline{0.22}$$

Because 5.60 >4.43, the precisions are different.

A pooled standard deviation of .087 was calculated from these and past data for Labor tory #2 and it was used in all subsequent calculations because the precision for the WCTM was much better than past measurement performance.

Calculation of Methods Means Based on RCTM

The two WCTM means $(\overline{X})$ are bias corrected for the differences observed on the RCTM analyses.

The 1976 RCTM reference value $(\underline{R})$ = 226.851 mg U/g from Table I

$$\overline{X}_2 = M_2\ (R/M_1) = 219.31\ (226.851/226.99) = 219.176 \text{ mg U/g}$$

$$\overline{X}_4 = M_4\ (R/M_3) = 219.39\ (226.851/226.99) = 219.256 \text{ mg U/g}$$

$$\overline{X}_{2+4} = \underline{219.205}$$

Calculation of the Equality of the Means

The approximate variances (V) and degrees of freedom (f) for each mean are calculated.

$$V_2 \simeq \overline{X}_2^{\,2} \left(\frac{S_1^{\,2}}{(n_1)M_1^{\,2}} + \frac{S_2^{\,2}}{(n_2)M_2^{\,2}}\right)$$

$$V_2 \simeq (219.157)^2 \left(\frac{(0.030)^2}{(6)(226.99)^2} + \frac{(0.067)^2}{(6)(219.30)^2}\right) \simeq \underline{0.00088}$$

$$V_4 \simeq \overline{X}_4^{\,2} \left(\frac{S_3^{\,2}}{(n_3)M_3^{\,2}} + \frac{S_4^{\,2}}{(n_4)M_4^{\,2}}\right)$$

$$V_4 \simeq (219.256)^2 \left(\frac{(0.087)^2}{(9)(226.99)^2} + \frac{(0.087)^2}{(9)(219.39)^2}\right) \simeq \underline{0.0016}$$

$$f_2 \approx \frac{V_2^{\,2}}{\dfrac{\left(\dfrac{\overline{X}_2^{\,2}\ S_1^{\,2}}{n_1\ M_1}\right)^2}{n_1-1} + \dfrac{\left(\dfrac{\overline{X}_2^{\,2}\ S_2^{\,2}}{n_2\ M_2}\right)^2}{n_2-1}}$$

$$f_2 \approx \frac{(0.00088)^2}{\dfrac{\left(\dfrac{(219.18)^2\ (0.030)^2}{(6)(226.99)^2}\right)^2}{5} + \dfrac{\left(\dfrac{(219.18)^2\ (0.067)^2}{(6)(219.39)^2}\right)^2}{5}} \approx \underline{5}\ *$$

$$f_4 \approx \frac{V_4^{\,2}}{\dfrac{\left(\dfrac{\overline{X}_4^{\,2}\ S_3^{\,2}}{n_3\ M_3^{\,2}}\right)^2}{n_3-1} + \dfrac{\left(\dfrac{\overline{X}_4^{\,2}\ S_4^{\,2}}{n_4\ M_4^{\,2}}\right)^2}{n_4-1}}$$

$$f_4 \approx \frac{(0.0016)^2}{\dfrac{\left(\dfrac{(219.26)^2\ (0.087)^2}{(9)(226.99)^2}\right)^2}{8} + \dfrac{\left(\dfrac{(219.26)^2\ (0.087)^2}{(9)(219.39)^2}\right)^2}{8}} \approx \underline{8}\ *$$

unded to the nearest integer.

5. Compute the T Statistic with f Degrees of Freedom Using the Following Equation:

$$T = \frac{|\overline{X}_2 - \overline{X}_4|}{\sqrt{V_2 + V_4}} \quad \text{in which} \quad T = \frac{|219.176 - 219.256|}{\sqrt{0.00088 + 0.0016}} = \underline{1.60}$$

$$f \approx \frac{(V_2 + V_4)^2}{\frac{V_2^2}{f_2} + \frac{V_4^2}{f_4}} \quad \text{in which} \quad \frac{(0.00088 + 0.0016)^2}{\frac{(0.0008)^2}{5} + \frac{(0.0016)^2}{8}} \approx \underline{13} \; *$$

T from T-Table @ $T(1-\alpha/2, f) = T(0.975,13) = 2.16$

Because 1.60 <2.16, the means are not different.

6. Assignment of WCTM Concentration Value (A) by Weighting the Bias Corrected Means fr each Method

$$A = W_2\overline{X}_2 + W_4\overline{X}_2$$

$$W_2 = \frac{\frac{1}{V_2}}{\frac{1}{V_2} + \frac{1}{V_4}} = \frac{\frac{1}{0.00088}}{\frac{1}{0.00088} + \frac{1}{0.0016}} = \underline{0.6452}$$

$$W_4 = 1 - 0.6452 = \underline{0.3548}$$

$$A = (219.176)(0.6452) + (219.256)(0.3548) = \underline{219.204 \text{ mg U/g solution}}$$

7. Calculation of the Standard Deviation (S_A) Associated with A, with f_A Degrees of Fr

$$S_A \approx \left[\frac{1}{W}\left\{1 + 4\, W_2 W_4 \left(\frac{1}{f_2} + \frac{1}{f_4}\right)\right\}\right]^{\frac{1}{2}}$$

$$W = \left(\frac{1}{V_2} + \frac{1}{V_4}\right) = \underline{1761}$$

$$S_A \approx \left[\frac{1}{1761}\left\{1 + 4\,(0.6452)(0.3548)\left(\frac{1}{5} + \frac{1}{8}\right)\right\}\right]^{\frac{1}{2}}$$

$$S_A \approx \underline{0.027 \text{ mg U/g}}$$

Na is the number of degress of freedom used in calculating the limit of error for A.

$$Na \approx \frac{1}{\frac{W_2^2}{f_2^2} + \frac{W_4^2}{f_4}} \approx \frac{1}{\frac{(0.6452)^2}{5} + \frac{(0.3548)^2}{8}} \approx \underline{10} \; *$$

8. Calculation of the Limit of Error (LE) and Relative Limit of Error (RLE)

$$LE = 2S_A = 2(0.027) = \underline{0.054 \text{ mg U/g}}$$

$$RLE = \frac{100\%\ LE}{A} = \frac{(0.0540)100\%}{219.204} = \underline{0.025\%}$$

9. Test to Determine if the RLE Meets the Requirement of <1/3 of the Plant RLE of 0.2 which is 0.08%

The target RLE of 0.08% is >0.025% of the WCTM, therefore the WCTM characterizatio satisfactory .

* Rounded to the nearest integer.

Calculation of the 95% Confidence Interval (CI) for the Assigned Value

$CI = A \pm t\ (1-\alpha/2,\ N_a)(S_A)$

$t\ (0.975, 10) = 2.228$

$CI = 219.20 \pm 2.228\ (0.027) = \underline{219.14 \text{ to } 219.26 \text{ mg U/g Solution}}$

APPENDIX II

STATISTICAL TREATMENT OF THE WCTM CHARACTERIZATION ANALYSES

1. Data Collected in Confirmation Work from 1978 In-house Analyses

The Mean (M) and Standard Deviation (S) of each set of results were calculated usin following equations:

$$M = \frac{\Sigma X_i}{n}$$

$$S = \frac{\Sigma (X_i - M)^2}{n-1}$$

n = number of samples in each set

Gravimetric Results		Titrimetric Results	
RCTM	WCTM	RCTM	WCTM
216.555	219.209	216.660	219.057
216.584	219.153	216.583	219.363
216.509	219.192	216.490	219.193
216.519	219.247	216.660	219.057
216.521	219.324	216.490	219.193
216.658	219.182	216.607	219.237

M_1 = 216.558	M_2 = 219.217	M_3 = 216.582	M_4 = 219.183
S_1 = 0.057	S_2 = 0.061	S_3 = 0.077	S_4 = 0.116
RSD_1 = 0.026	RSD_2 = 0.028	RSD_3 = 0.036%	RSD_4 = 0.053%

2. F-Test of Precision

Calculated F ratios for both methods are compared to tabulated F values at the 95% confidence level.

Method (1)

$$F = \frac{S_1^2}{S_1^2} = \frac{(0.057)^2}{(0.061)^2} = \underline{0.873} \qquad \frac{1}{F} = \underline{1.15}$$

$$F(1-\alpha/2,\ n_1-1,\ n_2-1) \quad \text{or} \quad F(0.975,5,5) = \underline{7.15} \qquad \frac{1}{F} = \underline{0.14}$$

Because 0.873 <7.15 and >0.140, the precisions are not different.

Method (2)

$$F = \frac{S_3^2}{S_4^2} = \frac{(0.077)^2}{(0.116)^2} = \underline{0.44} \qquad \frac{1}{F} = \underline{2.27}$$

Because 2.27 <7.15 and >0.140, the precisions are not different.

3. Calculation of Method Means Based on the RCTM

The two WCTM means ($\overline{X}$) are bias corrected for the differences observed on the RCTM analyses.

The RCTM reference value ($\underline{R}$) = 216.578 mg U/g from Table II.

$$\bar{X}_2 = M_2\ (R/M_1) = 219.217\ (216.578/216.558) = \underline{219.237}$$

$$\bar{X}_4 = M_4\ (R/M_3) = 219.183\ (216.578/216.582) = \underline{219.179}$$

$$\bar{X}_{2+4} = \underline{219.208}$$

Calculation of the Equality of the Means

The approximate variances (V) and degrees of freedom (f) for each mean are calculated.

$$V_2 \approx \bar{X}_2^{\,2} \left(\frac{S_1^{\,2}}{(n_1)M_1^{\,2}} + \frac{S_2^{\,2}}{n_2 M_2^{\,2}} \right)$$

$$V_2 \approx (219.237)^2 \left(\frac{(0.057)^2}{(6)(216.558)^2} + \frac{(0.061)^2}{(6)(219.217)^2} \right) \approx \underline{0.00118}$$

$$V_4 \approx \bar{X}_4^{\,2} \left(\frac{S_3^{\,2}}{(n_3)M_3^{\,2}} + \frac{S_4^{\,2}}{(n_4)M_4^{\,2}} \right)$$

$$V_4 \approx (219.179)^2 \left(\frac{(0.077)^2}{(6)(216.582)^2} + \frac{(0.116)^2}{(6)(219.183)^2} \right) \approx \underline{0.00325}$$

$$f_2 \approx \frac{V_2^{\,2}}{\frac{\left(\frac{\bar{X}_2^{\,2}\ S_1^{\,2}}{n_1\ M_1}\right)^2}{n_1 - 1} + \frac{\left(\frac{\bar{X}_2^{\,2}\ S_2^{\,2}}{n_2\ M_2}\right)^2}{n_2 - 1}}$$

$$f_2 \approx \frac{(0.00118)^2}{\frac{\left(\frac{(219.237)^2 (0.057)^2}{(6)(216.558)^2}\right)^2}{5} + \frac{\left(\frac{(219.237)^2 (0.061)^2}{(6)(219.217)^2}\right)^2}{5}} \approx \underline{10}\ *$$

$$f_4 \approx \frac{V_4^{\,2}}{\frac{\left(\frac{\bar{X}_4^{\,2}\ S_3^{\,2}}{n_3\ M_3}\right)^2}{n_3 - 1} + \frac{\left(\frac{\bar{X}_4^{\,2}\ S_4^{\,2}}{n_4\ M_4}\right)^2}{n_4 - 1}}$$

$$f_4 \approx \frac{(0.00325)^2}{\frac{\left(\frac{(219.179)^2\ (0.077)^2}{(6)(216.582)^2}\right)^2}{5} + \frac{\left(\frac{(219.179)^2\ (0.116)^2}{(6)(219.183)^2}\right)^2}{5}} \approx \underline{9}\ *$$

Compute the T Statistic with f Degrees of Freedom Using the Following Equation:

$$T = \frac{|\bar{X}_2 - \bar{X}_4|}{\sqrt{V_2 + V_4}} \quad \text{in which} \quad T = \frac{219.237 - 219.179}{\sqrt{0.00118 + 0.00325}} = \underline{0.871}$$

$$f_4 \approx \frac{(V_2 + V_4)^2}{\frac{V_2^{\,2}}{f_2} + \frac{V_4^{\,2}}{f_4}} \quad \text{in which} \quad \frac{(0.00118 + 0.00325)^2}{\frac{(0.00118)^2}{10} + \frac{(0.00325)^2}{9}} \approx \underline{14}\ *$$

Rounded to the nearest integer.

T from T-Table @ $t(1-\alpha/2,\ f) = T(0.975,14) = \underline{2.145}$

Conclude the two means are not different since $0.871 < 2.145$

6. Assignment of WCTM Concentration Value (A) by Weighting the Bias Corrected Means fro each Method

$$A = W_2\overline{X}_2 + W_4\overline{X}_4$$

$$W_2 = \frac{\frac{1}{V_2}}{\frac{1}{V_2} + \frac{1}{V_4}} = \frac{\frac{1}{0.00118}}{\frac{1}{0.00118} + \frac{1}{0.00325}} = \underline{0.73363}$$

$$W_4 = 1 - 0.73363 = \underline{0.26637}$$

$$A = (219.237)(0.73363) + (219.179)(0.26637) = \underline{219.22 \text{ mg U/g solution}}$$

7. Calculation of the Standard Deviation (S_A) Associated with A, with f_A Degrees of Fre

$$S_A \approx \frac{1}{W}\left[1 + \left\{4\ W_2W_4 \cdot \left(\frac{1}{f_2} + \frac{1}{f_4}\right)\right\}\right]^{\frac{1}{2}}$$

$$W = \frac{1}{V_2} + \frac{1}{V_4} = \underline{1155.15}$$

$$S_A \approx \frac{1}{1155.15}\left[1 + \left\{4\ (0.73363)(0.26637)\left(\frac{1}{10} + \frac{1}{9}\right)\right\}\right]^{\frac{1}{2}} = \underline{0.0318 \text{ mg U/g}}$$

Na is the number of degrees of freedom used in calculating the limit of error for A.

$$Na \approx \frac{1}{\frac{W_2^{\,2}}{f_2} + \frac{W_4^{\,2}}{f_4}} \approx \frac{1}{\frac{(0.73363)^2}{10} + \frac{(0.26637)^2}{9}} \approx \underline{16}\ *$$

8. Calculation of the Limit of Error (LE) and Relative Limit of Error (RLE)

$$LE = 2S_A = 2(0.0318) = \underline{0.0636 \text{ mg U/g}}$$

$$RLE = \frac{100\%\ LE}{A} = \frac{(0.0636)100\%}{219.22} = \underline{0.029\%}$$

9. Test to Determine if the RLE Meets the Requirement of <1/3 of the Plant RLE of 0.25% which is 0.08%

The target RLE of 0.08% is >0.03% of the WCTM, therefore the WCTM characterization i satisfactory.

10. Calculation of the 95% Confidence Interval (CI) for the Assigned Value

$$CI = A \pm t\ (1-\alpha/2,\ n_a)\ (S_A)$$

$$t\ (0.975,16) = 2.120$$

$$CI = 219.22 \pm 2.12\ (0.0318) = 219.15 \text{ to } 219.29 \text{ mg U/g solution}$$

* Rounded to the nearest integer.

Preparation of Uranium Standard Solutions for X-Ray Fluorescence Analysis*

by

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ABSTRACT

A method has been developed for gravimetrically preparing uranium nitrate standards with an estimated mean error of 0.1% (1 sigma) and a maximum error of 0.2% (1 sigma) for the total uranium weight.

Two source materials, depleted uranium dioxide powder and NBS Standard Reference Material 960 uranium metal,[1] were used to prepare stock solutions. The NBS metal proved to be superior because of the small but inherent uncertainty in the stoichiometry of the uranium oxide. These solutions were used to prepare standards in a freeze-dried configuration suitable for x-ray fluorescence analysis.[2] Both gravimetric and freeze-drying techniques will be presented. Volumetric preparation was found to be unsatisfactory for 0.1% precision for the sample size of interest.

One of the primary considerations in preparing uranium standards for x-ray fluorescence analysis is the development of a technique for dispensing a 50-μl aliquot of a standard solution with a precision of 0.1% and an accuracy of 0.1%. The method developed corrects for variation in aliquoting and for evaporation loss during weighing.

Two sets, each containing 50 standards have been produced. One set has been retained by LLL and one set retained by the Savannah River Project (SRP).

KEYWORDS: X-Ray fluorescence analysis; actinides; high accuracy; freeze dried; particle size effects; gravimetric standards; radioactive samples

INTRODUCTION

The purpose of this study was to develop a method of preparing uranium standards for ay fluorescence analysis to meet the requirement of the Safeguard Programs at Lawrence ermore Laboratory (LLL). Some of these requirements were that the standards source erial must be of high purity; the method of preparation of the standard solution must be urate; the aliquoting technique must be precise; the standard configuration must be table for x-ray fluorescence measurement; and, the maximum error associated with all ects of preparation must be minimal and well known.

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s suggested by S. S. Yamamura, private communication.

. L. Pickles and J. L. Cate, Jr. Quantitative Nondispersive X-Ray Fluorescence Analysis Highly Radioactive Samples for Uranium and Plutonium Concentration, Lawrence Livermore oratory, Report UCRL-47417 (1973) , and in Advances in X-Ray Analysis, C. L. Grant, C. Barrett, J. B. Newkirk, and Co., O. Rudd, Eds. (Plenum Press, New York, 1974), Vol. 17, 337-347.

I. STANDARDS SOLUTIONS PREPARATION

A. Uranium Oxide Standards

To make our initial trial uranium standards, we used some 15-year-old depleted ura oxide that was 99.93% pure UO_2. The sample was spectrographically analyzed for impurities (see Table I).

The uranium oxide was initially prepared according to the following standard metho (1) The oxides are converted to U_3O_8 by heating in a cleaned platinum crucible at 800°C for one hour; (2) The crucible is removed from the oven and the powder stirred a mixed well; (3) The crucible is returned to the oven and heated for one hour; and (4) U_3O_8 is allowed to cool in a desiccator and then weighed. The weight of the UO_2 before heating was 201.859 g and the weight of U_3O_8 after heating was 208.967 g. There was a weight gain of 7.108 g which indicates a 99.6% theoretical conversion of UO_2 to U_3O_8, and according to the equation $3\ UO_2 + O_2 \rightarrow U_3O_8$, the gain in weight should have been 7.973 g. This difference may indicate that the original UO_2 contained a small amount of U_3O_8. The stoichiometry as well as the isotopic composition were established by mass spectroscopy.

A weighed aliquot of the U_3O_8 was dissolved in sub-boiled distilled 8 N HNO_3, and a stock solution was prepared using sub-boiled distilled H_2O to dilute to volume at 1 N HNO_3. Sub-standards from 0.1-10 mg U/g of solution were then prepared from the stock solution.

All aliquots and dilutions were made by powder weight. Aluminum foil pans and fun were used for initially weighing the UO_2 and U_3O_8 to eliminate the static charge that the powder exhibited. Next, the solutions were pipetted, weighed, freeze-dried, and analyzed by x-ray fluorescence.

Table I. Spectrochemical Analysis for Impurities in UO_2 (ppm).

Fe	100	Al	5	B	<1
Ni	30	Mg	5	Sr	<1
Ca	20	Cu	4	Pb	0.5
Mo	20	Mn	3	Ti	<0.3
Cr	15	Sn	3	Be	<0.1
Si	15	Zn	2	V	1

The following elements were not detected:

	Detection limit
Ba	<30
Zr	<10
Nb, Sb	<3
Bi, Co	<1
Cd	<0.3

B. Uranium Metal Standards

The uranium metal, NBS Standard Reference Material 960, was obtained from the National eau of Standards and cleaned of surface oxide according to the following NBS procedure: dip the uranium metal in 1:1 HNO_3 for ten minutes to remove surface oxide; (2) ise in distilled water; (3) etch in 1:3 HCl for five minutes; (4) rinse thoroughly in stilled water; and (5) remove excess distilled water and place in a vacuum desiccator to ain constant weight. Removal of surface moisture is accelerated and reoxidation of the al surface is retarded by drying under vacuum for a suitable length of time proximately 1/2 hour).

After constant weight is attained, a weighed aliquot of the uranium metal was ssolved in sub-boiled distilled 8 N HNO_3 and sub-standards were prepared. These utions were pipetted, weighed, freeze-dried, and analyzed by x-ray fluorescence in the ne manner as the uranium oxide. The metal-based standards proved to be far more precise n the oxide-based standards.[3]

II. WEIGHING ACCURACY

We checked our H-16 Mettler balance and our weighing method to determine the sistency of the balance in weighing and the individual bias in reading the weights. st, one person alternately weighed a series of empty vials, and then a series of vials h containing 50 µl of distilled water. This procedure was repeated ten times for each l. Second, two people did the weighing, rezeroing the balance and alternately reading weights. The results in Table II show that the slight variance in weight read by two ple or by the same person is not great enough to exceed the 0.1% precision and accuracy weight that we hope to achieve.

Table II. Average Deviation in Reading Weights

Reading by	Empty Vials	Vials + H_2O
One person	± 0.00002 g	± 0.00003 g
Two people	± 0.00003 g	± 0.00005 g

III. DISPENSING PRECISION AND ACCURACY

The accuracy and precision of three high-precision microdispensers were measured by ghing each aliquot on a Mettler H-16 balance. To standardize the effects of weight loss m evaporation while weighing, the following procedure was used: (1) open vial; (2) rt electric timer; (3) pipet 50-µl aliquot of distilled water; (4) dispense sample o vial; (5) place on balance pan; (6) weigh; (7) read weight when timer is exactly 0 min. The Brand A pipet proved to be far superior to the Brand B and Brand C pipets, shown in Table III. However, none of the three pipets are capable of delivering 0.1% uracy or precision volumetrically, therefore, the accuracy had to be achieved vimetrically, weighing each sample individually.

. L. Pickles, J. W. McClure, R. H. Howell, A Non-Linear Method for Including the Mass ertainty of Gravimetric Standards and the System Measurement Errors in the Fitting of ibration Curves, Lawrence Livermore Laboratory Report, UCRL-80375 (1977), and in the ceedings of the American Chemical Society, Symposium on Non-Destructive and Analytical mical Techniques in Nuclear Safeguards (1978), 175 ACS.

Table III. Pipet Precision and Accuracy for Delivery of 50 µl Water Samples

Pipet	Number of Measurement	% Accuracy[a]		Average % Precision
		Range	Av	
Brand A	70	-1.38 to 1.72	-0.48	0.47
Brand B	60	-6.62 to 7.28	-2.27	3.03
Brand C	20	-9.46 to 1.16	-1.42	2.65

[a] Corrected for H_2O density variation at room temperature (22°C).

IV. EVAPORATION CORRECTION IN WEIGHING

The evaporation rate of 50-µl aliquots of several solutions was determined by repeated weighings over a five-minute interval for each sample. It is apparent from Fig that the evaporation loss becomes significant for a weighing time greater than 15 s.

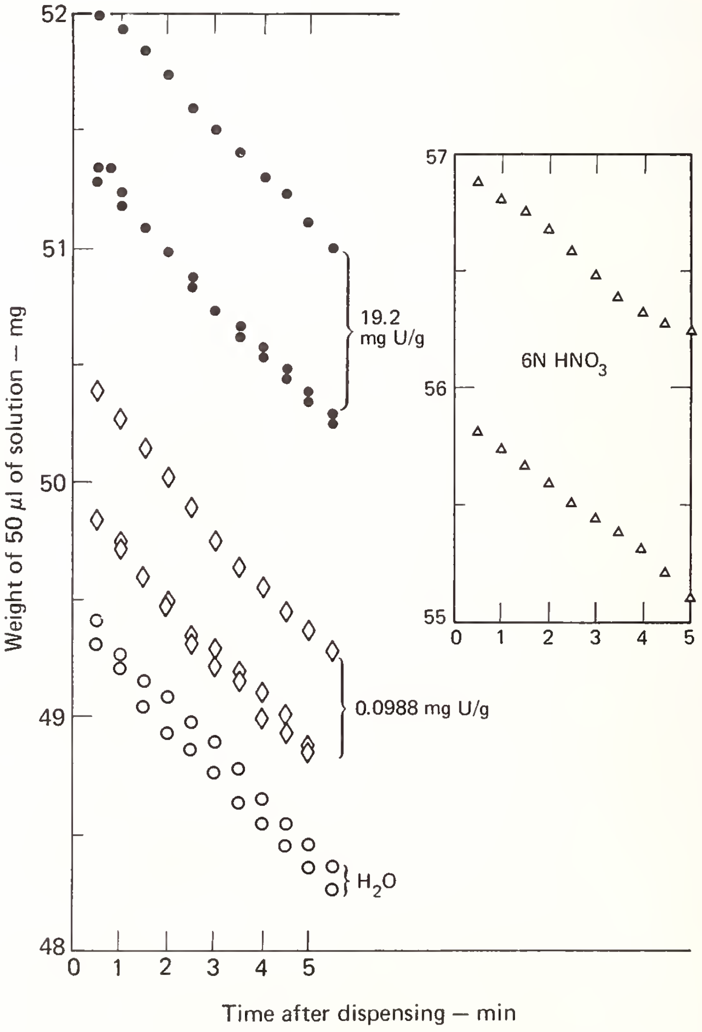

Fig. 1. Weight changes of solution during weighing.

The evaporation rates of 50 µl of pure water and of 100 ppm, and 19000 ppm (in 0.25 N HNO_3) uranium solutions vary between 0.19 and 0.21 mg/min (a slightly lower rate of 0.15 mg/min was observed for 6 N HNO_3). In actual practice, the minimum time required for conveniently dispensing (with an automatic pipet) and weighing the 50-µl aliquot is about 30 s. Therefore, within 30 s, 0.10 mg of solution would have been volatilized, or 0.2% of a 50-mg aliquot, for solutions with the above evaporation rate. To achieve the 0.1% accuracy, as desired by the Safeguards Programs, it is necessary that this kind of correction be incorporated into the weighing procedure.

The 50-µl aliquot was chosen because this volume best meets the requirements of the sample mounting and counting procedure developed by LLL for x-ray fluorescence analysis of uranium-bearing solutions.[2] Briefly, this procedure involves mounting an adhesive Kapton polyimide film on a 35-mm slide with a 1.27-cm diameter circle of polycarbonate film centered on the adhesive side of the Kapton. The polycarbonate film was wiped with a dilute (1:100) solution of aerosol-OT-dispersant, then dried and tared. The standard solutions were then dispensed onto the circle of film, weighed continuously every 30 s for five minutes, freeze-dried, and covered with another layer of adhesive Kapton (Fig. 2). After the procedure was completed the samples were analyzed by x-ray fluorescence.

V. FREEZE-DRYING TECHNIQUE AND PHYSICAL SAMPLE CHARACTERISTICS

After weighing, the sample was quick-frozen by placing it on an aluminum chill block that was at LN temperature. The chill block and sample were then placed in the vacuum apparatus and kept under vacuum until the sample was completely dry — from 6 to 16 hours (Fig. 3).

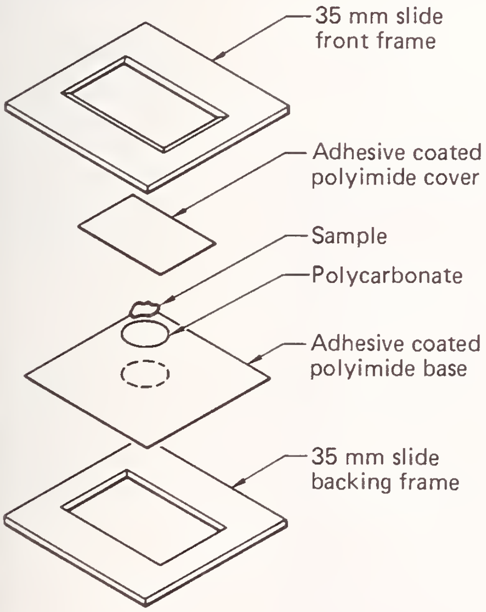

Fig. 2. Mounting procedure for an x-ray fluorescence analysis sample. This is a convenient procedure that provides primary containment for hot samples.

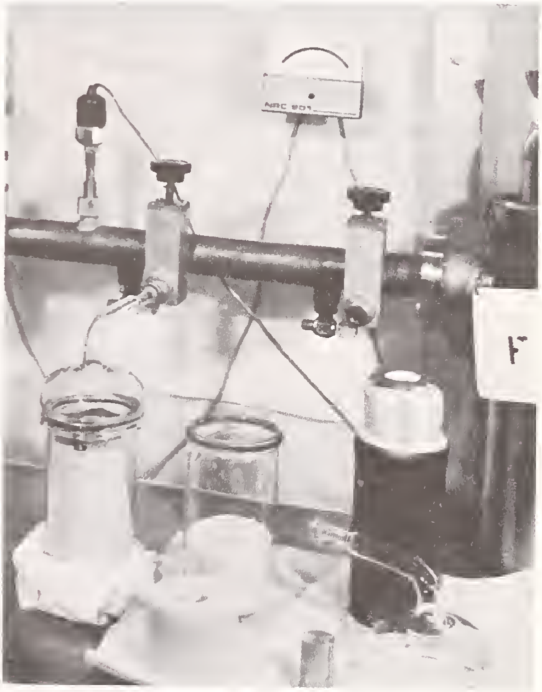

Fig. 3. Freeze-drying apparatus. The apparatus consists of a vacuum manifold, a sample evacuation jar, a foam insert, and an aluminum heat sink at LN temperature.

Some of the sample standards were gold coated by vacuum-deposition techniques and th crystals examined under various magnifications with a mini-scanning electron microscope. The optical photographs showed details of the fibrous, snow-like crystalline structure which is an important consideration for understanding the type of particle-size effects t expect in the x-ray fluorescence analysis of these samples (Fig. 4). The diameter of the sample is 12.7 mm. Figure 5 is a magnified view of the edge of the sample showing the fibrous nature of freeze-dried U-NO_3.

The use of excessive concentrations of dispersant in preparing these samples was discontinued after discovering that it caused the center portions of the sample to freeze in an irregular way (Fig. 6).

Fig. 4. Optical photograph of a 12.7-mm-diameter freeze-dried U-NO_3 sample.

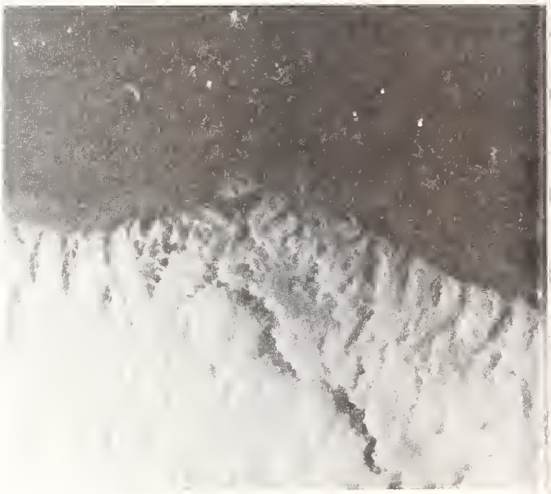

Fig. 5. Highly magnified, optical photograph of a freeze-dried U-NO_3 sample. Note its fibrous nature.

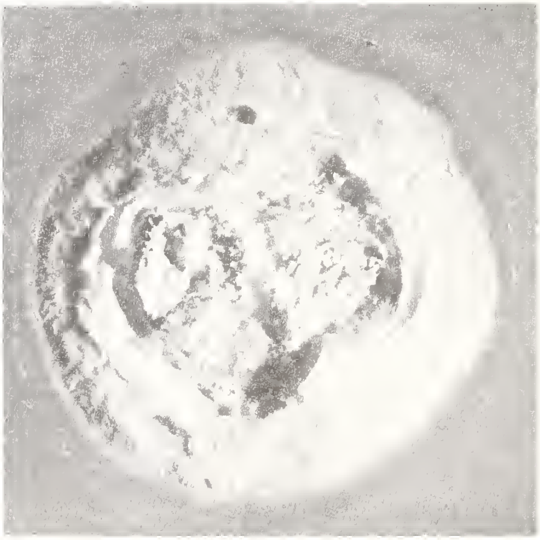

Fig. 6. Freeze-dried U-NO_3 sample that has been collapsed to expose the interior structure.

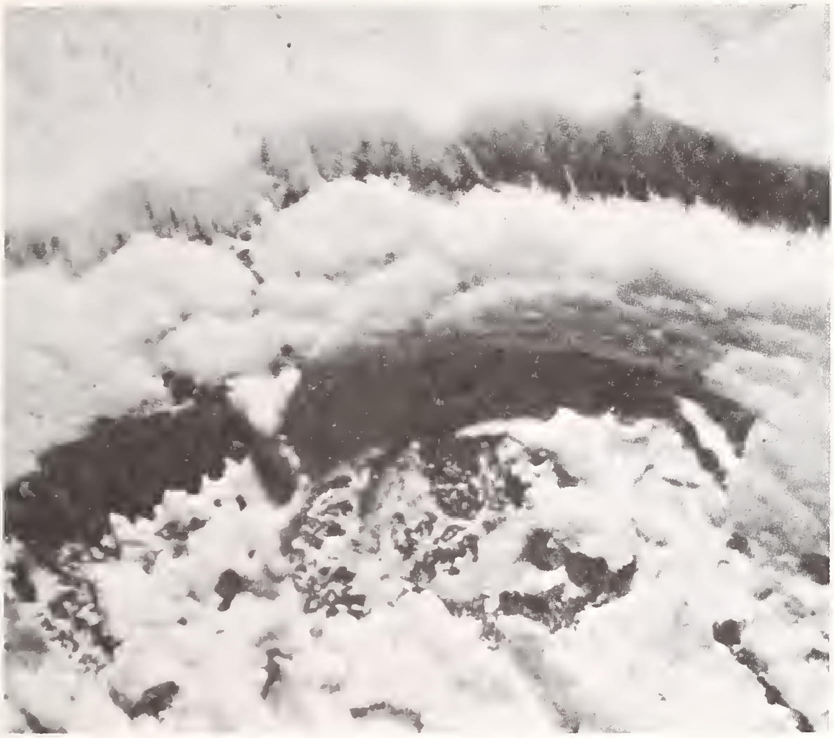

Fig. 7. A highly magnified, optical photograph of a crushed, freeze-dried U-NO_3 sample. Note the fibrous nature of the sample and the crevice at the top.

Most of the information about the structure of the freeze-dried samples was obtained by physically crushing the center and photographing the exposed interior using high magnification. As shown in the fissure on the left in Fig. 7, freeze drying U-NO_3 results in long twisted fibers that are generally perpendicular to the plane of the sample. A simple exponential absorption model, with an increased effective sample thickness, may be used to describe the effect of freeze-dried U-NO_3 on the XRFA instrument response.[3]

SUMMARY

In conclusion, we have demonstrated that highly accurate, freeze-dried U-NO_3 standards that are suitable for x-ray fluorescence analysis can be prepared in the mass range from 4 µg to 1000 µg. Gravimetric methods, using NBS 960 U metal, have proved to be the most accurate preparation technique; standard reference material accuracies of approximately 0.2% can also be achieved by this method.

Use of a Non-Linear Method for Including the Mass Uncertainty of Gravimetric Standards and System Measurement Errors in the Fitting of Calibration Curves for XRFA with Freeze-Dried UNO_3 Standards

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ABSTRACT

At LLL we have used a sophisticated non-linear multiparameter fitting program to produce a best fit calibration curve for the response of an x-ray fluorescence analyzer to uranium nitrate, freeze dried, 0.2% accurate, gravimetric standards. The program is based on unconstrained minimization subroutine, VA02A. The program considers the mass values of the gravimetric standards as parameters to be fit along with the normal calibration curve parameters. The fitting procedure weights with the system errors and the mass errors in a consistent way. The resulting best fit calibration curve parameters reflect the fact that the masses of the standard samples are measured quantities with a known error. Error estimates for the calibration curve parameters can be obtained from the curvature of the "Chi-Squared Matrix" or from error relaxation techniques. We have shown that non-dispersive XRFA of 0.1 to 1 mg freeze-dried UNO_3 can have an accuracy of 0.2% in 1000 sec.

KEYWORDS: Non-linear least squares, x-ray fluorescence analysis, uranium, two-dimensional calibration.

INTRODUCTION

The goal of the work described here was to be able to produce highly accurate (0.1 to 0.2%) calibration curves of non-destructive assay instruments where the accuracy of the standards available is the limiting factor, or at least a major source of calibration error.

In reaching the ultimate accuracies possible for a particular NDA measurement system, the instrument long-term precision is often not the limiting factor. The variability of sample preparation and the accuracy and applicability of the standards used for calibration of the instrument usually create the greatest source of uncertainty.[1]

We have developed a mathematical method of dealing with these types of errors in a statistically correct way. Our first test of this method was with standards accuracy for x-ray fluorescence analysis of freeze-dried[2] UNO_3. The method can also be used to evaluate the importance of sample variability errors. The type of computer code we have used in this method is commercially available from several sources[3,4] as a package which requires only a small amount of input-output user generated software.

METHOD

Our LLL XRFA system[5] has a repeatable precision which has been measured to be 0.1% (two standard deviations). In attempting to utilize this system for accountability measurements in the nuclear fuel cycle, we were continually frustrated by the lack of high accuracy solid samples in the mass range from 10 to 1000 μg. We were finally able to produce UNO_3 standards by a freeze-drying method with an NBS traceable accuracy of 0.2% (one standard deviation).[1] These samples were thought to have particle size absorption, but because of the uniform fibrous nature[1] of these freeze-dried samples it was expected that these absorption effects would be calculable to high accuracy. We have used 100 of these standards to calibrate our XRFA instrument.

Since the mass accuracy error of the standards was estimated to be twice as large as the instrument precision errors, we felt it was particularly important to include the mass certainty in the calibration procedure. Our approach was to treat the mass values of e standards in exactly the same way as we normally treat the instrument's response to ose standards. That is, the mass value of each standard is a gravimetrically measured antity. The gravimetrical mass value, M_i, is not the "true mass" of the standard. It ffers from the true mass in a normal way. The gravimetrically measured mass, M_i, has a % probability of deviating from the true mass value by less than 0.2%. We therefore eated a set of parameters which represent the true mass values,

$$\left\{X_i\right\}$$

ere is one X_i, or true mass, for each standard. It is now possible to use these new para-
ters in expressing the instrument response calibration curve equation, YFUN.

$$\text{YFUN} = G(A,B,C,\mu_1,\mu_2,X_i)$$

e true mass X_i of the standard is one of the variables in the calibration function instead being a fixed constant. Consequently, the true mass, X_i, may be fit along with A,B,C,μ_1 d μ_2, the "usual" calibration curve fit parameters.

The result of this technique is to start from a set of gravimetrically measured standard ss values and measured XRFA instrument responses to those standards and arrive at both the st probable, or true mass, of the standard, and the most probable system response values. is is diagrammed schematically in Figure 1.

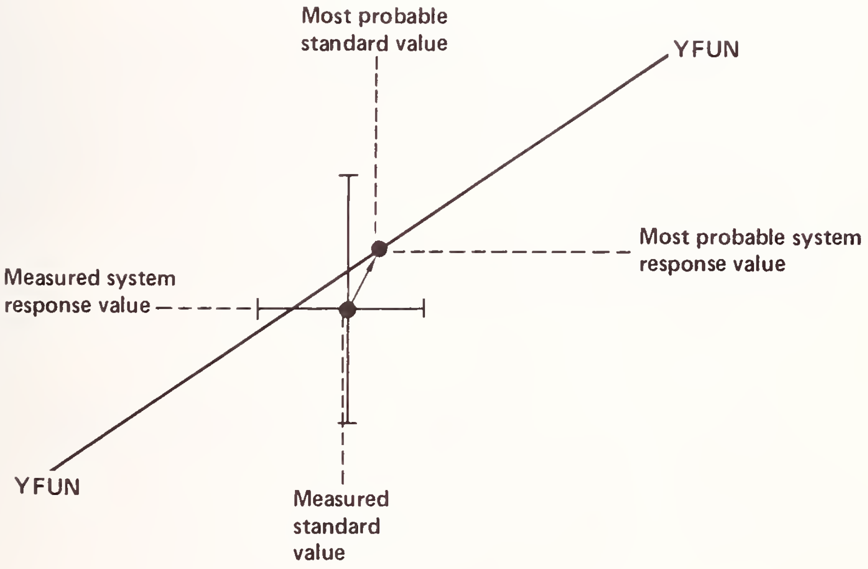


Figure 1. Overall result of non-linear least squares fitting is a most probable system response value and a most probable standard mass value.

The fitting procedure is accomplished by a commercially available,[2] non-linear, uncon-
rained minimization, computer program. The program minimizes the quantity chi-squared. r chi-squared not only involves the deviations in the instrument response from the cali-
ation curve as is usual, but must also include the deviations of the gravimetric mass lues from the true mass. The value of chi-squared per degree of freedom is a measure of e "goodness" of fit of the calibration curve and true masses to all the experimental data. r chi-squared is defined in Figure 2. The expression for chi-squared has two sums of ighted, squared deviations. The first of these terms is similar to the whole expression ed for fitting programs in the past. It is different in that the true mass, X_i is used place of the gravimetrically measured mass, M_i. The second term is new, and is the sum

TO CONSISTENTLY USE BOTH TYPES OF ERRORS CHISQUARED MUST INCLUDE THE STANDARDS MASS ERRORS

System response

$$Q \equiv \sum_i \left[\frac{R_i - \mathrm{YFUN}\,(A_1, B_2, \mu_1, \mu_2, C, \boxed{X_i})}{2\,\sigma_i} \right]^2$$

Almost normal CHISQUARED

Standards variations

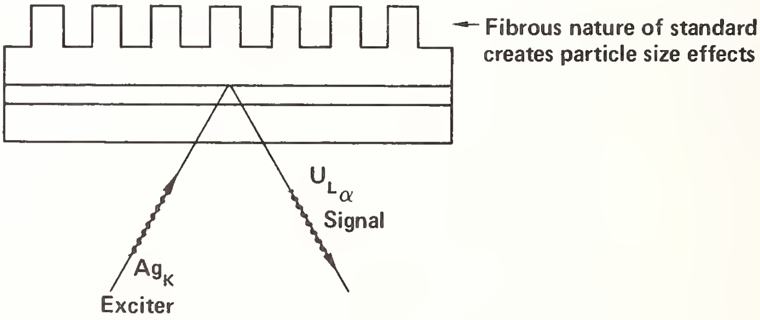
$$+ \sum_i \left[\frac{\boxed{X_i} - M_i}{2\epsilon_i} \right]^2$$

New contribution to CHISQUARED

Figure 2. New two-dimensional definition of chi-squared used in the non-linear fitting technique. Note the use of true rather than gravimetric mass.

of the squares of the deviations of the measured mass from the true mass, weighted by the gravimetric errors. The actual calibration curve function, YFUN, which we used in this wor is shown in Figure 3. The function contains three terms; the first term is a constant, the second is a term that represents simple mass absorption, and the third term allows for absorption in the long thin fibers of UNO_3 oriented perpendicular to the plane of the sampl The fact that the free parameters in this function $A,B,C,\mu_1,\mu_2,\{X_i\}$ appear as products and that the expression for chi-squared contains X_i's which are free parameters, dictates the use of a non-linear fitting program.

FOR XRFA OF FREEZE DRIED UNO_3 STANDARDS WE CHOOSE A PHYSICALLY REALISTIC MODEL



$$\mathrm{YFUN} \equiv A + B[1-e^{-\mu_1 m}] + C[1-e^{-\mu_2 m}]$$

Background | Normal mass absorption | Fibrous particle size absorption

- Thus the function becomes

$$\mathrm{YFUN} = A + B[1-e^{-\mu_1 X_i}] + C[1-e^{-\mu_2 X_i}]$$

Figure 3. The actual calibration curve used in this work has a term for normal mass absorption and also a term for fibrous particle size absorption.

RESULTS

The final results of using this technique is a "best-fit" value for A,B,C,μ_1,μ_2 all the X_i's as shown in Figure 4 numerically and Figure 5 graphically. As can be seen Figure 5, 40% of the under response is due to simple mass absorption and 60% is due to ticle size absorption.

THE FINAL RESULT OF THIS TECHNIQUE IS

- A set of most probable model parameters

$$\mathrm{YFUN} = \underbrace{1.02 \times 10^{6}}_{\text{Background}} + 4.6 \times 10^{5}\ \underbrace{[1-e^{-2.1\times 10^{-4}\,x}]}_{\substack{\text{Normal}\\ \text{mass absorbtion}}} + 5.6 \times 10^{5}\ \underbrace{[1-e^{-7.3\times 10^{-4}\,x}]}_{\substack{\text{Fibrous particle}\\ \text{size absorbtion}}}$$

- A set of most probable standard values

```
  X DATA       X FIT       RES/SIGMA      SIGMA
4.454E+00    4.294E+00     1.599E+00    1.000E-01
4.459E+00    4.341E+00     1.186E+00    1.000E-01
9.521E+00    9.594E+00    -7.339E-01    1.000E-01
    •            •             •            •
    •            •             •            •
    •            •             •            •
    •            •             •            •
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Figure 4. Actual numerical results of our fitting method showing our best fit parameters.

PARTICLE SIZE AND MASS ABSORBTION ARE APPROXIMATELY EQUAL

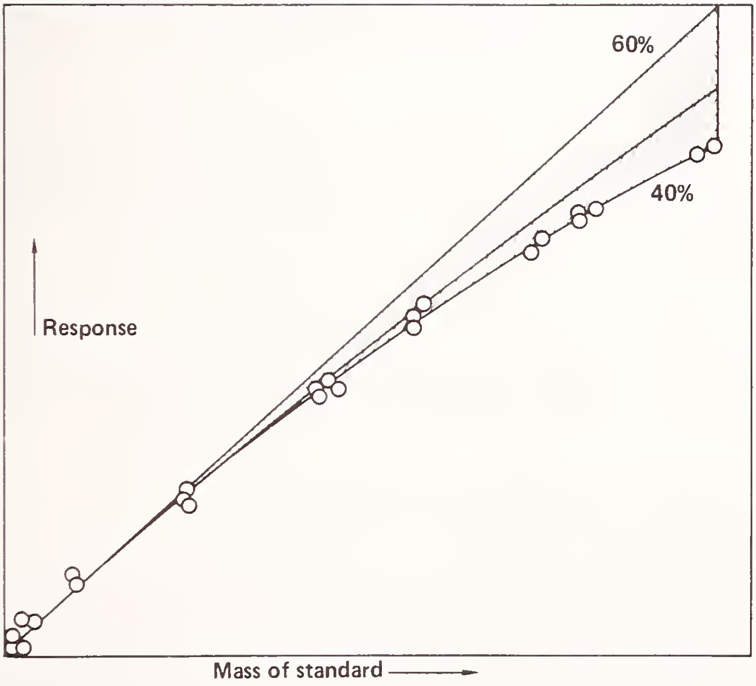

Figure 5. Graphical representation of our best fit calibration curve showing the normal mass absorption, 40%, and the fibrous particle size absorption, 60%, under responses from the linear.

ERRORS

A non-linear least squares fitting program does <u>not</u> use simple matrix inversion to obtain a unique best fit value for each free parameter and consequently does <u>not</u> produce a unique error matrix for the free parameters. However, estimates of the overall error is possible by two methods. In the first method, the curvature of chi-squared space near the best fit value of each parameter is an indication of the sensitivity of the fit to that parameter. The second and more useful method is to relax the errors on the gravimetric masses and/or the instrument response precision until a chi-squared per degree of freedom of approximately <u>three</u> is obtained. A chi-squared per degree of freedom of three means th probability that all the fit parameters are within one standard deviation of their "correc value is 67%. We were able to obtain a chi-squared per degree of freedom of three by relaxing the instrument response errors to 0.2%. The conclusion we draw from this is we should accumulate counts on an unknown sample until the precision of the response is 0.1% and then the error we assign to the measurement of that sample will be 0.2% (1 sigma).

SUMMARY

We have found the non-linear fitting techniques as described here to be a powerful method of creating realistic calibration curves for an NDA instrument and a particular standards set. The method uses both the gravimetric mass errors and the instrument respon errors in a statistically consistent way. It incorporates the independent gravimetric measurement of the standards in the calibration curve parameters thus extracting all the experimental information available for the instrument response and the standards set. It determines the actual most probable value of each standard mass. It allows sensitive selection among the calibration curve models. It eliminates the need to cross measure standards, and it allows a realistic appraisal of the overall accuracy error of an NDA instrument and it's standards.

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3. International Mathematic and Science Library--XCSSQ Routine.

4. National Bureau of Economic Research--NL2SOL Routine.

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Future Approaches to Material Control and Accounting

by

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ABSTRACT

This paper presents a short description of the safeguards responsibilities and activities of the U.S. Nuclear Regulatory Commission (NRC), the NRC regulatory requirements for safeguards in the area of material control and accounting (MC&A), and the current NRC efforts which may result in significant changes in the current U.S. safeguards system. The preliminary results of NRC staff and contractor MC&A activities will be discussed, as well as the recommendations of a recent NRC task force on MC&A.

ORDS: Nuclear safeguards, material control and accounting, fuel-cycle regulation

INTRODUCTION

U.S. Nuclear Regulatory Commission is responsible for ensuring that there is appropriate ection against radiological sabotage at commercial nuclear facilities and theft of ear materials. The Commission meets this responsibility through a safeguards program rised of four major elements--regulatory development, licensing, inspection and evalua- of licensee operations, and coordination with other agencies. Material control and unting activities comprise a significant part of the NRC program in each of these ents. As background prior to addressing future approaches to material control and unting in this paper, a brief overview is first provided of the current NRC safeguards ram and activities.

first major element of the NRC safeguards program is the development of a regulatory . This element includes developing safeguards policies, requirements which reflect e policies, and guidance to assist licensees in meeting these requirements. In this , several major policy activities and supporting technical studies are underway which ess MC&A. These studies will be described in detail later in this paper.

second major element of the NRC safeguards program is licensing which includes the ew and approval of proposed safeguards plans in order to assure that appropriate safe- ds will be implemented. Reviews of such plans occur when licensees respond to new lations, when applicants apply for new licenses, or when application is made for license fication or renewal. In this area, the major current licensing activity for MC&A is the ementation of new requirements for measurement quality control, which includes specific bration and statistical procedures.

third major element of NRC's safeguards program is the inspection and evaluation of the guards systems, procedures and practices of current licensees. These NRC activities two objectives: (1) to insure that current safeguards practices are in compliance with requirements, and (2) to insure that NRC's requirements themselves are adequate through evaluation of the vulnerabilities and capabilities of present systems. In this area, is currently conducting a major evaluation program at facilities possessing plutonium high-enriched uranium (greater than 20% in the U-235 isotope). Included in this program comprehensive evaluations of the material accounting and internal control systems at e facilities. The evaluation findings and recommendations are fed back into the regula- development and licensing activities previously discussed.

The final major element of the NRC safeguards program encompasses the activities which NRC accomplishes with extensive coordination with other government agencies. These activities include threat assessment, planning for nuclear emergencies, and international safeguards matters. In the international area, NRC is currently preparing a new regulation to implement the US/IAEA safeguards agreement which will provide for IAEA inspection at selected facilities and will require that certain information be reported to the IAEA. The information to be reported includes design information and data concerning inventories, inventory changes, and material balance reports, among others. Certain U.S. facilities are already supplying design information, on a voluntary basis. Once the agreement comes into force, all eligible facilities will be required to report design information and material account data.

SUMMARY OF CURRENT REGULATIONS

All of the current NRC regulations concerning material control and accounting for special nuclear material are contained in Title 10 of the Code of Federal Regulations under Part 7 It is contemplated that the requirements needed to implement the pending US/IAEA agreement for safeguards will be published in Part 75.

Most persons and organizations authorized to possess at any one time and location more tha one effective kilogram* of special nuclear material in unsealed form are required to compl with comprehensive material control and accounting regulations. An applicant must include in his license application a full description of his proposed program plan to show how compliance with the regulations will be accomplished. After review and approval by the NR the plan is incorporated as a condition of the license.

In discussing the control and accounting of SNM, it should be recognized that the first li of protection against theft or diversion is provided by a comprehensive physical security program. Classical security measures are utilized, including perimeter barriers and alarm armed guards, access controls, vaults, portal monitors, surveillance and secured communications. Time does not permit a detailed discussion of physical security programs in this paper.

Material Control

The material control measures used for safeguarding SNM are similar in many respects to those used by industry for the internal control of valuable assets. The basic features of the present NRC material control program are summarized as follows:

- Assignment of overall responsibility for the material control and accounting program a single individual
- Separation of staff functions to provide internal checks
- Approval and maintenance of a manual which specifies current safeguards procedures
- Designation of specific control areas for the physical and administrative control of material in sufficient number to localize losses
- Assignment of custodial responsibilities for SNM within each control area to single designated individuals
- Establishment of storage and handling controls to provide current knowledge of the identity, quantity and location of all SNM in discrete items and containers

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*"Effective kilograms of special nuclear material" means: (1) For plutonium and uranium-2 their weight in kilograms; (2) For uranium with an enrichment in the isotope U-235 of 0.0 (1%) and above, its element weight in kilograms multiplied by the square of its enrichmen expressed as a decimal weight fraction; and (3) For uranium with an enrichment in the isotope U-235 below 0.01 (1%), by its element weight in kilograms multiplied by 0.0001.

Unique identification of items

Annual audit of the material control program

Material Accounting

ccounting program for special nuclear materials contains many of the basic elements of ntional accounting applied in the business community. Special emphasis is placed on easurement of SNM for generating accounting source data. The basic features of the nting program may be characterized as follows:

Physical measurement of SNM received, produced, transferred between control areas, shipped or discarded

Measurement quality control program to assure the quality of accounting data and to generate measurement uncertainty information

Material balance and item control areas to assess and localize losses through the accounting system

Documented system for transfer of material between control areas

Physical inventories based on measurements

Centralized accounting system employing double-entry bookkeeping

Material balance closures with accounting adjustments to incorporate physical inventory results

Statistical limits based upon measurement errors

Evaluation and investigation of differences between the material records and the physical inventory

Review and reconciliation of statistically significant shipper- receiver differences

Immediate investigation of losses of discrete items and containers

Annual accounting and measurement system audits

Retention of records for five years

licensees are presently required to establish and maintain plant accountability systems that the measurement uncertainties (limits of errors) associated with a plant material ce do not exceed 0.5% of material throughput.

cal inventories and material balance closures must usually be performed bimonthly for nium and high-enriched uranium and semiannually for low enriched uranium.

Measurement Quality Control

prehensive quality control program is required by current regulations on physical rements utilized in the safeguards accounting program. Weight, volume and nondestruc- assay measurements performed on the production line and on shipments and receipts for ntability are covered by these requirements as well as analytical laboratory measure- . The requirements are summarized as follows:

Assignment of overall responsibility for the program to a single individual

Performance of process and engineering tests to assure adequate mixing and sampling

Engineering analyses and evaluations to assure adequacy of each measurement system

- Ongoing use of standards for calibration and control of systematic errors
- Generation of current data for estimation of random and systematic errors for each material balance period, and for the establishment of bias corrections
- Statistical control, including control charts, over each measurement system
- Investigation and correction of performance outside of control limits
- Discontinuing measurements not covered by the quality control program for SNM accou
- Retention of records for five years
- Maintenance of training and personnel qualification programs
- Annual management reviews and system audits

CURRENT DEVELOPMENT PROGRAMS*

NRC's current development programs for material control and accounting can be separated the following four categories: (1) development of improved evaluative methodologies, (2 development of new approaches to performing material control and accounting operations, development of new techniques for analyzing material control and accounting data, and (4 development of improved measurement and measurement quality control techniques. Each of these four categories of the current development program will be summarized in this sect

Evaluation Techniques

Three evaluation techniques are currently being assessed by the NRC: (1) Diversion Path Analysis (under development for the Department of Energy by the National Bureau of Standards), (2) the Material Control System Assessment Procedure (under development for by Lawrence Livermore Laboratory), and (3) Insider Collusion Methodology (under developme for NRC by Science Applications, Inc.).

Diversion Path Analysis (DPA)

DPA is a structured procedure developed by the National Bureau of Standards for the Depar ment of Energy to systematically consider methods (paths) by which special nuclear materi (SNM) can be covertly removed from its authorized location in a facility (Ref. 2). It considers various methods by which the removal could be concealed and identifies operatic procedures or safeguards mechanisms necessary to detect such diversion attempts. DPA dea predominantly with those insiders who have hands-on access to material and/or records, bu also directs consideration to other personnel who may be in the area. By forcing a detai and systematic, although judgmental, examination of the facility, assurance is gained tha all diversion paths within the scope of the analysis have been considered.

Material Control System Assessment Procedure

Development of a systematized means to determine the effectiveness of material control systems is the major thrust of this work sponsored at the Lawrence Livermore Laboratory (LLL) by the NRC (Ref. 3). It is LLL's intent to provide the needed assessment tools and procedures, and the data base necessary for application of the assessment methodology.

The methodology is intended to consider the integration of material control, material accounting, and physical protection safeguards systems; meet user needs; provide assuranc of the adequacy of its results; and deal with the requisite spectrum of threats to materi control and material accounting safeguards. The methodology is planned to be well orient toward dealing with the types of facilities of interest to NRC. It also is intended to provide reasonable ease of use and good allocation of analysis resources.

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*A more detailed description of the material contained in this section can be found in Reference 1.

er Collusion Methodology

methodology, developed by Science Applications, Inc. (SAI), provides a good analysis work for integration of material control and physical protection safeguards against sion (Ref. 4). The SAI methodology consists of analyzing both physical protection and ial control safeguard components in terms of the individuals who are in a position to de their effectiveness. The safeguards components also are represented in terms of location within the facility. The methodology then analyzes paths from locations SNM is accessible to the facility boundary, determining the individuals who have s to SNM and those who can control the safeguards along these paths. By considering ndividuals responsible for safeguards components along a path, the conspiratorial group dividuals who can most effectively degrade safeguards is determined. When all such date paths for theft are analyzed, the method is designed to locate and list the paths vulnerable to collusion by any specified group of employees and to list the remaining uards along the path. Since the methodology considers both physical protection and ial control safeguards, it provides an integrated safeguards approach to the analysis cility vulnerability to collusion.

New Approaches to Performing MC&A Operations

esent, there are two programs being sponsored by the NRC and one by the Department of y to develop new approaches to performing material control and material accounting tions. They are studies concerning: safeguards use of process control and quality ol data, controllable unit accounting, and rapid nuclear material control systems. The se and status of each program will be discussed briefly.

RC study on possible safeguards use of process and quality control data is intended to ate the potential safeguards utility of such data currently generated by licensees for ss control and quality control purposes. A short-term preliminary evaluation of this ot has just been initiated. If this study produces significant results, a more ehensive evaluation will be undertaken as a follow-on to this initial study.

RC study on controllable unit accounting is intended to develop a technique for dividing see production operations into controllable units to improve certain material control aterial accounting capabilities. The basic concept of controllable unit accounting is onversion of the measurement uncertainty around a process or a portion of a process controllable unit) into a numerical measure which represents the degree of accountty control which can be attained with a specific processing and measurement system. concept makes it possible to partition the process into specific controllable units size and throughput depend upon the degree of control required for safeguards purposes.

ontrollable unit concept has been computer simulated for a hypothetical high-throughput cation plant (Ref. 5). The model indicates that the technique may be quite useful in ding rapid checks for material loss. A test application of the concept in an operating is being initiated.

Department of Energy sponsorship, the Los Alamos Scientific Laboratory (LASL) is oping a "model" rapid nuclear materials control system, called DYMAC (for DYnamic ials Control) (Ref. 6). The system, under development at the Plutonium Processing ity (TA-55) at LASL, consists of a plant-wide surveillance system and a network of onnondestructive assay (NDA) instruments interfaced to a computerized materials accountty and control system. DYMAC incorporates the following key elements: (a) an in-line t-line measurement system relying heavily on newly developed NDA instruments to provide assay data at key measurement points, (b) direct automated transfer of data from the floor into a central computer via interactive display terminals at selected measurestations, and (c) an automated accounting system to provide rapid status on material ces around "unit processes" which are defined on the basis of process logic and ial residence time in the process and accessibility for measurement.

urrent Department of Energy schedule projects a completion date of December 1979 for ssessment of the practicality of the DYMAC system at the LASL TA-55 plutonium facility. DOE processing plants and laboratories (e.g., Rockwell International at Rocky Flats, Colo.; and the Y-12 plant at Oak Ridge, Tenn.) are also pursuing the implementation of computerized material control and accounting systems similar to DYMAC and on similar schedules. Also, a few licensees are developing or have implemented rapid, computerizec material-control or process-control systems in their facilities (e.g., GE at Wilmington, N.C.; Westinghouse at Columbia, S.C.; and AGNS at Barnwell, S.C.). Therefore, rapid nuc material control and accounting is a useful safeguards concept for the present generatic high-throughput processing plants, as well as for future plants.

New Techniques for Analyzing Data

There are three current NRC development programs which relate to possible new techniques analyzing material control and material accounting data. One of these is a program to provide statistical analysis packages to the NRC and licensees for their use in analyzir material control and material accounting data. The other two programs are a time series analysis study and a study of the implications of strategic analysis.

The program which provides NRC and licensees with statistical analysis packages is desig to present, in a series of reports, a set of statistical analysis techniques including a discussion of such topics as the power of the statistical test, the individual confidenc from a negative test that no loss has occurred, the probable amount and process locatior the loss for a positive test, and comparisons to other candidate statistical tests. The tests presented in the reports will not only address plant statistics such as inventory differences and their associated uncertainties, but will also address the modeling of specific in-plant processes such as conversion of UF_6 to U_3O_8. This set of statistical packages is scheduled for completion by the end of FY78 and should prove extremely usefu both licensees and NRC in establishing procedures for analyzing material control and accounting data, as well as for safeguards analyses of process control data.

The basic concept of time series analysis in the context of material accounting is that proper data analysis techniques, based upon the properties of a time ordered series of inventory differences, can provide greater power than the current test of inventory diff ence as compared with its uncertainty in detecting continuing losses of small quantities material. A number of candidate analysis techniques of this type are under investigatio These include the statistical analysis of cumulative inventory differences (CUSUM), a nu of minimum-variance unbiased estimation techniques (Kalman Filtering and Minimum-Varianc Inventory Estimates), and Box-Jenkins modeling (Ref. 7).

Another complementary approach to data analysis involves strategic analysis. The basic concept of strategic analysis is to model safeguards in a competitive environment contai a safeguards defender and an adversary. It formulates the safeguards problem as a serie actions (moves) by the safeguards defender and the adversary. These actions result in varying costs and benefits to each, depending upon the actions taken. The analysis then makes use of the theory of games to develop optimum strategies for both the adversary an the safeguards defender (Ref. 8).

Measurement and Measurement Quality Control

In addition to the more sophisticated material control and material accounting methods a data analysis procedures discussed previously, material control and material accounting detection sensitivity can be improved by simply improving measurement techniques and measurement control programs. Recent material accounting assessments by NRC and several studies of licensee material accounting programs (Ref. 9) have indicated that improvemen in this area are within the state-of-the-art at relatively low costs. NRC has a number on-going development projects in this area whose FY78 and FY79 products will be the deve ment of coordinated measurement assurance programs; standardized procedures and calibrat techniques for nondestructive assay; a safeguards measurement handbook which covers all bulk, destructive assay, and nondestructive assay measurement techniques for safeguards purposes; NUREG documents on accountability methods and preparation of working calibrati and test materials; and an empirical study of systematic errors.

TASK FORCE RECOMMENDATIONS

e development of material control and accounting programs for special nuclear material is dynamic process of research, testing and rulemaking. Recently a special task force of NRC ecialists completed a comprehensive review of the roles and objectives of material control d accounting in safeguards (Ref. 1). It recommended goals, development programs and stem upgrades for strategic special nuclear material (SSNM)* covering the next five years. the short time I have left, I would like to highlight some of the major recommendations the Task Force.

e major new thrust recommended by the Task Force is the development of material control stems to provide continuous cognizance of the status of nuclear material in a facility. e roles of material control are to provide for the timely detection of material diversion om authorized uses and locations, rapid assessment of possible losses or alleged thefts, d assurance that no significant loss of material has occurred during intervals between ysical inventories. The proposed detection goals are set at two kilograms for plutonium d uranium-233, and five kilograms for high-enriched uranium. The major goals recommended material control include the following:

Provide shift monitoring of processing operations and associated records

Assure close vigilance over material

Ensure that as much material as is practicable is maintained in items or otherwise measurable and controllable forms

Assign direct responsibility and accountability for SSNM to custodians who shall maintain effective stewardship over the material

Detect within one shift, with high assurance ($\geq$ 90%), a loss of five formula kilograms** of SSNM in the form of items or sealed containers accessible to theft

Detect within a day, with high assurance, a loss of five formula kilograms of bulk SSNM from any controllable unit within a facility

Detect with high assurance a cumulative loss of five formula kilograms of SSNM from any controllable unit within the period between physical inventories

Maintain procedures and information sufficient to evaluate, within one hour, process conditions and material records for possible diversion

principal roles ascribed to material accounting by the Task Force are those of after-the-t detection, assessment of significant losses of SSNM, and assurance that material is sent in assigned locations and in correct amounts. As with material control, detection abilities are focused on two kilograms for plutonium and uranium-233, and five kilograms high-enriched uranium. With respect to inventory differences, action limits of three mula kilograms were recommended for reinventory, and five formula kilograms for plant tdown and cleanout inventory. For the assurance functon, considerable emphasis is placed the control of cumulative inventory differences to prevent systematic trends away from o. In addition to the above, the following goals were included in the Task Force ommendations:

Secure and limit access to accounting records to those who have a need to know

Verify the presence and integrity of all items and containers of SSNM within one working day of receipt of shipments

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SNM is plutoniums uranium-233, and uranium which is $>20\%$ in the U-235 isotope (ie., high-nriched uranium).
ormula kilograms = (kilograms contained U-235) + 2.5 (kilograms U-233 + Kilograms lutonium).

- Detect within ten days of receipt with high assurance ($\geq$ 90%) a loss of five formula kilograms of SSNM from any shipment

- Monitor cumulative shipper-receiver differences to ensure that these values do not exceed five formula kilograms for any period of twelve months.

- Resolve statistically significant shipper-receiver differences during the inventory period in which they are identified

- Detect, with high assurance ($\geq$ 90%) through bimonthly material-balance accounting, a loss of five formula kilograms of SSNM from designated accounting areas

- Validate the accuracy of waste discards

- Assure the recovery of poorly measured scrap during the inventory period in which it i generated

- Establish within NRC a capability for monitoring and analyzing shipper/ receiver and inventory differences across the licensed fuel cycle to detect and investigate trends and biases

In the long term, the Task Force recommended that the overall safeguards program be goal oriented with close integration between the physical security, material control and materia accounting functions, and that future planning take into consideration the interactions tha may exist in terms of redundancy, diversity and synergism to provide a cost effective syste of in-depth protection.

NRC staff is currently reviewing the Task Force recommendations and is developing an action plan for a detailed evaluation of each recommendation. The specific areas for upgrading of the material control and accounting regulations will be determined on the basis of these evaluations.

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Evaluation of Analytical Capabilities For Accurate Prediction of Isotopic Correlation Ratios

by

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ABSTRACT

This study looks at the feasibility of using existing physics methods and data to verify and/or deduce reactor history as in safeguards applications. Investigation indicates that adequate physics methods exist for verification calculations but that they are sophisticated, requiring care to achieve the necessary precision. The accuracy of the physics data (therefore, the adequacy) will vary with isotope; this imposes restrictions and necessitates care in the choice of isotopes. Deductive calculations will rely on mostly the same physics methods and data as the verification calculations. Limited study of deductive (backwards) calculations to date shows that they provide valuable insight into the isotope ratios best suited for the verification (forward) calculations.

KEYWORDS: Isotope correlation ratios; burnup calculations; reactor history verification; reactor history deduction; safeguards

INTRODUCTION

The purpose of this study was to evaluate the availability and accuracy of existing methods for predicting fission product, cladding-mutant, and actinide concentrations and isotopic ratios in discharged reactor fuel elements, as determined by chemical analyses after various irradiation and cooling (minimum of three months) times. This type of calculation involving theoretical predictions may be referred to as a forward calculation. The overall goal is to be able to identify fuel and reactor types and reconstruct irradiation history (backwards calculations) from correlations of key nuclides. Initial attention is centered on the forward calculation: this is the area where significant work seems to have been done. It would also seem to necessarily precede the backward calculation.

Numerous empirical correlations of chemical analysis data exist in the literature. These are not of interest per se except that they may serve as benchmarks and they do indicate sensitivities of correlations to parameters (like moderator ratio). Very few attempts at prediction and subsequent comparison to measurement have been made.

Initially one seeks methods suitable for analyzing individual cases. Later, one might develop a data set of predicted correlations for use in recognizing fuel element and reactor types when unknown. Finally, unfolding techniques could be attempted with such data sets as bases.

To predict the various mutant concentrations, the methods must
(1) produce suitably - averaged reaction rates and decay data for each transmutation chain step of interest. This implies a cross-section processor and a neutronics calculation,
(2) carry out the calculations in some burnup code, preferably with capability for
    (a) reading in the transmutation chains of interest,
    (b) fuel management (e.g., fuel shuffling, reprocessing/recycling),
    (c) adjusting the flux level as fuel is consumed, and
    (d) flux-spectrum re-averaging or otherwise getting burnup-dependent cross sections.

The actual mutant concentrations in discharge fuel and blanket elements may be expected vary with axial length, and location in the reactor. Early cores, for which chemical lysis data are already available, have been irradiated on a batch basis. Present core adiations tend to utilize fuel shuffling techniques to maximize burnups and minimize er peaking factors. Anticipating that most chemical analysis data will be for whole l elements, or batches of such, it may be important to include multi-dimensional cap-lity in the burnup/fuel management (movement and inventory) computer programs; should al drill-samples or pellets be analyzed, multi-dimensional capability becomes even more ortant.

The mutants of specific interest in this study were isotopes 99-104,6 of Ru, 133-5,7 Cs, 140-2,4 of Ce, 142-6,8,50 of Nd, and 150-6 of Eu. Analysis of all major reactor cepts is of interest, but prime concern must be LWR's whose fuel is already being rocessed. As BWR analysis tends to require an extra spatial dimension, the specific mination is further focused on PWR's.

METHOD OF INVESTIGATION

To determine the required and desired features of the theoretical tools, two principal hods are used:

(1) intuition derived from general neutronic calculational experience
(2) comparison to measurements of predictions from various theoretical methods. The latter data base is presently quite small.

Several questions come immediately to mind:

(1) What is the uncertainty in the measurements?
(2) What is to be compared? Absolute contents are not generally measurable. Isotopic compositions - e.g., ^{238}Pu/Pu, etc. - are usually measured only for the element Pu. Certain isotopic ratios seem to be of interest; however, these are generally chosen so as to be linear with burnup and independent of intervening reactor downtime gaps. Thus, they do not reflect reactor history, only the cumulative burnup.
(3) What is the relationship of success in predicting ratios which are of interest elsewhere to success in predicting ratios of interest here?
(4) What is the uncertainty in the nuclear data used in theoretical calculations?

These and other pertinent questions are all examined in detail here. Many detailed siderations come into play. Advantage is taken wherever possible of related work in the erature.

RESULTS

Sources of Information

Current Activity

Table I lists some recognized centers of related activity. Many of these organizations together under the umbrella organization ESARDA: European Safeguards Research and lopment Association. Its purpose is to coordinate the research and development work ited to safeguards carried out by those laboratories operated directly by the European ission and by other organizations within the European Economic Community.

One ESARDA Working Group has set up an isotopic correlation data bank at the Ispra blishment so that information provided by European utilities can be evaluated to pro- a better understanding of the correct correlations. The data collection has concen-ed on heavy isotope correlations but the working group is encouraging experimental vities in the fields of fission gas correlations and other fission product correlations. group is also considering the relationship between input analyses and isotopic correla-s using linear regression analysis and statistical tests. This will provide a link the Working Group on Integral Experiments. One goal is the selection of a small er of key correlations containing a maximum of information. Members of the group are assisting the International Atomic Energy Agency (IAEA) in setting up a similar data

Table I
Centers of related activity

Organization	Location	Leaders	Areas of Interest
ENEL (JRC*)	Ispra	A. Cricchio	Measurements Theoretical Parameter Studies Evaluation of FP Nuclear Data Needs Establish an isotope correlation bank at Ispra.
European TU, GfK, Project Spaltstoff-flusskontrolle (JRC*)	Karlsruhe	Lothar Koch	Study of Correlations in Whole Fuel Cycle, esp. Transplutonium: Theoretical & Empirical
CEN, Eurochemie	Mol, Belgium		Correlations of U & Pu with FP Spect in MOL IV
CNEN	Bologna, Italy		Use of iso corrlns in MTR fuel repro BU vs. Eu 154/155 ratio
RCN	Netherlands		Corrln of U/Pu w γ spectra for BWR's
BNWL	Richland, Washington	D. E. Christensen R. P. Matsen D. L. Prezbindowski	Empirical isotope correlations, Theoretical calculations
INEL	Idaho Falls	W. Maeck W. Emel	High precision FP yields and analyti measurements on fuels, isotope correlations
SGAE	Austria	K. Goroncek F. Pichlmayer G. Falta M. Lammer G. Eder	"Backward" reconstruction of fuel an reactor types and history
WCAP	Pittsburgh	Nodvik Miller, D. L.	Saxton Core II, III San Onofre YankeeRowe V, VI, VII
ORNL	Oak Ridge	S. Raman	Actinide XSCS waste production

*The Euratom Joint Research Center is located (jointly) at the ENEL lab in Ispra and at the Transuranium Institute (TUI) at Karlsruhe.

The ESARDA Working Group on Integral Experiments is concerned with the development and execution of experiments in which various safeguards techniques are employed on a controlled production campaign over a significant period of time. In general, the main objectives of such experiments include the evaluation of measurement errors, the testing of different instruments and techniques, and the analysis of "operating losses", all directed towards closing the material balance for an actual campaign.

The Oesterreichische Studiengesellschaft fuer Atomenergie GmbH (SGAE), Reaktorzentru Seibersdorf has studied backward calculations and their inter-relationship with forward calculations. In each case the use of a gamma spectrometer was assumed for measuring the mutant concentrations. Thus, their mutants of interest and their conclusions are not necessarily ours. In particular they require that their mutants emit γ-rays with energie greater than 500 keV.

Reactor Fuels Measured

Existing reactor fuel chemical measurements represent potential benchmarks for verif cation of calculational tools. To qualify, however, they should include nuclides of interest and be accompanied by complete model descriptions of the reactor and its history These are difficult to obtain.

Table II lists the commercial reprocessors. These complement the organizations of ble I in measuring spent fuel compositions. To date fuels have been mainly reprocessed the NFS plant (U.S.A.), the Eurochemic plant (Mol), the WAK plant (Karlsruhe), and the FL plant (Windscale).

Table II
Oxide-fuel-reprocessors

erator	Site	Purex separation via	Capacity metric tons U/yr	In service
S	West Valley, N.Y.	PC*	300	1966-1972
	West Valley, N.Y.	PC	600 (total via expansion)	uncertain
NS	Barnwell, S.C.	CE/PC	1,500	uncertain
FL	Windscale, U.K.	PC/MS	150	1970-73
	Thorp, U.K.	PC/MS	1,000	uncertain
A	La Hague, France	CE/MS	800	uncertain
	La Hague, France	CE/MS	1,600	1984-1986 completion
K	Karlsruhe, W. Germany	MS	35	1971-
WA	not yet decided	PC/MS	1,400	1985 completion
rochem	Mol, Belgium	PC	60	1966-1974
lgoprocess	Mol, Belgium	PC	60	1981-1983 (restartup of above unit)
	Tokai Mura, Japan	MS	210	uncertain

C=pulsed column; MS=mixed; CE=centrifugal extractor

Theoretical Activity

Much activity in empirical correlation of spent fuel measurements is evident in the erature. This forms a solid base of valuable information for many applications, but es not relate to the goals here except as: (1) a source of possible benchmarks and (2) a ssible indicator of the sensitivity of an isotope ratio to various reactor parameters. addition to the empirical activity, some theoretical activity has also been evident at L (Washington), GFK-Karlsruhe, and JRC-Ispra. This stems from the desire to extend relations to higher burnups and different fuel types.

The theoretical analysis performed at JRC-Ispra especially deals with heavy isotope relations; a wide range of PWR and BWR fuels was analyzed up to a burnup of 40,000 MWd/t, the results were compared to experimental data with adequate agreement. For correla- ns concerning PWR fuels, a systematic investigation was made of their dependence on the lowing parameters:

-- fuel enrichment (in the range 2% - 4%)
-- moderator-to-fuel volume ratio (in the range 1.2-2.2)
-- cladding material (Zircaloy or stainless steel)
-- control system (poison in the moderator or fixed absorbers)

Similar studies were underway at GFK-Karlsruhe, but with main emphasis on the burnup endence of effective cross sections which control linear correlations of heavy isotopes. ethod was being developed for the evaluation of cross section ratios from experimental a for isotopic ratios which have been observed to be linearly independent.

Existing Burnup Codes and Code Systems

Table III lists most of the burnup codes which have been encountered. Some include l management. There are far too many to allow detailed analysis of all within the scope this study.

Table III
Some (not all) of the current burnup codes

Code Name	Yr	Source	Code Name	Yr	Source
ABBRAND		IKE	HEXBU		FINLAND
ACTIN		EURATOM	HYLAS		
AIMFIRE		AI	IKEV		IKE
ANALYT		IKE	ISOCRUNCH		
ANDROMEDA	72	JAERI	ISOGEN		
APOLLO	74	JAERI	ISOSEARCH		
ASB 71	73	KFK	ISOTEX-1	74	ISPRA
ASSAULT		ORNL	ISOTOPES		
BABS		UK	JOSHUA	68	UK
BASS		UK	LASER	65	West
BOXER	74	EIR	LASER/HIC		
BRUTUS		BOLOGNA	LEOPARD		West
BUG2			LEOPARD/SPOTS		West
BUPO	71	UK	MAFIA-1		
BURP2	66		MANDI		KFK
BURSQUID	72	ENEL(IT)	MEDIUM	71	SIEMENS
CACA-2	76	ORNL	NEUTRA	72	GEESTHACHT
CAPHE	75	FRANCE	NUCY		ORNL
CHAINS			ORIGEN	73	ORNL
CINDER		LASL	PABUC		AI
CITATION	71	ORNL	PANDA	71	WEST.
CLUB	72	ORNL	PDQ7		
CONDOR3	70	ITALY	PDQ8		
CRACKLE	73	UK	PENELOPE/CITAT.	75	SPAIN
CREAM-7	71	UK	PHENIX	69	LASL
2DB		BNWL	RAD2		
3DB		BNWL	RAPFU		
DBUFT11			REBUS2	74	ANL
DDB			REST	72	KFK
EDDT			RIBD		UNI
DELIGHT-2	74	JAPAN	RIBD-II	75	HEDL
DTFBURN			RLT-4		
DWARF	72	INEL	RSYST		IKE
3DXT/DEP3			SINBAD	69	INEL
FABGEN	75	ORNL	SIZZLE		AI
FARED			SPECTAR	74	YUGOSLV.
FEVER7			SYN		GE
FISSPROD-2	75	AECL	SYNBURN	76	ANL
FLARE	64	GEAP	SYNTRON	72	RISOE
FREVAP6			SYNTRONVOID	74	RISOE
FUMBLE			TRIBU	73	BELGIUM
FURNACEJ	72	JAERI	TRISIC	73	ARGENTINA
GAD,REV.			TURTLE 24.0	71	WEST.
GAFFE			VARMU-1		BELG.
GARGOYLE		EIR	VENTURE-BU		ORNL
GAUGE		GA,EIR	XPOSE(LEOPARD)	75	EXXON
			XTG	75	EXXON

Existing Comparisons of Theoretical Calculations with Measurement

Few comparisons have been reported in the literature. Of those which do exist, the calculations are generally either zero-dimensional or 3-dimensional. There is little i between. The zero-dimensional approach appears to suffice in asymptotic flux regions (a from core boundaries or control rods), but is inadequate elsewhere. The limited 3D calc lations made so far have been compared to measured axial distributions with reasonable success. Somewhat strangely, integral comparisons from whole fuel elements or groups of such have not been found yet in the literature. Comparisons to date are listed in Table

Table IV
List of existing comparisons of calculation to measurement

thors	Lab	Reference	Reactor Fuel	Calculational Methods	Measurements
Ariemma Bramati Galliani Pacletti-Gualandi Zaffiro Cricchio Koch	ENEL(Ispra) Euratorn (TUI)	Reaktortagung 1971, Bonn EUR-4638 (1971)	Garigliano (BWR)	2D neutronic & BY EQUIPOISE, SQUID 3D FLARE feedback RIBOT cross sections: 2G,5G,2K, 10K mesh	F_T* by ^{137}Cs γ-spectrometry ^{83}Kr/^{86}Kr and ^{84}Kr/^{83}Kr by mass spec anal of pellets Actinides and ^{148}Nd by mass spec
N. Fox	Winfrith	1971 BNES Conf at Canterbury	SGHWR	σ: WIMS (69G→7G), METHUSELAH ϕ: DSN(7G), ID cell calcs. Feedback: JOSHUA II	Actinides
Davis,Jr W. Kee C.A. Vaughn L. Tobias	ORNL	ORNL/TM-5691 (1976)	Peach Bottom HTGR FTE-4 Fuel Rods(2)	ORIGEN	U isotopic composition from head-end reprocessing γ-scanning for ^{85}Kr, ^{90}Sr, ^{95}Zr, ^{95}Nb, ^{106}Ru, ^{110}Ag, ^{125}Sb, ^{134,7}Cs, ^{144}Ce, ^{152,4,5}Eu
	England	--	Calder Hall	ARGOSY vs WIMS-D vs WIMS-D	^{240,1}Pu
ggi	Ispra	IAEA-SM-201/44	Garigliano Trino Vercellese VAK	point burnup ISOTEX-1, GGC-2	F_T, ^{84}Kr/^{86}Kr, ^{86}Kr/^{83}Kr, ^{84}Kr/^{83}Kr, ^{132}Xe/^{134}Xe, ^{134}Xe/^{131}Xe, ^{132}Xe, ^{131}Xe, ^{146}Nd/^{148}Nd, ^{148}Nd/^{148}Nd, ^{145}Nd, ^{146}Nd/^{145}Nd, ^{154}Eu/^{137}Cs, ^{134}Cs/^{137}Cs
P. McNeece	United Nuclear Industries, Inc. Richland Wash.	UNI-436 (1975)	N Reactor: Mark IV, Mark 1A Fuels	DCODE (ID-TT) RIBD(FP)	$^{238-42}$Pu

$_T$ is atom % BU

On the basis of existing experience with prediction of actinides and a few burnup indi-
tors, multi-dimensional techniques appear to be needed for computational accuracies better
an 5-10%. Whether this is needed to predict fission products mentioned in Section 1.0,
pecially their ratios, remains to be seen. It may not be worthwhile to use a < 10%-error
chnique with nuclear data containing > 10% error.

Problem Understanding: What Are the Mutant Parameters of Interest?

Given the goals described in the introduction, the question arises - just which mutant
ameters are of interest? More specifically, is there a complete or near-complete basis
of parameters which will sufficiently characterize a reactor and its history. This
ses more questions:

(1) What, specifically, do we desire to know about a given reactor fuel?
(2) how does one go about finding the basis set?

(3) can one select just a few parameters (the ones with the most inherent accuracy) and find permutations through a Gram-Schmidt type of orthogonalization process which will then give a "complete" set? Hints at the feasibility of using such permutations are already evidenced in existing papers. Such a complete set ma form a basis set for the "backward" unfolding techniques also.

What Do You Really Want to Know About a Given Reactor Fuel?

A basic question arises at the outset - are we interested in general reactor behavi or are we looking for some local substitution or diversion? By general reactor behavior mean abnormal conditions like downtime, reduced rating, overpower, and excursions. By local behavior we mean:

(1) Was any irradiated fuel element replaced other than as scheduled?
(2) Has any fuel been diverted?
(3) Were any special samples introduced?

This and other similar questions should show up as deviate chemical results in a batch o elements. One might however have to specify the limit to the number of elements in a chemical dissolution batch.

The significance of the local vs general question is in the complexity of the nucl model. The answer to the question is that we are interested in both. However, it is wo while to note that the local solution requires considerable more complexity in the model than that for the general reactor. This is discussed further in the next section.

Determining the Complexity of the Nuclear Model

In the case of fast reactors, axial and radial blankets will also be present. Tabl shows the calculated equilibrium fuel discharge composition for a 1000 MWe LMFBR. As ca be seen, the isotopic weight fractions vary considerably among the different core and blanket regions. Note particularly how different are the "Isotopic Weight Fractions in Each Chemical Element" for:

(a) (inner) core Zone 1 vs (outer) core Zone 2.
(b) inner radial blanket vs outer radial blanket
(c) individual zones vs "total reactor".

These results were obtained with a one-dimensional neutronic calculation plus burnup and fuel management routines. Runs were separately made in both the radial and axial direct

As the axial blankets are a part of the fuel element, they may be expected to be mi in with the core in the chemical analysis. The radial blanket, however, is physically separate. By excluding the explicit calculation of radial blanket concentrations (just use a transverse buckling), a one-dimensional axial calculation may suffice. Indeed, it doubtful that the radial blanket concentrations can add significant information to that the core in characterizing the nature or history of the reactor. One question remains however: Do we need to check the radial blanket to see if special samples have been int duced or if diversion has occurred? In those cases, we are probably back to multi-dimen al calculations.

For LWR's one can divide the fuel elements into two categories:

(1) those in an asymptotic flux spectrum,
(2) those in a perturbed flux spectrum.

This is quite important. By asymptotic we mean as in the cell of a large lattice, far from control rods or enrichment zone boundaries. The latter corresponds to perturbed fl situations. In practice, perturbations are always present due to reactor finiteness, bu they are frequently insignificant. This is particularly so for earlier cores which are operated on a once-through batch basis. Current cores tends to be divided into radial f shuffling (management) zones of differing enrichment, thereby introducing more boundarie within the core region.

The importance of this all is that for asymptotic flux spectra, zero-dimensional techniques calculate isotopic concentrations well whereas perturbed flux regions require one- or more-dimensional representation.

Table V
Equilibrium fuel discharge composition, 1000-Mwe LMFBR advanced design

	Core Zone 1	Core Zone 2	Axial Radial Blanket	Axial Blanket Above Inner Radial Blanket	Outer Radial Blanket	Axial Blanket Above And Below Core	Total Reactor
Isotopic Weight Fractions							
U^{232}	2.60^{-9}	1.60^{-9}	2.46^{-10}	2.27^{-12}	1.69^{-10}	1.069^{-12}	5.202^{-10}
U^{237}	1.04^{-5}	7.60^{-6}	2.68^{-6}	2.86^{-6}	7.30^{-7}	2.250^{-6}	1.126^{-6}
U^{238}	1.00^{+0}	1.00^{+0}	1.00^{+0}	1.00^{+0}	1.00^{+0}	1.00^{+0}	1.00^{+0}
U^{239}	4.85^{-6}	3.01^{-6}	2.62^{-6}	1.64^{-6}	7.94^{-7}	8.142^{-7}	1.486^{-6}
Np^{236}	1.83^{-7}	1.52^{-7}	4.38^{-8}	1.43^{-8}	1.35^{-6}	3.162^{-16}	1.11^{-7}
Np^{237}	4.35^{-1}	4.89^{-1}	4.05^{-1}	1.25^{-1}	4.59^{-1}	5.026^{-9}	4.40^{-1}
Np^{238}	7.31^{-7}	5.08^{-4}	2.62^{-4}	7.85^{-5}	1.70^{-4}	2.64^{-14}	4.46^{-4}
Np^{239}	5.64^{-1}	5.11^{-1}	5.94^{-1}	6.77^{-1}	5.40^{-1}	[illegible]	5.60^{-1}
Pu^{238}	8.66^{-6}	3.609^{-6}	4.561^{-6}	1.548^{-7}	1.607^{-6}	2.751^{-10}	5.221^{-6}
Pu^{238}	4.675^{-4}	2.219^{-4}	2.922^{-4}	1.953^{-5}	2.026^{-4}	[illegible]	[illegible]
Pu^{239}	6.410^{-1}	6.086^{-1}	9.636^{-1}	9.221^{+0}	9.568^{-1}	9.699^{-1}	7.150^{-1}
Pu^{240}	2.940^{-1}	3.174^{-1}	3.529^{-2}	4.047^{-1}	4.199^{-2}	2.961^{-2}	2.336^{-1}
Pu^{241}	4.281^{-2}	4.869^{-2}	8.496^{-4}	1.026^{02}	1.065^{-3}	6.259^{-4}	3.406^{-2}
Pu^{242}	2.177^{-2}	2.431^{-2}	1.254^{-5}	1.685^{-4}	1.750^{-5}	6.914^{-6}	1.707^{-2}
Pu^{243}	1.730^{-6}	1.164^{-6}	1.255^{-10}	3.995^{-9}	4.145^{-10}	1.985^{-10}	1.064^{-6}
Am^{241}	5.090^{-1}	6.467^{-1}	1.00^{+0}	1.00^{-0}	9.94^{-1}	9.662^{-1}	7.13^{-1}
Am^{242}	3.30^{-4}	2.55^{-4}	2.52^{-7}	1.90^{-15}	1.57^{-4}	2.607^{-4}	2.93^{-4}
Am^{243}	4.919^{-1}	3.521^{-1}	3.61^{-6}	5.14^{-10}	6.70^{-2}	1.422^{-2}	4.25^{-1}
Am^{244}	1.210^{-4}	5.293^{-5}	1.876^{-7}	4.83^{-20}	1.40^{-5}	5.046^{-4}	8.85^{-5}
Cm^{242}	5.96^{-1}	9.64^{-1}	1.72^{-1}	2.96^{-2}	5.44^{-1}	2.515^{-1}	6.43^{-1}
Cm^{243}	1.37^{-2}	1.50^{-3}	1.34^{-1}	1.67^{-1}	9.76^{-2}	3.766^{-2}	1.26^{-2}
Cm^{244}	3.90^{-1}	3.62^{-2}	6.94^{-1}	8.04^{-1}	3.58^{-1}	7.106^{-1}	3.64^{-1}
Element Weight Fractions							
Fission Products	1.08^{-1}	9.80^{-2}	8.17^{-1}	9.84^{-4}	6.58^{-3}	2.72^{-3}	3.02^{-2}
U	7.219^{-1}	6.67^{-1}	9.91^{-1}	9.92^{-1}	9.56^{-1}	9.79^{-1}	9.003^{-1}
Np	8.919^{-4}	5.62^{-4}	3.76^{-4}	2.65^{-4}	2.03^{-4}	2.30^{-4}	3.46^{-4}
Pu	1.678^{-1}	2.33^{-1}	3.59^{-2}	8.23^{-3}	3.56^{-2}	1.88^{-2}	6.864^{-2}
Am	9.83^{-4}	5.63^{-3}	6.58^{-7}	1.28^{-9}	1.84^{-6}	2.61^{-7}	3.01^{-4}
Cm	1.30^{-4}	9.14^{-4}	1.17^{-7}	1.48^{-6}	1.25^{-7}	3.93^{-6}	3.36^{-5}
Total							

For safeguards considerations, however, there is no doubt that one must calculate all R core regions and all LMFBR core and blanket regions: not for reactor type and history entification purposes, rather to check that no Pu has been diverted. Thus, we see that e purpose may need only a simple calculational tool; another purpose requires an elab-ate tool: all for the same reactor and history.

Some of the early reactor cores have been reprocessed and analyzed. These fuels were radiated on a batch basis with no fuel shifting. Even where fuel-shifting management is heduled, the first batch of elements out of a reactor will have been exposed only at one actor location. However, as it is very attractive to shift fuel to increase the rnup while simultaneously minimizing peaking, one must assume this philosophy predominate for the future. This can be readily accommodated in a forward calculation. backwards calculation would seem to be very hard to accomplish if any fuel shifting was neduled. The direct approach would be to incorporate fuel shuffling into a backwards story model. This would add one or more additional parameters, however.

Another potential problem area is recycled fuel (more of a problem for LMFBRs than r LWRs). There the feed compositions may change with time. These can depend on such ings as reprocessing techniques: some labs may reprocess blanket Pu separate from core , while others mix the two. This will significantly affect the Pu isotopic compositions the feed.

Different reprocessing techniques also affect the spent fuel analyses. WAK (Germany) es a chop and leach process which homogenizes fuel. This has the effect that the isotopic stribution of fission gases is constant throughout a dissolution.

How Might One Go About Deducing Reactor Type and History?

We assume we are confronted with one or more black box (no apriori knowledge) reactor ments. A remote gamma scan can give an axial radiation profile to tell us if there are heterogenities: graded enrichment steps or blanket zones, or special materials. Also, will indicate fuel column length, relative power distribution, and fission product ration. Neutron radiography can tell of local hydrides, H_2-containing impurities, fuel ensions, and fuel structure.

Assuming homogeneity, the element is next presumably dissolved and the inquirer is sequently presented with the chemical analysis. Mass spectrometry subsequently reveals isotopic analysis. Repeating both the chemical separation and the mass spec analyses at later times would give time-dependence as well. Alternately, this may be feasible thr gamma spectrometry of small "thin" samples.

We now would attempt to characterize the reactor. Actinide composition should speci the original kind of fissile and fertile fuels present, and the approximate neutron spect Combined with the differences in fission product yields per fissile isotope and spectrum one would try to deduce the original composition. Possibly the condition of the cladding outer surface and its composition can help to identify the reactor coolant. Coupling the above with the residual compositions of cladding, fuel, and blanket (if present), one sho be able to pinpoint the type of reactor including the gross characterization of the neutr spectrum. Isotopic composition and fuel diameter can distinguish between a PWR and a BWR With that, an accurate spectrum-averaged set of fission product yields is obtained for ea fissionable nucleus of interest. This is very important to determining the original comp osition and time-dependent history.

Many isotopic ratios are strongly dependent upon enrichment, fuel-to-moderator ratio and fuel pin diameter. Weaker dependences on clad and control method may also be utiliza This should help determine the reactor composition and associated nuclear data base. Fir through ratios of isotopes with a variable array of half lives one can try to reconstruct irradiation history, especially in terms of deviations from full-power operation.

Mutant Parameters for Backward Calculations

Note that the following has been derived from a program which relied on a gamma spectrometer for measuring mutant concentrations.

The selection of mutants to be used for interpretation is guided by the following considerations:

(1) Accuracy of the nuclear data;

(2) Accuracy of the measurement;

(3) A range of half-lives among the mutants so as to yield information about different periods of the reactor history: irradiation times and shutdown times. Most fission products will only yield information about the later part of the irradiation history.

(4) At least some mutants with significant cross sections are desirable as that makes them sensitive to down times.

(5) Fission products must have adequate yields from fission.

(6) Burnup may be inferred from long-lived fission products. In a gamma spectromet program the following conclusions were made.

^{137}Cs (30 yr.) is far superior with respect to the amount of additional information needed for interpretation: it requires no knowledge of neutron spectrum or fuel compositions and almost no knowledge of irradiation history. However, one must be sure that no significant loss (<10%) of ^{137}Cs has occurre Also migration of ^{137}Cs in very bulky fuel elements could cause errors if smal local samples were taken.

^{106}Ru - ^{106}Rh (1.0 yr.) is next best with respect to half-life, but has much higher fission yield for Pu fissions than for U fissions.

^{144}Ce - ^{144}Pr (285.4 d) is only useful if the irradiation history is ei known or rather short.

^{95}Zr - ^{95}Nb (65.5/35.15 d) is only useful for very short irradiations.

^{134}Cs is also used with ^{137}Cs as a ratio.

(7) Cooling time can be determined from measured activity ratios of fission produc of various half-lives if it can be assumed that they were in saturation immediately before shutdown. Figure 1 shows some typical curves.

(8) Methods to determine flux ϕ and irradiation time T require a constant neutron or a rather accurate knowledge of the neutron spectrum. The ^{134}Cs/^{137}Cs activ ratio gives the integrated neutron flux with low accuracy.

(9) Methods exist to determine the fraction of Pu fissions. The fission yield for ^{106}Ru - ^{106}Rh varies by an order of magnitude between U and Pu fissions. ^{144}C ^{144}Pr is a fission product of comparable half-life and its fission yield is ra independent of the type fission. By using the ^{144}Ce - ^{144}Pr/^{106}Ru - ^{106}Rh rat a first order cancellation of decay correction errors is achieved. The activi ratio decreases very slowly during cooling with an effective half-life of 3.3

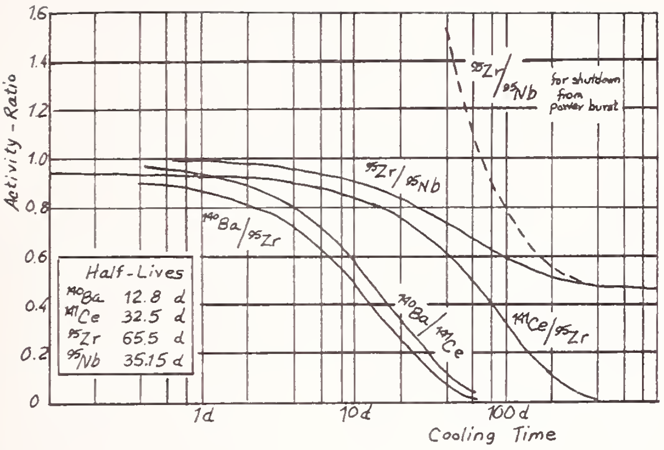


Figure 1. Dependence of activity ratios of several fission products on cooling time.

years; therefore, only an approximate decay correction is needed.

Similar attempts with ^{140}Ba - ^{140}La/^{111}Ag or ^{140}Ba - ^{140}La/^{156}Eu ratios failed.

The mutants may be nominally divided into three classes:

a. Primary fission products (P): all precursors have relatively short half-lives,
b. Secondary (decay) fission products (S): immediate precursor was a Primary.
c. Secondary (absorption) fission product (A): obtained by P(n,γ)A reaction.

Now in principle each mutant FP is a function: f(BU,t,λ,σ,φ) where:

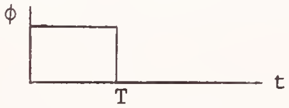
BU = burnup
t = time
λ = decay rate
σ = destruction cross section } fairly well known
φ = flux

This assumes there is only one process leading to formation of the nuclide. Although
tivity to each of the parameters (BU,...φ) is needed through one nuclide or another,
also desirable to limit the sensitivity for each individual nuclide. For the case
, if $\sigma = \lambda = 0$, then P = P(BU) only. For S, one desires $\sigma_P = 0 = \lambda_S = \sigma_S$ such that
(P, λ_pt) = S(BU,λ_pt) only. For A, one desires $\lambda_p = 0 = \lambda_A = \sigma_A$, such that A =
$_p\phi$t) = A(BU,$\sigma_p\phi$t). Now, in principle, we have P(BU), S(BU,λ_pt), and A(BU,$\sigma_p\phi$t), which
be orthognalized to f_1(BU), f_2(t), and $f_3(\phi)$.

One parameter (BU) deductions are straightforward and frequently done. BU is in
ce,

$$\int_0^T \sigma_f \quad \phi(t)\ dt$$

sberger and Bruneder* showed how to deduce several parameters. First, they devised
-parameter model:



J. Higatsberger and H. Bruneder, Acta Physica Austriaca 28, 94 (1968)

With it, forward calculations yielded typically Figures 2 and 3 for ^{103}Ru and ^{137}Cs. sider the case where [^{103}Ru] = 1x10^{15} and [^{137}Cs] = 3.16x10^{16} ([] denotes concentrati at time T. Upon overlaying the two curves, these two lines of concentration intersec T ∿ 2 years and ϕ ∿ 4x10^{19} n cm^{-2} years^{-1}.

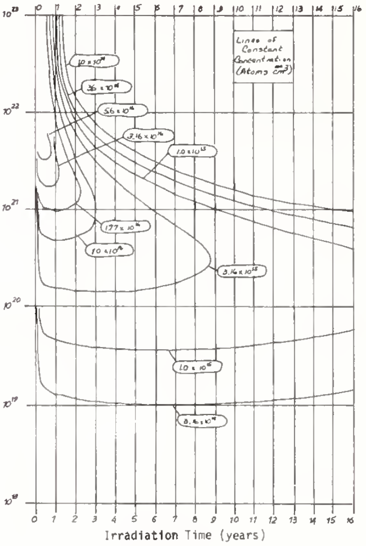


Figure 2. ·^{03}Ru buildup (short-lived primary fission product, 40 days).

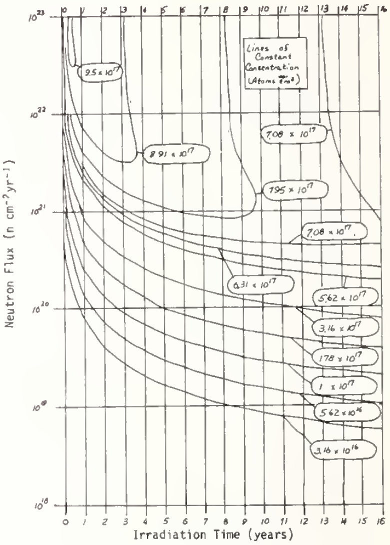


Figure 3. ^{137}Cs buildup (long-lived primary fission product, 30 years).

Instead of overlaying curves one could parameterize [^{103}Ru] as f(t,ϕ), a surface three-dimensional space. Then by some computerized mathematical technique the inters of the ^{103}Ru and the ^{137}Cs surfaces would (hopefully) uniquely and sharply determine values of T and ϕ. To maximize the sharpness (the angle between the surfaces at thei intersection), inspection of Figures 4-5 shows that t$_{1/2}$ should vary as much as possibl between different P. Also an "A" surface is quite different (Figure 5).

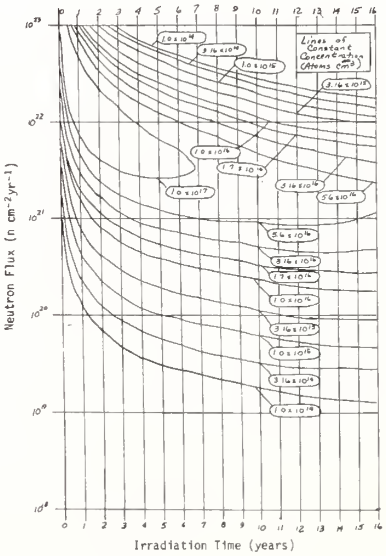


Figure 4. ^{134}Cs buildup (n,γ product of ^{133}Cs, 2.3 years).

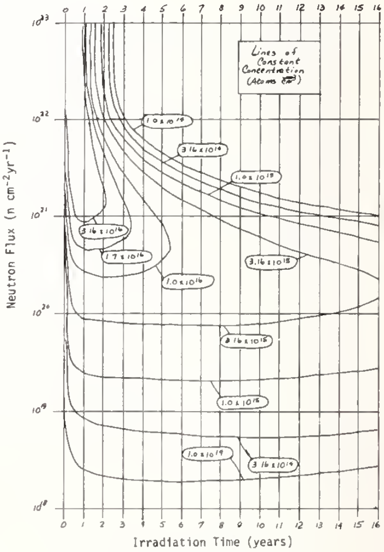
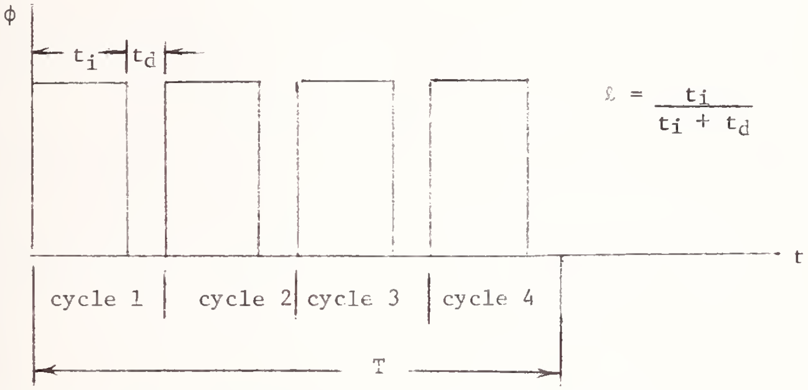


Figure 5. ^{95}Nb buildup (short-lived secondary product of ^{95}Zr, 35 days).

In similar fashion, one would hope that the intersection of the $f(X_1, X_2, X_3)$ (volumes our-dimensional space) for three isotopes would sharply and uniquely determine the meters X_1, X_2, and X_3. However, we note complexity was rapidly increased just in going one parameter (BU) to two parameters (ϕ,T).

Actually, Higatsberger and Bruneder present a formalism for four and more parameters, its practicality remains to be demonstrated. In each case one has to assume a historical l or pattern. For 4 parameters one possible model has a continuous "load availability" ern:



parameters are then T, ϕ, n, ℓ. Desirable isotopes for analysis would presumably ude some with time constants (λ or $\sigma\phi$) of the order of t_d, t_i, and T.

The problem with the above is that Figures 2-5 are for a point reactor (reactor average). e $\{\sigma_f\}$ for the fuels and $\{\sigma_\gamma\}$ for the fission products are involved, the analyses are ron spectrum dependent; and the spectrum is spatially dependent.

One solution to the dilemma would be spectrum-independent ratios of isotopes. This e feasible for thermal reactors where σ_γ for most materials behaves as $\sigma_\gamma(E)$ = . However, the heavier fission products tend to be somewhat deformed resulting in er level densities; that leads to some thermal region resonances (non-1/V behavior).

Another path is to find additional isotope ratios which indicate that the spectrum is from turbed region (near a boundary or control rod); a suitably-determined correction to the trum-independent" ratio would then be made. As additional uncertainty would be oduced, the "E-½" solution (above) is to be preferred.

What Mutant Parameters are Available

This study has assumed that chemical analysis data are the most accurate and reliable, s therefore predicated on this. Accuracy will vary with chemical element and depend the composition: e.g., two chemical elements may be hard to separate from one another. mplete recovery of a given chemical element is infeasible, results become relative. pic composition in a chemical element can be determined through mass or γ spectrometry.

Thus, the most accurate information will be for ratios of two isotopes whose atomic stries evidence similar high recovery rates.

In summary, we see that we must concentrate our methods on the information from pe/isotope ratios ($^AX/^BY$), and isotopic compositions ($^AX/X$). The latter should be the accurate.

It is also important to know the relative yields of mutants in typical spent fuel ses, i.e., just what is available. Table VI lists the few isotopes which have been fically measured in reactors for isotope correlation purposes and such. In addition e above, ^{148}Nd is frequently measured for burnup determination. It is popular because, l the other fission products, it is the only one presenting the following main cteristics:

- Its cumulative fission yield is practically identical for uranium and plutonium and is independent of neutron energy.

- Neodymium and its chain members do not change location in the fuel by diffusi other transport mechanisms during irradiation.
- It is stable and neutron capture by the chain members is practically negligib compared to their beta decay. Thus it is rather insensitive to neutron flux changes and shutdown periods in the fuel irradiation.
- Its chemical separation and analysis by isotope-dilution mass spectrometry is relatively simple.

Table VI
Isotopic measurements reported in the literature for spent fuels

Reactor	Measurements
Latina (gas-graphite)	U, D_5, Pu
Chapelcross (gas-graphite)	25, 28, 25
Garigliano (corner and std. rods, BWR)	^{132}Xe, ^{131}Xe, ^{241}Pu
Kahl (BWR)	^{131}Xe, ^{132}Xe, ^{241}Pu, ^{84}Kr, ^{83}Kr, D_5, F_t
Gundremmingen (BWR)	^{131}Xe, ^{132}Xe, ^{241}Pu
Trino Vercellese (PWR)	Pu, U, ^{134}Cs, ^{137}Cs, ^{131}Xe, ^{134}Xe
Dresden (BWR)	Pu, U, D_5
Humboldt Bay (BWR)	Pu, U, D_5

F_t = fractional heavy atoms burnt
D_5 = fractional ^{235}U depletion

Sensitivity of Mutants to Reactor Parameters and Conditions

The fractional composition of a given Pu isotope can fluctuate 10-20% about a no value due to parameters such as:
(1) moderator-to-fuel volume ratio (MFR) which ranges from 1.2 to 2.2
(2) ^{235}U enrichment (ENR) which ranges from 2-4%
(3) fuel pin diameter (OD)
Reactivity control, e.g., boron concentration, and cladding (zircaloy vs. stainless s affect composition only by a few percent.

For the specific isotopes Np-237 and Pu-238 the atom densities are dependent as
[Np-237] = f(1/MFR, ENR, 1/OD, clad (weakly))
[Pu-238] = f(1/MFR, 1/ENR, OD, clad (weakly))
Figure 6 from Foggi and Frandoli (EUR 5071) graphically illustrates some sensitivitie

Tables VII and VIII list some key parameters for existing PWR's and BWR's. Note consistencies. Thus, within a given class (PWR or BWR) the most sensitive parameters not vary considerably. This should help to distinguish PWR from BWR fuel.

As one might expect, any recycling of Pu leads to an increase in the production actinides with A>242, which should not be very different between the two LWR types. an enormous accumulation of Cm-242 in later TRINO VERCELLESE samples was caused by a shutdown of the reactor, which consequently led to an Am-241 buildup of Pu-241 decay. Other similar tell-tale decays should be present both in the actinides and in fissio products as well.

Nuclide concentrations are inherently sensitive to cross sections, flux, and ti The cross sections and flux are, in turn, sensitive to numerous reactor parameters. of this sensitivity can be removed by considering ratios of one isotope to another; numerous ratios are found to exhibit linear dependence upon burnup. This can be usef that it reduces dependence to one or two variables which can be accurately determine the other hand, these same linear ratios may be now independent of flux level and ti (irradiation history information). Thus, a combination of concentrations (or isotop compositions) and isotopic ratio information should be of interest here.

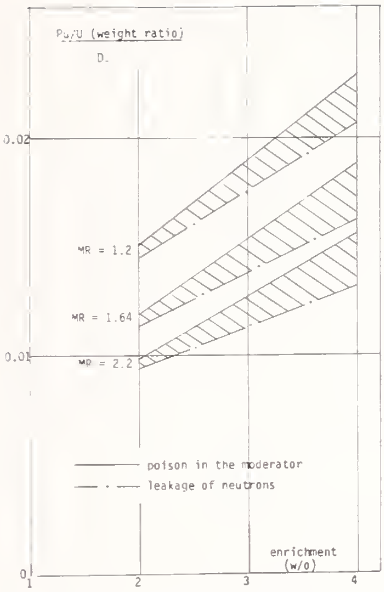


Figure 6. Pu/U to ^{235}U depletion ratio for different lattices and different reactivity control methods (Zircaloy cladding).

TABLE VII SUMMARY TABLE ON PWRs

Reactor	Fuel Diameter (in)	Moderator/ Fuel Ratio	Enrichment Outer Region Initial Core	Enrichment Equilibrium
Beaver Valley	0.3669	1.67	3.2	3.2
Calvert Cliffs	0.382		3.03	
Connecticut Yankee	0.3835	1.533	3.67	
Crystal River-3	0.362	1.68	2.90	2.94
Donald Cook				
Diablo Canyon-1	0.3669	1.67	2.67	
Diablo Canyon-2	0.3669	1.67	3.70	
Fort Calhoun	0.383	1.60	2.95	3.05
Indian Point-2	0.3669	1.67	2.68	2.92
Indian Point-3	0.3669	1.67	3.20	
Kewaunee	0.3669	1.60	3.15	3.38
Main Yankee	0.382	1.61	3.01	
Midland-1	0.370	1.65	2.64	
Oconee-1	0.362	1.79	2.77	
Oconee-2	0.362	1.68		2.47
Oconee-3				
Oyster Creek-2	0.362	1.68	2.90	2.94
Palisades	0.359	1.70	2.74	2.74
Point Beach-1	0.3669	1.60	2.80	
Point Beach-2	0.3669	1.60	2.80	3.05
Prarie Island-1	0.3669	1.60	3.15	3.38
Prarie Island-2	0.3669	1.60	3.15	3.38
Robinson-2	0.3669	1.675	2.73	
Russellville	0.362	1.68	2.90	2.94
Salem-1	0.3669	1.67	3.20	
Sequoia-1	0.3659	1.68	3.20	
Sequoia-2				
Surry-1	0.3669	1.675	2.94	3.38
Surry-2	0.3669	1.675	2.94	3.58
Three Mile Island	0.362	1.67	2.90	2.94
Turkey Point-3	0.3669	1.67	2.73	
Turkey Point-4	0.3669	1.67	2.73	
Zion-1	0.3669	1.72	3.20	
Zion-2	0.3669	1.72	3.20	
Yankee Rowe Core I & II	0.286	1.286	3.41	
Average	0.3678	[illegible]	2.968	3.099

TABLE VIII SUMMARY TABLE ON BWRs

Reactor	Fuel Diameter (in)	Moderator/ Fuel Ratio	Average Enrichment Initial Core
Arnold	0.487	1.587	2.23
Bell	0.488	1.586	2.23
Big Rock Point			
Brown's Ferry-1		1.548	2.19
Brown's Ferry-2			
Brown's Ferry-3		1.58	2.19
Brunswick 1	0.487		2.25
Cooper	0.488	1.578	2.15
Dresden-1			
Dresden-2	0.488	1.47	2.36
Dresden-3	0.488	1.47	2.36
Fitzpatrick	0.487	1.587	2.23
Hatch			
LaCrosse	0.350	2.038	3.63
Millstone Point	0.488	1.47	2.07
Monticello	0.488	1.55	2.03
Nine Mile Point	0.488	1.47	2.10
Oyster Creek-1	0.488	1.40	2.10
Pilgrim	0.488	1.58	2.18
Quad Cities I & II	0.488	1.586	2.18
Shoreham	0.488	1.586	2.28
Vermont Yankee	0.488	1.56	2.29
Peach Bottom-1	0.488	1.586	2.19
Peach Bottom-2	0.488	1.586	2.19
Peach Bottom-3	0.488	1.586	2.19
Average	0.4805	1.580	2.263

Isotopic Ratios vs. Isotopic Compositions

The buildup and depletion of a given isotope is dependent upon exponential terms and $e^{-\lambda t}$

λ = decay constants

t = time

$\overline{\sigma}$ = microscopic spectrum-averaged transmutation cross section

ϕ = neutron flux

In as much as all theoretical calculations are to be compared to measurement, it is imp to recognize that considerable uncertainty lies in the physical quantity ϕ. As illustr consider a reactor fuel reportedly exposed to a burnup of 30 MWd/kg U. This is probabl uncertain by at least 5% just due to uncertainties in knowledge of exact calorimetric p levels of operation. Now analytically burnup is just the integral

$$\int \sigma_{fiss}\ \phi\ N_{fuel}\ \ d\underline{r}\ dt.$$

Thus, uncertainty in the power levels results in similar uncertainties in the deduced f (σ_{fiss} and N_{fuel} are rather certain). Transmutation is generally proportional to term like:

$$[1 - \exp(-\sigma\phi t)] \text{ (one-step process)}$$

$$\text{If}\quad \left.\begin{array}{l} \sigma \sim 10 \text{ barns} = 10^{-23}\ \text{cm}^2 \\ \phi \sim 10^{14}\ \text{n cm}^{-2}\ \text{sec}^{-1} \\ t \sim 10^{7}\ \text{sec (1/3 year)} \end{array}\right\} \quad \begin{array}{c}\text{typical power reactor}\\ \text{conditions}\end{array}$$

such that $\sigma\phi$ is in the neighborhood of 0.01, then

$$[1 - \exp(-\sigma\phi t)] \sim \sigma\phi t$$

and production is linear with burnup ($\sigma_f\phi t$).

As example, for $^{238}U \rightarrow {}^{239}Pu$

$$\frac{^{49}N}{^{28}N_o} \sim \left\langle \sigma_{28}{}^{n,\gamma} \right\rangle \phi t$$

For a two-step process $^{238}U \rightarrow {}^{239}Pu \rightarrow {}^{240}Pu$

$$\frac{^{40}N}{^{28}N_o} \sim \left\langle \sigma_{28}{}^{n,\gamma} \right\rangle \left\langle \sigma_{49}{}^{n,\gamma} \right\rangle (\phi t)^2$$

If one now takes ratios of mutant production, ϕt frequently cancels out. Thus, ratios much more dependent on the $\overline{\sigma}$ (t) involved than on the precise history. Thus the ratio $(Pu/U)/(^{239}Pu \cdot {}^{242}Pu/(^{240}Pu)^2)$, employed in the correlation literature, reduces to constant times $(\phi t)/(\phi t \cdot [\phi t]^4/[\phi t]^2)^2 = 1$. For fission products as previously classif "P" $\propto \phi t$, while "S" and "A" are of the form:

$$S(t) = a\left(t - \frac{[1 - e^{-\lambda_p t}]}{\lambda p}\right). \qquad a = \text{constant}$$

For small t, $S(t) \sim a \dfrac{\lambda p}{2}\ t^2$. For A, λ_p becomes $\sigma_p\phi$.

The $\{\overline{\sigma}\}$ are strongly dependent upon spectrum which is affected by moderating rati enrichment, and pin diameter, and to a lesser extent on cladding and leakage control mechanism.

In summary, isotopic compositions will depend on both flux and cross section. Fl should generally be the more uncertain, especially, in trying to relate to experiment values. Ratios eliminate problems of flux dependency, but carry little history inform

Preliminary Choice of Mutant Parameters

Parameters involving two groups of mutants quickly come to mind: the Group I act for which much experience and data already exist, and the fission products of original interest in this study because of the high accuracy with which they can be measured.

Before an accurate and general approach to the problem of constructing or choosi isotopic ratios can be defined the important question of the sensitivity of an isotop ratio to diversion (or other unreported behavior) must be examined. Any one isotopic will have zero sensitivity to certain types of diversion; this zero sensitivity is ca a "blind spot". Methods for identifying and compensating for "blind spots" in the isotopic ratio require the solution of a system of equations which predict the possib combinations of overall isotope changes that will produce no response in the isotopic ratios being used. The use of a number of distinct ratios that is greater than the n isotopic concentrations that the diverter may conceivably manipulate insures that the ind spots" to diversion are covered. Two or three ratios may be all that are required practice since other constraints may eliminate many mathematically-possible but ctically-impossible diversions.

Problem Understanding: Considerations in Comparing Theory to Measurement

Several factors may adversely affect the comparison of theoretical prediction to eriment: First of all, there exist uncertainties in both the theoretical calculation in the measurement. Second, there is the question of whether to even consider some -central reactor zones. Third, problems of mutant migration (diffusion) can occur. ally, there is the question of how to relate success in predicting ratio A/B (done in literature) to success in predicting C/D of interest here.

Measurement Uncertainties

Measurement errors may be expected to arise in chemical separation and analysis, and the mass spectrometric analysis. In part the uncertainty will be due to different nical recovery efficiencies. In the Diablo Canyon analysis appreciable Xe, Kr, I, U, Pu were lost.

Isotope migration effects. For some fission products axial and radial migration can ır. One underlying mechanism can be simple diffusion from a hot region towards a colder . In the well known case of Cs, this is probably due to the gaseous and chemically t nature of its precursor Xe and the tendency to diffuse from a hotter temperature ards a cooler one. Other elements with low chemical affinity may also diffuse. (The other case with an inert gas precursor is Kr → Rb.)

To avoid this problem in general it will be better to always analyze the whole fuel ent. In the specific case of Cs, it will also be important that the cladding integrity not violated resulting in loss of Xe gas through it.

Reported measurement uncertainties: Table IX. In the analysis of Saxton Core II, inghouse used mass spectrometric analysis to determine the U and Pu isotopic distribu- and the ^{239}Pu/^{238}U and ^{148}Nd/^{238}U atom ratios in each spent fuel sample. ^{137}Cs was ured radiochemically. Alpha spectrometric and radiochemical analyses were made for u, ^{238}Pu, ^{237}Np, ^{241}Am, ^{243}Am, ^{242}Cm, and ^{244}Cm.

HEDL and ARHCO analyzed the same samples and reported their uncertainties. A German rt gives the measured uncertainty in uranium enrichment. Karlsruhe and Ispra both yzed the same sample for two fission products. The difference in their results is n as a measure of uncertainty.

Table IX summarizes these data and makes some rough estimates of the state of the art. conclusion is that the standard "plutonides" are quite accurately measurable. Exotic nides and fission products are less so. The table is somewhat misleading for the ion products as a ratio is not involved. Presumably, with proper choice of elements, ical uncertainties can be virtually eliminated leaving only those from mass spectrometric ysis.

Theoretical uncertainties: Computer precision

The length of a computer word is 32 bits for IBM, 60 bits for CDC. Each word is di- d into a mantissa and an exponent, which give the precision (ε) and range (R) of the ers representable. For IBM this is:

$$\varepsilon_I = 10^{-7} \qquad 10^{-78} < R_I < 10^{+75}$$

CDC,

$$\varepsilon_C = 10^{-15} \qquad 10^{-294} < R_C < 10^{+332}$$

Table IX
Measurement uncertainties (%)

Parameter	W(a) Saxton	(b) HEDL	(b) ARHCO	(c) German	Karlsruhe[(d)] vs. Ispra	Estimated 2 Range (%)
Pu-238/Pu	2.3	8.8, 3.4	10, 9.8			2-10
Pu-239/Pu	0.03	0.1, 0.06	0.3, 0.06			0.03-0.10
Pu-240/Pu	0.2	0.53, 0.5	2.1, 0.13			0.2-0.5
Pu-241/Pu	0.3	0.42, 0.5	3.4, 2.8			0.3-0.5
Pu-242/Pu	0.9	3., 3.0	7.4, 3.3			0.9-3
Pu-239/U-238	0.7					0.7
Np-237/U-238	15					15.
Cm-242/Pu-239	10					10.
Cm-244/Pu-239	20					20.
U-234/U	29.4					29.
U-235/U	0.9			1.08		1.
U-236/U	5.6					6.
U-238/U	0.01					.01
Cs-137	8				7	8
Nd-148					9	9

(a) WCAP-3385-56 (pt.2), uncertainty is 2σ.
(b) UNI-436, uncertainty basis not given.
(c) uncertainty basis not known.
(d) 1σ estimate from comparison of two different measurements on the same sample.

In examining computer programs we must consider various sources of error. For a burnup code, ordinary differential equations are generally solved by finite difference techniques. This implies several sources of error:

(1) (truncation) error in the finite difference approximation to a differential operator. This depends on the number of terms in the formula and on whether is implicit or explicit. Generally, implicit formulas have less truncation error than corresponding explicit formulas; however, implicit formulas usuall require iteration, and are thus prone to propagation of roundoff error.

(2) roundoff error arises from the finite nature of the computing machine which c only deal with finitely represented numbers. This is expressed explicitly in the word sizes (in bits), and the number of those bits devoted to precision (range). The greatest loss of significance in numbers occurs when two numbers about the same size are subtracted so that most of the leading digits cancel Unless care is taken in advance, this can happen almost any place in a long computation.

(3) instability (error propagation). Frequently, numbers produced at one stage a fed back into the computer algorithm to be processed again and again. The question then arises - will a small error grow or decay through the successiv iterations.

(4) range errors - exceeding the limits of the number system. These are not gene encountered. This arises from successive multiplication of small or large nu so as to exceed the range provided by the leading bits in the word.

In considering nuclide buildup and depletion, one often encounters terms like:

$$\frac{N_2(t)}{N_1(o)} = \frac{\alpha 2}{\beta_2 - \beta_1} \left[e^{-\beta_2 t} - e^{-\beta_1 t}\right]$$

where α, β are production and destruction coefficients of the form $\sigma\phi$ or λ.

For t small enough this simplifies to

$$\frac{N_2(t)}{N_1(o)} = \alpha_2 t$$

For a multiple step process, e.g., 1→ 2→ 3→ 4→ 5

$$\frac{N_5(t)}{N_1(o)} \simeq (\alpha_2 t)(\alpha_3 t)(\alpha_4 t)(\alpha_5 t) = \left(\prod_{i=2}^{m} \alpha_i\right) t^{m-1}$$

us burnup calculations involve: (1) the difference between small numbers, and (2) the oduct of numerous coefficients in a long chain process. In addition care must be taken th units: for (m-1)=6 one must calculate $\Pi(\sigma\ \phi)$ in units of $\sec^{-1}$ and not $0^{-24})^6 \times \Pi\ (\sigma_i(b)\phi)$. They both give the same result in theory, but the second, which lays the correction for units, would give an incorrect result on an IBM computer for -1) $\geq$ 6. Similarly, $\Pi\ (\sigma_i) \times \phi^6$ could also easily exceed the IBM single precision nge.

A realistic example is some calculations made on the IBM 360 computer in single ecision for the transmutation scheme shown in Figure 7. Most concentrations such as -243 build up smoothly (Figure 8) due to high concentration, direct paths, high fluxes, d appreciable cross sections: core regions "A"-"E" (see figure). In the remote (low x) blanket regions abnormal behavior is noted for distant chain members like Am-243.

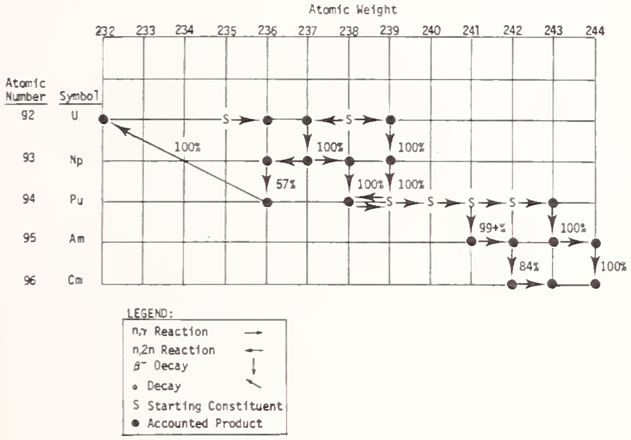


Figure 7. Branches of interest in FBR fuel burnup.

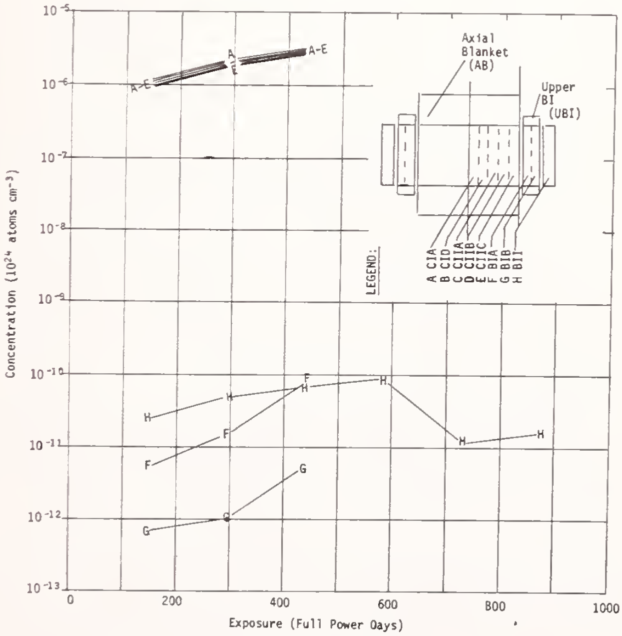


Figure 8. ^{243}Am buildup and burnup in 100 MWd/kg

In conclusion, then, it should prove less risky to do our calculations on a CDC machine than on the IBM one though the need is not fully demonstrated. One might especially be leary of a new IBM burnup code which has not yet stood the test of time for adequate accuracy.

Theoretical uncertainties: Nuclear data

Only a few cross sections are known to within 2%. For most one is lucky to get 10%. For rare off-the-beaten-path isotopes, much larger uncertainties may be expecte Fortunately, a recent demand for decay heat calculations has added some 800 fission product nuclei to the ENDF/B files, including n,γ cross sections for the nuclides of interest here.

Table X shows that a 1% error in cross section can lead to a greater than 1% error in production of a fission product nuclide (^{145}Nd). However, usually the error is reduced, not magnified.

Table X
Sensitivity of the computed production of stable fission products used in correlation techniques (in %) to an error of 1% in the yields and cross sections of the contributing fission products

contributing FP isotope	[^{145}Nd] sensitivity to FP yield	[^{145}Nd] sensitivity to FP cross section	[^{146}Nd] sensitivity to FP yield	[^{146}Nd] sensitivity to FP cross section
^{141}Ce	0.0038	-	0.0006	-
^{142}Ce	0.0023	0.0020	0.0004	0.0004
^{142}Nd	-	0.004	-	0.0006
^{143}Ce	0.149	-	0.0042	-
^{143}Pr	-	0.0007	-	0.0004
^{143}Nd	-	0.0290	-	0.0120
^{144}Ce	0.113	0.0073	0.03	0.0033
^{144}Nd	0.0003	0.26	-	0.0695
^{145}Nd	0.726	1.48	0.409	0.483
^{146}Nd			0.514	0.0362

Analysis of Existing Comparisons of Theoretical Predictions to Experiment

Virtually no comparisons have been made for fission product isotopes. Numerous comparisons have been made for actinides, especially for the more conventional isotopes of uranium and plutonium. For these agreement was quite good. For more exotic actinides, agreement is not good; one suspects that the nuclear data are inadequate.

Table XI summarizes some of the theory-to-measurement comparisons found. A wide ra of errors is seen. For ratios involving isotopes 239 through 241 of Pu, agreement is generally better than 10%, with some success indicated to the order of 1%; ^{242}Pu deviati are generally closer to 10%.

In Figures 9 through 10, errors are compounded: e.g., ^{240}Pu/^{239}Pu will have errors from both isotopes, in contrast to ^{240}Pu/Pu for which the error in Pu should be much smaller. The largest errors in this series occur in Figure 10 which involves high-error ^{242}Pu (∿ end of the chain) and ^{240}Pu (intermediate chain member). Error bands of ± 10% indicated to aid the eye of the reader.

Figure 11 shows similar information for the Calder Hall reactor and U.K. calculatic Two calculational methods are included. Agreement seems better for ^{241}Pu than for ^{240}P This emphasizes the compensating errors which must occur for each nuclide in the chain $^{238}\mathrm{U} \rightarrow {}^{239}\mathrm{Pu} \rightarrow {}^{240}\mathrm{Pu} \rightarrow {}^{241}\mathrm{Pu} \rightarrow {}^{242}\mathrm{Pu}$ as well as for $\mathrm{Pu} = \Sigma_i\, {}^{i}\mathrm{Pu}$. This limits the usefulr of this information to our concern of calculating fission product isotopes.

Table XI
Summary of Some Theory-to-Measurement Comparison Errors (%)

	Calc of N-Reactor at Rich, Wash.				VAK (BWR, 1971)		Yankee cores
atio	HEDL-1	HEDL-2	ARHCO-1	ARHCO-2	RMS	Signed Σ	4-6
-239/Pu	+0.1	+0.26	-0.1	+0.11	7.3	+4	+4.5
-240/Pu	-1.03	-1.5	+0.1	-0.5	11.2	+4	+1.5
-241/Pu	-0.52	-2.6	+1.9	-2.9	16.7	-17	+3.1
-242/Pu	+1.	+2.3	+10.5	+9.8	17.1	-7	-12.

VAK (BWR) 1975 Calc, Msmt. by WAK	KRB (BWR) 1975 Calc, Msmt. by Eurochemic	Saxton-II (20 GWD/MTM) W	Saxton III (50 GWD/MTM) Calc. by W (1973)	
			Range	Avg.
+1.1	+0.1	+0.86	-1.85 to 17.5	+4.0
-13.8	+2.6	+2.2	-15.0 to -3.1	-8.4
-39.9	+3.2	+3.6	0.8 to 9.8	+6.0
+5.8	-12.4	+0.4	-8.8 to 17.4	-13.8

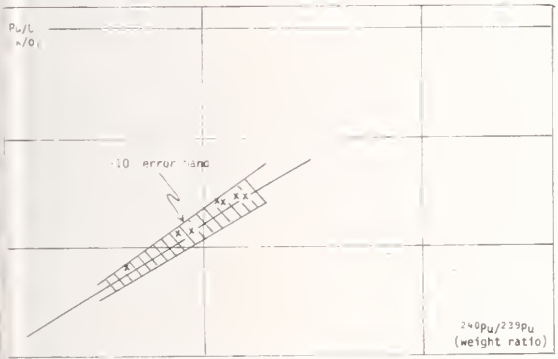


Figure 9. Pu/U vs ^{240}Pu/^{239}Pu; comparison with experimental results from Trino reactor (fuel enrichment 3.13 w/o).

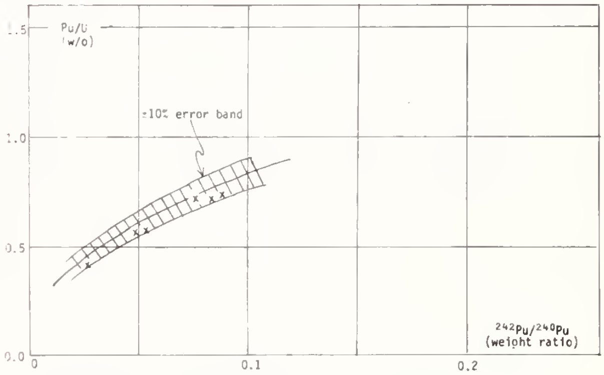


Figure 10. Pu/U vs ^{242}Pu/^{240}Pu; comparison with experimental results from Tino reactor (fuel enrichment 3.13 w/o).

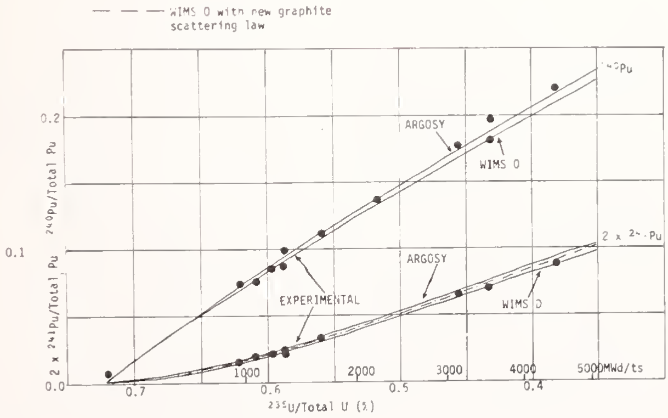


Figure 11. Fraction of ^{240}Pu and ^{241}Pu in total plutonium.

Table XII is significantly different: here one makes comparison for <u>absolute</u> concer trations. As expected for absolute values, agreement is worse for even these very standa nuclides.

Table XII
Comparison of calculation to isotopic data measured at the reprocessing plant on groups of PWR fuel assemblies

Fuel Assemblies	Depletions (kg/t(U))		Production (kg/t(U))	
	^{235}U	^{236}U	^{240}Pu	Pu fissile
	$\frac{C-E}{E}$ Dev.%	$\frac{C-E}{E}$ Dev.%	$\frac{C-E}{E}$ Dev.%	$\frac{C-E}{E}$ Dev.%
16-G5-E8	+3.0	+2.6	+6.8	+4.29
E4-15-H4	+4.3	+3.0	+9.5	+6.1
17-G10-F8	+2.9	+1.9	+4.8	+1.00
D5-D8-F4	+4.1	+3.1	+4.8	+1.8
H6-F7-F6	+2.3	+0.9	-1.0	-2.37
GP-F5-J6	+2.4	-0.05	+7.2	+4.14
E9-G4-E5	+3.9	+2.6	+5.5	+2.94
F9-I8	+3.9	+2.8	+5.8	+2.35
E11-K6-C8	+4.6	+0.2	-9.0	+4.1
E8-I10-F11	+3.8	-4.5	+8.7	+4.12
G11-D4	+3.3	+0.6	+8.1	+4.66

Figures 12 through 15 show the ability of calculated ratios to follow variations due to

(1) initial fuel enrichment,
(2) BWR void fraction, and
(3) moderator ratio.

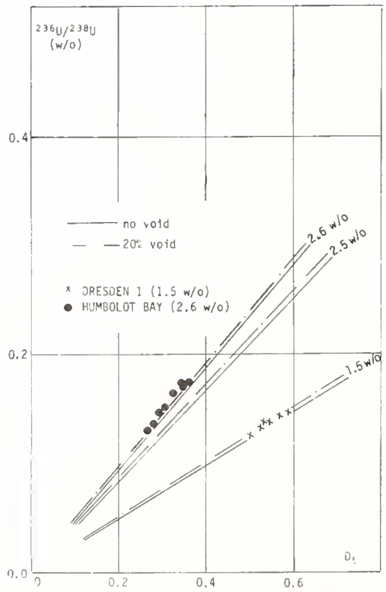


Figure 12. ^{236}U accumulation vs ^{235}U depletion (BWR reactors): comparison with experimental results.

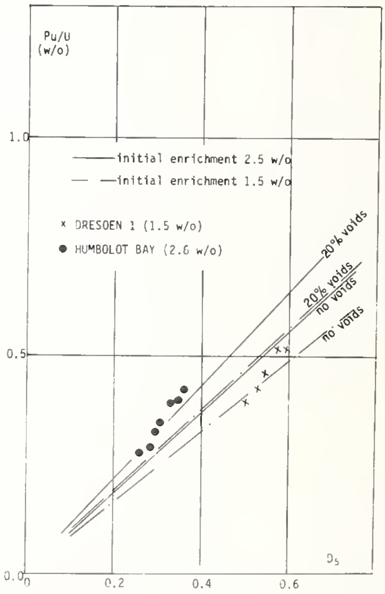


Figure 13. Pu/U ratio vs ^{235}U depletion (BWR reactors): comparison with experimental results.

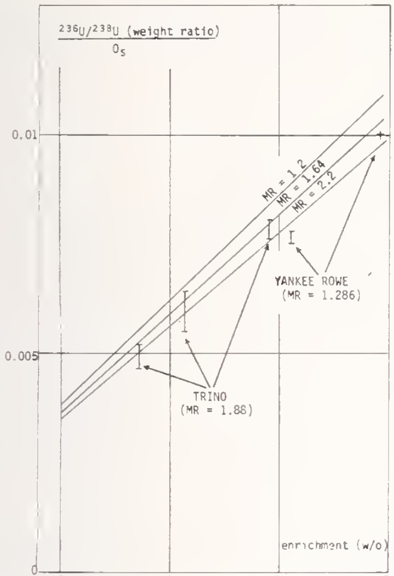


Figure 14. ^{236}U accumulation/^{235}U depletion ratio; comparison with experimental results from Trino and Yankee Rowe reactors.

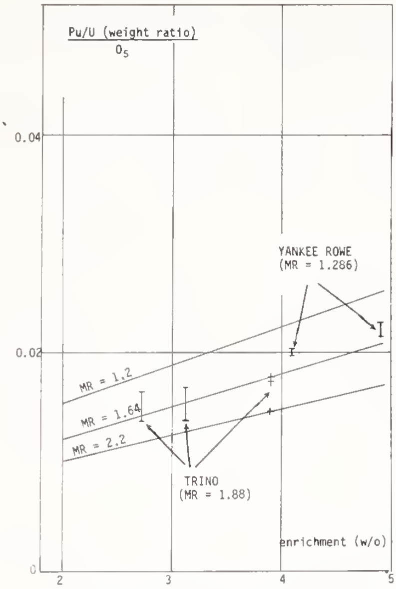


Figure 15. Pu/U to ^{235}U depletion ratio; comparison with experimental results from Trino and Yankee Rowe reactors.

that D_5 means depletion of ^{235}U. Dresden and Humboldt Bay are BWRs; Trino and Yankee
are PWRS. Due to sophisticated codes like CONDOR-3, they are able to reproduce some
e sensitivities, but not all. The same sort of success is shown (Figures 16 and 17)
ying to calculate spatial heterogeneity effects (pins near boundaries, control rods,
ecial channels). Codes like CONDOR-3 do show that they can reproduce some of the
tivity but they are not exactly right on the money.

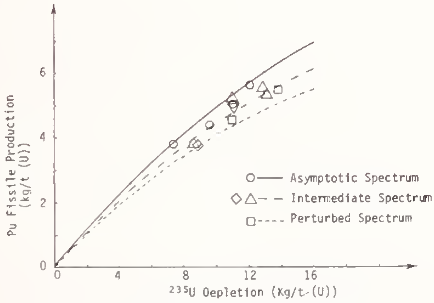


Figure 16. Fissile plutonium production vs ^{235}U depletion in different spectra.

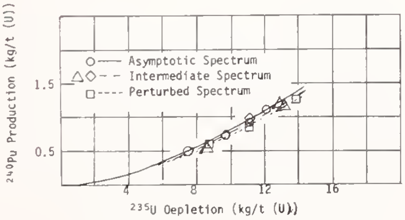


Figure 17. ^{240}Pu production vs ^{235}U depletion in different spectra.

Table XIII shows the marked improvement one can achieve on perturbed (corner) rods increasing the spatial and group mesh. Note that for the higher isotopes agreement get worse with better techniques - indicating that some, but not all, of the compensating errors are being removed.

Table XIII

Comparison of several calculations to several experiments: (C-E)/E (%)

	(Coarse) BURNY Code		(Fine) BURSQUID Code	
	Corner Rod	Stand. Rod	Corner Rod	Stand. Rod
BURN-UP (Cs)	1.82(-)	1.17(+)	0.60	1.60(+)
(Nd)	3.25(-)	0.49	1.35(-)	
[U-235]	6.04(-)	1.15(-)	1.24	1.42(-)
[U-236]	2.65(-)	2.66(-)	3.60(-)	2.21(-)
[U-238]	0.10(+)	0.05(+)	0.04(+)	0.02(+)
[Pu-239]	16.5 (-)	6.41(-)	2.10(+)	1.17(+)
[Pu-240]	5.07(+)	2.00(+)	1.28(+)	1.09(+)
[Pu-241]	6.35	2.27	4.43	3.43(+)
[Pu-242]	6.90	1.98	9.22(+)	8.35(+)

Figure 18 tends to show simply that its much harder to predict for a sample from t end of a rod vs. from its middle.

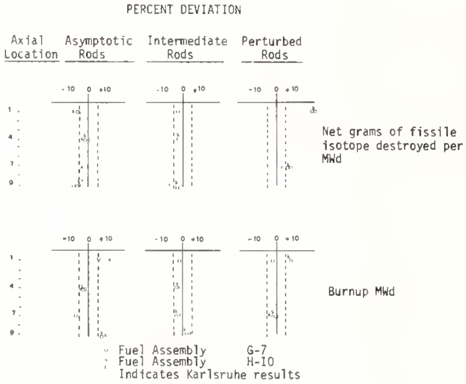


Figure 18. Relative predicted-measured errors on net grams of fissile isotopes destroyed per MWd and on local burnup.

In summary this section shows that success in accurate prediction of measurements not come easily. It will necessitate sophisticated techniques to eliminate calculation errors. The trick will be to get advanced techniques which are well suited to the task and avoid any expensive overkill. Once that is done it becomes important to choose nuclides for which nuclear data uncertainties are small. The use of sensitivity calcul tions with the ENDF/B covariance files may be necessary for full understanding. Thus t job can be done, but it requires considerable care, patience, and money.

Decay Chains of Interest and Their Requirements Upon Computer Codes

Existing Information on Transmutation Chains and Associated Nuclear Data

For the moment it is convenient to reclassify mutants as follows:

1. actinide mutants
2. radioactive fission products, generally measured by non-destructive gamma spectrometry.
3. stable and neo-stable fission products, generally measured by chemical analyse and mass spectrometry.
4. cladding mutants

stigation of production of the main actinides has been motivated by concern over fuel
ntory, hazards, and economics. Thus decay chains and nuclear data necessary for
retical calculations have been developed. Cross sections and decay constants for the
exotic actinides are being added to ENDF/B-5 (available in 1978). Similar data for
radioactive fission products have been built into zero-dimensional codes like ORIGEN
CINDER whose purpose is to calculate decay heat. Personal communication with the
ent authors indicates that the stable and neo-stable fission products are also ade-
ely represented and the specific chains of interest here are included. ENDF/B-IV
ided the first cut at yields, decay constants, and cross sections for 800+ fission
uct nuclides. ENDF/B-V will include numerous improvements. Little data development
the cladding mutants has occurred due to lack of interest.

Thus for the chemical analysis data of interest here, the nuclear data and transmuta-
chains needed for prediction tend to be well developed though still undergoing some
ges. The data libraries existing in a few codes are mostly for LWRs, especially PWRs.
cally they are in the form of four-group (or less) constants, having been previously
ced over a typical PWR spectrum. With that, the zero-dimensional codes tend to predict
distributions within 5% and heavier nuclei within 20% in asymptotic spectra. FP
arisons have not been made.

Unfortunately, the incorporation of these chains and associated data into codes like
ER and ORIGEN does not in any way facilitate incorporation into other burnup codes.
data are still described in only one place: ENDF/B and limited accompanying
mentation.

On Looping

Chain steps are very dependent upon the product of σ and ϕ. Given the fact that we
usually considering fuels which have been exposed to their full burnup potential, then
suspects the possibility of some chain looping where a chain path can lead to a previous
er. Most codes cannot handle this. This may occur in both FBR's and LWR's: In the former
high; for the latter, σ is. Still the problem is known to be more serious for actinide
ns than for fission product ones.

Decay Chains for Use in Predicting Fission Products of Prime Interest

Figures 19 through 23 show five chains deduced in this work for the isotopes of
rest. The data displayed on the figures represents typical values used to determine
prevalent paths. The latest data are available in the ENDF/B library (current
ion) or from EG&G's Nuclear Physics Branch (current evaluators).

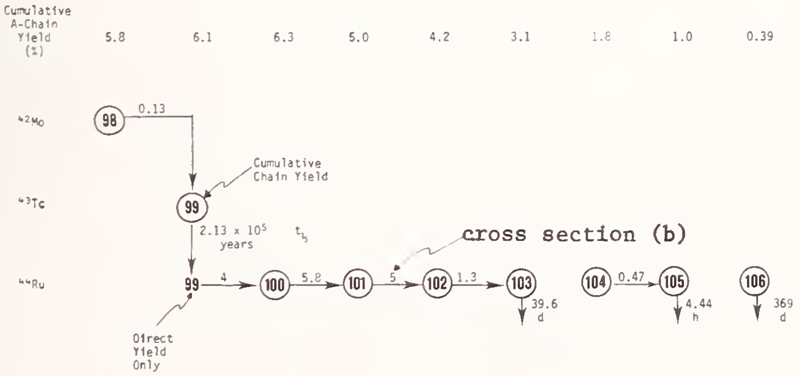


Figure 19. Decay chains for pertinent Ru isotopes.

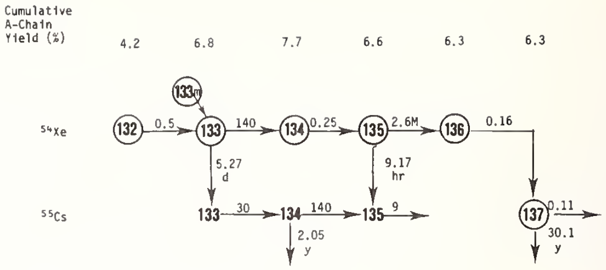


Figure 20. Decay chains for pertinent Cs isotopes.

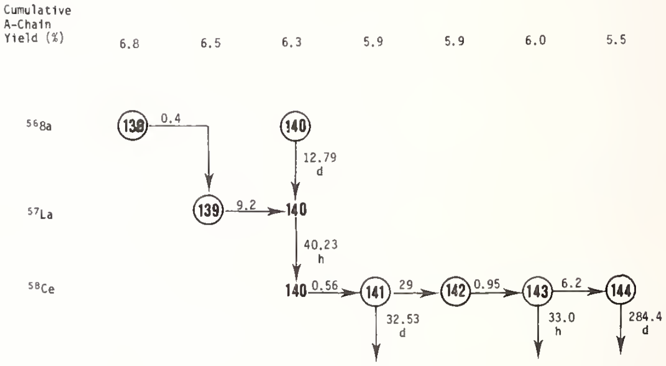


Figure 21. Decay chains for pertinent Ce isotopes.

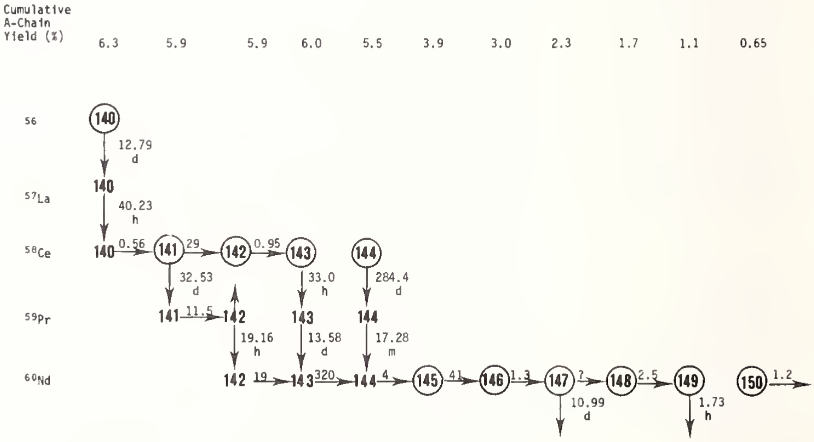


Figure 22. Decay chains for pertinent Nd isotopes.

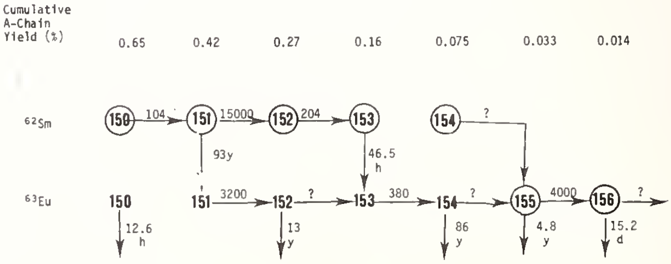


Figure 23. Decay chains for pertinent Eu isotopes.

In deducing the chain paths, neutron absorption is in competition with decay. For sorption to be significant (>1%) it is necessary that

$$\sigma > \frac{1}{100} \frac{0.693}{\phi \cdot t_{1/2}}$$

Taking $\phi \simeq 10^{14} n\ cm^{-2} sec^{-1}$ one gets

$$\sigma > \frac{2.2}{t_{1/2}\ (\text{years})} = \frac{802.}{t_{1/2}\ (\text{days})} = \frac{19{,}250}{t_{1/2}\ (\text{hrs})}$$

Examination of these chains leads to some first-order conclusions:

(1) much cross section information is relatively unknown.
(2) most of the isotopes of interest have time constants (from decay or neutron absorption) of the order of years - of little value here.
(3) the production of some isotopes stems from more than one path controlled by cross sections. The accompanying data uncertainty will probably limit seriously their usefulness. For history deductive purposes the best ratios should involve a neo-stable isotope in the denominator and ones with a time constant of the order ∿ 2 to 50 weeks in the numerators. For the denominator the element may also suffice as it is relatively stable.

For Ru, ^{103}Ru/Ru and ^{106}Ru/Ru are of interest. Isotopes 100, 101, 102, or their n might also suffice in the denominator. For Cs, beware the problem of Xe precursor gration. The best Cs is therefore ^{135}Cs whose Xe precursor has a half-life of only 12 hour and ^{137}Cs (precursor $t_{1/2}$ = 3.84m). However ^{137}Cs also is produced through the = 136 chain where the Xe is stable, and ^{137}Cs migration is already known to be a oblem.

For Ce, ^{141}Ce and ^{144}Ce have attractive time constants. ^{142}Ce should make a good ference. For Nd, only ^{147}Nd comes close to having an acceptable time constant. For a number of isotopes look interesting, especially because of large cross sections sotopes 151, 153, 155). Their true value would take more extensive investigation to termine due to the complexity of production and destruction paths.

Analysis of Code Features Under Consideration

On Multi-dimensional Capability

It was earlier shown that isotope production is sensitive to regions of different richment. In a comparison of calculation and experiment, one saw a difference in conntrations between asymptotic spectra (near the center of a region), and perturbed spectra ear a boundary or control rod). The two-dimensional methods employed were able to culate most of these differences. Although one might be able to find mutant ratios ch are insensitive to these effects, they would then also be insensitive to phenomena of terest to this study. Thus, although zero-dimensional calculations may suitably calate some isotope correlation ratios, those of interest to this work will require tiple dimensions. The question now becomes what will suffice? We certainly can't ford 3D transport theory recalculations at each burnup step (the extreme).

Table XIV indicates a fine point: for PWR's adequate representation of radial terogeneities appears to be more important than full axial representation.

Table XIV
Regionwise Burn-ups Evaluated With Different Methods (MWd/t(U))

Region	Inferred from in-core instrum.	r,z-CONDOR-3 calculation	x,y-CONDOR-3 calculation
Inner	12 933	12 528	12 985
Intermediate	13 192	13 183	13 104
Outer	8 648	9 068	8 675

Tools Needed for PWR and BWR Analysis

There are important differences between PWR and BWR which significantly affect the prediction of transmutations. In the modern PWR, reactivity is primarily controlled by dissolved B which is uniformly distributed in the moderator. The reactor is designed to avoid significant boiling in the moderator such that the variation in moderator-to-fuel volume ratio is small axially and radially. Dissolved B control and variable radial fuel enrichment minimizes radial and axial peaking. These features make the calculation of element averaged concentrations for a PWR relatively straight forward. In a BWR the moderator-to-fuel ratio varies substantially in 3D. Also, rod insertion is used for control.

A saving simplification in BWR analysis lies in the high degree of standardized similarity between BWR's, especially the later standardized designs (Table VIII). A large uncertainty remains in the control rod patterns. If some nominal control configuration could be standardized, the BWR's could be characterized by 3 or 4 FLARE-ISOCHECK calculations.

Outline of a Typical Complete Set of Burnup Prediction Methods

The techniques for detailed burnup evaluation are essentially based on:

(a) burnup dependent cross section library calculations whose fundamental tools ar a multigroup treatment of slowing-down; a representation of the resonance capture; a lattice-thermalization law together with a fine-group representatio of the disadvantage factors; and solution of the time-dependent equations for variable isotopes using cross-sections collapsed into four groups.

(b) power- and burn-up-dependent corrections to cross-sections. Mainly the ^{238}U cross-section dependence on power shapes through life-time is evaluated.

(c) power- and burn-up shapes evaluation during life-time using a coarse or detailed representation of the core. The main codes for this purpose are: a one-dimensional diffusion-depletion code (radial or axial) including special features like spatial Doppler variation; spatial moderator temperature variation; burn-up-dependent cross-section libraries; criticality searches; an two-dimensional diffusion-depletion codes with the same features as the one-dimensional above, together with composition-and burn-up-dependent cross-secti libraries.

Sometimes an iteration procedure between spectrum and local flux evaluation is applied in order to define the proper spectrum for each composition. When survey calculations or experimental data are available, the composition- and burn-up-dependent library evaluation is performed using the critical spectrum in conditions very near to the real ones (local power, poisoning and leakage), otherwise spatial flux distributions are evaluated using average cross-section libraries and the appropriate spectrum for eac composition is calculated again.

A simplified synthesis technique is often used to estimate three-dimensional power and burn-up shapes. The model consists of the detailed x, y-representations of the cross-sections of the core, using local poisoning (for the representation of partial control rod insertion) corresponding to the reactivity effect of the absorbers, diluted poison as required, composition-dependent axial leakage (obtained through survey calculations), burn-up- and composition-dependent cross-section libraries. The point-wi burn-up evaluation is carried out, and the compression of the results by compositions or regions during burn-up gives the inputs (local power, fast-to-thermal flux ratio, leakag poisoning) for the axial representation in the regions of interest. The axial burn-up calculation gives all the burn-up dependent characteristics at a given point or region in the core.

A more sophisticated model is used when perturbations due to control rods are predominant during burn-up. The model includes an x, y-calculation as previously and, wher a cylindrical representation is possible, an r-z or radial calculation during burn-up, or a wide-mesh three-dimensional burn-up evaluation.

Extensive use of the mixed number density model is made. Problems related to burnable ons behavior are treated with special routines for burnup of poison spheres and nders.

Deduced Code Requirements and Desirable Features

Required Code Features

1. 1-D for PWR's, LMFBR's
   3-D (FLARE) for BWR's
2. Multiple groups for LMFBR's
3. Adequate numerical ability
4. Burnup plus HARMONY-type representation of burnup-dependent cross sections, or ability to recalculate fluxes periodically.
5. Available or easily-implementable nuclear data library
6. Error propagation stability with time step
7. Feasible cost of running

Highly Desirable Code Features

1. Able to input different fission yields for ^{234,6,8}U and $^{239-42}$Pu.
2. Calculation of BU in fuel elements next to control rods, water reflectors, or other large-flux change regions.
3. Could use zero-dimensional capability for exploratory surveys such as
   - effect of excursions
   - effect of reduced power operation
   - which fissiles contribute the most?
4. Available on a CDC computer
5. Ability to read in chains and associated data

Other Desirable Features

1. Checked out on IBM as well as CDC (for possible use on IBM if numerical error is not a problem to chain members of interest).
2. Pre-fabricated modern chain library, ready to go.
3. 3D inventorying.
4. Multi-dimensional fuel movement and inventory representation.
5. Looping ability of burnup chains.
6. Local experience.

Recommended Code Systems

From all of the information above, it appears that a code system which includes i-dimensional neutronics calculations is needed for the purposes defined here. A good ple is Ispra's system built around CONDOR-3. An American equivalent of CONDOR-3 d be PDQ-7 or -8. The use of HARMONY for burnup-dependent cross sections with PDQ s a powerful tool. Indeed, this package has been used for many light water tor calculations.

What this package might lack is
(1) routines or codes to handle fuel management
(2) automation of intermediate steps
(3) a cheap way to do BWR calculations which require an extra spatial dimension (possibly a synthesis option in some PDQ versions may help).

Another attractive solution is the new EPRI-sponsored ARMP package. Designed to be by public utility engineers it
(1) removes many headaches of data handling,
(2) is designed for light water reactor calculations,
(3) has a FLARE (GE BWR code) - type subroutine to allow economical calculation of a third dimension (for BWR's especially), and
(4) includes fuel management routines.

Indeed, this package was designed for a purpose which highly overlaps that declared e. It presently uses a cross section library of ENDF/B caliber, but a new one from

ENDF/B-4 is imminent. Further, it is logical to expect that EPRI will continue to keep both methods and data current for a long time.

To calculate the fission product nuclei of interest will still require some chain formulation read-in along with appropriate nuclear data processing. However, this will be true of all codes except for ORIGEN, RIBD, and CINDER which calculate everything under the sun. Their inadequacy lies in their zero-dimensionality for neutronic calculations. (Actually CINDER plays a small role in the ARMP package in preparing burnup-dependent cross sections for HARMONY).

The ARMP system is proprietary to EPRI and NAI, a CDC subsidiary. It will be available at all CDC utility computer service centers (at their computer rates) and at three ERDA/NRC computer installations: BNL, ANL (Chicago), and UC-Berkeley.

SUMMARY CONCLUSIONS

Sources of Information

Numerous individuals and labs have been active in fields related to this area of concern. A large number of spent fuel analyses have been made but it is a difficult task to locate the results and a description of the reactor and its history, and then to develop an appropriate nuclear model. Much of the information does not appear to be in the open literature. One major source would be the data bank at Ispra. A similar bank may develop in the U.S.

The numerous empirical correlations could prove useful as benchmarks, but the original data is to be preferred. Presently the empirical data would seem more useful as indicators of the sensitivity of an isotope ratio to various reactor parameters.

Cursory survey of the large number of burnup codes and code systems indicates some basic trends. Comparisons of theoretical calculations with measurement are rather limited for fission product nuclei.

Workers at SGAE-Austria are among the very few active in the field of a backward (deductive) calculations.

Problem Understanding: What Are the Mutant Parameters of Interest?

Interruptions to a reactor's operation may be detectable through analysis of spent fuels with zero - or one-dimensional techniques. To sense where fuel substitution or diversion has occurred, appears to require multi-dimensional techniques. In the situation where one knows (or wishes to assume) nothing about the origin or history of a fuel element, it is important to perform visual and gamma spectrometric analyses. These can help identify the type of element and determine important heterogeneities. Neutron radiography is also a possibility. A logical sequence of analysis should be developed leading to identification of reactor type and composition before attempting to resolve detailed history. This is important so that the correct weighting spectra are used in the latter effort.

In studying the spent fuel analyses one can use isotope/isotope ratios (${}^{A}X/{}^{B}Y$) and isotopic compositions (${}^{A}X/X$). The latter are more accurate from the measurement point of view as the element and isotope should have the same chemical recovery efficiency. Theoretical uncertainties also should be smaller for the denominator X (errors partially cancel when summing up the isotopes of a given element) than for ${}^{B}Y$.

Most of the isotopes of declared interest in this study have not been measured or predicted in other studies. ^{137}Cs and ^{148}Nd are the notable exceptions. Much valuable information in the past has been extracted from the actinides. As nuclear cross sections and decay data are well known for the more conventional nuclides and no fission product yields are involved, their use in forward and backward calculations can not be ignored. Also considerable experience including comparison of calculation with measurement has been developed for them.

The work to date on backward calculations provides some valuable insights. A key idea assume a pattern of history and parameterize it. One can then solve for the para- s using the same number of isotope ratios. Use of a larger number of isotope ratios overdetermine the problem: this should make up for the uncertainties in measurement heory. It should also indicate, by difference in answers, the validity of the ed model. Several models would be tried.

Judicious choice of isotope ratios is important: a scientific basis for logical e appears possible. A theoretical understanding of some standard nuclide concentra- behaviors was developed. To maximize the information obtainable -- to choose the ts of interest scientifically rather than by trial and error -- theoretical investi- n should be continued. Specifically one would like to develop permutational relation- which could approximate impulse functions of varying widths. Approximation of mathematical functions might also be possible and of interest.

Problem Understanding: Considerations in Comparing Theory to Measurement

It would be well to attempt to quantify the uncertainties due to (1) isotope migration n a rod and (2) viable chemical recovery efficiencies. Elements with similar high iencies and low variances would be particularly desirable for forming ratios. The ted variation in measurement uncertainty among isotopes of the same element should plained (for better understanding of the problem).

One tends to prefer the CDC computer for burnup calculations though an IBM code uble precision may be adequate; in any case we suspect a CDC code may be more ient here. Whichever computer code is chosen should be well documented and supported. which have stood the test of time tend to insure against errors stemming from ter word size or program logic.

Errors in nuclear data may be expected to play a significant role here. Sensitivity sis shows that uncertainties in yields are every bit as important as those in cross ons. Therefore, it behooves one to use the latest ENDF/B data, be aware of the tainties and eventually do sensitivity studies.

Evidence exists that key reactor lattice parameters sufficiently affect the neutron rum such that isotope concentrations are significantly affected. Furthermore, (at) American PWR's and BWR's each exhibit a narrow range of lattice parameters in their lass: this will facilitate distinguishing between the two. Direct evidence exists one can detect a long stand-still of a reactor by means of the nuclide compositions.

In seeking out mutant ratios to be studies, one should bear in mind that isotopic sitions (e.g., $^{A}X/X$) appear to be inherently more accurate than nuclide ratios Y). As both measurement and theoretical uncertainties exist, it will be necessary erdetermine the analyses. Also, any one nuclide ratio will have a blind spot or sensitivity to some reactor or history characteristic. This means using at least ore ratio than model parameter sought. A variety of time constants should be ded among the nuclide ratios.

Theoretical research should help to develop a scientific method for choosing nuclide s best suited for each question asked. To this end it would be well to set forth evelop a proper set of questions which is to be asked of the spent fuel cycle ses.

Information from Existing Comparisons of Theoretical Prediction to Measurement

Virtually no comparisons were found for fission products; only for actinides. In dering the conventional isotopes of plutonium, agreement varies. However in a ell, when reported in ratio to total Pu, isotopes 239-241 look pretty good ($\sim$ few or) while 242 exhibits $\gtrsim$ 10% error. This is not surprising as the 242 cross sections he least well known and its presence at the end of the chain has the effect of porating the errors of all its precursors as well.

Some significant evidence demonstrates that reasonably good agreement for higher actinides is entirely fortuitous and due to compensating errors: improvement in the calculational technique makes agreement worse.

Existing sophisticated calculational techniques are able to reproduce a good porti but not all, of the sensitivities of isotope ratios to spatial and spectral perturbatio The point is thus emphasized that one must carefully use the best techniques if the required precision is to be obtained. Judicious choice of the isotope ratios will also important to avoid those nuclides with large associated data uncertainties.

Decay Chains of Interest and Their Requirements Upon Computer Codes

The decay chains for the fission products of declared interest here were deduced and examined. In the context of other sections of this report, it was found that most isotopes would give the same information, and therefore be redundant. Others were clearly unique. Thus it is very important that the characteristics desired of the isotope ratios be further investigated, classified and applied to the set of isotopes of possible interest to the situation to be analyzed.

The resultant set must also satisfy data requirements as indicated above. Sensitivity analysis should prove to be valuable: first, sensitivity of isotope concentrati to the different chain paths so as to define its appropriate class and time constant; second, sensitivity of isotope concentration to the uncertainties of the underlying nuclear data to see if it will be useful.

Analysis of Code Features Under Consideration; Requirements and Desirable Features

Multidimensional neutron calculations seem to be a requirement. An appreciable number of codes will be required for cross-section processing, 2D neutronic calculation, 3D coarse mesh neutronic calculation, burnup calculation, and inventorying with or with fuel shuffling. Linked systems of codes are available which can significantly facilitate the whole process.

Recommended Code Systems

Items of major significance observed here are:
(1) limitations of zero-dimensional codes
(2) excellent suitability of the EPRI ARMP package to this problem.
(3) the large number of nodal method codes coming into existance. These allow one to perform a 3D calculation with suitable approximations and reasonable cost (compared to a 3D finite difference calculation).

The recommended calculational system would be one which includes:
(1) 2D neutronics (like CONDOR-3 or PDQ-7), and
(2) coarse mesh, nodal code for 3D (possibly 3D synthesis will suffice)

By far the best system seems to be the EPRI-ARMP: it has virtually everything needed, it is highly automated and human engineered, and doesn't overkill the problem (minimum cost to run). Should access to this semi-proprietary system be infeasible, other existing capabilities could be used: they're just not presently automated, and are less efficient. Modularized computing capabilities would facilitate assembly of a suitable code system.

In-Situ Transuranium Element Measurement Technique for Wastes Associated with Power Reactor Fuels

by

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ABSTRACT

A planar, 19 cm^2 intrinsic germanium detector has been used for in-situ analysis of plutonium and americium in contaminated laboratories and buildings. Detection limits depend on local background activity, but in typical surface measurements for decontamination work are about 0.005 nCi/cm^2 for ^{241}Am (59.5 keV) and 0.5 nCi/cm^2 for ^{239}Pu (17.2 keV). Specific analyses of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu are also possible using various gamma-rays. Attenuations equivalent to 10 cm of concrete can be tolerated for high levels of ^{239}Pu and ^{241}Am.

KEYWORDS: In-situ analysis, americium, plutonium, detection limits, germanium detector, x-rays, gamma-rays

INTRODUCTION

Increasing precautions being taken in nuclear materials handling and management have red the development of instrumentation for rapid, sensitive analyses of various trans- c waste elements from both power and breeder reactors. Such instrumentation is re- d to analyze residual solids in high and low level waste streams and on contaminated ment, and to provide accountability. Since gross beta, alpha, or even neutron flux rements frequently give insufficient information about the concentrations of transuran- ements, the analytical capabilities of x-ray and low energy gamma-ray spectrometry have investigated. Transuranic elements which are readily identified in this manner include ., ^{239}Pu, ^{241}Pu, and ^{241}Am.

This paper describes the first field tests of an intrinsic germanium detector for in- analysis of low energy photons from ^{239}Pu and ^{241}Am in fissile material storage and atory buildings and in a building undergoing decontamination. The sensitivities, de- on limits, and other information such as the depth of the activity in an absorbing m are given.

METHODS

A planar 19 cm^2 intrinsic germanium detector, attached to its cryostat by an adjustable ing (Princeton Gamma-Tech, Princeton, NJ) permitting 180° adjustment from up-looking to looking or at intermediate positions, was used for all x-ray and gamma-ray analyses. etector preamp was coupled by a 30 m cable to the amplifier. Pulses were stored in a ble multichannel analyzer which was interfaced to a portable cassette recorder (Model Techtran Industries, Inc., Rochester, NY) for storage of spectral data. Nominal de- r resolution at 59.5 keV was 0.68 keV FWHM with this apparatus. Unfortunately, just to the field tests a defect developed which degraded the system resolution to 1.04 keV. ovable annular lead collimator (1.27 cm thick by 10.2 cm long) was placed around the tor head to reduce background and restrict the detector's field of view.

Laboratory calibrations were accomplished with thin sources of ^{241}Am, ^{238}Pu, ^{239}Pu, and , counted at various distances from the detector for geometry assessment and through us absorbers for determination of attenuation. The attenuation measurements for ^{241}Am used to estimate linear coefficients relating L x-ray peak areas and relative attenua- factors to the observed 26/60 keV peak area ratio. This permitted attenuation correc- for the ^{241}Am measurements and interference correction of the plutonium L x-ray peak . Once corrected for interference by the partially resolved L x-rays from ^{241}Am, the L s from plutonium decay could be similarly corrected for attenuation using the L_β/L_γ peak ratio.

Besides correction for photon absorption, the peak ratios were also used with appro mate attenuation coefficients to estimate the thickness of any absorbing material over t transuranic element source, or in the case of a uniformly distributed source, the mean d of the activity. Attenuation coefficients required for these depth estimates were measu in the laboratory using various materials such as concrete, wood, sand, steel, lead, luc glass, and floor tiles. Additional sources consisting of several transuranic species mi in coarse sand or finely packed dunite were also analyzed to verify the attenuation calc tions. Details of the calibration and calculation methods have been described elsewhere

Analysis of contaminated surfaces consisted of positioning the detector, acquiring for 1-10 min, recording the spectrum on a magnetic tape cassette, and moving to a new lo tion. Analyses both with and without the lead collimator were done to evaluate its use effectiveness. Although prominent peaks such as the L x-rays and the 26 and 60 keV gamm rays were immediately observed, detailed analysis of the data for plutonium activity and depth was done following transfer of the spectra from the cassettes into a PDP-15 comput

RESULTS

The first of three field experiments was an attempt to measure surface contaminatio a concrete room containing large arrays of steel drums of fissile material. Background this room created ∿60% dead time in the unshielded detector and prevented observation of photopeaks below the intense 60 keV ^{241}Am peak. Although the annular lead collimator reduced the dead time to ∿30%, it was still not possible to measure low level local surfac contamination.

The second experiment consisted of a series of measurements near a pair of contamin hoods in a chemical separations laboratory area. Measurements were made at three locati (60 cm intervals) on the floor in front of the hoods and also looking horizontally into hoods. The contaminated portion of the room was isolated by a thin plastic cover which not significantly attenuate the observed peaks. Spectra collected at a location on the both with and without the lead collimator, are illustrated in Figure 1 (Table I, Locatio

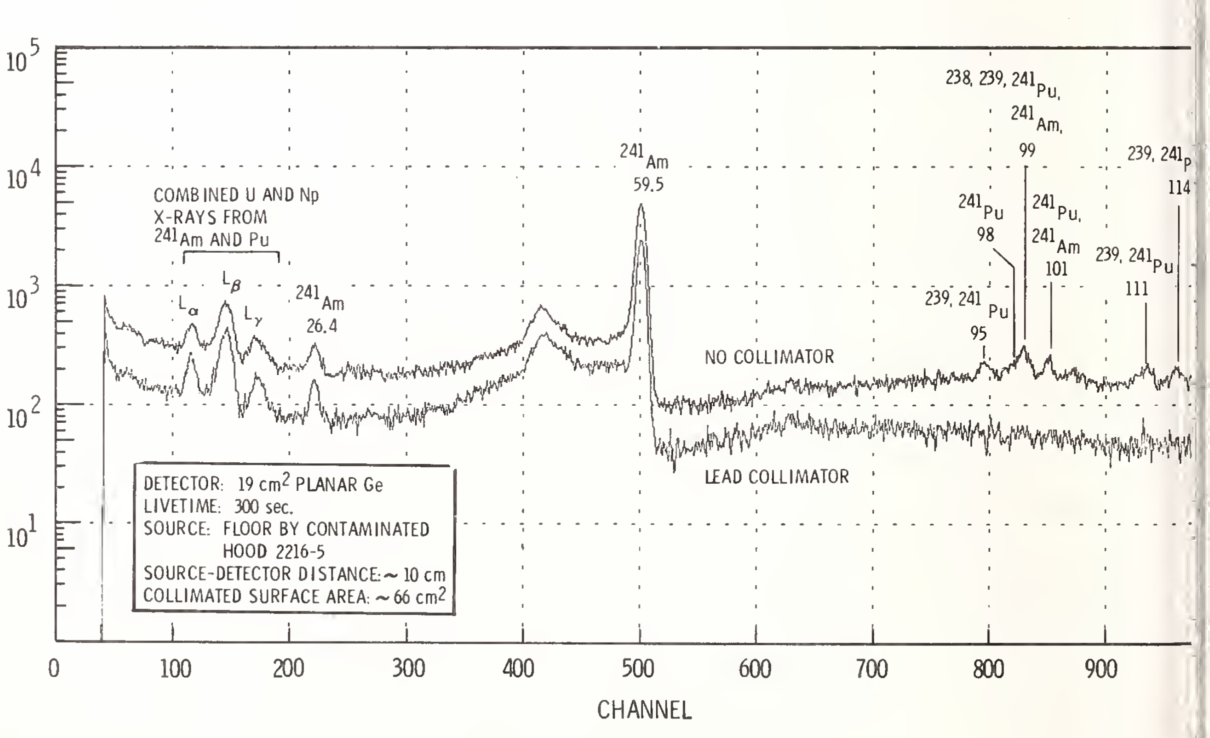

Figure 1. Low Energy Photon Spectrum from a Contaminated Floor Area

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[1] K. K. Nielson, C. W. Thomas, N. A. Wogman and R. L. Brodzinski, "Development of a Pluto Americium Monitor for In-Situ Soil Surface and Pond Bottom Assay," Nucl. Instr. and Met 138, 227-237 (1976).

As can be seen, the x-ray peak areas are not appreciably reduced by collimation, which icates that the surface contamination of this particular area is local and confined to viewing area of ~66 cm^2. The elimination of the higher energy plutonium gamma-rays -120 keV) and attenuation of the 59.5 keV ^{241}Am peak by the collimator indicates detec- n of these higher energy photons from beyond the 66 cm^2 viewing area, most likely through sides and top of the unshielded detector head. The observed concentrations and depths activity of the contaminated floor areas are summarized in Table I as calculated by the k ratio method,[1] using L x-rays for plutonium determination and the 26 and 60 keV peaks ^{241}Am determination.

TABLE I

Floor Activity (nCi/cm^2)$^{(a)}$

Sampling Location	1	2	3
^{241}Am	0.083 ± 0.013	0.48 ± 0.05	1.9 ± 0.1
^{239}Pu	1.2	1.9 ± 0.4	29 ± 4
Mean activity depth	Remote[b]	2.8 mm	2.8 mm

[a] Statistical uncertainties only.
[b] No peaks were observed below 60 keV indicating activity was deep or, more likely, simply background.

The hoods themselves were examined at a distance of ~25 cm, yielding a collimated view- area of ~400 cm^2. The results of the hood analyses are listed in Table II. For Hood A, of the lead collimator greatly affected the observed spectrum, as illustrated in Figure nd Table II. In this case, the entire spectrum was attenuated, including the x-ray ks, indicating the activity to be spread over a large area which was geometrically re- icted by the collimator.

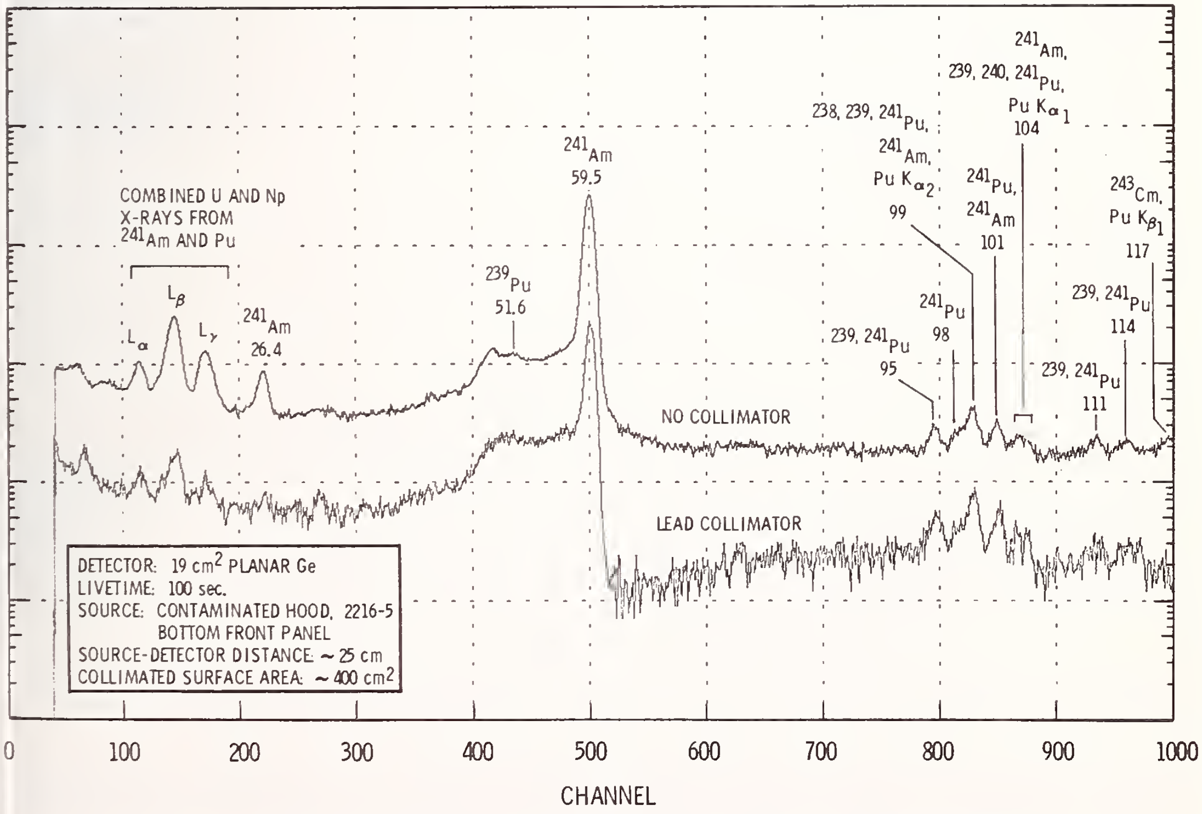

Figure 2. Low Energy Photon Spectrum of a Contaminated Laboratory Hood

The minimal reduction in photopeak intensities made by the collimator in analyzing Hood B indicates the activity was almost entirely confined to the ~400 cm^2 viewing area.

TABLE II

Hood Activity (nCi/cm^2)

	Hood A		Hood B	
	Without Collimator	With Collimator	Without Collimator	With Collimator
^{239,241}Pu (95 keV)	20700	5450	33900	33400
Pu (L x-rays)	5811	318	1090	446
^{241}Am (60 keV)	590	44	730	690

An additional spectrum collected from Hood B at a lower gain is illustrated in Figure 3 and includes a variety of higher-energy gamma-ray peaks from ^{239}Pu, ^{241}Pu, and ^{237}U (^{241}Pu). These peaks extend the depth determination capability for ^{239}Pu by a factor of 10 and could potentially permit limited attenuation or depth profile modeling.

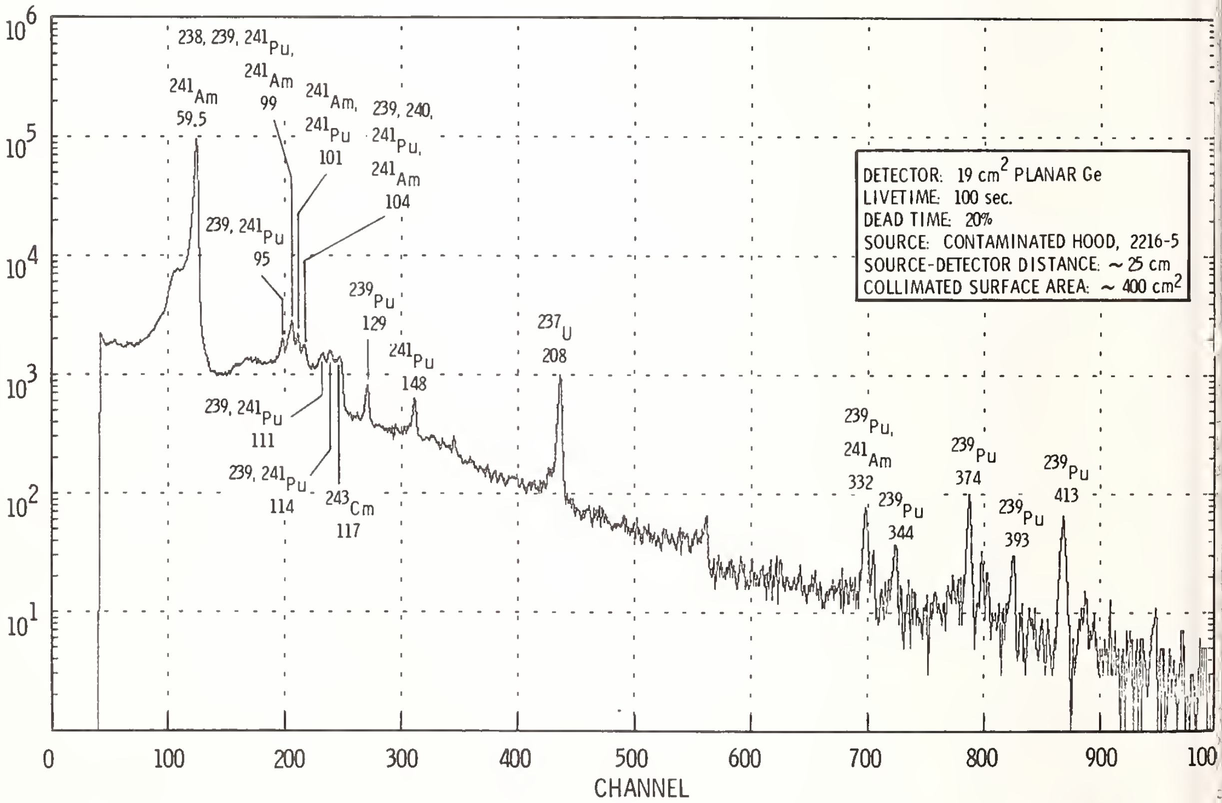

Figure 3. Gamma-Ray Spectrum of a Contaminated Hood Using 0.47 keV/Channel Energy Scale

The third experiment was conducted inside a concrete cell which was undergoing extensive decontamination efforts including paint removal and, in some cases, removal of surface layers of concrete. Two areas of suspected residual contamination were found to contain

.023 ± 0.002 and 0.022 ± 0.002 nCi/cm^2 of ^{241}Am. Although plutonium L x-ray peaks were bserved, the corresponding activity was below the 3σ detection limit of ∿0.46 nCi/cm^2. he ^{241}Am 3σ detection limits were 0.004 nCi/cm^2 for these ten-minute counts. In the absence of x-ray interference from ^{241}Am, the ^{239}Pu detection limits would drop to ∿0.13 Ci/cm^2.

DISCUSSION

The in-situ detection limits of the field system described here are similar to those stimated earlier[1] based on a smaller laboratory germanium detector housed in a lead cave. hree sigma detection limits for ten-minute counts have been computed from the background ntensities of the in-situ spectra and are plotted in Figure 4 as a function of concrete bsorber thickness to illustrate the relative depth of penetration of the various photons. he detection limits were computed as

$$\text{Detection Limit} = \frac{3\sqrt{2B}}{S}\exp(\mu X),$$

here S is the sensitivity (counts per nCi/cm^2), B is the ten-minute background intensity or the peak integration region, μ is the linear attenuation coefficient for the given hoton, and X is the thickness of the absorbing medium. As shown, ^{241}Am is readily detec-ed in the 0.005-0.1 nCi/cm^2 activity range at depths to ∿4 cm, while plutonium detection equires activities ∿100 times greater for surface counting and ∿1000 times greater at epths of a few centimeters.

The surface detection limits depicted in Figure 4 for the 59.5, 17.7, 17.2, and 26.4 eV peaks were estimated from the spectral backgrounds observed in the concrete cell exper-ment. The remainder of the detection limits for transuranic element photons are based on ackground intensities observed in analyzing the contaminated hoods in order to more realis-ically assess the practical limits of plutonium detection. Since ^{241}Am is generally found n any plutonium contaminated area, the conservative plutonium detection limits given in igure 4 are more appropriate. Plutonium detection limits would be much lower than indica-ed by Figure 4 if computed on an interference-free basis. For example, in the concrete ell where the ^{241}Am activity was low, background intensities were lower at 50, 100, 200, nd 400 keV by 0.055, 0.012, 0.057, and 0.20, respectively. Detection limits for ^{240}Pu and ^{238}Pu were calculated from relative intensity data[2] since significant peaks were not ob-erved for these isotopes in this weapon's grade material. Both of these isotopes are much ore abundant in high-burnup power reactor fuels.

Although the detector system used for these measurements was not operating with optimum esolution, its efficiency and detection limit capabilities were not greatly affected. Al-hough improved resolution would reduce interferences in the L x-ray peaks and also in the 5-117 keV region, the overlaps would still not be well resolved and analysis of these peaks ust include some form of interference corrections. These are especially important for the four peaks in the 95-104 keV region which are potentially composed of up to 14 x-ray and gamma-ray peaks.[3]

Continued development of this in-situ analysis method for ^{241}Am and plutonium will in-clude modification of the lead collimator to provide better definition of the surface area being counted. In addition, quantitative measurements will be further aided by computer analysis of the spectra for rapid activity and depth estimates. Semi-quantitative or qualitative estimates of the nuclide activities and depths can also be made in the field using analyzer-integrated peak regions or by visual inspection of the data as illustrated in Figures 1 and 2. Approximate on-the-spot assessments of the quantities and locations of specific nuclides are frequently adequate for decontamination work. However, in the areas of nuclear safeguards or decommissioning of nuclear facilities, the ability to analyze specific transuranic nuclides at the 0.005-1 nCi/cm^2 level may be important.

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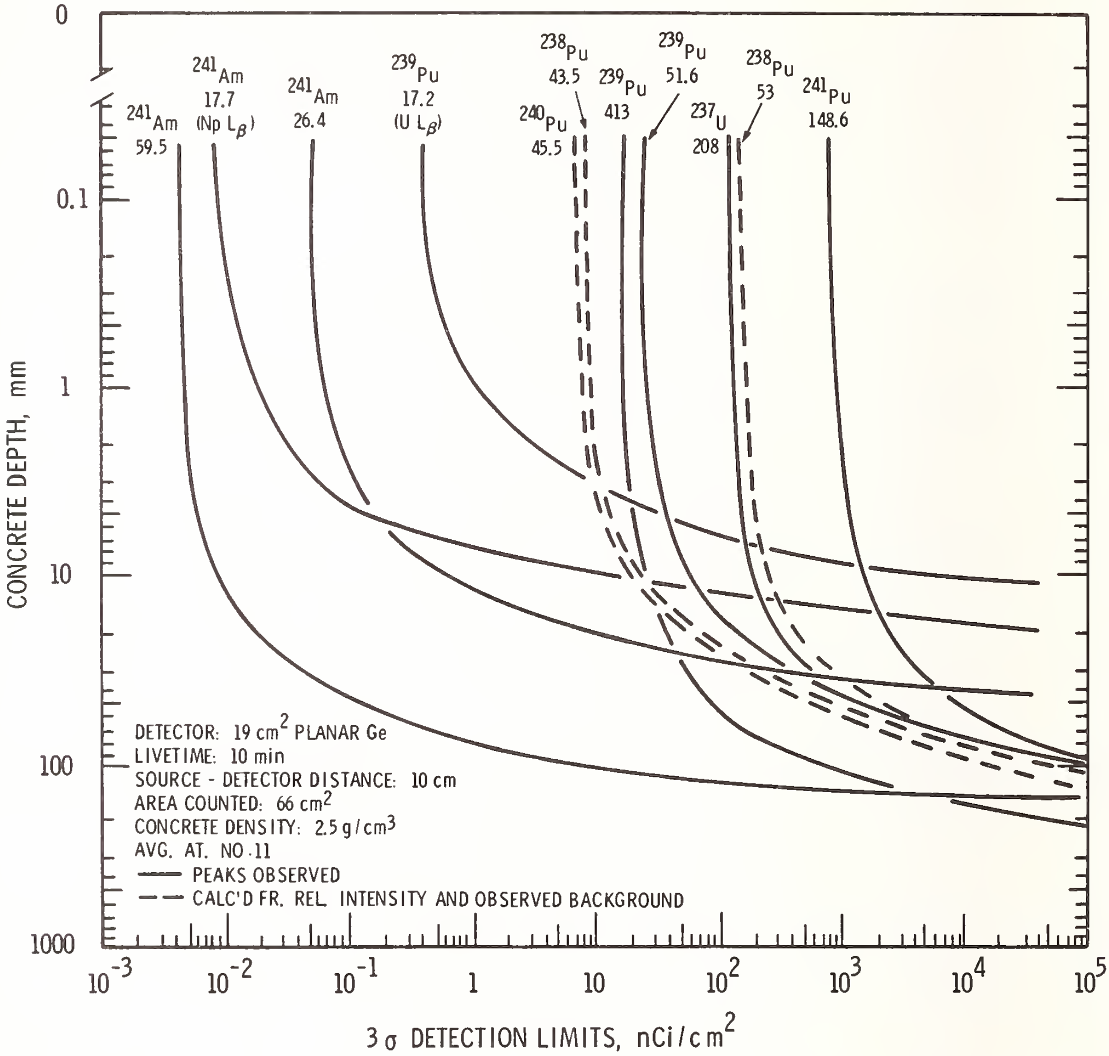
[2] G. Erdtmann and W. Soyka, "The Gamma-Ray Lines of Radionuclides Ordered by Atomic and Mass Number," J. Radioanal. Chem. 27, 137-286 (1975).

[3] R. Gunnick and J. E. Evans, "In-Line Measurement of Total and Isotopic Plutonium Concentrations by Gamma-Ray Spectrometry," UCRL-52220, Lawrence Livermore Laboratory (1977).

FIGURE 4

Pu AND Am DETECTION LIMITS VERSUS DEPTH IN A CONCRETE ABSORBER



ACKNOWLEDGMENTS

We appreciate the assistance of H. L. Nielson in making the in-situ measurements. Thi work was performed under U. S. Department of Energy Contract EY-76-C-06-1830.

Experiences With a Counter for Plutonium in Crates [1] [2]

by

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ABSTRACT

Some contaminated waste generated at the Rocky Flats Plant has been put into crates for shipment to storage and disposal. Previous estimates of plutonium contamination in these wastes has been conducted with hand-held survey instruments. That practice was time consuming and expensive in terms of manpower.

A counter to assay plutonium in 1.22 by 1.22 by 2.13 mm crates was constructed. A previous report[3] described the counter and preliminary experiments which indicated the counter could detect 0.7 grams of ^{239}Pu in 6 hours or 10 grams in 20 minutes at a 0.95 confidence level. These sensitivities assumed the plutonium would be reasonably well distributed throughout a crate as opposed to concentrated in the center or in a corner.

The counter was made with 51 mm thick polyethylene walls. A standard crate was rolled inside and measurements of instrument response made with PuO_2 sources in various locations. Ten detectors, installed outside the walls, were lithium-loaded zinc sulfide screens (NE-422^R) 305 mm diameter. These detectors responded to thermal neutrons. Their scintillations were passed through conical light pipes to 127 mm diameter photomultiplier tubes. Signals from the tubes were processed through conventional amplifying electronics. Discriminators were used to practically eliminate any response to gamma rays. The standards crate for the counter was used to simulate combustibles waste crates which have had a mean weight and standard deviation of 658 ± 200 kg, respectively.

Since the previous report[3], experiments have been conducted to better measure the counter responses with plutonium concentrated in unfavorable locations and responses with plutonium in noncombustibles matrices. These laboratory-type experimental results will be described. Operating history of the counter under routine conditions will be discussed.

Having this counter as a final assay device has the potential of reducing assay efforts in certain plant operations. Such benefits will also be discussed.

KEYWORDS: Analyses; counter, neutron; plutonium; waste

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[1] Sponsor: J. D. McCarthy

[2] Work supported by U.S. Department of Energy under Contract No. EY-76-C-04-3533

[3] R. A. Harlan, Journal of the Institute of Nuclear Materials Management, 1977, in press

Requirements for Near-Real-Time Accounting of Strategic Nuclear Materials in Nuclear Fuel Reprocessing

by

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ABSTRACT

A Purex-based nuclear fuel reprocessing plant has been studied for possible incorporation of near-real-time accounting to supplement conventional accounting procedures. Near-real-time accounting of special nuclear materials relies on in-line or at-line flow measurements and plutonium assay of product and waste streams, complemented by conventional analytical chemistry for daily instrument calibrations. In-line alpha monitors could be used for waste stream measurements of plutonium, even in the presence of high beta-gamma fluxes from fission products. X-ray absorption edge densitometry using either K- or L-absorption edges could be used for plutonium concentration measurements in main product streams. Some problem areas identified in waste stream measurements include measurements of leached hulls and of centrifuge sludge. Conventional analytical chemical methods for measuring plutonium in weapons grade material can be modified for reprocessed plutonium. Analytical techniques requiring special precautions will be reviewed.

Some suggested areas for improvements in process design to facilitate materials accountability in future plants will be discussed.

KEYWORDS: Nuclear safeguards; dynamic materials accounting; in-line analysis; nuclear fuel reprocessing.

INTRODUCTION

Safeguards has become an increasingly important consideration in the public acceptanc of nuclear energy. This is particularly true in the back end of the nuclear fuel cycle where large amounts of fissile material are available in a relatively pure, concentrated form. The Safeguards Systems Group at the Los Alamos Scientific Laboratory has been tasked by ERDA and DOE to design integrated materials accounting systems for various plants in the back end of the fuel cycle. To date, studies have been completed for plutonium handling in a LWR fuel fabrication plant, a nitrate-to-oxide conversion plant, and a LWR fuel reprocessing plant. Each system is based on a specific facility -- for the fu reprocessing plant the AGNS plant at Barnwell, South Carolina (BNFP) was selected. This plant is one of the most modern reprocessing plants in the world. It was designed to reprocess 1500 MT of irradiated fuel per year, producing approximately 15 tonnes of plutonium, or on the basis of 300 operating days per year, approximately 50 kg per day of plutonium.

Design concepts and evaluation methods were developed for advanced nuclear materials management systems to safeguard in-process materials in current and future fuel reprocessing facilities. The concepts are based on a thorough evaluation of the Barnwell plant an represent minor extrapolations of existing fuel-reprocessing technology, conventional analysis, state-of-the-art nondestructive assay (NDA), and data-processing and analysis systems. Concepts applicable to domestic and foreign commercial or government-owned facilities to be built in the next decade were evaluated with simulated production data.

THE PUREX RECOVERY PROCESS

All present and currently proposed aqueous separations facilities including the BNFP e based on the Purex solvent-extraction process, developed by the US Atomic Energy Comission (AEC) in the late 1940s to satisfy military needs for weapons-grade plutonium. In e Purex process both uranium and plutonium are recovered, and the radioactive waste olumes are reduced by minimal use of nonvolatile salting agents and reactants.

Purex and its subsequent variants are based on dissolution of the irradiated fuel in itric acid, oxidation of the contained plutonium and uranium, and coextraction of the xidized species into an organic phase consisting of a hydrocarbon diluent containing triutyl phosphate (TBP), which forms extractable complexes with the oxidized species. The rganic phase is scrubbed to remove most of the nonextractable fission products and transranics from the coextracted fissile materials; then it is contacted with an aqueous phase hat selectively reduces the plutonium, stripping it from the organic phase. The partiioned phases, the organic uranium and the aqueous plutonium, are then individually subected to additional extraction, ion exchange, and other purification steps that eventually roduce two pure product streams containing uranyl nitrate and plutonium nitrate. The crubbing and stripping solutions from the purification and "polishing" steps are recycled long with the spent solvent streams to give a total recovery of uranium and plutonium roduct that can be approximately 99.9% with a net fission-product decontamination factor f more than one million.

Solvent damage from radiation exposure in the first extraction (co-decontamination) tage has always been an important problem in the operation of a Purex process. This olvent degradation poses problems for analytical chemistry as well as for the process ngineer because the dibutyl and monobutyl phosphate plutonium complexes do not behave n extraction or chemical analysis schemes as does the normal TBP complex. After most of he fission products have been removed, contact time in subsequent extraction, partition, nd purification steps is not nearly so important, and less vigorous means of attaining quilibrium are used in the interest of reduced mechanical complexity.

Other areas receiving attention in modified Purex processes have been the selection of uitable reductants for the partitioning step and the postpartition purification and olishing operations. The desire for reductants having minimal effect on product purity nd waste volumes has resulted in the use of organic reductants that decompose to volatile roducts, of uranium-IV reductants that add no new material to the product, and, ultiately, of electrolytic reduction, which adds nothing to the process stream, as in the roprietary AGNS Electropulse System.[1]

BNFP is pure state-of-the-art Purex: chop-leach head end with continuous dissolution, entrifugal extraction, and electrolytic partitioning. There are two uranium-extraction ycles plus a silica-gel polishing column and two plutonium-extraction cycles. First-stage xtraction is performed with the Robatel centrifugal contactor; subsequent co-decontaminaion, partition, and purification contactors are pulsed columns, including a proprietary lectropulse partitioning column. In this system, partition is effected by electrolytic eduction of uranium-VI to uranium-IV, which subsequently reduces plutonium-IV to pluonium-III. Considerable uranium is stripped along with the plutonium, necessitating an dditional plutonium-purification step and significant back cycle. The plant uses remote aintenance at the head end and through the first cycle, and anticipates no maintenance in ther areas of the plant except those in which the products have been decontaminated to he level where direct maintenance is feasible.

Because details of the AGNS design and materials flows are available and because the lant itself is in an advanced state of completion, it was selected for our safeguards odeling and design purposes.

CONVENTIONAL MATERIALS ACCOUNTING AT BNFP

The conventional materials accounting system at BNFP is based on daily analysis of the ccountability tank, waste streams, and plutonium nitrate product tanks. The measurement oints and precisions of analytical methods are summarized in Table I. NRC regulations

TABLE I

CONVENTIONAL MATERIALS ACCOUNTABILITY AT BNFP

Tank	Frequency	Method	Measurement Error, 1σ
Accountability	3/day	Mass spectrometry	0.2 to 0.5%
Leached hulls	1/batch	^{144}Pr	?
HAW surge	6/day	Mass spectrometry	5 to 3%
Pu nitrate	each batch	Coulometry, amperometry	0.3 to 0.1%

specify 1% error in measuring plant throughput. Throughput is verified semiannually by flushout-cleanout and measurement of in-process holdup. Based upon a plutonium throughput of 50 kg per day, the allowable material-unaccounted-for between cleanouts is 75 kg.

Thus, one is faced with the problem that a divertor could hide sufficient plutonium fo several weapons in the measurement uncertainty, and it could take up to six months before one could detect missing material. Clearly, this is an uncomfortable situation for the nuclear materials manager.

DYNAMIC MATERIALS ACCOUNTING

The basic philosophy behind dynamic materials accounting is to provide sufficient instrumentation that one can obtain near-real-time measurements of material flow rates and concentrations in all streams leading into the process area. Furthermore, the process could be divided into as many materials accounting areas as one can successfully instrument. Thus, timely material balances can be drawn about relatively small amounts of SNM. For a plant such as BNFP, the most desirable areas to instrument would be those containing the largest amounts of plutonium in a form most attractive to the divertor. The plutonium at the head end of the process is not attractive because it contains lethal concentrations of fission products and is diluted approximately 100-fold with uranium. However, after the 1B column, the bulk of the fission products have been removed and the uranium/plutonium ratio has been reduced to 2/1. From this point the plutonium becomes increasingly attractive as it proceeds through the process to the plutonium nitrate storage tanks. Hence, this area was selected for design of a dynamic materials accounting system.[2]

System Design

A schematic of the BNFP is shown in Figures 1 and 2. To isolate the plutonium purification process (PPP) (Figure 2) as a unit process requires flow and concentration measurements at the 1BP tank (input) and 3P concentrator (output). In addition, acid recycles (2AW, 3AW, 3PD) and organic recycle (2BW, 3BW) must be monitored for flow and concentration. The nominal flow rates and plutonium concentrations for these streams are summarized in Table II.

TABLE II

CONCENTRATIONS AND FLOW RATES IN THE PPP

Stream	Flow (L/h)	Plutonium Concentration (g/L)
1BP	400	5
3PCP	8	250
2AW	500	trace
3AW	215	0.1
3PD	32	trace
2BW	150	trace
3BW	105	trace

Flow Measurement

The precisions for flow measurement in the input and output streams should be 1% (1σ) etter. For the 1BP stream this can be attained with a calibrated orifice meter in the surge tank or with in-line ultrasonic or magnetic flowmeters. The flow measurement isions for the recycle streams are less stringent; possibly air lifts could be cali- ed to the order of 5-10%.

Concentration

The plutonium concentrations of input and output product streams of the PPP can be ured using absorption-edge densitometry. The Pu concentrations in the 1BP stream can easured at the L_{III} edge using either x-ray tube[3] or bremsstrahlung sources.[4] For onium concentrations of approximately 5 g/L a precision of 1-2% can be obtained.[3] The stream also could be measured at the K edge using longer cells. For highly radioactive itions a curved crystal spectrometer may be used as an energy filter for an energy dis- ive detector.[5] Additional research and development is required to evaluate the effect ission products on the method and to measure the precision and accuracy under plant itions.

The plutonium isotopic composition and concentration at concentrations representative he 3PCP stream for reprocessing samples can be measured using a radioisotope source at K-absorption edge. Using a ^{75}Se-^{57}Co source as suggested by Canada,[6] Hofstetter, et obtained a precision (1σ) of 0.2 to 0.5% for plutonium concentrations between 150-500 The plutonium isotopic composition of these samples was similar to that expected for t-cycle LWR fuel.

The recycle stream concentrations generally are expected to be less than 0.1 g/L, hence er measurement precision can be tolerated than for the product streams. In-line alpha tors have been installed in these streams for process control to assure that columns operating properly. These alpha monitors are being evaluated at the BNFP for the ititative measurement of plutonium in flowing streams. They have been shown to have a ear response to plutonium concentration in the range between 10^4 to 10^8 dpm/mL with an a/beta discrimination factor of 10^4.[8] A relative precision of 5-10% (1σ) for plutonium centrations should be obtainable.

One area that presents a problem in measuring plutonium in the plutonium purification is the determination of in-process holdup. Capacities of the tanks and columns in area are shown in Table III.

Approximately 22 kg of the 41-kg holdup is in the 1BP tank and the concentrator, and be estimated from the in-line concentration instruments and tank volumes. However, the int in the columns cannot be measured accurately, and can contribute significantly to uncertainty in plutonium content of the PPP.

An alternative to actually measuring plutonium concentration is the estimation of con- rations from a knowledge of column operation.[9] The feasibility of this approach was ed by mathematical simulation of column operation for the 2A column. A schematic of 2A column, with flow rates into and out of the column, is shown in Figure 3. The onium holdup as a function of 2AF, 2AS, and 2AX flow rates was modeled using the SEPHIS e,[10] and results are summarized in Figure 4.[11] The largest variations in holdup occur low 2AX (organic) flow rates. However, the data indicate that from a knowledge of the it stream flow rates the plutonium holdup in the column can be estimated. The accuracy the estimate has to be verified with actual column operation.

DISCUSSION AND RESULTS

The operation of the plutonium purification process was mathematically modeled using te Carlo techniques.[9] The measurement points and associated errors for each point are arized in Table IV. Four different strategies were used to evaluate the diversion sitivity, and are summarized in Table V. The measurement errors for the four cases are

TABLE III

IN-PROCESS HOLDUP IN TANKS AND VESSELS OF THE PPP

Identification[a]	Volume (L)	Plutonium Concentration (g/L)	Plutonium Holdup (kg)
1BP tank	1500	4.942	7.4
2A column	700	b	4.6
2B column	500	b	2.8
3A column	600	b	5.4
3B column	440	b	4.8
3PS wash column	20	58.70	1.2
3P concentrator	60	250.	15.

---

[a] See Figure 2.

[b] A model of the concentration profiles and the holdup in the pulse columns is described in Reference 9.

These values are not flowsheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flowsheet.

TABLE IV

MEASUREMENT ERRORS FOR DYNAMIC MATERIALS ACCOUNTABILITY IN THE PPP

		Precision (1σ), %	Calibration Error (1σ), %
1BP	Flow	1	0.5
	Concentration	1	0.3
2AW	Flow	5	1
2BW			
3AW	Concentration	10	2
3BW			
3PCP	Flow	1	0.5
	Concentration	1	0.3

TABLE V

MEASUREMENT STRATEGIES

Case	Balance Period	Recalibrate Flow	In-Process Inventory Measurement Precision (1σ), %
1	8 h	--	10
2	8 h	24 h	10
3	8 h	24 h	5
4	1 h	24 h	5

Measurement of concentration and flow every 0.25 h.

marized in Table VI, and show that in each case measurement error is dominated by uncer-
nties in in-process inventory. The diversion sensitivity was determined using decision
lysis theory described in a preceding paper ("Decision Analysis for Dynamic Accounting
Nuclear Material" by James P. Shipley), and is shown for cases 1 and 4 in Table VII.
rovement in diversion sensitivity is obtained by increasing measurement frequency. Note
t for case 4 (1-h measurement frequency) a diversion sensitivity of 4.2 kg at the end of
week is obtained. This can be compared to the conventional sensitivity of 75 kg per
-month inventory period.

TABLE VI

MEASUREMENT ERRORS IN FOUR DYNAMIC-ACCOUNTABILITY CASES

	Variance (kg^2 Pu) (standard deviation, kg Pu)			
	Case 1	Case 2	Case 3	Case 4
transfers ne-week average	0.022 (0.15)	0.022 (0.15)	0.022 (0.15)	0.00073 (0.027)
process inventory ne-week average	0.98 (0.99)	0.98 (0.99)	0.36 (0.60)	0.36 (0.60)
erial balance ne-week average	1.99 (1.41)	1.99 (1.41)	0.74 (0.86)	0.74 (0.86)
um				
nd of day	2.13 (1.46)	2.13 (1.46)	0.89 (0.95)	0.89 (0.95)
nd of week	8.51 (2.92)	3.29 (1.81)	1.98 (1.41)	1.98 (1.41)

TABLE VII

DIVERSION SENSITIVITY[a] FOR THE PLUTONIUM PURIFICATION PROCESS

surement Case	Average Diversion per Balance (kg Pu)	Detection Time (h)	Total at Time of Detection (kg Pu)
(8 h)	4.2	8	4.2
	0.30	168 (1 week)	6.3
	0.15	672 (4 week)	12.6
(1 h)	2.6	1	2.6
	0.075	24	1.8
	0.025	168 (1 week)	4.2

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s determined consistently with ERDAM Appendix 7401-C, "Nuclear Materials Management and
afeguards System Handbook."

The safeguards materials accountability improvements described in this report are based
a measurement overlay for an existing reprocessing plant. Hopefully, the system could
improved if it could be incorporated into the plant design at an early stage. The fol-
ing were identified as areas of safeguards concern for future facilities of this type.

Location of Centrifuge

One source of sampling error at the input accountability tank results from the suspended
ticulates in the dissolver solution. Solids could account for as much as 0.3% of the
countability-tank volume and 0.8 kW of heat per tonne of dissolved fuel. Consideration
uld be given to installing the centrifuge between the dissolver and the accountability
k, as has been done for the Japanese plant at Tokai and the proposed EXXON Nuclear Com-
y plant.

Accountability Tank

Further consideration should be given to using load cells to measure the volume of input accountability tank. The design must, as much as possible, isolate the tank from associated piping. If practicable, mass measurements using load cells would be particu ly advantageous for processing fuels with higher burnup or shorter cooling times, which would have higher intrinsic heat-generating capacities.

Flowmeters

Flowmeters having provision for periodic recalibration should be installed in speci crucial process streams; a measurement accuracy of 1% or better is required. A 5-10% m urement accuracy is acceptable for flowmeters in waste streams.

Concentration Sensors

In-line or at-line detectors should be incorporated to measure plutonium concentrat in major process streams with a measurement accuracy of 1% or better, and in waste stre with an accuracy of 5-20%.

Instrument Accessibility

All in-line or at-line instruments, including flowmeters and concentration sensors, should be installed in a manner that permits ready accessibility for recalibration and maintenance by plant personnel or inspection by the national or international safeguard staff. Sensors should be directly interfaced to the safeguards computer system for dyn materials accounting.

HA Contactor

An improved decontamination factor may be attainable at the front end of the separa tions process by increasing the number of stages in the HA contactor, or by providing a second decontamination cycle before partition, as has been done effectively in some oth facilities. The reduced radioactivity in the uranium-plutonium product stream might pe mit inclusion of an additional accountability point before the plutonium-process area a the HS column. This would be highly desirable both for process control and for safegua in the event that a co-processing mode of plant operation is selected.

3P Concentrator

Concentration of the final $Pu(NO_3)_4$ from 60 to 250 g/L is primarily for convenience storing and shipping. Under current NRC regulations co-location of reprocessing and nitrate-to-oxide conversion facilities will be required. If the concentration of the f plutonium-product solution from the reprocessing plant is maintained below 50 g/L, this solution can be used directly as feed for the conversion plant, and the 3P concentrator associated heater and feed tanks can be eliminated. From a safeguards viewpoint, this would increase the amount of solution required to divert 1 kg of plutonium by a factor 4 to 8, and would decrease holdup by the volume of the concentrator. In order to provi a 3- to 6-month product-storage capacity, the number of nitrate-storage tanks would hav to be increased proportionally unless the plutonium-product output were directly couple to the input of a contiguous conversion plant.

Centrifugal Contactor

In general, in-process inventory can be reduced by a factor of 20 by using centrifu contactors in place of pulsed columns in the plutonium-purification area.[12] Using a French-designed eight-stage contactor, the pulsed columns in the plutonium-purification rea could be replaced as follows:

2A column - 9 contactors
2B column - 3 contactors
3A column - 4 contactors
3B column - 2 contactors.

n addition to low holdup, centrifugal contactors provide added advantages of rapid drain-own with negligible drain-down volume, and rapid startup after shutdown. Disadvantages nclude relatively low flow rates of 100 L/h in both aqueous and organic phases, greater ccessibility of material to possible diversion, and more stringent design requirements for ptimizing organic/aqueous flow ratios.

CONCLUSIONS

The primary conclusion from this study is that current technology can provide improved rocedures for safeguarding strategic quantities of SNM in a nuclear-fuel reprocessing acility at a reasonable cost and with minimal disruption of production processes. The ystem design must be facility-specific for each reprocessing plant, taking into considera-ion such features as plant throughputs, side streams, materials control philosophy, and quipment maintenance features. The formation of a dynamic materials balance area around he plutonium-process area adds another level of safeguards protection of plutonium in its ost concentrated and pure form, the form most attractive to a potential divertor.

The study has also identified generic features and processes in the reference facility hat contribute most importantly to measurement uncertainties and that could be improved in uture facility designs if they were to be optimized for their safeguardability.

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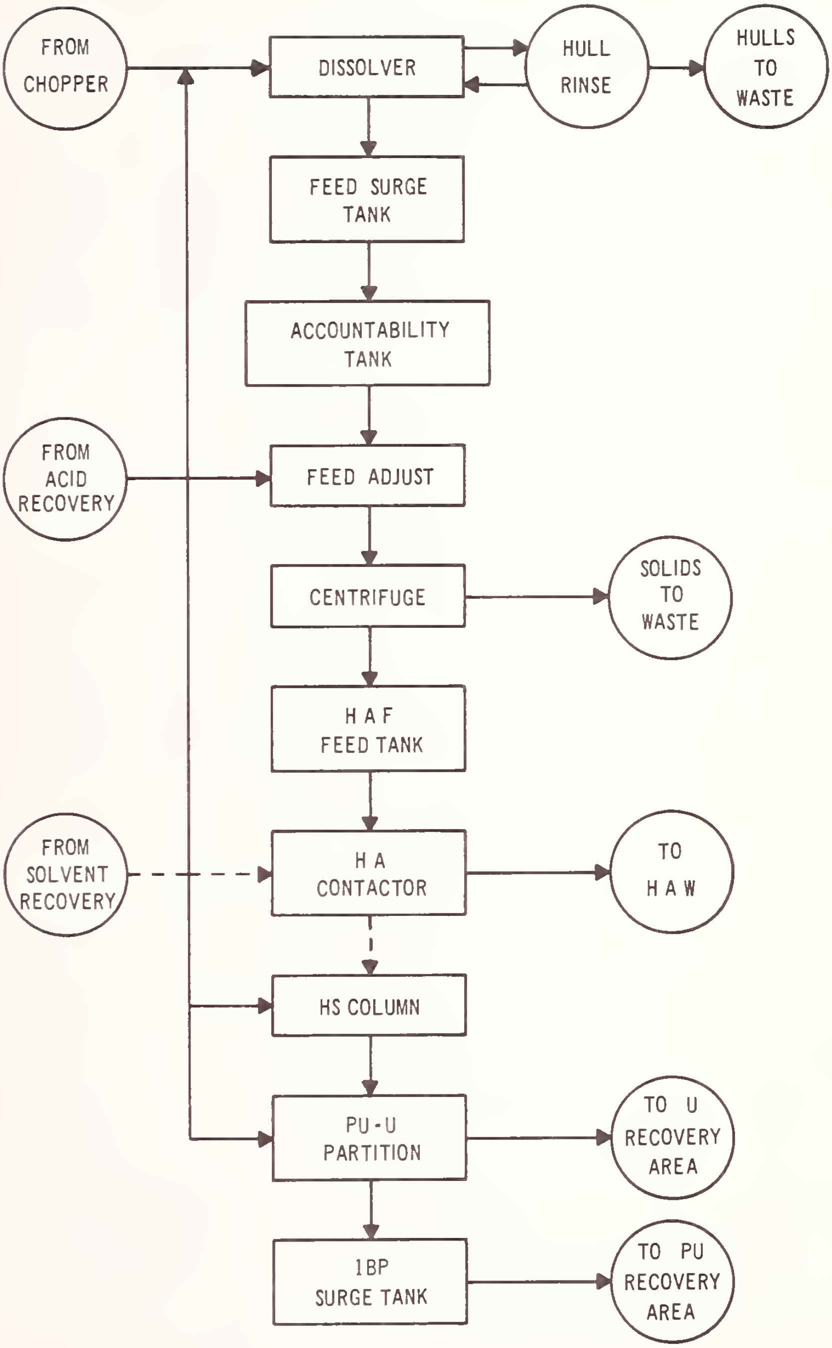


Figure 1. Dissolver-separations process block diagram.

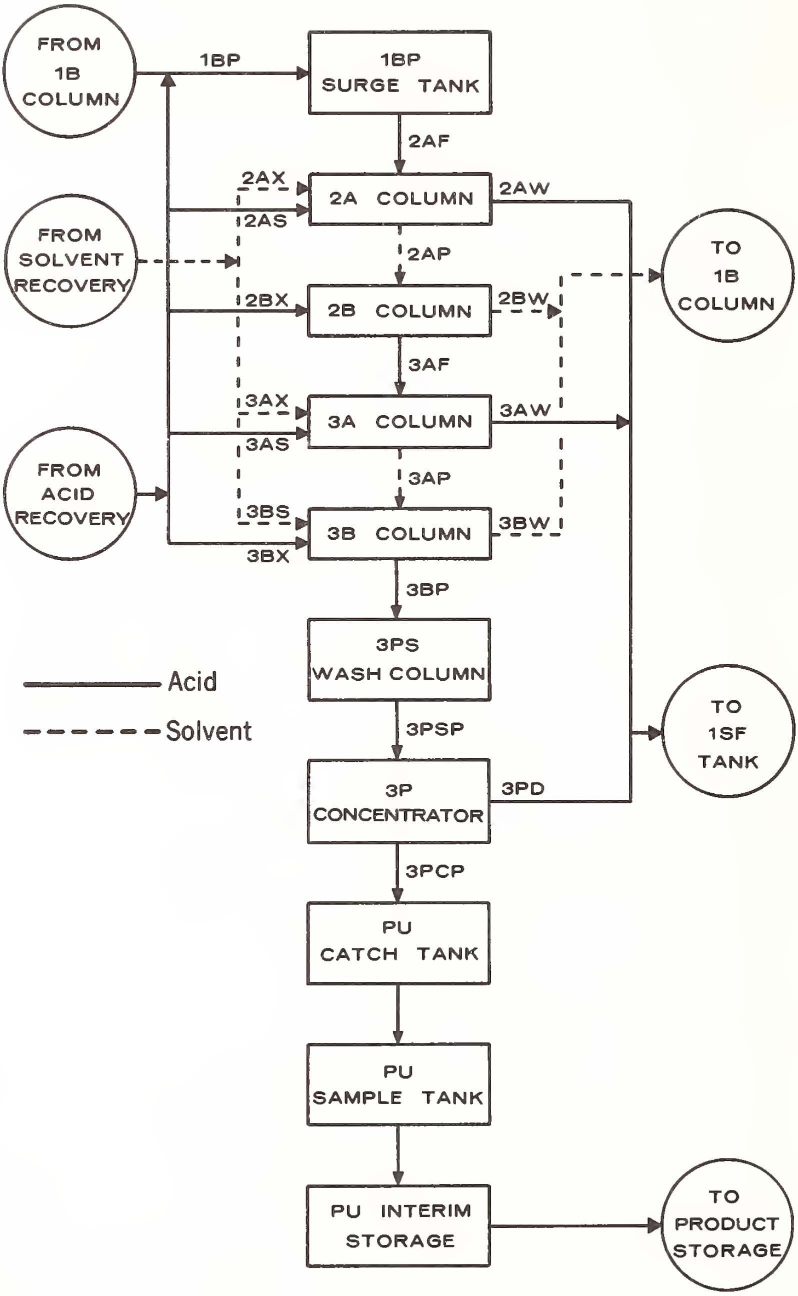


Figure 2. Plutonium purification process block diagram.

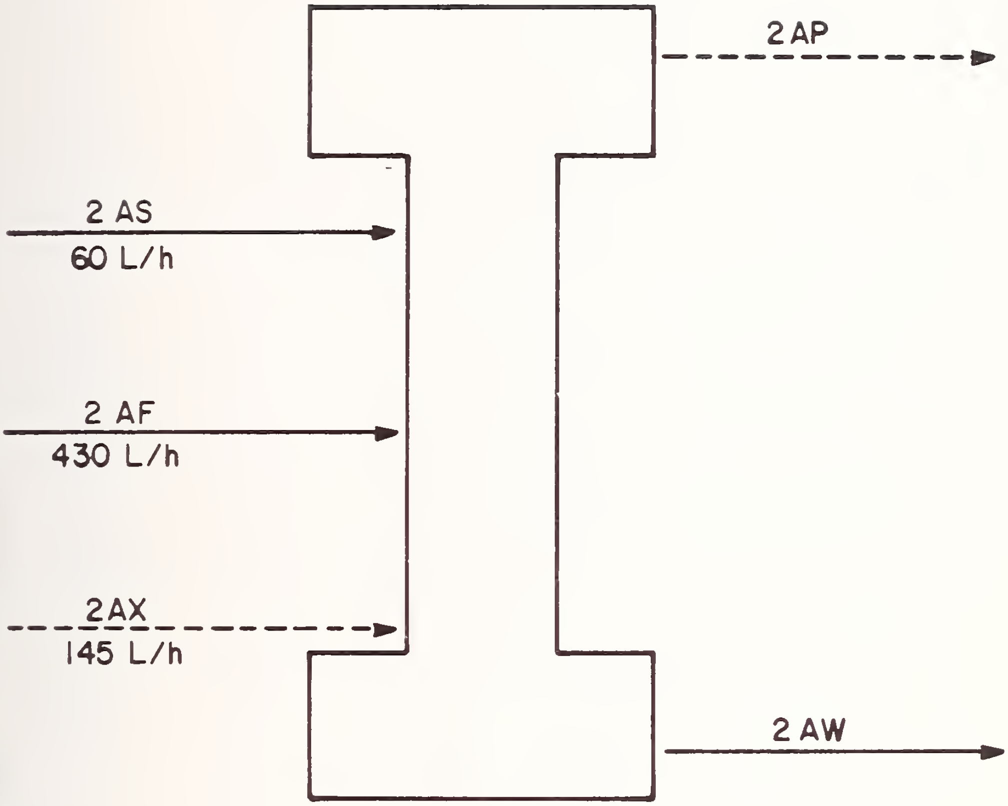
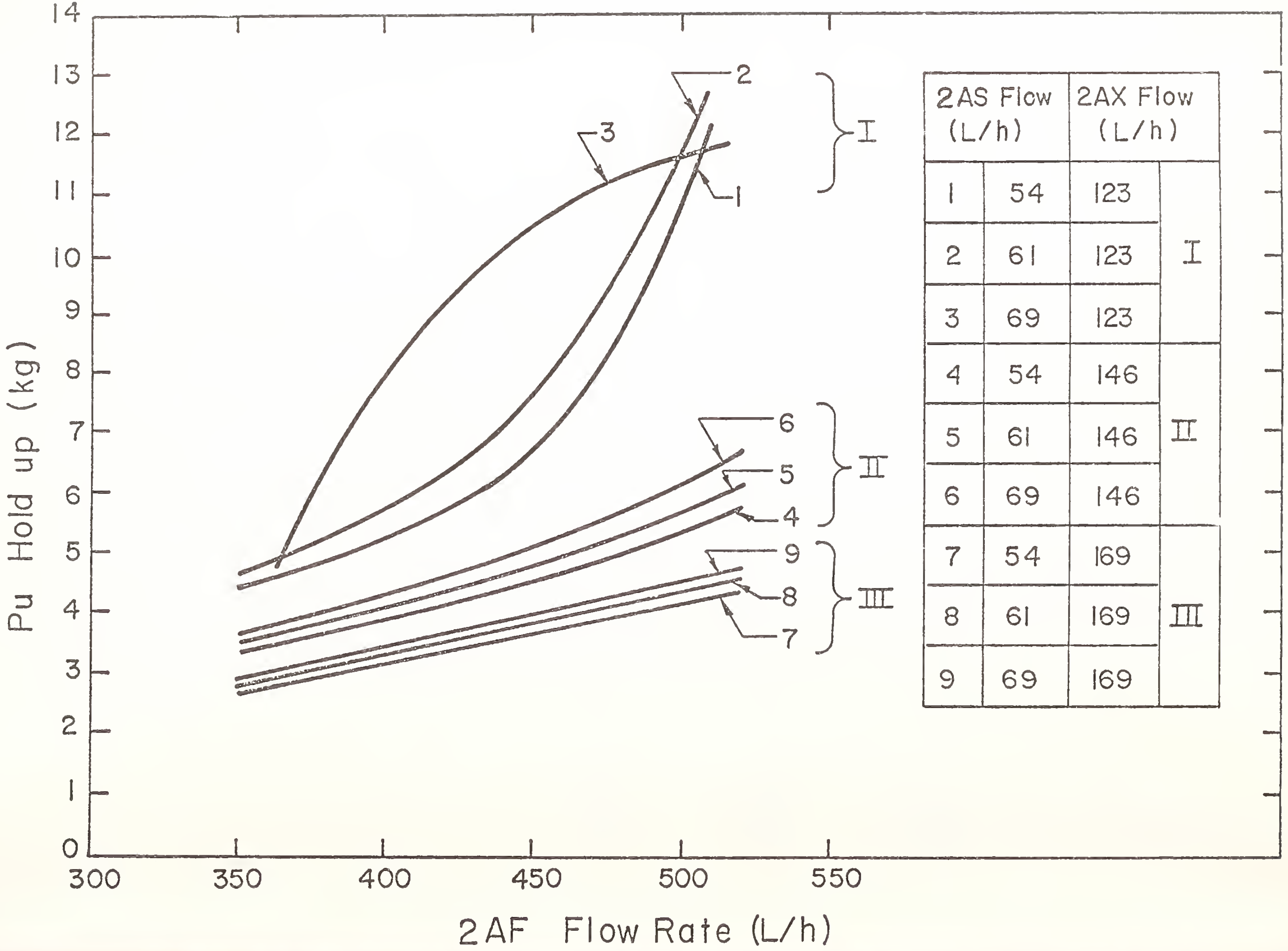


Figure 3. Schematic of 2A column.


Pu Hold up (kg)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
2AF Flow Rate (L/h)
300
350
400
450
500
550
1
2
3
4
5
6
7
8
9
I
II
III
2AS Flow (L/h)
2AX Flow (L/h)
1 54 123 I
2 61 123
3 69 123
4 54 146 II
5 61 146
6 69 146
7 54 169 III
8 61 169
9 69 169

rification of ^{235}U Enrichment in SNM Receipts at the DOE Feed Materials Production Center

by

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ABSTRACT

A diversity of uranium-bearing, nonirradiated materials with ^{235}U assays from fully depleted to a maximum of 10 wt % ^{235}U, is routinely returned to this DOE site for reprocessing. It is necessary to confirm the ^{235}U isotopic content of Special Nuclear Material (SNM) receipts both for accountability and nuclear criticality safety purposes.

Methods and instrumentation have been developed for an isotopic verification facility by which ^{235}U isotopic content is rapidly and nondestructively determined. The 185 keV gamma photon emitted by ^{235}U is measured using a dual-channel gamma spectrometer which incorporates automatic background subtraction and an optimized collimator/NaI(Tl) detector assembly. Measured activities are then related to ^{235}U isotopic content by means of appropriate standards that have been destructively analyzed in the laboratory.

Use of the described facility for the past seven years has resulted in improved nuclear safety procedures, better use of storage space and more stringent nuclear materials accountability.

KEYWORDS: Gamma spectrometry; ^{235}U enrichment; nondestructive analysis; sodium iodide detection; isotopic verification

INTRODUCTION

e National Lead Company of Ohio is the contract operator of the Department of Energy (DOE) ed Materials Production Center (FMPC). The FMPC is located near the village of Fernald, proximately 20 miles northwest of Cincinnati, Ohio. Nonirradiated uranium materials, th ^{235}U enrichments of less than 10 wt %, are routinely returned to the FMPC for recovery uranium, which is subsequently returned to the nuclear fuel cycle.

the past difficulties have been encountered with scrap receipts in the areas of both ecial Nuclear Materials (SNM) accountability and criticality control. Some of these fficulties were previously reported.[1] These problems are the results of several things: strumentation may not be available to perform ^{235}U isotopic assays and calculated values e therefore used; in other cases ^{235} U assays are not obtained because enrichment values e thought to be reasonably documented; another, and perhaps the most common reason for ^{5}U isotopic discrepancies is human errors involved in handling both the material and its companying paperwork.

. L. Dunaway. "Enrichment Errors in Interplant Shipments". USAEC Report NLCO-1083 June 29, 1971).

Since it was felt that these problems could continue in the future, and their consequenc could have serious nuclear criticality potential in our processes, a program was initiat to check the ^{235}U isotopic content of virtually all incoming SNM receipts. Rigid materi handling and operational procedures have been adopted to preclude the accidental (or sur titious) loss of SNM's or the acceptance of highly enriched materials by mistake.

EXPERIMENTAL

It became apparent several years ago that a rapid, nondestructive means of verifying th ^{235}U isotopic content of uranium receipts was needed. Requirements for the method were it should be inexpensive and relatively simple to operate. Nontechnical personnel were operate the instrumentation on a day-to-day basis.

Theory of Operation

A technique based on the measurement of the 185 keV gamma photon, emitted by ^{235}U (54% the time)[2], was chosen as the most economically and operationally acceptable method. T approach finally adopted was a refinement of a previously described method.[3] It can be easily demonstrated that the ^{235}U isotopic content is directly proportional to the meas 185 keV activity, for uranium in which the measured thickness greatly exceeds the 185 k e-fold attenuation distance (infinitely thick for our purposes).

Given the geometric configuration of Figure 1, we readily conclude that the incremental count rate "d(cr)" arriving at the NaI(Tl) detector from uranium metal can be described

$$d(cr) = \varepsilon \Gamma I \rho A \exp[-(L-x)/\lambda]dx \qquad (1)$$

where,

cr = count rate (c/s)
ε = detector efficiency for 185 keV gamma rays
L = slab thickness (cm)
λ = e-fold attenuation distance (cm) for 185 keV gamma rays in uranium (mean-free-path)
Γ = specific 185 keV gamma ray activity (4.255×10^4 gamma rays/s - g ^{235}U)
I = ^{235}U weight fraction
ρ = uranium density (g/cm^3)
A = area viewed by the detector (cm^2)
μ = uranium linear attenuation coefficient (cm^{-1})

Integrating over the slab thickness L yields

$$cr = \varepsilon \Gamma I \rho A \lambda (1-e^{-L/\lambda}) \qquad (2)$$

assuming $L >> \lambda$, attentuation with regard to spatial distances can be disregarded and

$$cr = \varepsilon \Gamma I \rho A \lambda \qquad (3)$$

or, since $\lambda = 1/\mu\rho$, and rearranging terms we have:

$$I = \frac{\mu}{A\varepsilon\Gamma} \cdot (cr) \qquad (4)$$

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[2] C. M. Lederer, J. M. Hollander, and I. Perlman. "Table of Isotopes", 6th ed., New York: Wiley (1967).

[3] B. L. Twitty and H. W. Humphrey. "A Self-Correcting Inspection Monitor for Determin the ^{235}U Level in Reactor Fuel Cores". USAEC Report NLCO-1011 (May, 1968).

[4] R. B. Walton. Personal Communication to H. W. Humphrey from R. B. Walton of LASL, Los Alamos, N. M. (March 5, 1971).

t is interesting to note: (1) that in this form (Equation 4) the ^{235}U isotopic content does ot depend explicitly on the density, and (2) all the terms in the first portion, of the ight side of the equation are constants, therefore the ^{235}U isotopic content is directly roportional to the measured 185 keV gamma activity.

nfortunately, most of the materials received at this site are not merely uranium metal. ranium in practically every conceivable geometric configuration and chemical composition as been returned for reprocessing at one time or another. Some of the materials received or reprocessing are listed in Table I. The listing does not, of course, include all the orms and matrices returned to this site for reclamation of uranium values. The physical imensions of receipts have varied from several mils (uranium wire) to large railroad tank ars. Uranium concentrations ranging from several hundred ppm (contaminated copper) to ure metal (100% U) have been encountered.

ince the matrices to be measured are quite varied, a means of correcting for geometry, ontainer (cladding), and composition is necessary. Variations in both size and shape can e minimized using a series of graded lead collimators. The largest size collimator is ormally used, consistent with both the surface area of the specimen and the ability to eproducibly place the specimen on the detector. The greater the area viewed, the greater ill be the measured count rate (hence the more precise will be the reading).

mathematical model has been formulated to compensate for heterogeneous regions (voids) ormed by nonuranium materials localized in the detector viewing area. Since the procedure s based on the assumption of a point source of radiation, working relationships should be etermined empirically using actual broad-beam conditions.

ne inverse square law states that radiation intensity is inversely proportional to the quare of the source-to-detector distance (D). The ratio of activity measurements (A) aken at two distances "a" and "b" are then given by

$$A(a)/A(b) = \left[\frac{D(b)}{D(a)}\right]^2 \qquad (5)$$

calculations were made at one inch increments and the results plotted, the lower (no void) urve shown in Figure 2 would result. Moving the source 1/2 inch upward to simulate the isplacement due to a 1/2 inch void, and so on for the other void thicknesses, would yield ne other indicated relationships. To use the algorithm, one determines the activity ratio or an unknown material at two different source-to-detector (S-T-D) distances. Referring Figure 2 should provide the approximate void size (if any); the appropriate void correcion factor can then be determined using the upper family of curves.

should be noted that the affect of voids within a container can be minimized by judicious ljustment of the S-T-D distance. For instance, if we measure the activity of a point ource located 1 inch from a detector and then move the source 1-1/2 inches away from the etector and take a second measurement (simulating a 1/2 inch void) the activity ratio would e

$$A_{1.5} / A_1 = 0.444 \qquad (6)$$

epeating the measurements at 12 inches and 12-1/2 inches we find

$$A_{12.5}/A_{12} = 0.922 \qquad (7)$$

, less than 8% error is introduced into the measurement at a S-T-D distance of 12 inches, a 1/2 inch void is present.

practice, the selection of the S-T-D distance is usually a compromise. This is seen more early using the above example. Increasing the S-T-D distance from 1 to 12 inches reduces ne activity reaching the detector by more than 99%. This of course means that measurement mes must be increased to insure adequate counting statistics. The minimum S-T-D distance defined in practice by the thickness of the collimator employed.

In addition to the 185 keV photon emitted by ^{235}U, most uranium compounds also emit radia- tions of 765 keV and 1001 keV (exceptions would be freshly purified materials). These tw gamma rays are emitted during the decay of ^{234m}Pa (UX_2), the granddaughter of ^{238}U, and account for most of the sample background via Compton interactions. The ^{235}U photopeak rests upon this Compton continuum from higher energy photopeaks. The collimator thicknes is therefore selected to maximize the difference between ^{235}U and ^{234m}Pa transmissions (Figure 3). Lead was chosen for the collimator material due to its high density, availab and malleability. Sodium iodide (thallium activated) was the detector of choice due to i high gamma ray efficiency, relative availability, simplicity, and low cost. The detector thickness was optimized by differentiating the expression for the difference between the two transmission curves (Figure 4) and setting the first derivative equal to zero to find the maximum. An optimum thickness of 0.53 inch was thus calculated.

Although spatial effects play a very important part in nondestructive gamma spectrometry, equally important (and often overiding) effect is the sample composition itself.

It was shown earlier that for uranium metal, the 185 keV count rate was independent of th density of the matrix emitting the radiation. In the case of uranium compounds and resid however, this is not the case. Equation (4) must be modified to include the effect of th nonuranium components of the matrix. Quantitatively this becomes[5]

$$I = \left[\frac{\mu}{A\varepsilon\Gamma}\right]\cdot(F)\cdot(cr) \tag{8}$$

where,

$$F = \left[1 + \frac{\mu_m\rho_m}{\mu\rho}\right]^{-1} \tag{9}$$

μ_m and ρ_m are the mass absorption coefficient and density of the nonuranium matrix mater respectively, and μ and ρ are as previously defined.

The mass absorption coefficient is a slowly varying function of atomic number[6] up to abou $Z = 30$; beyond that it is seen to increase rather rapidly (Figure 5). Although the chem composition of receipts is not always known, quite often it is not required. From Figur we see that the ratio of $\mu_m/\mu \simeq 0.08$ for $Z \leqq 30$. If $\rho_m/\rho \leq 1.0$ (50% U or more) the affec upon the analysis would be an error of less than 10%. In practice this means that the 2 isotopic content of uranium compounds and rich residues ($\geq$ 50% U) can be determined by comparison with a single standard without making a correction for matrix absorption. If the matrix and uranium concentration are known, "F" can be evaluated; if a standard and unknown are of the same material, "F" may be neglected. The technique is not applicable materials containing high Z elements in unknown concentrations or to mixtures containing less than an "infinite" thickness of material, unless the values of these parameters are known.

An "infinite" thickness of material "T", for purposes of this assay, is defined as that quantity (thickness) necessary to give 95% of saturation. Quantitatively this becomes

$$T = \frac{10 \ln 0.05}{-\mu}\ \text{mm} \tag{10}$$

Infinite thicknesses for several of the more common uranium compounds are listed in Tabl

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[5] J. L. Parker. Personal Communication to H. W. Humphrey from J. L. Parker of LASL, Los Alamos, N. M. (December 31, 1970).

[6] J. H. Hubbel. "Photon Cross Sections, Attenuation Coefficients, and Energy Absorption Coefficients from 100 keV to 100 GeV". NSRDS-NBS-29. (August, 1969).

ation (5) must also be modified to reflect the effect of container attenuation. The net ect of container attenuation is to lower the measured count rate. If the container (or adding) thickness is known (or can be measured) the container activity transmission is lculated using the relationship

$$C = C_o e^{-\mu_c t} \qquad (11)$$

ere,

C_o = The unattenuated count rate (c/s)
C = The attenuated count rate (c/s)
μ_c = Linear absorption coefficient of the container material (cm^{-1})
t = Container thickness (cm)

corporating this into equation (8) we have

$$I = \left[\frac{\mu}{A\varepsilon\Gamma}\right] \cdot \frac{(cr)\ e^{\mu_c t}}{\left[1 + \frac{\mu_m \rho_m}{\mu\rho}\right]} \qquad (12)$$

effect of container thickness upon the measurement of ^{235}U enrichment is vividly ustrated in Figure 6. Metal thicknesses of greater than 0.025 inch produce results that low by 10% or more.

above analytical expression (Equation 12) serves as the basis for the measurement of nown enrichments. In practice, however, there are other considerations that must be en into account.

Instrumentation

the gamma activity of an aged uranium sample is measured with a NaI(Tl) detector, a ctrum similar to Figure 7 is obtained. As seen in the figure, the ^{235}U peak rests upon izeable Compton continuum. At equilibrium, the contribution of ^{234m}Pa to the ^{235}U peak a is fairly constant. If the uranium is freshly purified, the dotted spectrum of Figure ould result upon gamma activity measurement. Following purification, the ^{234m}Pa activity a uranium matrix will continue to grow for 5 or 6 months until equilibrium is once again ched (Figure 8). Since the ^{234m}Pa contribution to the ^{235}U peak area is also dependent enrichment, geometrical configuration and composition, a Compton background subtraction t be made. Several different approaches have been taken by various analysts to determine s background contribution, for as many different reasons. The method chosen for our use to perform a Compton background measurement in the area immediately adjacent to the 185 photopeak area, on the high energy side.

hough a single channel analyzer (SCA) system would be the simplest and least expensive, s type of system requires more work from the analyst and provides additional opportuni- s for error. A dual channel analyzer (DCA) system (Figure 9) was ultimately chosen since was still relatively inexpensive and did not suffer from the aforementioned deficiencies the SCA system.

of the electronic components of the system were manufactured by Harshaw Chemical Co. and of the NIM type (except of course for the integral probe assembly). The NJ-20 Up-Down nter automatically subtracts the background from the gross count yielding the net count its output. The total cost of the instrumentation was approximately $2,950 when chased in 1970.

IVF Facility. The above DCA system is permanently housed in the southwest corner of warehouse near the receiving dock which is dedicated to temporary storage of SNM receipts. The nuclear instrumentation and associated materials handling equipment are referred to by personnel at the FMPC as the Isotopic Verification Facility (IVF).

Figure 10 illustrates the layout of the IVF. A conveyor is located behind the monitoring table which permits large objects (e.g. drums, ingots, etc.) to be moved from the outside and positioned above the NaI(Tl) detector with the aid of the overhead hoist. The table c the right is adjustable to accommodate long, or irregularly shaped objects. A calibrated vernier under the table permits reproducible adjustments to the height of the radiation detector. A large overhead door permits easy access to the IVF by fork lift trucks to br in bulky materials or larger quantities of receipts. Provision has been made to change collimators on the NaI(Tl) detector to permit analysis of the various geometrical configu tions received. The temperature of the IVF is controlled year-round to approximately ± 5 to insure instrumental stability.

Support Instrumentation. The weight and piece count of each shipment is verified ju outside of the IVF in Building #71, prior to ^{235}U enrichment verification. For nuclear safety purposes, materials are stored in the same configuration in which they were shippe until the ^{235}U content can be verified.

Should it be necessary or expedient to monitor ^{235}U enrichments in the field, a recently acquired portable Eberline dual channel gamma spectrometry system (SAM-II) is employed. This instrument employs a two inch diameter by one-half inch thick NaI(Tl) scintillation crystal embedded in a lead collimator/shield probe assembly (RD-19). The NaI(Tl) crystal is doped with ^{241}Am to provide instrumental stabilization in the presence of electronic o ambient environmental changes.

If materials, or assays, are suspect for any reason, corroborating analyses are performed at the analytical laboratory. A 20 cc Ge(Li) detector system is available to perform non destructive gamma analyses. This instrument, mainly because of its superior resolving ability, has proven to be extremely useful over the years in diagnosing spectral difficul In addition, where materials can be sampled, destructive gamma and mass spectrometric analyses are often used.

Verification Procedures. All verification procedures are governed by FMPC Standard Operating Procedure 1-C-908 "Checking the ^{235}U Isotopic Identification of Materials Received from Off-Site", dated January 12, 1973.

Both analyzers are calibrated each day prior to use. The calibration procedure requires approximately 15 minutes per day and involves taking 20 second measurements at varying threshold readings on each SCA with a relatively small window setting. A completed calib tion sheet is illustrated in Table III and plotted in Figure 11. The data points marked L, P, and L' represent the low, peak, and equivalent threshold points, respectively. Sir the shape of the spectrum is dependent on the enrichment, material composition and geomet the uranium calibration should be conducted using a specimen from the shipment to be veri

It will be observed in Figure 11 that there is a 0.05 difference in threshold settling be tween the two analyzers. This difference is taken into account when the background setti is determined for #2 SCA as seen in Figure 12. The gross count threshold "E", is simply "L_1"; the gross count window is

$$\Delta E_1 = L_1' - L_1 \qquad (13)$$

The background count threshold is $(L_1'-0.05)$ and the background window $\Delta E_2 = \Delta E_1$. Having established the calibration, the instrument can now be standardized.

ardization normally takes one of several forms: (1) if all of the units within a ship- are similar in physical and chemical properties and have the same stated enrichment, a element statistical standardization is performed, (2) if the units of a shipment are eved to be similar, but with varying enrichments, several representative units are cted for use as standards, (3) shipments with varying uranium concentration and enrich- require additional information to effect an assay. Verifications can often be performed aterials in this latter category using assumed uranium compositions from shipping docu- s.

selecting the appropriate collimator, materials with the same chemical and physical erties as well as identical ^{235}U enrichments are standardized after randomly selecting its from the group. The net count rate is then determined for each unit to a coeffi- of variation of ±1.5% (3σ), or better.

ength of time necessary to attain a relative counting precision of ±1.5% is a function th the gross ^{235}U count "G" and the Compton background count "B". Since the net count s

$$N = G - B \tag{14}$$

tandard deviation "σ" associated with the net calculated count rate, is determined by gating the errors involved in both measurements. Or,

$$\sigma_N = \pm\sqrt{\sigma_G^2+\sigma_B^2} \tag{15}$$

ince for a random Poisson distribution the precision can be estimated by

$$\sigma_G = \pm\sqrt{G} \qquad \sigma_B = \pm\sqrt{B} \tag{16}$$

σ (99%) precision associated with a net activity measurement is then

$$3\sigma_N = \pm\, 3\sqrt{G + B} \tag{17}$$

fficient of variation of 1.5% is attained when

$$1.5 = \frac{100 \times 3\sqrt{G + B}}{(G - B)} \tag{18}$$

fining k ≡ B/G, the gross count necessary to obtain a coefficient of variation of 1.5%

$$G = 40{,}000\,\frac{(1 + k)}{(1 - k)} \tag{19}$$

ength of time necessary to attain a 1.5% counting precision is seen to double (using ion 19) as the background increases from 20% to 50% of the gross count.

g measured the net count rate of 10 randomly selected units from the shipment, the one which most nearly represents the average for the group is selected as the standard. lly, since there are so many undefined variables, a small specimen is taken from the ard and destructively analyzed. All subsequent assays are then compared to the remain- ortion of the standard in the following manner. Ten consecutive net activity measure- are taken for the standard and the dispersion of the data determined at the 99% (3σ) dence level. The upper and lower acceptance limits are then simply

$$\begin{aligned} \text{UAL} &= \bar{x} + 3\sigma \\ \text{LAL} &= \bar{x} - 3\sigma \end{aligned} \tag{20}$$

where "$\overline{x}$" is the average value computed for the ten measurements. An unknown activity measurement "C_x" is acceptable when

$$LAL \leq C_x \leq UAL \tag{21}$$

The ^{235}U isotopic enrichment corresponding to count "C_x" is calculated from the simple tionship

$$\frac{I_x}{C_x} = \frac{I_s}{C_s} \tag{22}$$

where,

I = ^{235}U isotopic enrichment (wt %)
C = Integrated count rate
s = standard
x = unknown

Occasionally, when the number of units within a shipment is prohibitively large, or the history of the material suggests a uniformity of ^{235}U enrichment, a relatively poorer precision will be found acceptable. For example, a recent shipment contained 4,123 ni clad uranium plates enriched to 1.865 wt % ^{235}U. The average net count rate for the standard was 11,850 counts/15 seconds and the 3σ precision was ± 0.108 wt % ^{235}U (5.79 coefficient of variation). Had this shipment been counted to a relative precision of a 2.5 minute count per unit would have been required. Operationally this would have required 170 mandays, compared to the 17 mandays actually used.

The decision to either accept or reject an assay is based upon a predetermined, object criterion. If the shipper's claimed ^{235}U enrichment agrees with the determined value within ± 0.5 wt % ^{235}U (99% C.L.), it is accepted. Obviously an accuracy of ± 0.5 wt % would be unacceptable from an SNM accountability standpoint since large MUF's could re from such a procedure. Although the shipment is accepted if within ± 0.5 wt % ^{235}U, t actual nondestructive assay is performed to a precision of ± 0.1 wt % ^{235}U, or better. this way questionable results are identified and destructive assays are performed wher indicated.

Figure 13 illustrates the nuclear safety implications of the ± 0.5 wt % ^{235}U acceptanc criterion. Curve "A" represents the safe mass[7] storage relationship; curve "B" demons the critical mass for the indicated enrichments. Curve "C" represents the effect of s materials at a safe mass, for a stated enrichment of "I", when the enrichment could ac be (I + 0.5) wt % ^{235}U. It will be noted from the figure that for enrichments below 1 % ^{235}U the storage mass would exceed the critical mass, if the case of maximum error w assumed. This difficulty can be overcome in several different ways.

All materials containing less than 1.55 wt % ^{235}U can be stored at the safe mass for enrichment (approximately 360 lbs), or less restrictive criticality parameters may be as a means of control (if practical). Other means of criticality control, in additior mass, are: slab thickness, cylinder diameter, container volume, concentration, density mass per unit area.

A second type of standardization is employed for materials of similar chemical and phy properties but with varying ^{235}U enrichments. For this type of shipment a quite accu standardization can be performed by selecting several units that will be used as stan

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[7] D. L. Dunaway. "FMPC Nuclear Safety Guide". Unpublished. (Revised January 15, 1968

racket the anticipated range of ^{235}U values. A linear regression is then performed the method of least squares. Raw data is fitted to an equation of the form

$$y = a_o + a_1 x \tag{23}$$

,

x = wt % ^{235}U
y = net counts/3 minutes
a_o = y-intercept
a_1 = slope

oefficient of Determination "r^2" is calculated to obtain an objective determination of oodness-of-fit of the data to the assumed regression form ($r^2 = 1$ is a perfect fit). ample standardization for K-25 oxides is given in Table IV. All of the computations erformed using a programmable hand-held calculator. Analysis of the data contained in IV indicates that an assay could be performed to a relative precision of ± 2.1% (or r) in the ^{235}U enrichment range indicated.

ents of materials with both uranium and ^{235}U variations present an especially difficult Incinerator ashes are a good example of the type of shipment which requires special ment. Uranium concentrations in this type of material have been found to vary from as s a few tenths of a percent up to almost pure UO_2 (88.15% U). Accompanying this large um variation is a companion ^{235}U enrichment variation from < 1 to 10 wt % ^{235}U. As earlier in equation 12, the ^{235}U enrichment measurement is dependent on the matrix and composition; further information must therefore be available before a ^{235}U assay e effected when dealing with materials with such divergent uranium values.

tion that is always available is to measure the uranium concentration (either destrucy, or nondestructively)[8] or perhaps perform a density measurement.[9] The net result of type of approach is to perform two assays for each item received.

rly novel and inexpensive semiempirical approach is taken at the FMPC to the measureof enrichment in this type of material. This approach is based on the assumption that ally all receipts falling into this category consist of matrices with atomic numbers of less, and the mass attenuation coefficient is therefore fairly constant.

U_3O_8 standards were selected with known ^{235}U and uranium content which were representaof the full range of uranium values normally encountered (viz, 5.67%, 19.83%, and % U).

gamma ray attenuation is exponential in nature, a calibration equation of the following orm was assumed:

$$I = A \cdot \left[c + e^{a + bx} \right] \tag{24}$$

,

I = wt % ^{235}U enrichment
A = net 185 keV activity (usually per 3 minutes)
x = % uranium concentration
a,b,c = calibration coefficients

. Parker. "Nuclear Safeguards Research and Development-Status Report". USAEC Report 605-MS, p. 36. (September - December, 1970).

. Parker, et al. "Nuclear Safeguards Research and Development-Status Report". USAEC rt LA-4705-MS, p. 12. (January - April, 1971).

If L, M and H refer to the low, intermediate, and high uranium standards, then the cali tion coefficients are found from these relationships:

$$b = \frac{\ln\left[\frac{y_H - c}{y_L - c}\right]}{x_H - x_L} \tag{25}$$

$$a = \ln(y_L - c) - x_L b$$

where,

$$y \equiv \frac{I}{A}$$

and the coefficient "c" is found by iteration using the intermediate standard value of A seed value of 1.3×10^{-5} is assumed for "c" and it is either incremented or decrement units of 1×10^{-6} until y_M is attained, correct to six significant decimal places. All standardization calculations are performed electronically using an HP-9810A programmabl calculator.

Normally the assay is standardized once per day, following calibration, and all subsequ measurements that day are normalized to this initial standardization using the count ra the intermediate standard (M).

Since ^{235}U isotopic segregation has frequently been observed within containers, a measu is made of both the top and bottom of each container. This segregation was confirmed b Mobile Nondestructive Assay Laboratory (MONAL) when it was deployed by LASL at the FMP(November, 1970.[8]

In order to effect a ^{235}U enrichment measurement using Equation 24, we assume the vend claimed uranium value to be correct. This approach cannot be used with impunity since stated uranium concentration is not always correct. In the absence of additional and sophisticated instrumentation, this semiempirical approach works quite well for the ma of SNM receipts falling into this category. An example of a completely automated calcu is illustrated in Table V. Should differences exceed the ± 0.5 wt % ^{235}U acceptance criterion, messages will be printed indicating either segregation, or a discrepancy wi vendor's claimed value.

DISCUSSION AND CONCLUSIONS

With the advent of recent terrorist activities, the need for strict safeguards and SNM accountability have taken on new emphasis. Nondestructive SNM measurements are becomi increasingly popular as a viable means of control throughout the entire nuclear fuel c

Although the risks of potential diversion of SNM's are not as great at the FMPC as at ties handling highly enriched, weapons grade materials, our problems are very similar. natural uranium can be made critical, given the proper conditions of geometry and neut reflection.

The FMPC is licensed to handle materials containing up to 10 wt % ^{235}U. However, some ments have been sent to us containing greater than 10 wt % ^{235}U.

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[8] J. L. Parker. "Nuclear Safeguards Research and Development-Status Report". USAEC Re LA-4605-MS, p.36. (September - December, 1970).

ll over 40,000 items have been nondestructively examined during the seven years since the ception of the IVF, with exceptionally little down time. The simplicity of the system has doubtedly contributed to its reliability and longevity.

recent years the IVF instrumentation has been used for purposes other than originally tended. Such uses as inventory verification, sorting of uranium into scrap categories sed on its uranium content, identification of transition points in enclosed systems, etc. ve become increasingly more common.

of the instrument has resulted in the discovery of containers of tungsten that were belled as uranium, boron poison rods in reactor fuel assemblies, and other similar anomalies.

most recent innovative use of the IVF instrumentation has been its use as a uranium tector. Since the derivation of Equation 2 was general in nature, it will apply equally l to other gamma emitters. Since the count rate is directly proportional to both the otope weight fraction and density, if the former is know, the latter may be determined. ven an appropriate gamma ray signature, uranium content can then be determined if the ^{235}U ntent is relatively invariant.

hough ^{238}U has no useful gamma rays, it's granddaughter ^{234m}Pa does, as was discussed rlier. If the assumption that ^{234m}Pa is in radioactive equilibrium with ^{238}U can be made, en the Pa isotope can be used as a signature for uranium.

s principle has been applied to the sorting of aged metallic uranium scrap fuel cores o scrap categories. In this way low yield scrap can be segregated from materials contain- higher uranium concentrations. The cost savings resulting from the use of the IVF trumentation in this way alone has more than paid for the initial investment.

mally, because the IVF instrument is simple to operate, the day-to-day verification asurements are performed by a nontechnical chemical operator. Results are interpreted reports are issued by technical personnel. However, because of this simplicity the stem cannot be universally applied.

pletely unknown receipts, for which simplifying assumptions cannot be safely made, are ond the capability of the instrument. Difficulties also arise when portions of a ship- t contain gamma emitters (e.g. ^{137}Cs, or ^{60}Co) in either the matrix or containment vessel. the shipment is uniform with respect to extraneous gamma emitters the IVF standardization cedures will compensate for them. If, on the other hand, the gamma spectral interferences y within a shipment, an alternate approach such as Ge(Li) gamma spectrometry must be lied.

ce the IVF instrumentation is stationary, field verification work is performed using the viously described SAM-II DCA system. Some items monitored in-situ were 15 to 18 ft. long ium-bonded, uranium carbide rods and massive uranium ingots. The stabilized, dual channel ay system, with direct enrichment reading capability, greatly simplifies in-situ ^{235}U surements. Future plans also include an evaluation of a transmission measurement for the ification procedure to correct for matrix attenuation. This would require the acquisi- n of a third modular SCA system and a gamma emitter with energies resolvable using the (Tl) detection system.

conclusion, the IVF instrumentation has proven itself to be a reliable, accurate, relative- fast nondestructive means of veryfying the ^{235}U content of receipts returned to the FMPC reclamation of uranium values. The instrumentation has also found utility in the area uranium concentration measurements for materials possessing reasonably similar ^{235}U enrich- ts. The IVF is normally calibrated and standardized once daily by technical personnel, also supervise all nonroutine verification operations and calculate and report all ults. Nontechnical operators perform all routine measurements obtained on a day-to-day is.

TABLE I

SELECTED FMPC SNM RECEIPTS

Shipper	Matrix	Description
DUN	U Metal	Remelt scrap; Zr & Cu clad
NFS	UNH	Solution
ANL	UO_2	S.S. & Zr clad rods
ORGDP	Incinerator Ash	6" D. x 15" H., S.S. Containers
AI	UC	Slugs, wafers, Ni clad plates
BAPL	U Alloy	Foil; Nb/Zr alloy scrap
NBL	U Concentrates	5 gallon buckets
Y-12	UF_4 in Paraffin	Blocks, shot, wafers
SRP	Filter Cake	55 gallon drums
BNWL	Na_2UO_4	Powder & Chunks
PAD	Contaminated Scrap	Vacuum bags
RMI	U Residues	Quench sludge, sump cakes, extruded tubes
UNI	U in concrete	Saw fines & turnings in concrete blocks

TABLE II

MEASUREMENT PARAMETERS FOR COMMON URANIUM COMPOUNDS

	Metal	UO_2	U_3O_8	UO_3	UF_4	UF_6	"UNH"
U wt %	100	88.1	84.8	83.2	75.8	67.6	47.4
$\mu/\rho(cm^2/g)$	1.60	1.43	1.38	1.35	1.25	1.12	0.83
$\rho(g/cm^3)$	19.0	11.0	8.30	7.29	6.70	4.68	2.81
$\mu(cm^{-1})$	30.5	15.6	11.4	9.87	8.34	5.26	2.33
T (mm)	0.98	1.92	2.62	3.04	3.60	5.71	12.9

TABLE III

EXAMPLE OF IVF ANALYZER CALIBRATION

Voltage: 1.2 kV; Coarse Gain: 1/16; Fine Gain: 1.6;
ΔE: 0.30 Counting Period: 20 sec; Material: K-25 Oxide

E	No. 1 Analyzer	No. 2 Analyzer
1.0	76090	60671
1.1	56298	L_2 → 48819
1.2	L_1 → 53494	50513
1.3	61464	60749
1.4	73699	P_2 → 71467
1.5	P_1 → 77331	71271
1.6	70983	L_2' → 57400
1.7	L_1' → 52162	39894
1.8	38271	32104
1.9	32740	28155
2.0	29373	25875
2.1	26793	23701
2.2	25120	22186
2.3	23392	21012
2.4	21698	19427
2.5	20685	17922
2.6	18721	16628
2.7	17668	15246
2.8	15596	13916

TABLE IV

EXAMPLE OF K-25 OXIDE STANDARDIZATION

Wt % ^{235}U (x)	cts./3 min. Gross	cts./3 min. Bkg.	cts./3 min. Net (y)
1.011	465,966	270,350	195,616
1.347	498,516	264,416	234,100
1.598	542,059	280,459	261,600
1.856	570,181	274,286	295,895
2.168	601,398	267,460	333,938

$\Sigma x = 7.980$ $\quad\Sigma xy = 2{,}204{,}296$ $\quad\Sigma y = 1{,}321{,}149$

$\Sigma x^2 = 13.535$ $\quad N = 5$ $\quad\Sigma y^2 = 3.6057 \times 10^{11}$

$\bar{x} = 1.596$ $\quad\bar{y} = 264{,}230$

$$y = a_o + a_1 x$$

ASSUMED EQUATION FORM

$$a_1 = \frac{\Sigma xy - \frac{\Sigma x\ \Sigma y}{N}}{\Sigma x^2 - \frac{(\Sigma x)^2}{N}} = 119{,}825$$

$$a_o = \bar{y} - a_1\bar{x} = 72{,}988$$

$$r^2 = \frac{\left[\Sigma xy - \frac{\Sigma x\ \Sigma y}{N}\right]^2}{\left[\Sigma x^2 - \frac{(\Sigma x)^2}{N}\right]\left[\Sigma y^2 - \frac{(\Sigma x)^2}{N}\right]} = 0.999$$

$$x = \frac{y - 72{,}988}{119{,}825} \text{ wt \% } ^{235}\text{U}$$

CALIBRATION EQUATION

TABLE V

EXAMPLE STANDARDIZATION AND UNKNOWN CALCULATION FOR RECEIPTS WITH VARYING ^{235}U AND U CONTENT

(H) High Standard (c/3m)	=	167,651
(M) Intermediate Standard (c/3m)	=	149,473
(L) Low Standard (c/3m)	=	82,324
(c/3m) Bottom of Container	=	68,420
(c/3m) Top of Container	=	70,294
Vendor's % U Value	=	38.68
Vendor's wt % ^{235}U Value	=	1.3480
FMPC wt % ^{235}U Value (Bottom)	=	1.344
FMPC wt % ^{235}U Value (Top)	=	1.381
FMPC wt % ^{235}U Value (Average)	=	1.362
(FMPC - Vendor) wt % ^{235}U Value	=	+0.014

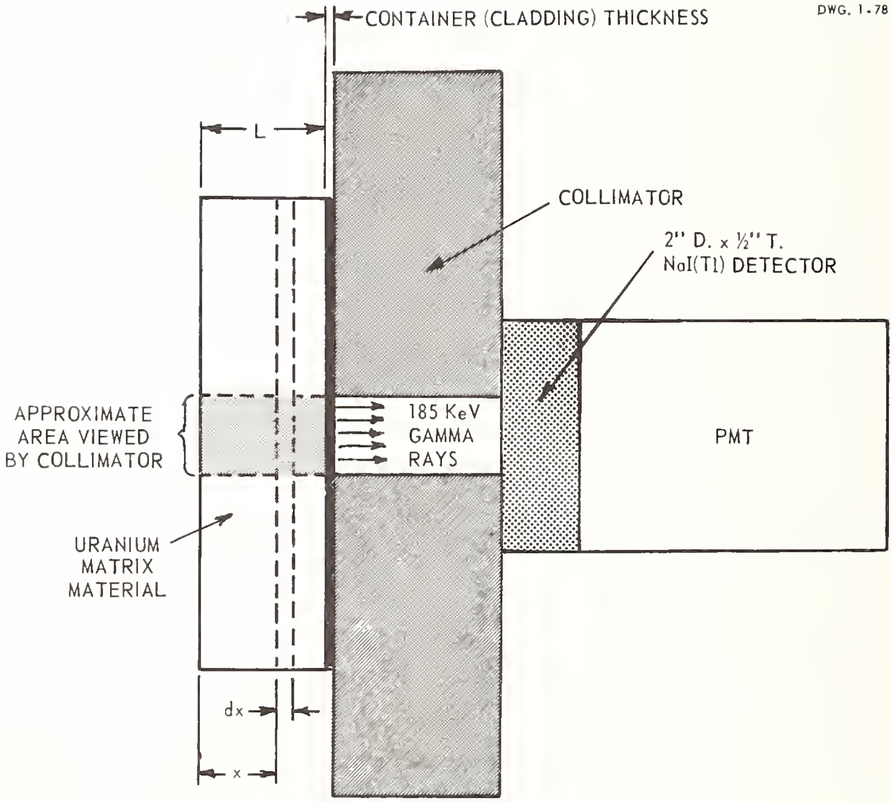


FIGURE 1 Detector Configuration for ^{235}U Enrichment Measurement

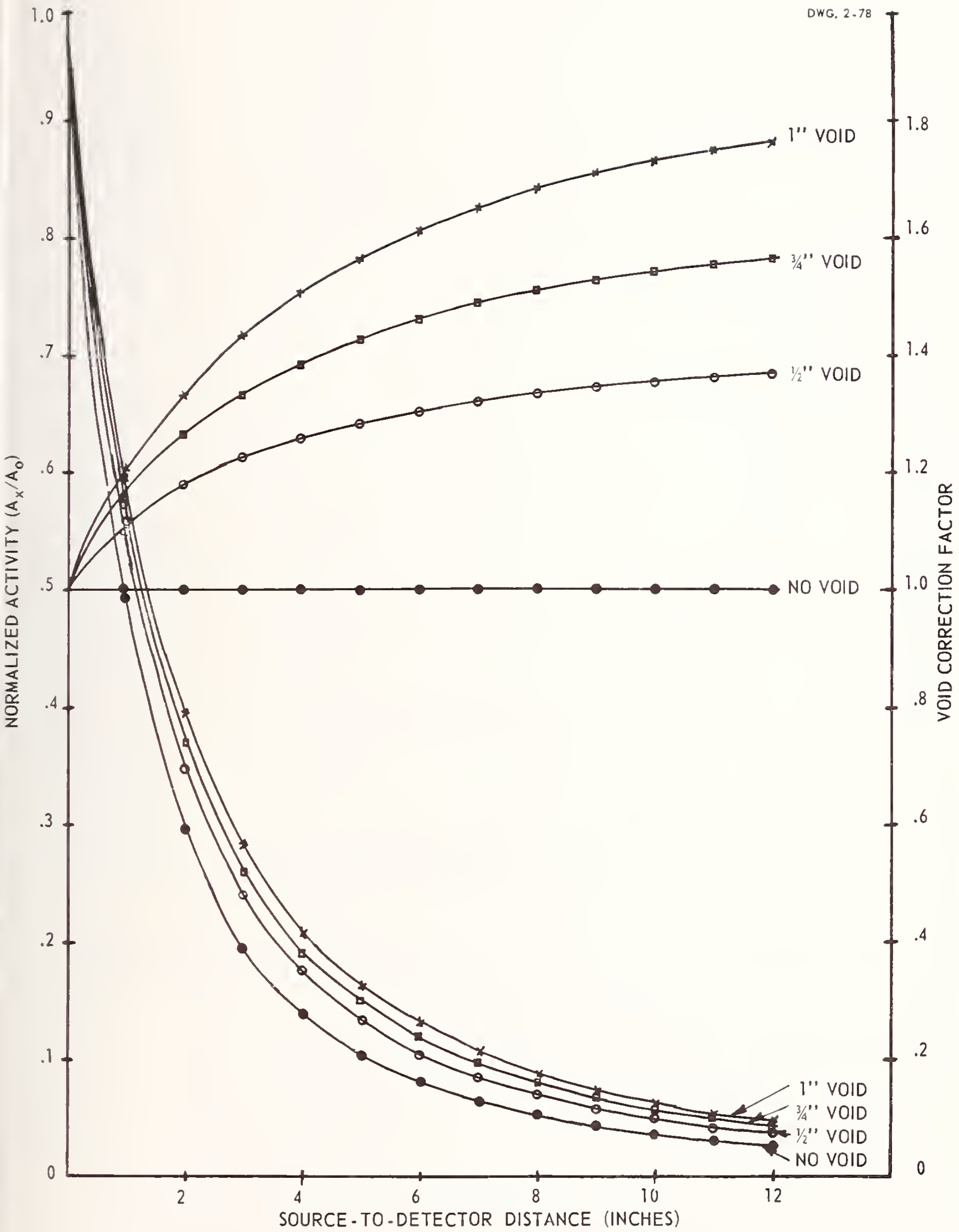


FIGURE 2 Void Correction Alogrithm

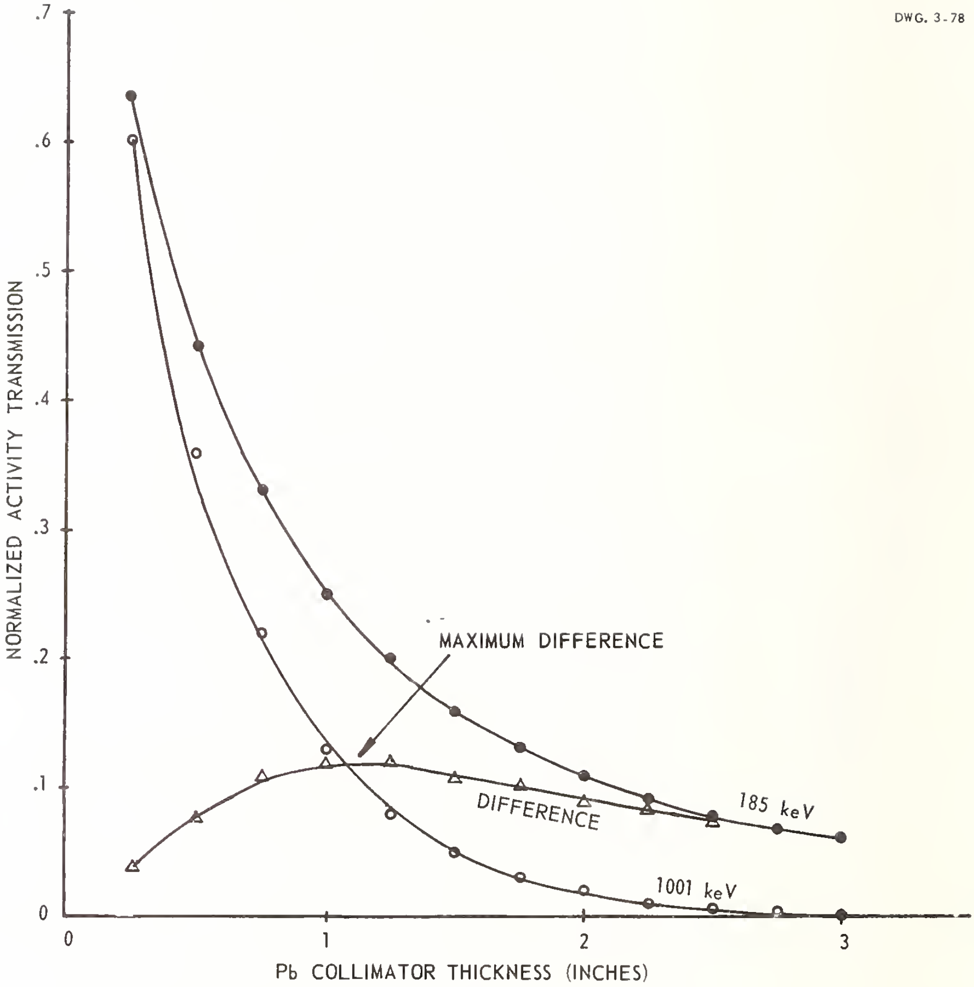


FIGURE 3 Collimator Thickness Optimization

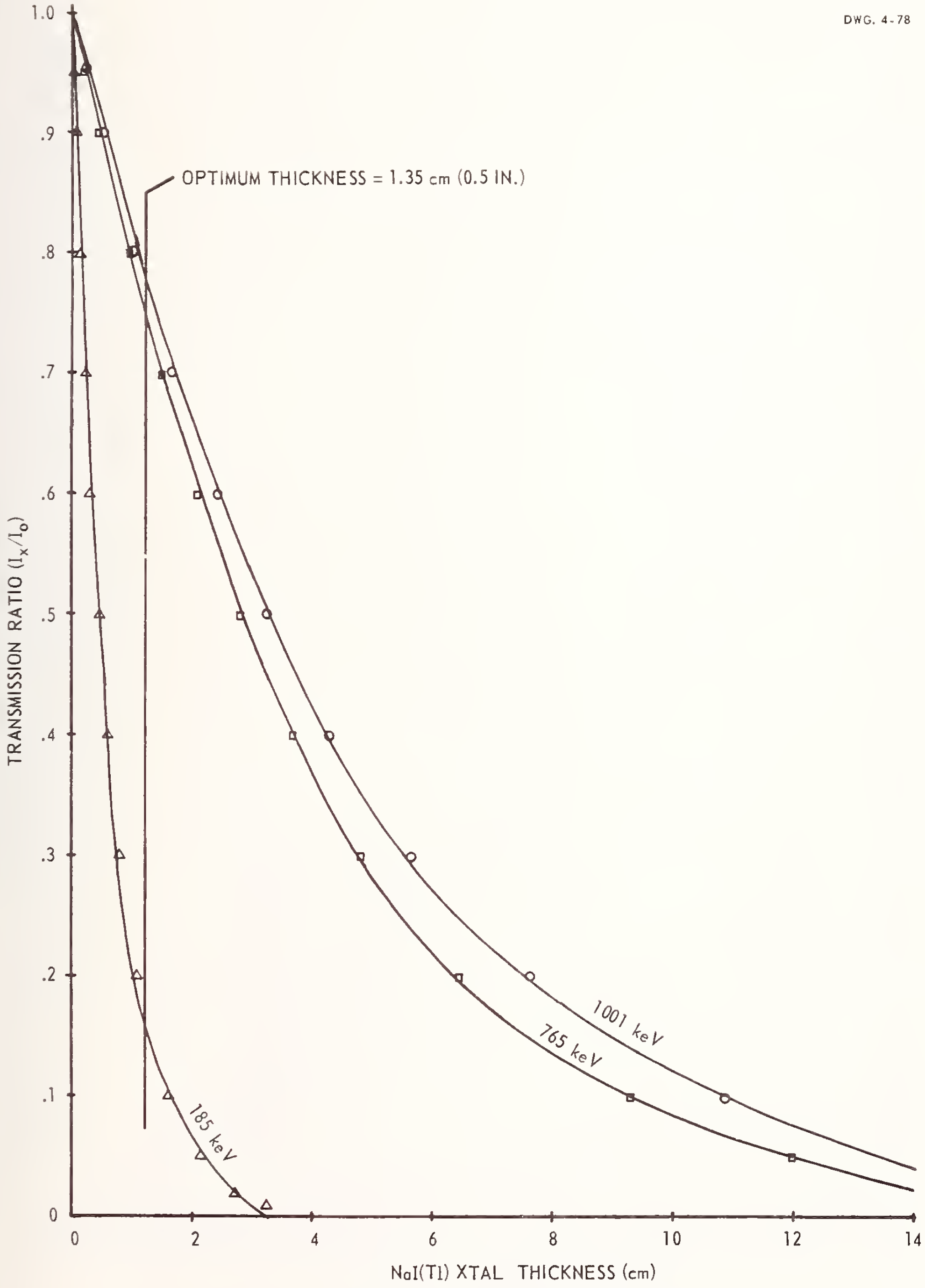
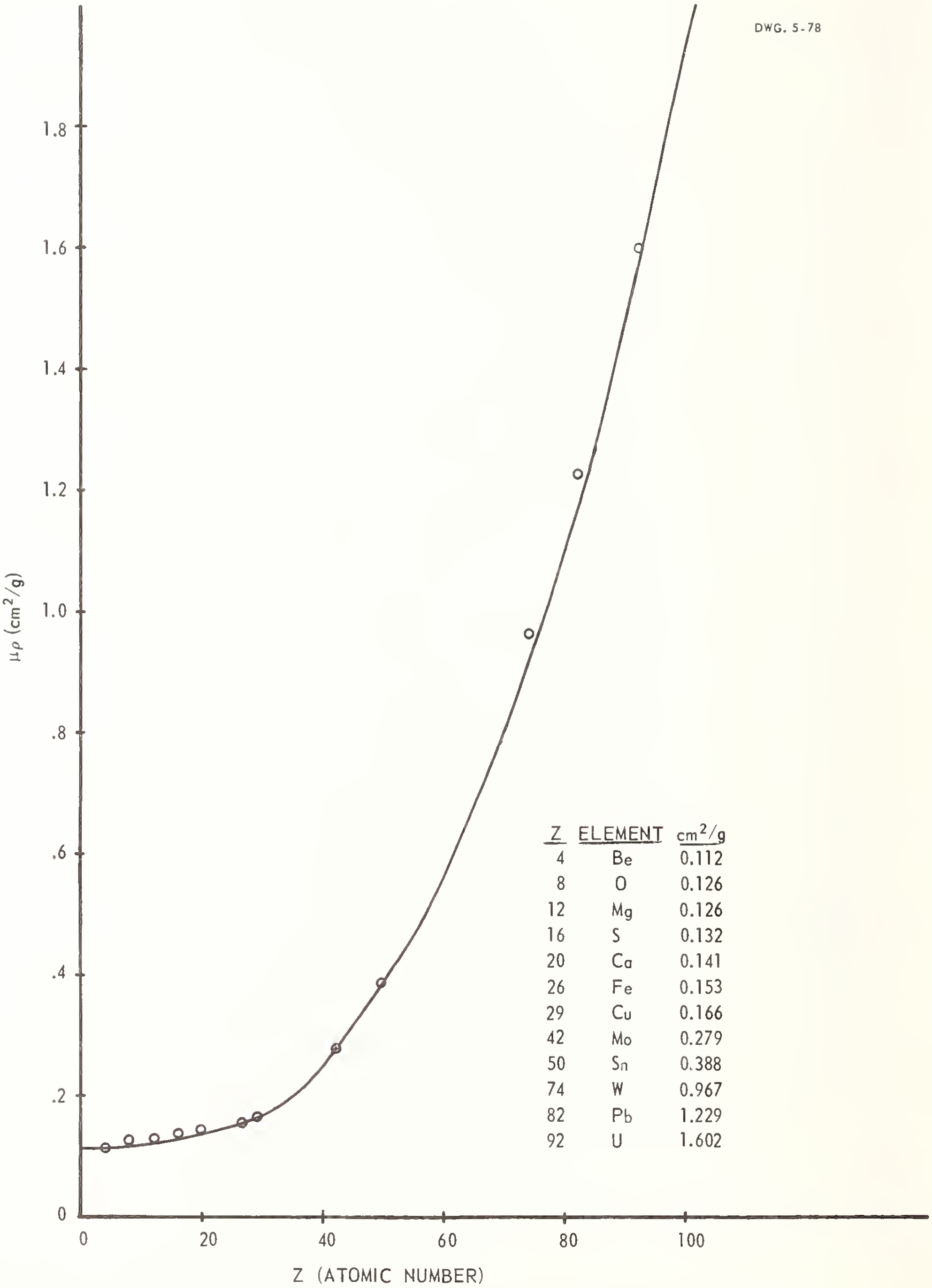


FIGURE 4 Detector Thickness Optimization



Z	ELEMENT	cm^2/g
4	Be	0.112
8	O	0.126
12	Mg	0.126
16	S	0.132
20	Ca	0.141
26	Fe	0.153
29	Cu	0.166
42	Mo	0.279
50	Sn	0.388
74	W	0.967
82	Pb	1.229
92	U	1.602

FIGURE 5 Atomic Number vs. Mass Attenuation Coefficient for 185 keV Gamma Rays[6]

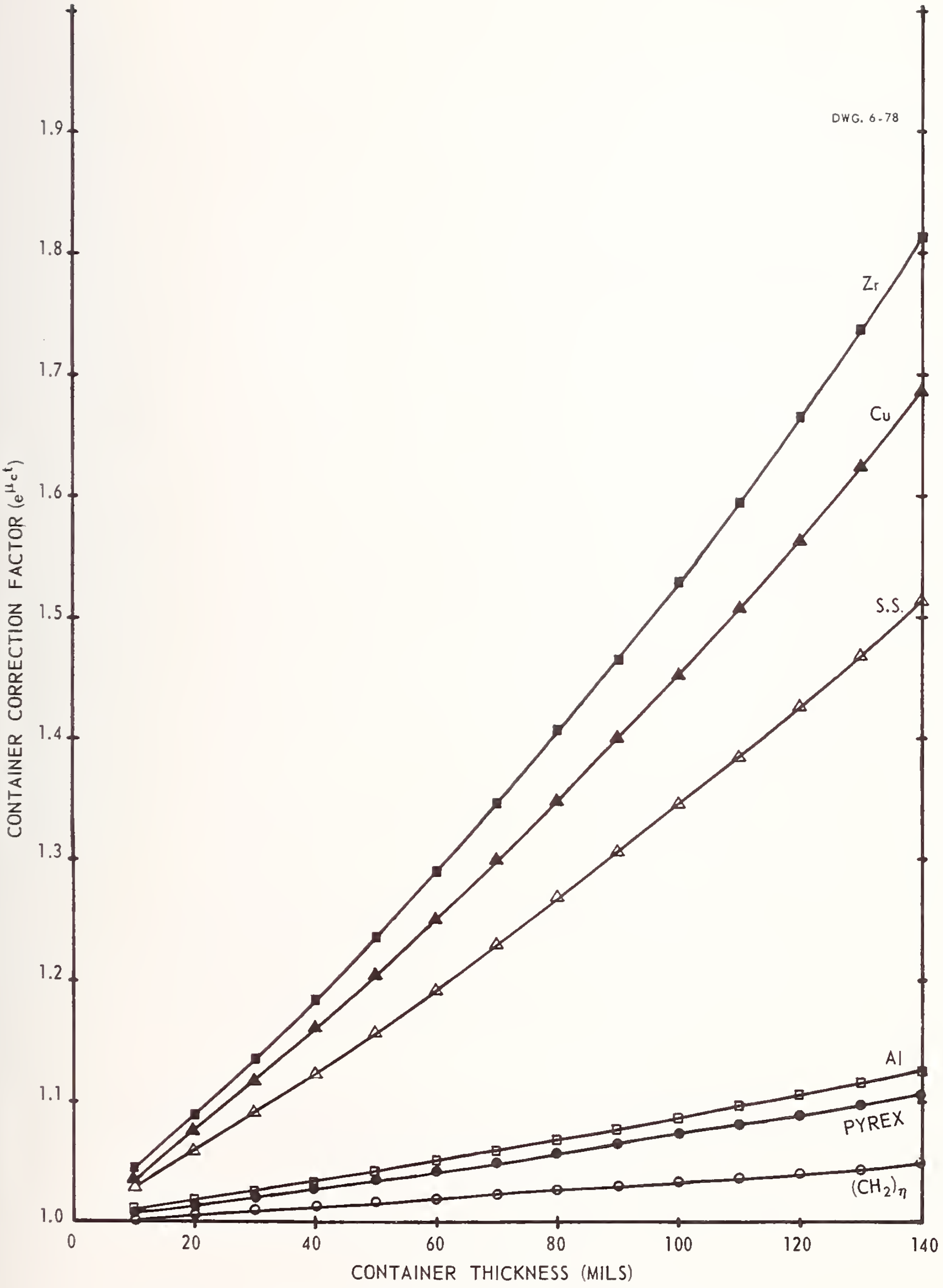


FIGURE 6 Effect of Container Thickness on ^{235}U Enrichment Measurement

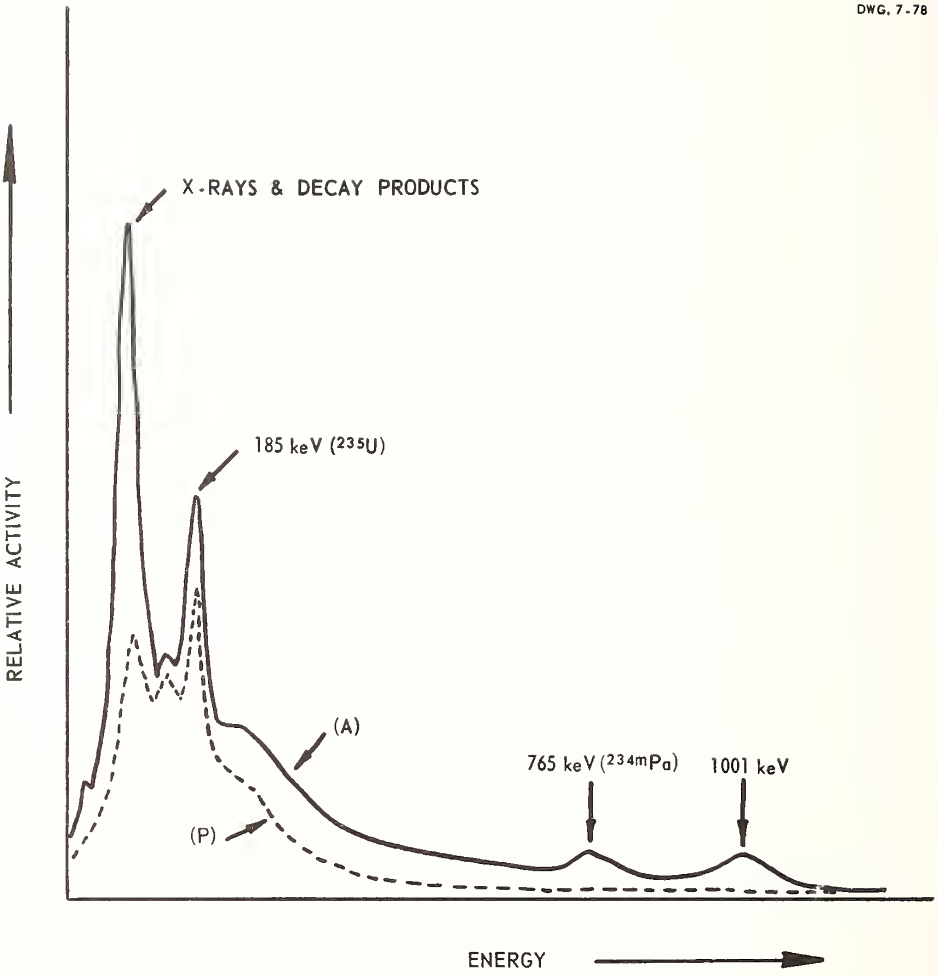


FIGURE 7 Aged (A) and Purified (P) Uranium Gamma Spectra Obtained with a NaI(Tl) Detector

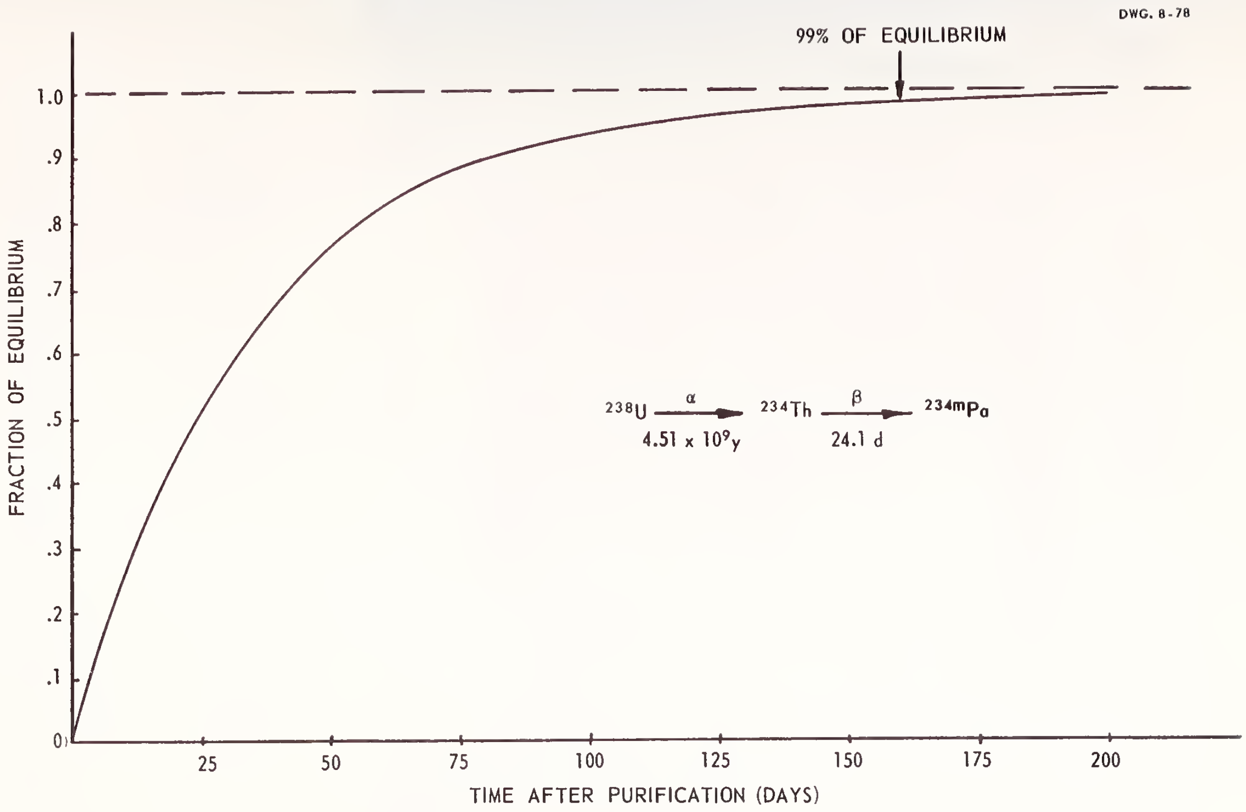


FIGURE 8 ^{234}Pa Ingrowth from Initially Pure ^{238}U

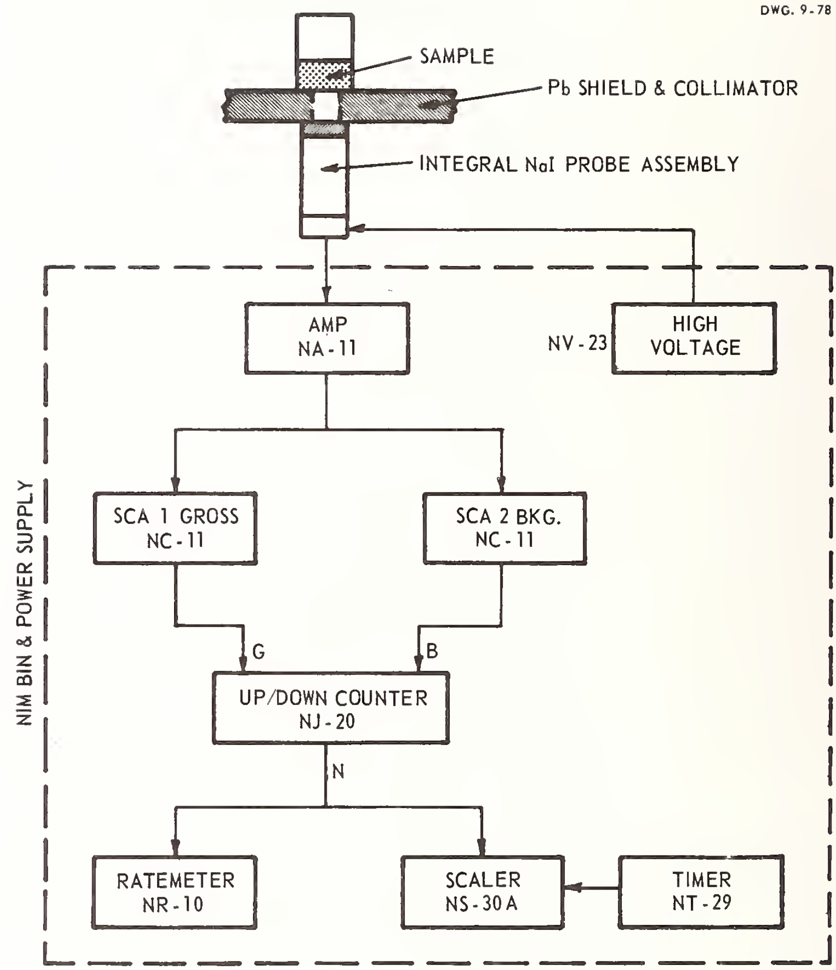


FIGURE 9 Schematic Diagram of ^{235}U Enrichment Verification Instrumentation

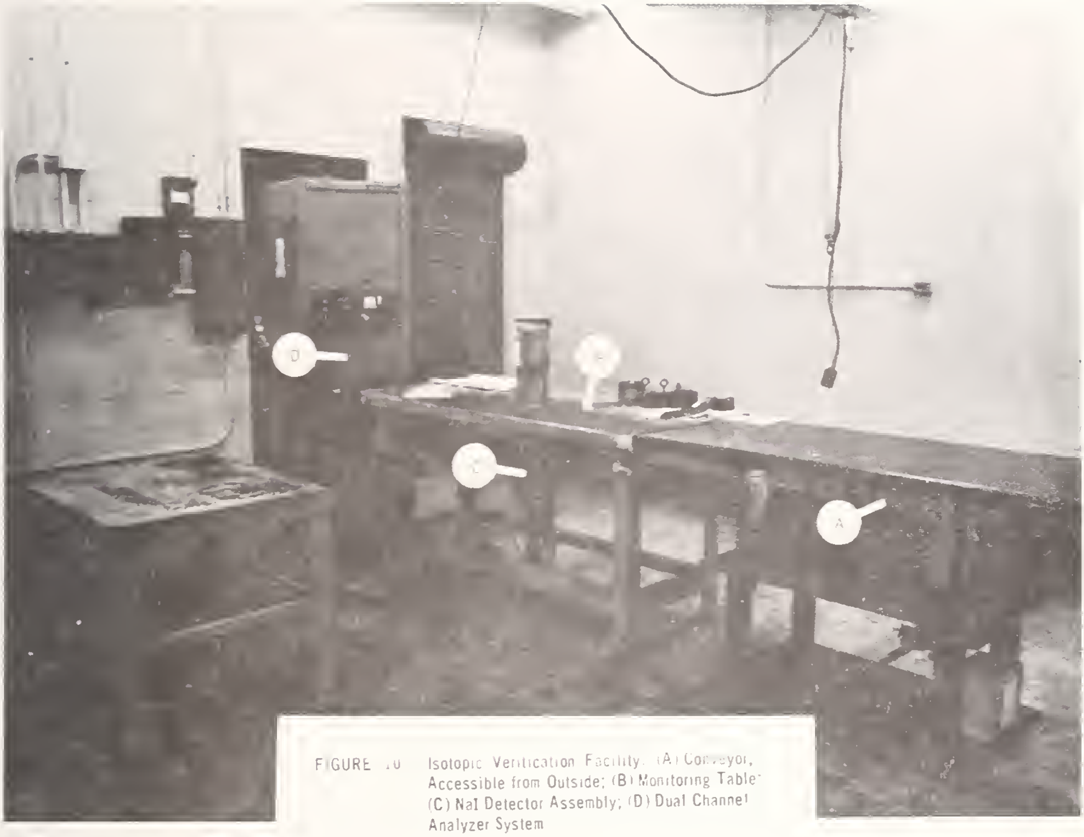


FIGURE 10 Isotopic Verification Facility: (A) Conveyor, Accessible from Outside; (B) Monitoring Table; (C) NaI Detector Assembly; (D) Dual Channel Analyzer System

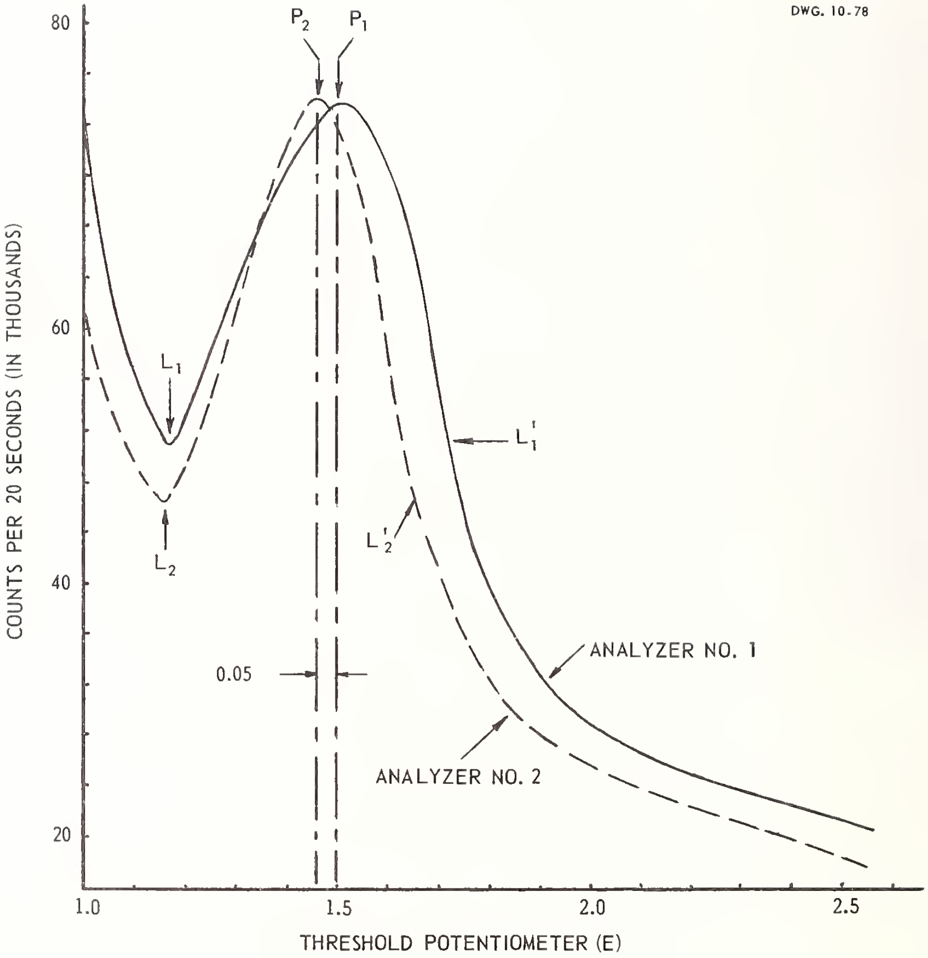


FIGURE 11 Uranium Calibration Spectra

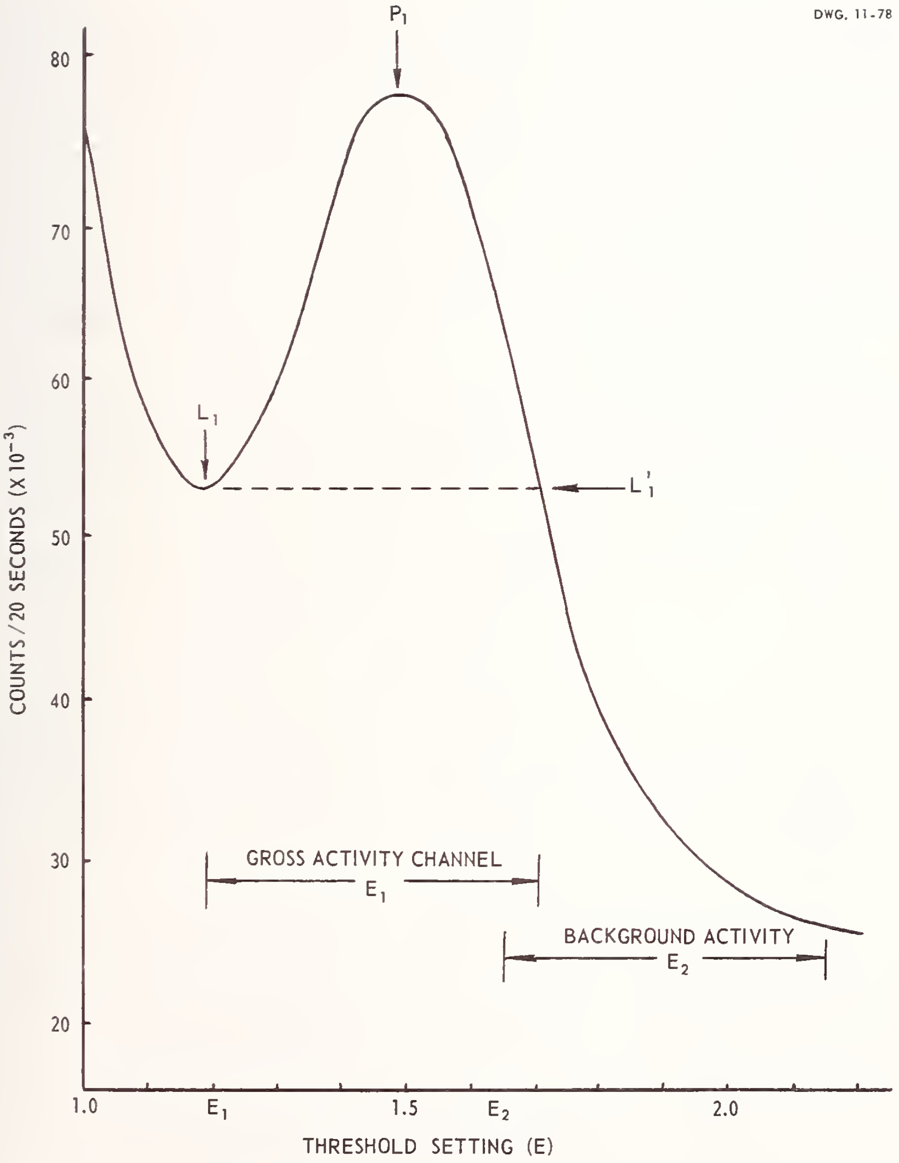


FIGURE 12 Determination of Single Channel Analyzer Settings

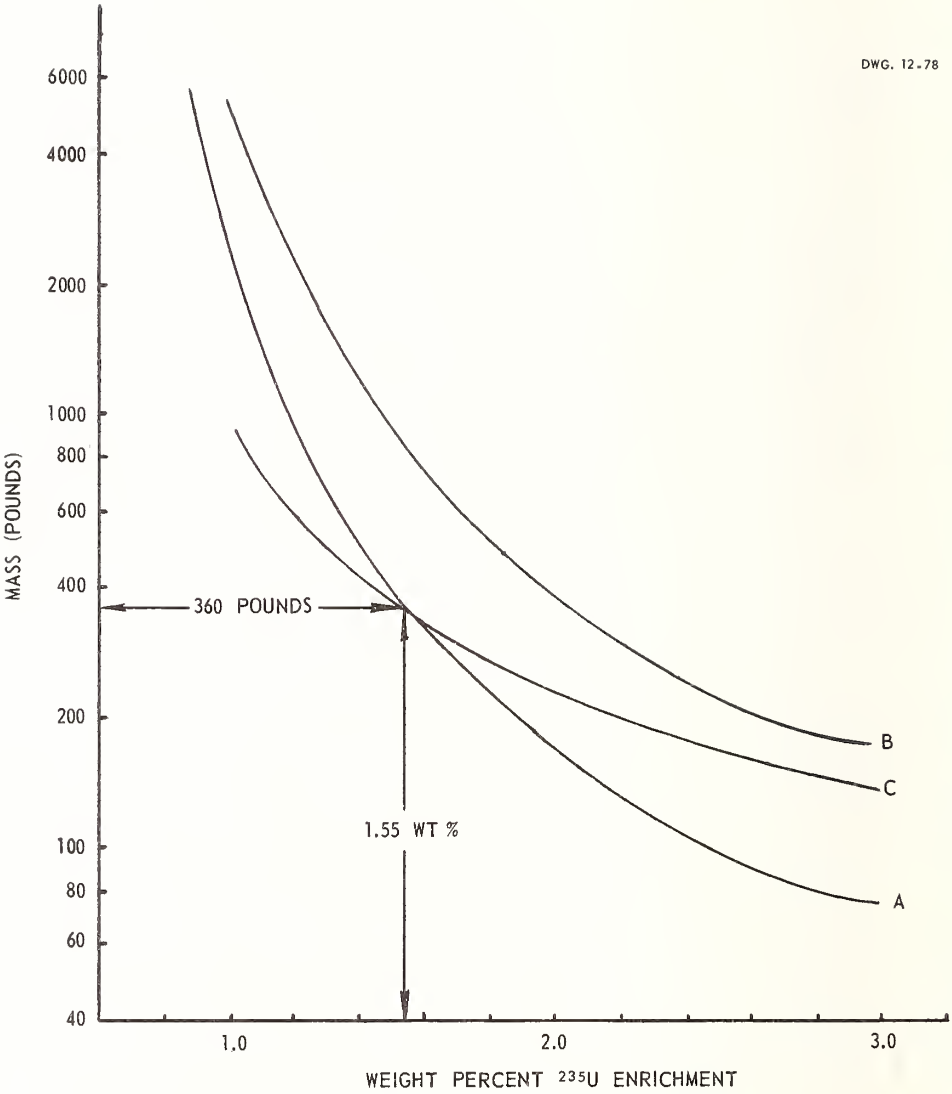


FIGURE 13 Nuclear Safety Considerations for IVF Acceptance Criterion: (A) Storage Mass, (B) Critical Mass, (C) Maximum Error in ^{235}U Value for Storage Mass

Accurate Determination of 5-25 mg of Uranium by Redox Titrimetry

by

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ABSTRACT

A precise and selective potentiometric titration method for determining 5-25mg of uranium has been developed. The method is essentially a scaled-down version of the modified Davies-Gray titrimetric method.[1] Our investigations extend the work of Slanina et al.[2] by identifying several critical steps where careful control of conditions is essential to obtain high precision. The method has been automated by interfacing a 10-mL Mettler buret with a pre-programmed HP-9830 calculator. The calculator controls the delivery of titrant so that the end point is approached as rapidly as possible, but delivers only small increments of titrant near the equivalence point. A hard copy of the data (mL of titrant vs. Electrode Potential) is printed as the titration proceeds, and the volume of titrant equivalent to the uranium in the sample is computed from the first derivative of the titration curve.

A precision and accuracy of 0.05% or better is obtainable with this method. The method is especially useful for the determination of uranium when the quantity available for analysis is limited. It has been used for verification of the uranium concentration of various standards used in analyses performed at the Idaho Chemical Processing Plant.

KEYWORDS: Uranium determination; computer controlled titration; low-level analyses

INTRODUCTION

To fill a need for an accurate independent verification of uranium concentration values for standards and the determination of uranium in accountability samples of limited size at the Idaho Chemical Processing Plant (ICPP), a search for a suitable analytical method was undertaken. The range of the method was to be limited to a few milligrams of uranium and an accuracy of about ± 0.05% was to be achieved with an analysis requiring a minimum of time.

Considerable experience had already been obtained by coworkers in the determination of uranium in standards prepared for distribution throughout the world as part of the Safeguards Analytical Laboratory Evaluation (SALE) Program. One of the most widely used procedures in this program is the titrimetric determination of uranium by a method developed by Davies and Gray[3] and modified and improved by Eberle, Lerner, Goldbeck and et al.[1] at the New Brunswick Laboratory. Although this method has been widely accepted as precise, accurate and selective for most nuclear fuel cycle materials, large amounts of uranium are used per analysis (50-300 mg) and large volumes of waste solution are generated (∿ 250 mL). It was reasoned that if this method could be scaled-down by a factor of ten and still retain the same accuracy and precision, it would be ideally suited to the present need. As an example, it would be practical to determine 233-U concentration in a stock solution used to spike samples for the determination of uranium by isotope dilution mass spectrometry.

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[1] Eberle, A. R., Lerner, M. W., Goldbeck, C. G. and C. J. Rodden, NBL Rep. 252 (1970).

[2] Slanina, J., Bakker, F., and W. A. Lingerak, "Safeguarding Nuclear Materials, Vol II 1976" p. 157.

[3] W. Davies and W. Gray, UKAEA Report TRG-716(D), 1964; Talanta 11, 1203, (1964).

In the modified Davies and Gray method uranium is reduced to U(IV) with Fe(II) in a phosphoric-sulfamic acid medium. Excess Fe(II) is selectively oxidized by nitric acid to Fe(III) in the presence of Mo(VI) catalyst and the uranium is subsequently oxidized to a potentiometric end-point with standard potassium dichromate solution. Vanadyl sulfate is used to catalyze the titration and sharpen the end point. The method is quite selective a if the sample is first fumed with sulfuric acid only silver and tin are reported to interfere.^{4,5,6,7}

In proceeding with the development of a scaled-down method, the provision for real-ti control of the potentiometric titration and data reduction by means of software rather tha strictly hardware was considered to be of prime importance. Such a software controlled system would permit maximum flexibility in performing the titration. An interface was designed and constructed by our Measurements Systems staff which permits a Hewlett-Packard 9830A programmable calculator to automatically control a Mettler DV-11 buret drive, acquir data after measuring equilibrium electrode potentials, and handle acquired data to determi the equivalence point in various titrations.

EQUIPMENT (CALCULATOR-CONTROLLED AUTOMATIC TITRATION)

Figure 1 is a block diagram of the programmable titration system. The electrometer amplifier has an input resistance of 10^{14}ohms and a unity-gain bandwith of 2K-Hz, and so i compatible with almost any electrode system. The programmable-gain amplifier has a software-selected gain of 1 to 16 in steps of one to enable use of the full analog/digital convertor resolution with any realistic electrode output. The ADC resolution is 1:4096 an and the full scale potential range is +2.5 to -2.5V.

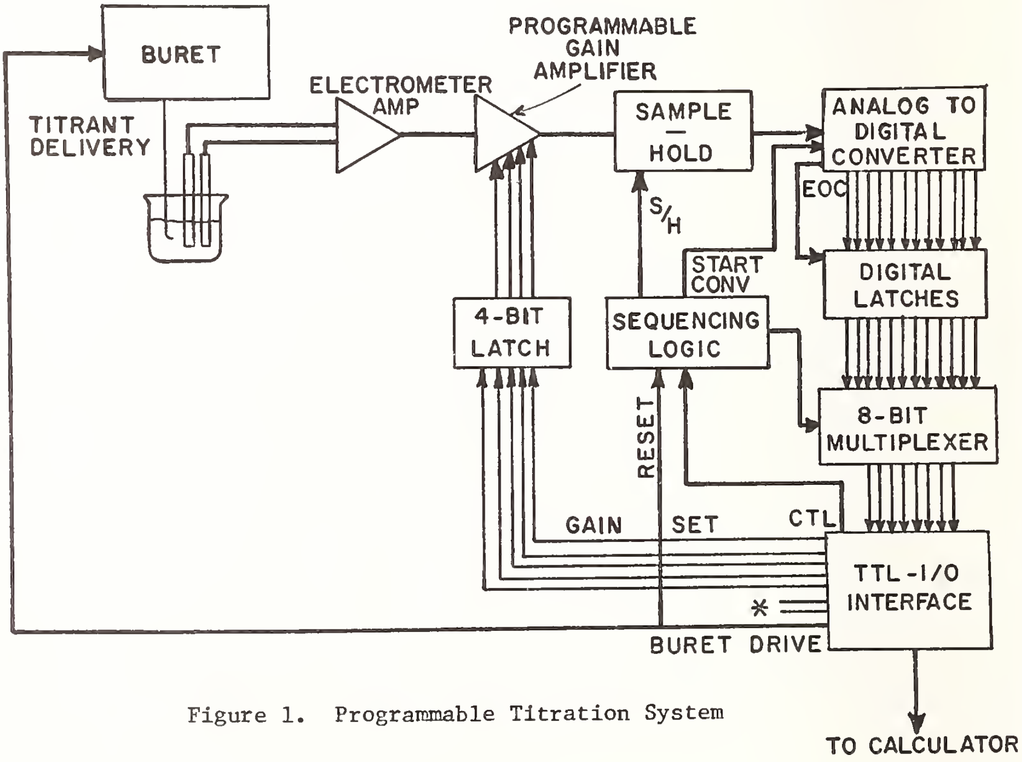

Figure 1. Programmable Titration System

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[4] A. R. Eberle and et al., NBL-252, 1970.
[5] A. R. Eberle and M. W. Lerner, NBL-262, 1972.
[6] L. Z. Badnar, J. M. Scarborough and M. W. Lerner, NBL-265, 1972.
[7] J. M. Scarborough and L. Z. Bodnar, NBL-267, 1973.

The calculator is programmed in BASIC language. Using the proper OUTPUT statements it direct the buret drive to deliver a specified increment of titrant, then input bits of ry information from the ADC and convert this information to electrode potentials. Data cquired and printed for each titrant increment only after equilibrium has been attained. is sensed by waiting a pre-selected time after addition of titrant before measuring the trode potential and then measuring the potential again after a second time delay. ential readings must agree within specified limits before a value is accepted and ner addition of titrant is possible. With a 10 mL buret, the Mettler DV-11 is capable elivering increments as small as 0.002 mL.

The calculator was initially programmed to add increments of titrant as manually red from the keyboard and then print out the total volume of titrant delivered vs. trode potential. As development work progressed and the results indicated that a able analytical procedure was possible, the calculator programs were extended to allow matic and systematic delivery of titrant, calculation of the end point (corrected for ant temperature and buret calibration), calculation of uranium concentration, plotting he data and data storage on magnetic tape. This hardware-software combination allows ations to be performed to a precise end-point in a minimum of time without the ibility of introducing human errors in manipulating or reading a buret or in determining potentiometric equivalence point.

J. Slanina et al.[2] have also reported on the use of a Mettler titrator in combination a programmable calculator to determine small quantities of uranium by a miniaturized es and Gray method. They used a complete Mettler System including a DK-15 incremental roller and apparently used the calculator only for recording and handling of data. They titrant continually until a preset potential is sensed and then add fixed increments each the equivalence point. We have found that the exact values of the potential prior he end point are quite non-predictable, as they depend on the condition of the platinum trode and the sample solution. A program which depends entirely on expected potentials potential changes to control the size of titrant increments was evaluated, but it did yield high precision results.

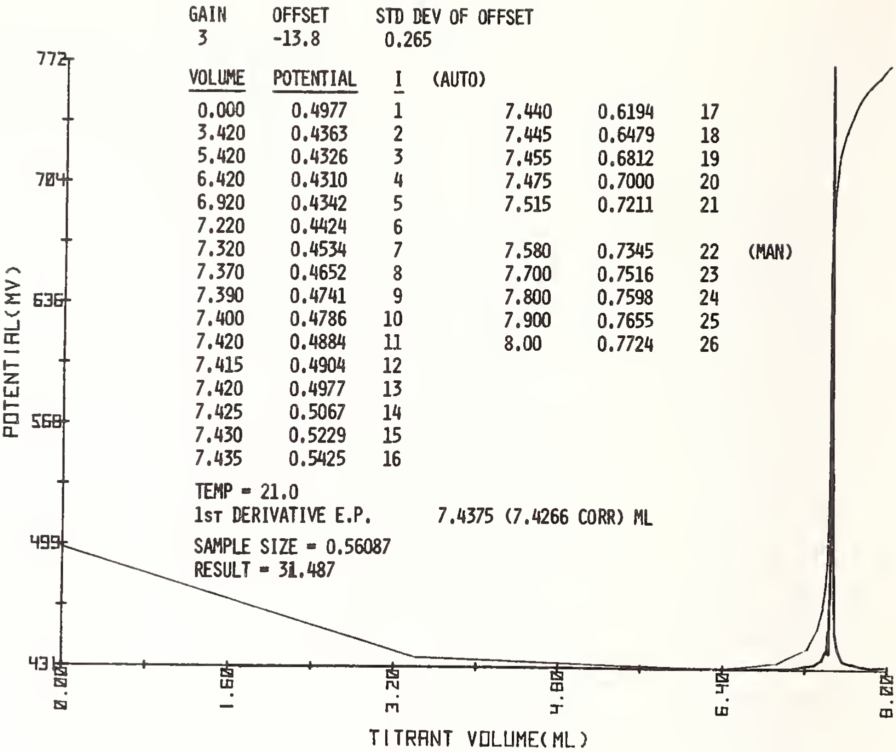
The best precision and accuracy has been obtained with a program which adds titrant redetermined increments to approach the end-point systematically. To use this program must have a close estimate of the volume of titrant required to reach the equivalence t. Since samples requiring accurate results are run in triplicate (or more) to obtain istical data, the first determination is run "manually", and the results are used to ulate the approximate equivalence point for additional determinations on the same sample. the systematic program the last 4 mL of titrant are first added in the order 2, 1, 0.5, 0.1, 0.05, and 0.02 mL. Increments of 0.004 mL are then added until the potential has eased from about 500 to 630 mV. The equilibrium potentials and corresponding titrant mes are printed out with an HP 9866A thermal printer. The maximum ΔE/mL usually occurs een 540 and 610 mV and approximately 5-7 minutes are required to complete an unattended ation.

Figure 2 is a facsimile of a typical set of data imposed on a plot made with a HP 9862A ter controlled by the HP 9830A calculator.

EXPERIMENTAL

In miniaturizing the Davies and Gray method to determine only about 5 to 25 mg of nium, the quantities of reagents specified in the New Brunswick procedure were initially uced by a factor of ten except that 0.02N standard dichromate solution was used as a rant instead of 0.05N. A 30-mL beaker was used as a vessel to carry out the preliminary mistry and the potentiometric titration. Miniature electrodes were mounted in a polyylene stopper which nested in the top of the beaker.

Although initial results with the scale-down procedure were generally within ± 0.3% cision and accuracy, considerable experimentation was required to reduce this spread to acceptable range. One major factor contributing to poor results was the improper control temperature during the molybdenum-catalyzed nitrate oxidation of excess Fe(II) reductant. emperature of 35-40°C is generated naturally in the large scale method from the addition sulfamic and phosphoric acids to the sample. In this temperature range the complete



```
GAIN      OFFSET      STD DEV OF OFFSET
3         -13.8        0.265

VOLUME    POTENTIAL     I    (AUTO)
 0.000     0.4977       1                 7.440      0.6194      17
 3.420     0.4363       2                 7.445      0.6479      18
 5.420     0.4326       3                 7.455      0.6812      19
 6.420     0.4310       4                 7.475      0.7000      20
 6.920     0.4342       5                 7.515      0.7211      21
 7.220     0.4424       6
 7.320     0.4534       7                 7.580      0.7345      22    (MAN)
 7.370     0.4652       8                 7.700      0.7516      23
 7.390     0.4741       9                 7.800      0.7598      24
 7.400     0.4786      10                 7.900      0.7655      25
 7.420     0.4884      11                 8.00       0.7724      26
 7.415     0.4904      12
 7.420     0.4977      13
 7.425     0.5067      14
 7.430     0.5229      15
 7.435     0.5425      16

TEMP = 21.0
1ST DERIVATIVE E.P.          7.4375 (7.4266 CORR) ML

SAMPLE SIZE = 0.56087
RESULT = 31.487
```

Figure 2. Typical Data Plot

destruction of excess Fe(II) occurs in a relatively short, predictable time without sim taneous oxidation of U(IV) to U(VI). In scaling down the procedure the smaller quantit of reagents do not provide and maintain the proper temperature for this reaction to pro predictably. The use of a small constant temperature water bath (35-38°C) effectively eliminated this problem and with other parameters held constant good precision was obta

The temperature of the sample during the titration was also found to affect the re If the sample is retained in the water bath at a temperature of about 37°C during the t tion, the results are low by about 0.1%. The error is less if the sample is removed fr the water bath but an accuracy of less than ± 0.05% is readily attainable if the sample rapidly cooled to about 18°C prior to titration. Partial air oxidation of uranium at t higher temperature is believed to cause the low results. A nitrogen atmosphere can be with a warm titration temperature but cooling the sample is preferred, since the electr response is generally more rapid.

High results are encountered when the phosphoric acid reagent contains dichromate- oxidizable impurities. This problem is effectively eliminated by dissolving enough sol potassium dichromate in the 86% phosphoric acid to give a persistent light yellow color The excess dichromate is reduced with uranium by ferrous ion and therefore presents no blem in the analysis.

PROCEDURE

The analytical procedure as presently developed is outlined below. The quantities concentrations of reagents specified have been optimized for the pure uranyl nitrate so tions studied. Close adherence to the instructions given for each step in the procedur given results that are better than the desired ± 0.05% (typically ± 0.02%) accuracy and relative standard deviation.

PROCEDURE	COMMENTS
Weigh an aliquot of the sample containing 5 to 25 mg of uranium into the bottom of a 30-mL beaker.	For maximum precision with a 10-mL buret select a sample aliquot containing 5 to 12 mg of uranium when working with $0.01\underline{N}$ $K_2Cr_2O_7$ and 10 to 25 mg of uranium when using $0.02\underline{N}$ $K_2Cr_2O_7$.
Add 0.2 mL of $9\underline{M}$ H_2SO_4 to the sample and gently mix. Evaporate the sample slowly on a hot plate until the appearance of heavy SO_3 fumes and solids begin to form in the beaker.	This step reduces all samples to a minimum starting volume and removes volatile potential interferences such as Br^-, Cl^-, I^-, and NO_3^-.
To the cooled sample are added 0.6 mL water, 0.4 mL of $1.5\underline{M}$ sulfamic acid, 5 mL of ∿86% phosphoric acid, and a ∿0.3 x 1.5 cm magnetic stirring bar.	The water and sulfamic acid may be used to rinse down the walls of the beaker. Do not rinse the walls with the phosphoric acid which has been treated with $K_2Cr_2O_7$ to remove oxidizable impurities.
Place the beaker in a small water bath positioned on a magnetic stirrer and adjusted to a temperature of 35±2°C. Stir the sample slowly for 30 s; then add 0.5 mL* of $1.4\underline{M}$ $FeSO_4$ in $2\underline{M}$ H_2SO_4 directly to the sample. Continue the gentle mixing for 1.5 min. *Add only 0.3-0.4 mL of $FeSO_4$ solution if the sample contains only 5 - 12 mg of uranium.	Uranium is reduced to U(IV) leaving an excess of Fe(II). In the absence of nitrate this reaction will proceed without sulfamic acid. If nitrate is present (i.e., H_2SO_4 fuming step is omitted) the sulfamic acid will prevent the interfering nitric acid oxidation of Fe(II) and U(IV) in the strong phosphoric acid solution.
Add to the sample 1 mL of a $8\underline{M}$ HNO_3-$0.15\underline{M}$ sulfamic acid - 0.5% ammonium molybdate reagent. Continue gentle stirring for 3 min after the brown coloration disappears.	Excess Fe(II) is selectively oxidized to Fe(III). Time and temperature are critical to this step. The temperature of the water bath should be 37±2°C.
Rinse down the walls of the beaker with 5 mL of $1\underline{M}$ H_2SO_4 containing 3 mg of $VOSO_4 \cdot H_2O$ per mL. Without delay, remove the sample beaker from the hot water bath and place it in a cold water bath which has a temperature of ∿10°C.	The sample is diluted with sulfuric acid in this step and vanadyl sulfate is added to catalyze the oxidation of uranium with standard potassium dichromate solution and sharpen the end-point. The solution is cooled to prevent air oxidation of uranium during the titration step.
Position the sample in the cold water bath under the buret and electrode assembly and swing the magnetic stirrer in place to support the sample for the titration. Adjust the stirrer to mix the sample at a moderate rate.	The buret should be filled, and the calculation programs loaded for execution.
Initiate the "automatic" or manual titration program and titrate the sample to the equivalence point.	For best results the titration should be completed in less than 10 min. The platinum electrode should be cleaned in conc HNO_3 and flamed in a Meeker burner after 3 or 4 determinations to assure rapid response and a large potential change at the equivalence point.

RESULTS

Following the procedure outlined previously the following set of results was obta using $\sim$0.02N $K_2Cr_2O_7$. The sample was an analytical control made from 99.995% natural containing $\overline{3}1.486$ mg of U per gram of solution.

Weight of Sample (g)	Conc. Found (U mg/g)
0.72099 (22.79 mg U)	31.487
0.63367	31.487
0.59630	31.489
0.57576	31.485
0.48628	31.480
0.43801 (13.79 mg U)	31.487

$\bar{X}_6 = 31.486$
$S = 0.0017$ rsd
$S,\% = < 0.01$ rsd
No significant bias

Using smaller samples of the above control and diluting the $K_2Cr_2O_7$ to $\sim$0.01N, the following set of data was obtained.

Weight of Sample (g)	Conc. Found (U mg/g)
0.23706 (7.46 mg U)	31.487
0.25595	31.486
0.31935	31.497
Next day	
0.26632	31.491
*0.27189	31.476
*0.30397	31.510
*0.32531 (10.24 mg U)	31.484

*Samples not fumed with H_2SO_4.

$\bar{X}_7 = 31.490$
$S = \pm 0.034$ % rsd

Although the results are more variable using $\sim$0.01N $K_2Cr_2O_7$ as the titrant, they a quite acceptable. The samples which were not fumed with sulfuric acid exhibit the larg variance from the mean.

CONCLUSION

The range of the Davies and Gray method for determining uranium has been successfu reduced by about a factor of ten without any loss in accuracy or precision. Since smal quantities of uranium are required there is little waste of this accountable element. titration under calculator control is considerably less tedious than manual titration, the method is especially suited to the determination of uranium in special nuclear mate requiring safeguarding and accountability.

In Situ Quantitative Determination of Transuranic Elements in Areas of High-Level Gamma Radiation*

by

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ABSTRACT

A technique is described for passive neutron monitoring of transuranic elements. The method provides quantitative determinations of transuranic element concentrations in a variety of field situations where no other measurement method is possible. The technique can measure concentrations of transuranic oxides as low as 8 nCi/cm^3 and is capable of operating in gamma radiation fields up to megarads per hour. Information on chemical and isotopic composition can also be obtained from the data. Several successful applications of the technique are discussed.

KEYWORDS: Transuranics; neutron monitoring

INTRODUCTION

The in situ detection and measurement of transuranic elements is an extremely difficult blem. These isotopes are primarily alpha-emitting nuclides which emit relatively low rgy gamma-rays through very low branching fractions. Transuranic elements also emit racteristic x-radiation in high yield, but this can only be measured in special circum- nces. Neutrons are the only characteristic radiations emitted by the transuranic elements ch are readily distinguishable in the presence of other radionuclides. These neutrons e from spontaneous fission or from (α,n) reactions on light isotopes such as ^{19}F, ^{17}O, or . For many applications, such as criticality, accountability, or waste management, re- ring the quantitative determination of plutonium or other transuranic elements, these neu- ns are the only radiations suitable for measurement. For example, the characterization of idual plutonium in process or fabrication hoods undergoing decommissioning is not possible alpha detection and is only occasionally possible by x-ray measurements. Although gamma ection will frequently work for fairly high quantities of plutonium, shielding by massive hinery may introduce substantial uncertainties. Neutrons are not as severely attenuated bulk quantities of steel, and remote pockets of plutonium may be detected by neutron mea- ements.

It may be necessary to measure plutonium concentrations for potential criticality eval- ion in trenches, cribs, or storage tanks which have received process wastes. These loca- ns frequently have large quantities of fission products present which would interfere h the detection of plutonium photons, and only neutrons can be unequivocally identified. ilarly, it may be desirable to measure the quantity of transuranic elements released to environs during an accidental discharge of fission product waste or to determine the nsuranic element content of fuel cycle fission product effluents for disposal purposes. high level gamma radiation present in these cases also restricts the detection of trans- nic elements to neutron monitoring.

This communication describes a technique for quantitatively measuring the neutrons tted by transuranic elements. This technique can evaluate the neutron energy spectrum thereby infer the chemical and/or isotopic composition of the transuranics in question.

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is paper is based on work partially supported by Rockwell Hanford Operations' Environment- Sciences Group, L. E. Bruns and H. H. Wang, Program Coordinators, under United States De- rtment of Energy Contract EY-76-C-06-1830.

Finally, this technique can make quantitative measurements of transuranic element concen tions at <10 nCi/g in gamma radiation fields exceeding megarads per hours.

EXPERIMENTAL

There are two basic detection techniques for measuring neutrons emitted by transura species. The first of these is the active technique, which incorporates real time measur ment of neutrons with ^{3}He, BF$_{3}$, fission chamber, or similar detectors and collection and storage of signals with appropriate electronic equipment. This technique is not applica to operation in high gamma radiation fields, since the electronic detectors will not fun properly. In addition, neutron energy evaluation is virtually impossible with this acti technique, since the detectors are generally operated in a moderating medium to effectiv utilize their enhanced efficiencies at thermal neutron velocities.

The second neutron detection technique, a passive neutron activation method, is the utilized in this work. The passive technique involves the exposure of various materials transuranic generated neutrons and subsequent remote determination of the neutron-induce reaction products. This technique is not influenced by high gamma fields and can yield gy related spectral information with appropriate use of threshold reactions.

The following criteria were considered in choosing appropriate materials for passiv neutron monitors. The neutron-induced reaction product had to be easily determinable. was quickly narrowed to radioactive products having distinctive gamma-ray emissions whic could be nondestructively determined in high sensitivity gamma-ray spectrometers. The p uct had to have a relatively high branching fraction through the gamma cascade of intere and a half-life between a few hours and a few days to allow the sample to reach near sat tion values within a reasonable exposure period. Time required for transfer from exposu to counting precluded very short half-lives. The material needed to be in a physically manageable and durable chemical form. The material needed to be readily available at re able cost; and cross sections for the neutron-induced reactions needed to be as large as sible in the interest of sensitivity.

After a thorough examination of the chart of the nuclides and a few preliminary exp ments, the number of suitable passive neutron monitors was narrowed to the four metals, magnesium, copper, zinc, and indium. The neutron reactions of interest in these metals listed in Table I along with the product half-lives, gamma-rays measured, and branching fractions. The copper and indium capture reactions monitor the thermal neutron flux and used in different situations rather than simultaneously. The copper reaction is used in cases where time and proximity to laboratory-based large crystal NaI(Tl) multidimensiona gamma-ray spectrometers permits. If rapid data acquisition or remote field measurements required, the indium reaction can be used in conjunction with a portable anticoincidence shielded NaI(Tl) well counter at nearly comparable sensitivity levels.

The zinc reaction has a practical threshold of 2.3 MeV, and the excitation function rises smoothly through a maximum of 280 mb at 10 MeV. The energy of the neutrons produc by (α,n) reactions on oxygen or fluorine is dependent not only on the kinetic energy of alpha particle but also on the excitation state of the residual nucleus. Therefore, the reactions result in a spectrum of neutron energies with the maximum being 3.22 and 5.76 for plutonium alpha particles on fluorine and oxygen, respectively. The spontaneous fis neutrons have a typical fission neutron energy distribution curve peaking at 1 to 2 MeV tailing up to ∿17 MeV. The zinc monitor reaction is therefore sensitive to both (α,n) a spontaneous fission neutrons.

The magnesium monitor reaction has a practical threshold of 6.2 MeV and is, therefo not sensitive to (α,n) neutrons but only to the small percentage of high energy spontane fission neutrons above this threshold level. The excitation function for this reaction smoothly through a maximum of 195 mb at 13 MeV, and although this monitor is not as sens as the others, it provides a specific measure of spontaneously fissioning isotopes such ^{240}Pu.

Table I. Passive Activation Neutron Monitor Reactions

Reaction	Product Half-Life	Gamma-Rays Measured (MeV)	Branching Fraction
^{63}Cu(n,α)^{64}Cu	12.8 h	0.511 x 0.511 coincidence	18.5%
^{15}In(n,α)^{116m}In	54.0 m	2.391 - 2.529 doublet	86.0%
^{64}Zn(n,p)^{64}Cu	12.8 h	0.511 x 0.511 coincidence	18.5%
^{24}Mg(n,p)^{24}Na	15.00 h	1.369 x 2.754 coincidence	99.85%

In order to quantitatively determine unknown transuranic element concentrations, iso- , or chemical composition from a measurement of induced activities in passive metal ors, it is necessary to calibrate the technique with known quantities of transuranic es under similar environmental conditions. This can be accomplished by constructing -up facilities virtually identical to the system being monitored and spiked with known ities of transuranic elements, by making rough mock-ups with "bugs" of transuranic ele- in strategic locations, or by monitoring an analogous field system that has been sam- and analyzed in the laboratory to determine its transuranic element composition. Al- h each of these techniques has been used successfully in this work, this paper will deal tail with only one of the more versatile calibrations.

The major demand for this passive activation technique thus far has been for the deter- ion of plutonium in soils, salt cakes, and waste tanks. Plutonium monitoring in soils ediments is of interest where high level fission product liquid wastes have leaked from ge tanks or where low level process streams have deposited accumulations over the years. minations of plutonium concentrations in high level liquid wastes or salt cakes are of rest from a potential criticality standpoint. These field situations all have the com- equirements that the monitoring must be done in situ from dry wells and in gamma-ray ls up to megarads per hour. These requirements mandate the use of the passive activation ique.

A calibration facility for the above applications has been constructed from a section of t (1.22 m) diameter corrugated culvert filled with local aggregate. A 6-inch (15.4 cm) ter dry well has been installed 11.1 cm off center of the culvert, and five 2½ inch cm) diameter source tubes are spaced on 12.7, 22.9, 34.9, 48.3, and 61.0 cm centers the dry well. Figure 1 shows a top view of this soil calibration facility. Nominal gram sources of plutonium oxides and fluorides of known isotopic composition are placed e source tubes, and the metal monitors are exposed to the neutron flux in the dry well. ed activities are determined by gamma-ray spectrometric methods. The plutonium in each e tube is assumed to be uniformly distributed throughout a spherical shell of soil hav- a mean radius equal to the source tube-dry well separation distance. By normalizing the ed activities from each spherical shell to the plutonium concentration in that shell and ng over all significant shells, the relationship between induced activities and an "in- e" source of uniformly distributed plutonium is determined. This method of calibration een verified experimentally for gamma radiation. A germanium diode "down well" probe imilarly calibrated using various gamma-ray sources, normalizing the data to each spher- shell, and summing all significant shells.[1] Subsequent calibrations of this diode in a 4 π facility filled with uniformly spiked soil yielded identical efficiency factors. alibration of neutron-emitting isotopes is completely analogous.

RESULTS

For the sake of brevity, only a single calibration experiment in this facility will be ssed in detail. However, the results of all other calibrations performed to date are . At this time, only calibrations in dry soil (4.1% moisture content) have been com- ed. However, it is planned to repeat these experiments at various soil moisture levels saturation values. Figure 2 shows the thermal neutron flux as measured in the dry by copper monitors for a 98.02 gram plutonium oxide source having the isotopic composi- of 0.588% ^{238}Pu, 72.659% ^{239}Pu, 19.373% ^{240}Pu, 5.427% ^{241}Pu, 1.907% ^{242}Pu, and 0.866%

. Nielson, N. A. Wogman and R. L. Brodzinski, Nucl. Instrm. Methods 143, 385 (1977).

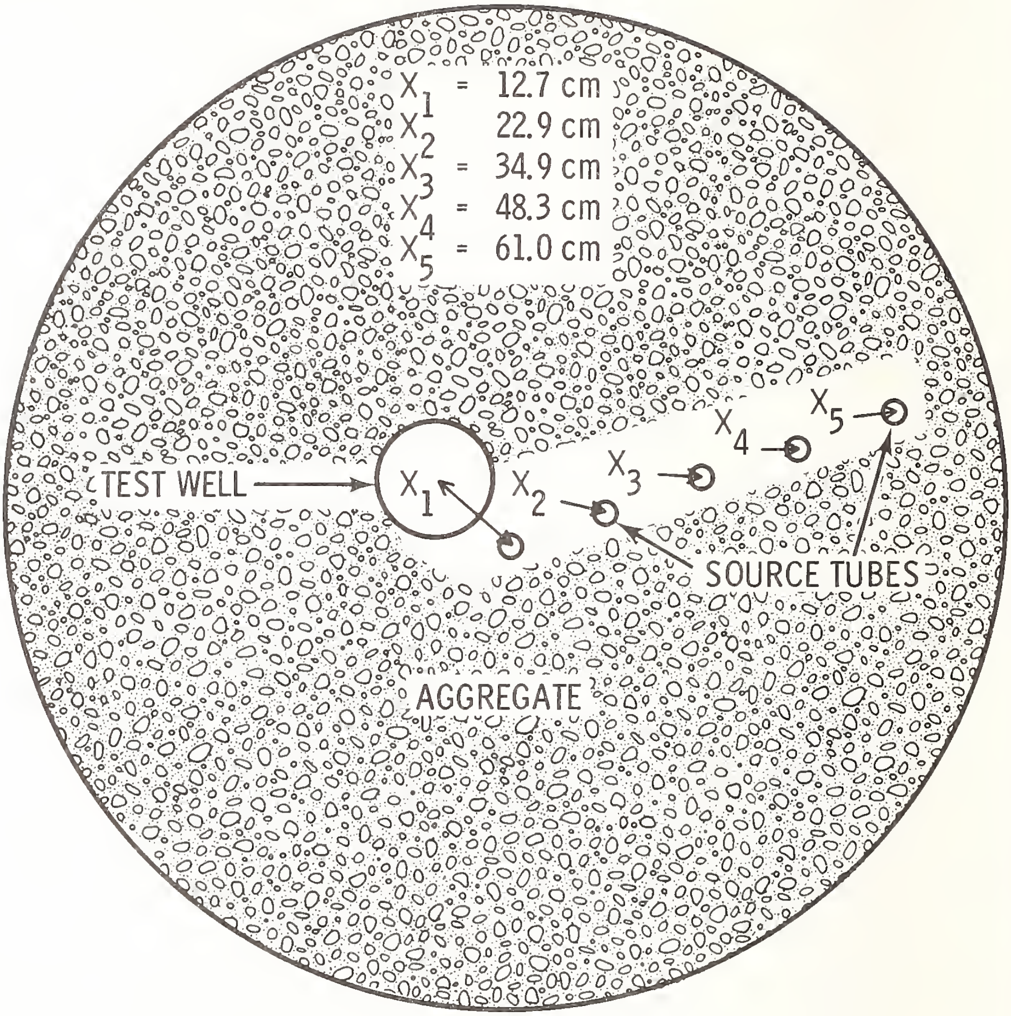

FIGURE 1. TOP VIEW OF SOIL CALIBRATION FACILITY FOR PASSIVE TRANSURANIC NEUTRON MONITORING SYSTEM

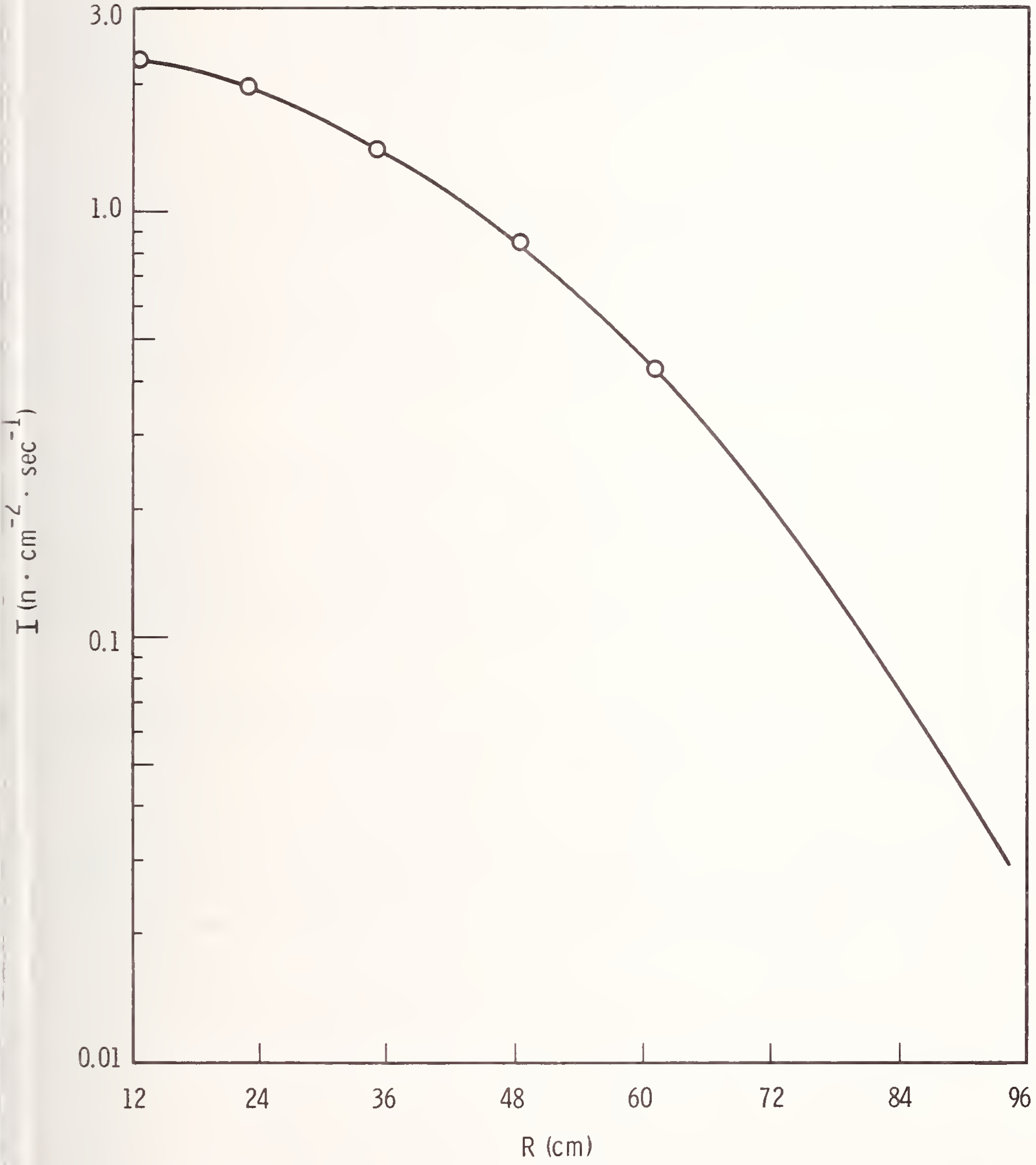

FIGURE 2. THERMAL NEUTRON FLUX FROM A PLUTONIUM OXIDE SOURCE MEASURED THROUGH VARIOUS THICKNESSES OF DRY SOIL

^{241}Am placed in each of the source tubes. In this experiment, a significant contributi to the total induced activity was obtained at the maximum source-monitor separation ava able, and it was necessary to extrapolate the data to a distance of 112 cm before the tribution became less than 1% of the total. This extrapolation, which amounted to 20% the total integrated value, was necessary due to the low moderating capacity of the dr and hence the long range of the fast neutrons. Extrapolation is not anticipated to be sary at higher moisture levels where the moderating ability of the soil will be greatly creased. The zinc monitor required a similar extrapolation which amounted to only 1.7 the total integrated value. No extrapolation was required for the magnesium monitor d because very few collisions are required to reduce the neutron energy below the reacti threshold.

For these calibrations, the monitors were all 15.24 cm diameter discs, 3.175 mm th for copper and 6.35 mm thick for zinc and magnesium. In practice, the geometry of the tor can be tailored to specific needs or requirements with no adverse effects. The onl necessary consideration, which has been included here, is the amount of self shielding sented by the monitor. An experiment offered in proof incorporated the exposure of a disc "facing" a plutonium source in the nearest position and another disc "edge on" to same source. Both discs yielded identical neutron fluxes which reflects the isotropic of the multiply scattered neutrons. Self-shielding corrections are normally not requi for zinc and magnesium monitors due to the low macroscopic cross sections for fast neu interactions.

Thermal neutron flux values are readily calculable from a determination of the qu of reaction products in the monitor, a knowledge of the cross section, and application standard radioactive growth and decay equations. The situation is somewhat more compl the zinc and magnesium reactions, however, since the measured activities are generated spectrum of neutron energies at widely varying cross sections. Therefore, it is most to determine the average product of the fast neutron flux and the cross section normal to a unit mass of monitor material. Such calibrations are determined from saturation ity data and are reported as the number of reactions per second per gram.

It was found that the most meaningful method of expressing plutonium concentratio the soil, activity per unit volume, also produced the most consistent relationship bet sources of different isotopic compositions. In the second column of Table II, the nor ized thermal neutron fluxes as measured by the copper monitors are given for one pluto fluoride source and three plutonium oxide sources of different isotopic composition. shown in the same column are two thermal flux values as measured by the indium monitor verification of the reliability of the technique. Two epithermal neutron fluxes, obta by enclosing the monitor discs in cadmium blankets during exposure, are also given. I should be recognized that the thermal/epithermal ratios are related to moderating capa (moisture level) of the soil and thus can be used to determine the appropriate set of bration curves in situations where soil moisture levels cannot be determined directly. the third column, the activity normalized reaction rates for zinc and magnesium monito are given, and in the last column, the magnesium reaction rates are normalized to the concentration since this is the only isotope which contributes to reactions in this mo

Agreement between the three plutonium oxide sources is excellent and average valu each monitor are shown in Table II. Similarly, the agreement between the oxide and fl source data is consistent with the predicted (α,n) neutron production rates in the two pounds except in the case of the magnesium monitor data which should be independent of ical composition since only spontaneous fission neutrons contribute to this reaction. can be seen in the table, this plutonium fluoride source yields approximately a factor three more high energy neutrons than the oxide sources, a phenomenon which is real and mains unexplained.

DISCUSSION

This technique has a practical detection limit of ~ 8 nCi/cm^3 for monitoring trans ic oxides with even lower values measurable in certain circumstances. A word of cauti regarding background measurements is advisable here. The normal cosmic-ray neutron fl sea level is ~ 0.017 cm^{-2}sec^{-1}, and a piece of copper taken from the laboratory shelf w

Table II. Neutron Reactions in Metal Monitors for Plutonium Sources in Soil Having 4.1% Moisture Content

e and Monitor	Thermal or Epithermal Flux $(n\ cm^{-2}sec^{-1}/nCi\alpha cm^{-3})$	Fast Neutron Reactions $(g^{-1}sec^{-1}/nCi\alpha cm^{-3})$	Fast Neutron Reactions $(g^{-1}sec^{-1}/mg^{240}Pu\ cm^{-3})$
(8.84% ^{240}Pu)			
Cu	$(2.30 \pm 0.29) \cdot 10^{-3}$		
In	$(2.29 \pm 0.39) \cdot 10^{-3}$		
Cu(Cd)	$(4.15 \pm 0.61) \cdot 10^{-4}$		
In(Cd)	$(4.53 \pm 0.54) \cdot 10^{-4}$		
Zn		$(5.52 \pm 0.65) \cdot 10^{-8}$	
Mg		$(2.29 \pm 0.65) \cdot 10^{-9}$	$(2.11 \pm 0.60) \cdot 10^{-3}$
(5.691% ^{240}Pu)			
Cu	$(4.5 \pm 1.0) \cdot 10^{-5}$		
In	$(3.64 \pm 0.95) \cdot 10^{-5}$		
Zn		$(1.03 \pm 0.22) \cdot 10^{-8}$	
Mg		$(7.3 \pm 4.6) \cdot 10^{-10}$	$(9.8 \pm 6.2) \cdot 10^{-4}$
(16.789% ^{240}Pu)			
Cu	$(6.8 \pm 1.4) \cdot 10^{-5}$		
Zn		$(1.00 \pm 0.21) \cdot 10^{-8}$	
Mg		$(8.8 \pm 4.3) \cdot 10^{-10}$	$(7.6 \pm 3.7) \cdot 10^{-4}$
(19.373% ^{240}Pu)			
Cu	$(6.0 \pm 1.2) \cdot 10^{-5}$		
Zn		$(1.01 \pm 0.22) \cdot 10^{-8}$	
Mg		$(6.7 \pm 2.8) \cdot 10^{-10}$	$(7.6 \pm 3.2) \cdot 10^{-4}$
ted Ave. PuO_2			
Cu	$(5.8 \pm 1.5) \cdot 10^{-5}$		
Zn		$(1.01 \pm 0.15) \cdot 10^{-8}$	
Mg		$(7.8 \pm 1.7) \cdot 10^{-10}$	$(8.4 \pm 1.8) \cdot 10^{-4}$

a measurable intrinsic ^{64}Cu activity. If this same piece of copper is kept 10 meters
ground for a day, the ^{64}Cu activity will be substantially reduced. It is therefore
sary when making very low level transuranic element determinations to derive all back-
d corrections based on monitors exposed under similar conditions but in transuranic-
nt free environments.

In certain instances, this technique can yield information on the chemical composition
e transuranic elements (i.e., metal, oxide, fluoride, etc.) by the copper/zinc, copper/
sium, or zinc/magnesium ratios. Similarly, it may be possible to determine the iso-
composition of a transuranic source by the magnesium/copper or magnesium/zinc ratios.

This technique has been successfully applied to the quantitative determination of plu-
m concentrations in a variety of field situations where other methods of analysis were
sible because of inaccessibility, excessive gamma radiation, or real potential for
ment contamination. Plutonium concentrations have been measured in high level fission
ct waste storage tanks, in cribs and trenches which have received plutonium-bearing
ss effluents, and in deep sediments which received accidentally released high level
on product wastes. A plutonium inventory has been performed on a building contamina-
uring a fire as a prelude to decontamination efforts. Process and fabrication hoods and
barrels have been examined and inventoried with remarkable accuracy. In these latter
, an element of directionality was introduced by "backing" the monitors with cadmium-
moderating collimators. In one waste barrel, a single slug of plutonium was located
th 3 cm, identified as plutonium oxide, and the weight was predicted to within 13%. In
ps the most spectacular success of the technique to date, a hidden "pocket" of plu-
m was found in a recess in a channel iron support beam of a fabrication hood being

decommissioned. The quantity and location of the plutonium was predicted, and the dat indicated it to be $\sim$75% oxide and $\sim$25% metal. When the hood was breeched, a pile of b oxidized plutonium metal shavings which had been generated over a period of years by t milling machine in the hood was recovered from where they had fallen through a crack a collected. The quantity recovered was $\sim$12% greater than predicted and from with 8 cm the identified location.

Neutron Correlation Counting for the Nondestructive Analysis of Nuclear Materials

by

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ABSTRACT

The technique of correlating the neutron pulse train from spontaneously fissioning material as an assay tool for nuclear material, its advantages, problems, and the underlying theory are discussed.

KEYWORDS: Spontaneous fission; plutonium nuclear material assay; neutron correlation counting; neutron coincidence counting

This report will discuss the use of neutron correlation counting as a way of assaying spontaneously fissioning nuclear material, usually plutonium, but also in certain situations U^{238} and other transuranic elements, particularly Cf^{252}. The intent is a broad rather than rigorous treatment of the theoretical and practical aspects, summarizing work done at many institutions, principally Brookhaven National Laboratory, the Naval Research Laboratory, Los Alamos Scientific Laboratory, and Gesellschaft für Kernforschung, Karlsruhe.[1] In a still developing technique there are still some matters of opinion. In these cases we have fallen back on the developments and experiences at Brookhaven.

The basic purpose of the neutron well correlation counter is to enable the neutrons spontaneously emitted material to be used as a valid signature for the amount of the isotope of interest present. While basically a method for measuring the spontaneously fissioning nuclides the amount of element present can be inferred if the isotopic composition is known. There is currently a strong effort to develop methods to determine isotopics by gamma spectroscopic techniques so that the neutron correlation assay method can be carried out in the field in a timely way without recourse to laboratory mass spectrographic analysis.

The neutrons coming from a typical sample have three origins:

i) spontaneous fission, which depends only on the amounts and proportion of the so-called even isotopes present in the sample (U^{238}, Pu^{240}, Cf^{252}, etc.)

ii) induced fission caused when neutrons (from whatever source) are absorbed by the isotopes present which as a result undergo fission. This depends not only on the isotopes present, but also on their concentration and the geometry of the sample

iii) (α,n) nuclear reactions caused by the bombardment of various (usually light element) nuclei (present in the sample either intentionally or as impurities) by the alpha particles copiously emitted by the transuranics nuclides present. This contribution to the neutron emission will depend on chemical composition and perhaps also the microstructure of the material in the sample.

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[1] At present the two most complete descriptions of the neutron correlation method are:

R. Sher, "Operating Characteristics of Neutron Well Counters", BNL 50332, Brookhaven National Laboratory (Long Island, New York, U.S.A.) (1972).

K. Böhnel, "Die Plutoniumbestimmung in Kernbrennstoffen mit der Neutronenkoinzidenzmethode" (Karlsruhe, F.R.G.), KFK 2203, Gesellschaft für Kernforschung M.B.H. (1975).

Both of these have extensive bibliographies to work done at BNL, LASL, Karlsruhe, and other institutions.

Concentrating for definiteness on the problems of Pu measurement, of these,
ly (i) is strictly tied to the Pu isotopic content alone, and so only the
ontaneous fission can be relied on in all cases to furnish a valid indication
the Pu content. Source (ii), induced fission neutron, cannot practically be
stinguished from the spontaneous fission neutrons since their multiplicity of
ission and energy distribution are quite similar. Fortunately it is only for
ssive and/or highly compact materials that this effect becomes appreciable.
en it does occur it is often possible to make approximate allowances, as will
discussed later.

It is the last contributor, the so-called uncorrelated (because they are
nerated singly in a Poisson distributed fashion) or (α,n) neutrons, which
use most of the trouble. Their energy spectrum is sufficiently similar to
at of fission neutrons so that discrimination on this basis is not practical.
ey will be present in any size of sample and since they depend on details of
emical content and physical structure are usually poorly related to the amount
Pu present.

Therefore a method using spontaneous neutron emission as a signature or
dicator of the amount of Pu present must be able to eliminate the (α,n) com-
nent (and hopefully find some accommodation with the induced fission).

The basic difference between fission neutrons (spontaneous or induced) and
,n) neutrons which is used is the fact that while the individual fissions
cur Poisson distributed in time, all the neutrons from a single fission are
itted almost instantaneously ($\sim 10^{-15}$ sec) compared to the scale of times we
e concerned with. They thus form a group in time which maintains its coher-
ce even after moderation. The basic scheme of the correlation counter ex-
oits this fact. It might be noted here that fissions emitting single neutrons
e of course indistinguishable from (α,n) neutrons, but the derivation of the
aracteristics of the instrument automatically takes this into account.

Before proceeding further, it is appropriate at this point to note that
nother perhaps more obvious way of exploiting the multiplicity is to use coin-
idence detection of emitted neutrons, and this has indeed been done. The pros
nd cons of coincidence versus correlation counting will be discussed later.

Several kinds of electronics have been developed to separate fission events
rom others producing neutrons. The simplest type just involves two scalers,
e with a dead time of the order of the lifetime of neutrons in the detector,
he other ideally having a vanishingly small dead time. Since the first scaler
ill miss closely spaced pulses caused by neutrons from a fission whereas the
ther will record every neutron, the difference in count rate between the two
calers can be related to the number of fissions detected. There are several
aults such a scheme has, particularly that it requires elaborate corrections
or count rate effects.

More efficient circuitry has been developed based on a correlation tech-
ique in which each incoming pulse from the neutron detector is in effect caused
o answer the question as to how many pulses preceded it in a time period of the
rder of the neutron lifetime in the detector and which therefore might have
ome from the same fission event. This type of circuit in its present form
sing shift registers to form the solid state equivalent of delay lines makes

efficient use of incoming information, is capable of high count rates, requires minimal correction for count rate effects, and will be the kind discussed below.

The neutron well correlation counter consists of a detector and associated electronics. The detector is essentially a cavity (into which samples to be assayed are placed) formed by moderator and proportional counters sensitive to neutrons. The purpose of the moderator is to slow the neutrons emitted by the sample so that they may be more efficiently detected by the counters. However, this moderation is accompanied with the introduction of a spread in the detection times of neutrons coming from the same fission, as well as a loss of neutrons to competing process such as leakage from the detector or by absorption by the moderator. The effect of the moderation, capture, and leakage, is to introduce a probability of detection per unit time which to a good approximation can be taken to be decreasing exponentially and characterized by a single time constant parameter known as the "die away time", τ_0. This is the neutron lifetime in the detector referred to above. Thus the probability of detection per unit time (normalized) may be written as $(1/\tau_0)\ e^{-(t/\tau_0)}$. The zero of time can be considered from when the first moderated neutron of a group from a single fission enters the detector region of the counter after passing through the moderator.

To describe the operation of the electronics: The pulses coming from the detector, each representing a detected neutron, are amplified and replaced on a one for one basis by uniform pulses of relatively short time duration. This pulse train enters a pulse correlation circuit. This latter circuit analyzes the pulse train from the detector by finding out and recording for each pulse as it arrives, how many pulses preceded it within a particular time period, set to be of the order .

The number in the register, after making allowances for counts generated by chance (i.e. uncorrelated) pulses, can be calculated exactly in terms of the amount of spontaneously fissioning material, q, the probability distribution function for the number of neutrons emitted per fission P_ν, the efficiency of the detector for detecting a single neutron ϵ, and a factor $0 \leq F \leq 1$ which pertains to particulars of the pulse correlation circuit and can be calculated knowing the details of the circuitry. In principle the calibration factor for the neutron well correlation counter, i.e., the proportionality constant between instrument's output the and the amount of material can be established without using standards.

In the following the constant of proportionality will be derived with emphasis on making the process of correlation seem physically plausable rather than on rigor. The derivation will be made with the simplifying assumption that events whether correlated or not (i.e. fissions or (α,n) reactions) do not appreciably overlap in time. The conclusions would be essentially the same even if they did. At first it will be assumed that the time over which correlations are measured is long compared to the die away time. These conditions imply a low counting rate, but in practice, the operation is as predicted by the formula to be derived here for count rates high enough to be at the limits of resolution for proportional counter pulses. The breakdown of the derived relation comes about from multiplication and at extremely high count rates from electronic problems.

Consider the simplified block diagram for the correlation circuit (Figure
.

Each pulse entering the circuit sets off a strobe signal which activates e adder. The pulse then enters three places; (1) a gross scaler, so called cause it counts every incoming pulse; (2) a delay line of length τ set by the erator in accordance with principles to be discussed later; (3) the additive put of an up-down scaler.

Pulses exiting the delay line are routed to the subtractive input of the -down scaler, thus the state of this scaler indicates the number of pulses in e delay line. When the adder is activated by a new incoming pulse it thus ds an amount equal to the number of pulses in the time τ preceding the incom- g pulses to the register.

Suppose an isolated group of k pulses within a time period less than proaches the correlation circuit. The first pulse activates the strobe, but nce there is no pulse then present in the delay line, no count is added to the gister. However, the advent of the second pulse in the group will find a lse already present on the delay line, hence a '1' will be added to the regis- r. The third pulse will find two pulses preceding, and cause a "2" to be ded to the register, etc., and so the increment to the R register by this oup of k pulses will be $0 + 1 + 2 + \ldots + (k-1) = k(k-1)/2$. The increment to e G scaler will of course just be k.

The contribution to the register R at the end of a measurement time inter- l t will be calculated by considering it to be made up of two contributions, $= R_f + R_\alpha$ where R_f represents the contribution due to fissions and R that e to (α,n) neutrons. Similarly, the gross count will be taken as $G = G_f + G_\alpha$.

The probability of ν neutrons being emitted by a fission will be symbolized P_ν. This distribution has been experimentally measured and is tabulated in veral publications. The conditional probability that if ν neutrons are itted, k will be detected, resulting in k pulses, is $P(k/\nu)=\binom{\nu}{k}\epsilon^k(1-\epsilon)^{\nu-k}$, where ϵ is the efficiency for the detection of a single neutron. Thus the oduct $P_\nu\binom{\nu}{k}\epsilon^k(1-\epsilon)^{\nu-k}$ represents the probability that k pulses result from fission in which ν neutrons were emitted. The sum over allvalues of ν of this oduct is then the probability that k pulses result from a fission regardless ν:

$$P(k) = \sum_\nu P_\nu \binom{\nu}{k} \epsilon^k (1-\epsilon)^{\nu-k}$$

ote that for $k>\nu$, $\binom{\nu}{k} = 0$ so that the corresponding term is identically ero.)

The average number of pulses resulting from a fission and added to the G aler is thus

$$\langle k\rangle = \sum_k k\, P(k)$$

$$= \sum_k k \sum_\nu P_\nu \binom{\nu}{k} \epsilon^k (1-\epsilon)^{\nu-k}$$

Interchanging summations:

$$\langle k\rangle = \sum_{\nu} P_\nu \sum_{k} k\binom{\nu}{k}\epsilon^{k}(1-\epsilon)^{\nu-k}$$

By appendix I(2), the sum over k can be evaluated exactly:

$$\langle k\rangle = \sum_{\nu} P_\nu\, \nu\epsilon$$
$$= \epsilon\,\langle\nu\rangle$$

Letting m be the mass of material present, λ the spontaneous fission rate per unit mass, then mλt is the number of fissions during the time period. Thus $G_f = m\lambda\epsilon\langle\nu\rangle\tau = q\epsilon\langle\nu\rangle\tau$ where q = mλ is the source strength for fission. There will also be (α,n) neutrons produced in some ratio (characteristic of the given sample) to the fission neutron production rate. It may be assumed that there is also a somewhat different detection efficiency for these neutrons due to their having a different energy distribution. Considering both these factors, an effective ratio of pulses produced by (α,n) neutrons to those produced by fission, α, may be introduced such that $G_\alpha = \alpha G_f$. Thus

$$G = G_f + G_\alpha = G_f(1+\alpha) = \epsilon\langle\nu\rangle(1+\alpha)(qt) \quad .$$

As described above, a fission which results in k pulses will add ½k(k - 1) counts to the R register. The average number added to R due to the fission component per fission is therefore

$$\langle \tfrac{1}{2}k(k-1)\rangle = \sum_{k} \tfrac{1}{2}k(k-1)P(k)$$
$$= \frac{1}{2}\sum_{k} k(k-1)\sum_{\nu} P_\nu\binom{\nu}{k}\epsilon^{k}(1-\epsilon)^{\nu-k}$$
$$= \frac{1}{2}\sum_{\nu} P_\nu \sum_{k} k(k-1)\binom{\nu}{k}\epsilon^{k}(1-\epsilon)^{\nu-k}$$

From Appendix I(3):

$$= \frac{1}{2}\sum_{\nu} P_\nu\, \nu(\nu-1)\epsilon^{2} = \frac{1}{2}\epsilon^{2}\langle\nu(\nu-1)\rangle$$

Since there were on the average (qt) such fissions during the time interval t, the contribution to R from this source is therefore

$$R_f = \frac{\langle\nu(\nu-1)\rangle}{2}\,\epsilon^{2}\,(qt)$$

This calculation implicitly assumed that an indefinite amount of time was available to collect every last one of the ½k(k-1) pulses. Actually it is advantageous from the standpoint of maximizing the "signal to noise" ratio of measurements to collect pulses only over a range of the order of the die away time . This will be discussed later in greater detail. Also for practical reasons having to do with the electronics, the start of the correlation time period is delayed a small amount of time. In other words, pulses preceding the incoming pulse within some fixed small amount of time are ignored. Thus the incoming pulse "interogates" the delay line only over a period of time $\tau_2 - \tau_1$, re $0<\tau_1<\tau_2$. Since the normalized probability per unit time for the arrival the fission pulses is $(1/\tau_o)\ e^{-(t/\tau_o)}$, the fraction of pulses which are not t and therefore contribute to R_f is therefore

$$F = \frac{1}{\tau_o}\int_{\tau_1}^{\tau_2} \exp(-t/\tau_o)\,dt = \exp(-\tau_1/\tau_o) - \exp(-\tau_2/\tau_o)$$

ere τ_1 and τ_2 are the beginning and end of the correlation time interval as sured from the incoming pulse. The factor F is determined by the die away e of the detector, τ_o, and the start and stop of the time period for correla- n τ_1 and τ_2 which are determined by the electronics. The quantity τ_1, termed initial delay, is built into the electronics, while τ_2 is adjustable in ed increments δ, selected by the operator, such that $\tau_2 = \tau_1 + n\delta = \tau_1 + \tau$. s

$$F = \left[\exp(-\tau_1/\tau_o)\right]\left[1 - \exp(-\tau/\tau_o)\right]$$

The quantity R_f is then modified by the factor F to be

$$R_f = \frac{\langle \nu(\nu-1)\rangle}{2}\,\epsilon^2 F\,(qt)$$

This is the contribution to R due to pulses which are correlated with one ther, i.e., arrive in groups. There is besides this the contribution to R m pulses randomly distributed in time. Suppose at the end of the t seconds counts have accumulated in the gross scaler. This implies an average count e G/t. Thus at any given time there must have been on the average $(G/t)\tau$ nts in the delay line of "length" τ. (This is actu- y a solid state realization of a delay line called a shift register.) Since re were by hypothesis G counts entering the detector, this is the number of es that a quantity of counts whose average value was (G/t) was added to the ister. Thus

$$R_\alpha = G(G/t)\tau = G^2(\tau/t)$$

l

$$R = R_f + R_\alpha = \frac{\langle \nu(\nu-1)\rangle}{2}\,\epsilon^2 F\,(qt) + G^2(\tau/t)$$

To recover the quantity R_f which is proportional to the amount of ssioning material we must therefore sutract R_α from the total in the register:

$$\begin{aligned} N &= R - R_\alpha \\ &= R - G^2(\tau/t) \\ &= \frac{\langle \nu(\nu-1)\rangle}{2}\,\epsilon^2 F\,(qt) \end{aligned}$$

ere N is the so-called net count . Thus the proprotionality between the ount of fission in the sample (qt) and the so called net count is

$$\frac{\langle \nu(\nu-1)\rangle}{2}\,\epsilon^2 F$$

This result has been experimentally verified in several ways. By successively disconnecting detectors the data for a plot of ln N vs. lnϵ can be obtained, and the ϵ^2 dependence verified to within a few tenths of a percent over several orders of magnitude of ϵ, limited only by counting statistics.

The dependence on $\frac{1}{2}\langle\nu(\nu-1)\rangle$ and F has been also verified to about one percent limited only by the accuracy to which a "known" source was calibrated, and by counting statistics.

The net count N is perhaps to be considered the primary correlation leading to the source strength because it accomplishes the basic purpose of the instrument, namely to allow the neutrons emitted spontaneously by the sample to be used as a signature for the amount of material present by eliminating (α,n) and other uncorrelated neutrons.

Another quantity can however be defined which has useful properties. If the square of the gross count is divided by net count as defined above, the ratio

$$(G^2/N) = [\epsilon\langle\nu\rangle(1+\alpha)(qt)]^2/\tfrac{1}{2}\langle\nu(\nu-1)\rangle F(qt)$$

$$= \left(\frac{2\langle\nu\rangle^2}{\langle\nu(\nu-1)\rangle}\right)\frac{(1+\alpha)^2}{F}(qt)$$

is seen to be independent of the efficiency, proportional to the amount of material (qt), but unfortunately dependent on (α,n) production and its ratio (including detection efficiency) to fission production.

The surprising independence with regard to efficiency is actually analogous to the principle made use of in the absolute calibration of gamma sources involving two gammas in cascade using double coincidence counting. The above result has been verified for neutron correlation counting to within the statistics of the counting process, for example, by deliberately changing the efficiency of the detector (disconnecting detectors) while monitoring the (G^2/N) ratio, and by other ways. (Of course, statistics do become poorer as ϵ is decreased, keeping counting times the same.) A use for G^2/N would be, for example, to eliminate the effects of the efficiency changing with respect to position within the cavity, or to render samples comparable as to Pu content which have different amounts of absorption or moderation.

Another useful quantity is the ratio

$$(G/N) = \frac{\epsilon\langle\nu\rangle(1+\alpha)(qt)}{\frac{1}{2}\langle\nu(\nu-1)\rangle\epsilon^2 F(qt)}$$

$$= \frac{2\langle\nu\rangle(1+\alpha)}{\langle\nu(\nu-1)\rangle\epsilon F}$$

It depends on the efficiency, and on the (α,n) production ratio, but not on the amount of material present. It is often possible, by considering N,G^2/N, and G/N for the same sample, to measure the (α,n) production rate for it. This t relation has been approximately verified (~10%) experimentally by suring (α,n) rates for materials for which the answer was known approxi- ely by other means.

We would now like to consider some of the practical aspects of neutron cor- ation systems. The detector portion of the neutron correlation counter can nade in many forms and sizes to accommodate different measurement problems. largest to date is one to assay ~ 200 liter waste drums, the smallest we w of assayed single metal clad Pu "coupons" which were about 5 cm X 5 cm X cm. Special ones have been made to assay 1 - 2 kg Pu buttons, and for fuel s. The typical so called neutron well counter type illustrates features com- to all (Figure 2). There is a central cavity for the sample surrounded by ayer of polyethylene moderator followed by one or more rings of proportional nters either He^3 or BF_3 filled in more moderator. The thickness of moderator ween the tubes and cavity is determined by the following consideration. As is increased, there will be a greater moderating effect on the fast neutrons or 2 MeV average energy) coming from fission, hence a greater sensitivity of detectors to the neutrons because of the 1/E (where E is the neutron energy) avior of the capture cross section of B^{10} or He^3 at low energies. However, greater the thickness of intervening moderator, the more chance for neutron ture by the polyethylene or scattering out of the reach of the detectors. As esult of these competing processes there is a maximum in the sensitivity of counter versus the thickness of moderator between the detector tubes and the ple cavity. This is at about 25 mm for Pu and 30 mm for Cf^{252} when BF_3 led tubes are used, the difference being the greater average energy of Cf^{252} trons. By making the thickness slightly less than that for maximum sensitiv- ("undermoderated") then if the sample has hydrogenous material in it there l be relatively little change in the sensitivity since the operating point of counter will be shifted about only in the vicinity of the maximum. Well nters for general purposes are usually designed with this in mind either ng a computer code or direct experimentation. If the counter is to be used moderator free materials, then it could be designed for maximum efficiency y. The combination of a '1/E' proportional counter together with moderator es typically neutron well counters which have an efficiency (20 - 30)% using and (30 - 40)% using He^3 tubes.

The choice between He^3 and BF_3 can often be decided on the basis of cost ectiveness. He^3 2.5 cm D. 4 atm. tubes, roughly speaking, will give about greater sensitivity than the 5 cm D 0.9 atm. BF_3 tubes (these are the opti- parameters for safeguards use), but at about a three times greater price. cost of proportional counters is the major item in a typical neutron corre- ion apparatus, even including the electronics. BF_3 proportional counters are s sensitive to gamma rays and produce faster rise time pulses. They have rer resolution and it is suspected a shorter lifetime (though it is still sured in years). For nearly all applications BF_3 tubes suffice.

External to the tube region there is a layer of ~.8 mm Cd followed by an er layer of polyethylene. This outer layer of polyethylene slows down neu- ns coming from outside the counter so that they can be more readily captured the Cd and prevented from entering the counter proper. The sample cavity ally has a ~.8 mm Cd lining to prevent thermalized neutrons from re-entering cavity where they could induce fissions in the sample.

The typical electrical arrangements of the detector and following electronics is illustrated in Figure 3. Proportional counters are run with the center wire positive with respect to the shell. While conventionally the shell is grounded, there are advantages to having it at a negative high voltage. When this is done the center wire will be essentially at ground voltage and can be fed directly into the charge sensitive preamplifier without the intervention of a decoupling resister and blocking capacitor, which are noise producing elements. Since the tube shells are embedded in polyethylene, an excellent insulator, there is no danger from having the shells at a high voltage.

The tubes are divided into groups, each group with its own preamplifier located right in the high voltage junction box. A multi-coax cable connects each preamp with a following amplifier and a fast output discriminator. The amplifier puts out a relatively slow gaussian pulse, $\sim 2\mu$sec FWHM, or a differentiated gaussian, designed to optimize the signal to noise ratio for the type of proportional counters used. This slow pulse is replaced by a standard 0.1 or 0.2μsec pulse from the discriminator. The discriminator pulses are combined together in an "OR" circuit which forms the pulse train analyzed by the following correlation circuitry.

Dividing the proportional counters into groups as described, each followed by its own preamp, amplifier, and discriminator accomplishes two objectives. The input capacitance per preamplifier is kept small for better signal to noise ratio. More important, the "amplifier dead time" caused by the possibility of pulses from different proportional counters overlapping is effectively divided by a factor almost equal to the number of groups that the counters are divided into, yet with no loss in pulse height resolution. This resolution is important in that it enables the discriminator bias to be set optimally between the noise level and the smallest neutron produced pulses occurring with appreciable frequency. A measure of the excellent signal to noise ratio achieved is the fact that proportional counter tubes designed by the manufacturer to operate at voltages of 2500 to 2800 volts with ordinary amplifiers, can be operated routinely at 1000 - 1500 V, and even give useful signals at as low as 500 V, although a portion of the pulse shapes then deteriorate because of poor electron collection. Lower tube operating voltages have practical consequences in reducing the incidence of high voltage leakage problems.

A problem with all well counters is that of variations in sensitivity within the counting volume. A small source of neutrons moved about within the volume will be counted with different efficiency depending on position; this is in fact a practical way to map out the efficiency as a function of location. For a cylindrical volume surrounded by proportional counters whose ative length is about twice that of the cavity height the fall off in sensitivity towards the ends of the counting volume can be about (10 - 15)% of the maximum it has at the midpoint of the axis. (The large overhang was for the purpose of minimizing this problem.) This fall off in sensitivity can be lessened somewhat by using "reflector" end plugs made of aluminum or graphite instead of polyethylene. In a radial direction along the midplane of the counter, the sensitivity will rise as the walls of the counter are approached, by roughly 10% more than the value on the axis. It isn't clear that anything in the way of design improvements could be made to alleviate this without compromising other aspects of the well counter design, such as azimuthal symmetry.

Both problems can be minimized by confining the dimensions of samples easured to be a small fraction of the volume, and making sure that samples are entered within the counting volume. In practice these are often not possible. ne typical well counter is already of the order of 500-600 kg in weight when uilt to accommodate 1-2 liter packages, and the lack of industry standards for ontainers guarantees there will be some oddly sized containers to be measured.

One approach to this problem is to develop a correction factor based on a apping of the counting volume sensitivity. Another method which will work if ne (α,n) contribution can be assumed constant is to use the (G^2/N) method escribed above. Finally, effort should be made to standardize packaging or to e cautious in comparing sample assay results where different geometries are nvolved.

An objection to the correlation circuit shown above (Figure 1), ore theoretical than practical, is that it assumes that the non-correlated ount is constant during the measurement so that it can be calculated as $^2\tau/t$. If this is not so, for example, caused by changes in the background ount of uncorrelated neutrons entering the counter from nuclear material eing moved about in the vicinity of the measurement apparatus, the fluctuations n background will give rise to a correlation, and the estimate $G^2\tau/t$ would e too small. This effect can be taken into account by monitoring the instantaneous alue of the correlation due to fluctuations in the uncorrelated neutrons y means of some additional circuitry as shown in Figure 4.

The basic action is the same as the previous but with an addition. The trobe signal activates the adder as before, but is also delayed for a period of ime long compared to the delay line (correlation time) τ, yet small compared to he time over which the background might be expected to change. Since τ is of he order (10-100) μsec, but it would take $\sim$(1 - 10) sec for changes to be made n the room inventory arrangements, such a choice can be made without diffiulty, say n $\sim$10. The delayed strobe is thus allowed to activate the adder gain via the OR logic circuit at a time such that the pulses in the delay line can have no relation to the incoming pulse from the pulse train, yet close nough in time to accurately sample the instantaneous value of the background. he prompt interrogation results are routed to a register R_p which is the same s the previous R, while the delayed interrogation results are routed to a regster R_d by the action of the AND circuits. Register 1 accumulates the count ue to (i) correlated and (ii) uncorrelated neutrons, and (iii), includes a conribution due to fluctuations in the uncorrelated neutron count rate, while regster 2 accumulates just the latter two contributions, (ii) and (iii). Thus the ifference $R_p - R_d = N$, the correlation count due to correlated neutrons.

Under normal circumstances where the background is constant it is preferble to use the formula $N = R - G^2\tau/t$ in preference to $N = R_p - R_d$ since its tatistical accuracy is better. This stems from R being subject to greater luctuations than G which is generally a very large number, which being a simple ross count, is a Poisson statistic.

When more than one isotope is present, the $\langle\nu(\nu-1)\rangle$ must be replaced by an ppropriate average taking into account the P_ν for the particular isotope information available from e.g. E.K. Hyde, "The Nuclear Properties of the Heavy lements", Vol. II, pp. 221-222 and others), the fraction of all the spontaneous fission nuclides that it contains , and the decay rate for fission for that nuclide. For perhaps most samples only the Pu^{240} content need be considered to give a fairly good answer. People do loosely speak of the Pu^{240} equivalent in terms of the other two isotopes but this is only in terms of neutron yield and would not be proper strictly speaking for $\langle\nu(\nu-1)\rangle$ since there are slight differences in P_ν for the different even Pu isotopes. For Cf^{252}, the P_ν are very different from that of the Pu isotopes.

The extension of the formula for the net count to the case where there is more than one contributing spontaneous fissioning nuclide present is straightforward

$$N = \frac{1}{2} L F t \sum_i \langle\nu(\nu-1)\rangle_i \epsilon_i^2 m_i \lambda_i / A_i$$

where L is Avogadro's number (no. of nuclei per g. nuclear mass), i refers to the nuclide species of mass m_i (g), nuclear mass A_i(g), and decay constant for spontaneous fission λ_i(sec^{-1}). If the total mass is m and the isotopic mass fraction is f_i, ($m_i = m f_i$), then

$$N = \frac{1}{2} L F t m \sum_i \langle\nu(\nu-1)\rangle_i \epsilon_i^2 f_i \lambda_i / A_i$$

Usually the efficiency ϵ_i can be considered the same, i.e., the neutron energy spectra are similar, for all species present (a good assumption if for example we were dealing only with Pu isotopes); then we can write the net correlation count per unit mass and time as

$$(N/mt) = \left(\frac{1}{2} L F \epsilon^2\right)\left(\sum_i \langle\nu(\nu-1)\rangle_i f_i \lambda_i / A_i\right)$$

The dimensionless first factor on the right is a property only of the instrument, the second factor having units (sec^{-1}g^{-1}) depends on the nature of the material. For example, a particular neutron correlation apparatus intended for mixed oxide fuel rod assay had (1/2 LF ^{2}) = 3.14 X 10^{22}, while some fuel rods made up of normal U with a few percent Pu had a value for the summation of $\sum$ = 2.19 X 10^{-23} sec^{-1}g^{-1}. Such calculations are necessary for example if the standard has a different isotopic mix than the samples being assayed.

Some values of parameters for Pu and U are cited below for example only. hey are not necessarily the best values; we have an ongoing request with he National Nuclear Data Center at Brookhaven National Laboratory to update he required data for the nuclides of interest.

TABLE I

Calculation of $\langle\nu(\nu-1)\rangle$ from P_ν

		Pu^{238}		Pu^{240}		Pu^{242}	
ν	$\nu(\nu-1)$	P_ν	$\nu(\nu-1)P_\nu$	P_ν	$\nu(\nu-1)P_\nu$	P_ν	$\nu(\nu-1)P_\nu$
0	0	.044	0	.041	0	.063	0
1	0	.175	0	.219	0	.192	0
2	2	.384	.768	.351	.702	.351	.702
3	6	.237	1.422	.241	1.446	.324	1.944
4	12	.124	1.488	.127	1.524	.033	.396
5	30	.036	.720	.020	.400	.036	.720
6	60			.001	.030		
$\nu(\nu-1)\rangle =$			4.398,		4.102,		3.762

A value of $\langle\nu(\nu-1)\rangle$ for U^{238} can be inferred from quoted values of Diven's parameter $D \equiv \langle\nu(\nu-1)\rangle/\langle\nu\rangle^2$ to be $\langle\nu(\nu-1)\rangle = 3.212$.

TABLE II

Summary of useful parameters for U and Pu
(λ is the fission decay constant on a per nucleon, not mass, basis)

isotope	$\langle\nu(\nu-1)\rangle$	$\lambda(\text{sec}^{-1})$	A(g)	$\lambda\langle\nu(\nu-1)\rangle/A$
Pu^{238}	4.398	4.481×10^{-19}	238.05	8.279×10^{-21}
Pu^{240}	4.102	1.877×10^{-19}	240.06	3.207×10^{-21}
Pu^{242}	3.762	3.138×10^{-19}	242.06	4.877×10^{-21}
U^{238}	3.212	2.197×10^{-24}	238.05	2.935×10^{-26}

TABLE III

Typical Values for a Mixed Oxide Fuel Rod

element or isotope	fractional composition element	(10^{-2}) isotope	$f\lambda\langle\nu(\nu-1)\rangle/A$ (sec^{-1}g^{-1}
Pu	2.83		
Pu^{238}		.506	1.186×10^{-24}
Pu^{240}		19.709	1.789×10^{-23}
Pu^{242}		1.766	2.437×10^{-24}
U	85.32		
U^{238}		99.29	2.486×10^{-26}
		$\sum =$	2.154×10^{-23}

It is also possible and usually more practical to calibrate the instrument with a single piece of material of known isotopic composition, or unknown composition if the weight is known and the isotopics are the same as the samples to be assayed.

When samples are large and or dense multiplication will occur as evidenced by an increase in the net count per gram of material over what it would be for smaller samples of the same type. The basic criterion is whether the geometry and macroscopic neutron cross section of the sample are such that neutrons arising from the sample have appreciable probability of reacting further with it. While people have spoken in terms of the amount of material beyond which one gets multiplication, actually in theory there is no threshold, and whether multiplication is observed or not depends on the precision with which the assy is carried out. As a practical matter one might expect to see significant multiplication in powdered PuO_2 weighing the order of 1 kg or so, while for Pu in metallic form (e.g. in the form of alloy plates or coupons with their flat areas in contact), a few hundred grams would suffice.

Attempts have been made to calculate the amount of multiplication in a sample using methods of reactor theory. One approach based on a simple idealized model of the sample in the counter geometry gives the result in the form of a complicated algebraic formula of uncertain accuracy when applied to an actual situation. Another approach using a Monte Carlo technique is capable of accuracy limited in principle only by computer size and running time but would seem impractical to apply to field use. Perhaps the answer is preparation using either approach of extensive tables covering a wide range of cases which the operator in the field can use to interpolate from to fit the actual cases met.

A practical way to counteract multiplication recognizes that it arises mainly from neutrons whose cross section for inducing fission was increased by slowing down in the well counter body, re-entering that cavity and interacting with the sample. This can be alleviated to an extent by lining the cavity with Cd or B^{10} (borax or boron carbide in some convenient way of containing the powder). The neutrons emitted in fission will pass through relatively unattenuated, but there will be a much higher attenuation for the backward diffusing thermal and epi-thermal neutrons. The attentuation of fast neutrons from the sample will be appreciable, perhaps 20% for $\sim$.8 mm Cd, with corresponding loss in the efficiency ϵ but this may still be a worthwhile sacrifice. The Cd lining can be made removeable for a slight advantage when small samples are being assayed.

The next line of attack with respect to multiplication is to accept that the calibration curve will depart from linearity and calibrate the system for samples of a given type by using a series of increasing weights as standards. The geometry should be kept as comparable as possible; for example, the container diameter might be kept the same while the depth of the material within is allowed to change.

What will be found is that the calibration curve will be initially linear, starting from the origin but will then depart at some point in the direction of giving a larger net count per unit weight of material. Neutron correlation well counter measurements have been made with samples of from 1 - 2 kg of PuO_2 with $Pu^{240}/Pu \sim 0.1$, where the multiplication, i.e. ratio of neutrons actually produced to those coming from spontaneous fission, have been as great as $\sim$1.2 or 1.3. Such samples can have count rates in excess of 10^5 s^{-1}. Samples larger than that, say $\sim$ 3 kg, have to be avoided anyway because they would constitute a criticality hazard if the neutron well counter should become flooded with water. The maximum allowable amount of Pu in metallic form would be considerably less from the criticality standpoint.

In neutron correlation measurements as in any other kind of measurement it is desirable to maximize the signal to noise ratio. In the present situation the "signal" are the correlated counts while the "noise" is made up of uncorrelated counts, due to (α,n) neutrons, neutrons from the environment, and also neutrons coming from fissions such that only one of the produced neutrons was detected. The correlation circuitry discriminates against uncorrelated events by calculating correlation over a period of time set to be of the order of the die away time of the detector. Typically the adjustment allowed by the circuitry is from 16 to 128 μsec. The detector die away time is a good first approximation as to what correlation time to use. This may be measured using the reactor physics technique called the Rossi-α measurement. In it the pulse train from the detector is used as input for a multichannel scaler. Assuming the MCS is not busy when a pulse enters, a time sweep is set off. The next pulse coming in during the sweep causes a count to be added to the channel the sweep is momentarily at. The result of this process repeated many times for a detector exposed to a source of correlated and uncorrelated neutrons will be a histogram as shown in Figure 5 consisting of a simple exponential atop a flat base. This can be interpreted as a plot of the relative probability per unit time of the time interval between the pulse initiating the sweep and the next following pulse. The exponential part is proportional to the probability density of detecting correlated neutrons with the detector and the decay constant of the exponential may be identified with the die away time of that detector. This is actually a practical way of measuring the die away time. It is also possible to calculate die away times with a Monte Carlo or other code, but the experimental way is probably more reliable. The flat portion of the histogram is proportional to the probability density of uncorrelated events. The action of the correlation circuitry can be interpreted in terms of measuring the total area between the vertical lines defining the correlation time interval and subtracting from it that portion consisting of just the uncorrelated contribution. This difference, the correlated count, divided by the uncorrelated count, is the signal to noise ratio for this type of measurement. Maximizing it thus depends on the relative sizes of the two areas. For small random contributions, one can increase the correlation time interval, for large random contributions it should be made smaller, in order to achieve optimum signal to noise ratio.

From this discussion it follows that an optimum counter design is one which maximizes the efficiency and minimizes the die away time. These goals are only partially at odds with one another, since if neutrons are "lost" to the detector volume by being absorbed by the detectors, resulting in counts, then both goals are being served. Reducing the die away time by introducing neutron poisons (as has been done) such as Cd sheeting is generally a poor practice, since the detection of correlated counts depends on the square of the efficiency, ϵ^2, whereas the uncorrelated counts will be detected as ϵ alone. Moreover in introducing the poison one is converting some good events (i.e., more than one detected neutron from a fission) into random events (only one detected) so the signal to noise decreases precipitously. Thus, poisoning the detector should only be used for count rates the electronics cannot otherwise handle.

The statistics of the correlation problem have been studied by various of the groups working in this field but with results which are not convincing to all the parties. One thing which is clear is that the correlation count is not a Poisson statistic and therefore the theoretical standard deviation is not given simply by the square root of the number of counts. Some groups however still use what amounts to a Poisson approach to calculating the statistical uncertainty, namely $\sqrt{(\text{corr.} + \text{uncorr.}) + \text{uncorr.}}$, i.e., the uncorrelated count is treated as a background to be subtracted from the total (correlated + uncorrelated), with each being respectively a Poisson statistic. Other formulae have been proposed, but this writer is skeptical and thinks at the moment the best approach is to experimentally determine what standard deviations might be expected in a given situation by repeated measurements.

We should consider correlation counting in comparison with other methods of assaying Pu^{240} and similar nuclides. The use of correlation counting as a measure of fissioning neutrons arose from the decision to use $B^{10}F_3$ or He^3 proporal counters to make up the detectors. While the original reason for using detectors mainly may simply have been that they were the classic neutron ctor, it is also true that they both have the virtue of being quite insensi- to the gamma rays which are always associated with plutonium and the other suranics. Both these counters depend upon the cross section of B^{10} and He^3 neutrons varying (for low enough energies) essentially as 1/E. To make e detectors have high efficiency, the neutrons have to be slowed down derated) by something like polyethylene. As mentioned before, this causes atistical spread in the arrival time of neutrons at the detectors. While erence is maintained over times (which depend on the geometry and materials he detector assembly) which are of the order of (10 - 100) μsec, this ead renders the usual coincidence techniques unuseable for such a detector e the accidental rate would be too great for such poor resolution. Thus, auto-correlation technique in this situation becomes necessary.

Applying the coincidence method requires dividing the detector into halves to be put into coincidence with one another. Hence, the efficiency the detection of single neutrons is also halved and the coincidence efficiency uced to a fourth of what it would be if the detector of the same bulk e used in an auto-correlation mode. Organic scintillator-photomultiplier e detectors would have to be used since proportional counters unmoderated would be insensitive. The detector would consist of a plastic or liquid scintillator ch operates either on the recoil principle or by slowing down the neutrons il they can be captured and cause the disintegration of some elements ^{0}, Gd, Cd) with which the scintillator is loaded. Organic scintillators sensitive to gamma rays. To some extent, the random gamma rays emitted the plutonium can be discriminated aainst by the resolving time of the ncidence circuitry, while those gammas which are emitted in the fission cess (an average of ~7.5 per fission) will give rise to valid coincidence nts. However, reliance on gammas will give rise to increased matrix dependence assay results compared to the case where the neutrons alone are used because y are more readily absorbed. Electronic neutron-gamma discrimination emes can be used but would add greatly to the complexity of the circuitry. ractical problem is the tendency of photomultiplier tubes to drift with perature and count rate, while proportional counters are notably stable er these conditions.

While more can be said on the question of using coincidence rather than relation counting for the purpose of assaying Pu by utilizing the spontaneous sion of the even isotopes, we feel that in summation there is no good son to develop organic scintillator-based coincidence schemes. There are worthwhile advantages to offset many disadvantages.

Active NDA equipment (random driver, ISAF etc. used in the passive mode h no neutron source) has been used to assay plutonium, but this is not the t way. The count rates tend to be low, the calibration relation is non- ear and matrix dependent and there is no longer the possibility of tracing basic instrument calibration back to a fundamental relation as is the case h the neutron well correlation counter.

APPENDIX I

Suppose one consider the sum (a + b), where a and b are any two numbers, raised to a power ν. From the binomial expansion formula

$$(a+b)^{\nu} \equiv \sum_{k} \binom{\nu}{k} a^{k} b^{\nu-k}$$

where

$$\binom{\nu}{k} \equiv \frac{\nu!}{k!(\nu-k)!}$$

and in particular

$$\binom{\nu}{k} = 0 \text{ for } k > \nu \text{ ; } \binom{\nu}{\nu} = 1$$

Take the derivative of both sides with respect to the parameter a:

$$\nu(a+b)^{\nu-1} = \sum_{k} k\binom{\nu}{k} a^{k-1} b^{\nu-k} \qquad (1)$$

Multiplying through by a:

$$a\nu(a+b)^{\nu-1} = \sum_{k} k\binom{\nu}{k} a^{k} b^{\nu-k}$$

Consider the special case a + b = 1, and let a = ϵ, then:

$$\epsilon\nu = \sum_{k} k\binom{\nu}{k} \epsilon^{k}(1-\epsilon)^{\nu-k} \qquad (2)$$

Taking the derivative of (1) again with respect to a:

$$\nu(\nu-1)(a+b)^{\nu-2} = \sum_{k} k(k-1)\binom{\nu}{k} a^{k-2} b^{\nu-k}$$

Multiplying through by a^2:

$$\nu(\nu-1)a^{2}(a+b)^{\nu-2} = \sum_{k} k(k-1)\binom{\nu}{k} a^{k} b^{\nu-k}$$

Again for the special case a + b = 1, a = ϵ:

$$\nu(\nu-1)\epsilon^{2} = \sum_{k} k(k-1)\binom{\nu}{k} \epsilon^{k}(1-\epsilon)^{\nu-k} \qquad (3)$$

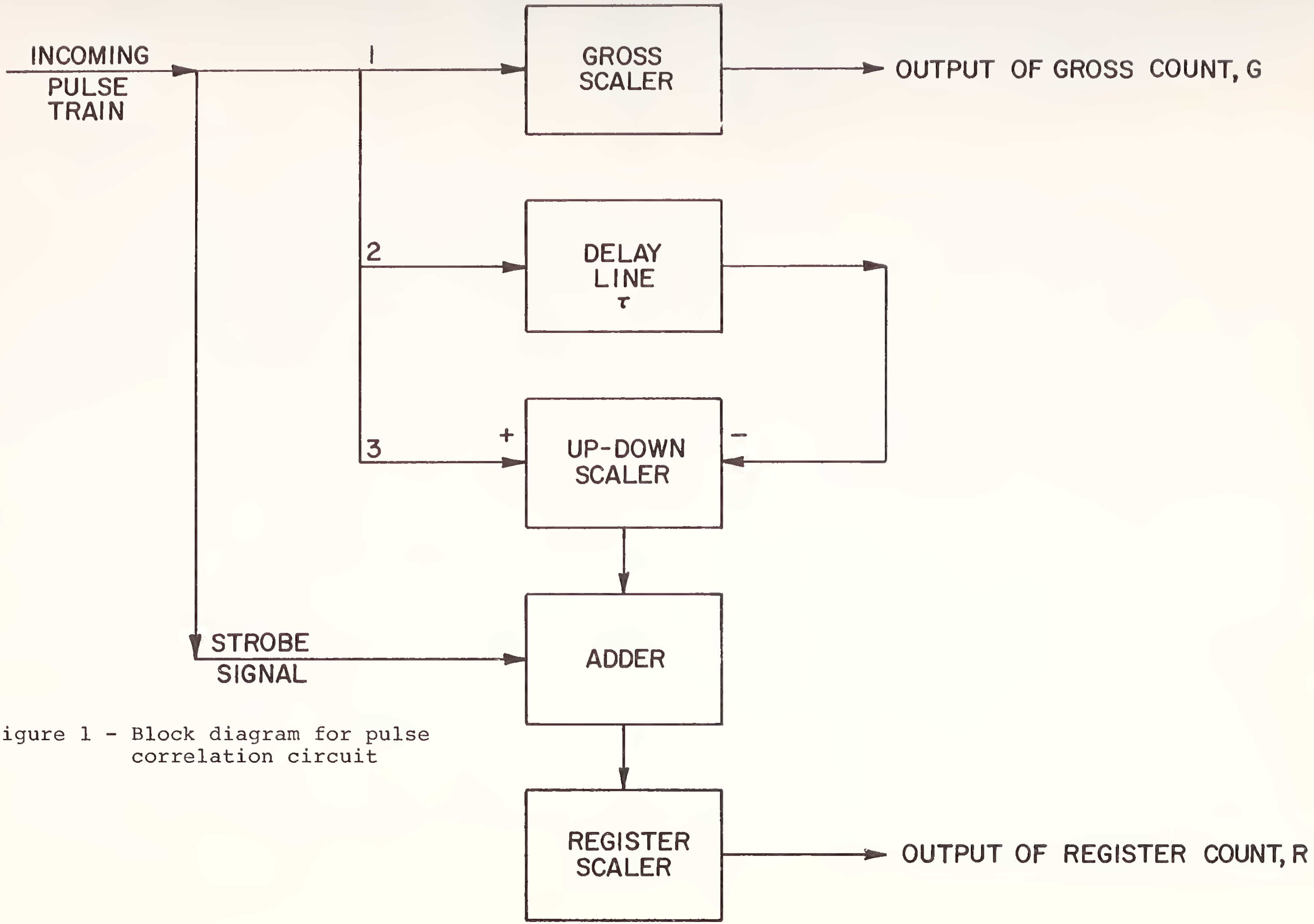


Figure 1 - Block diagram for pulse correlation circuit

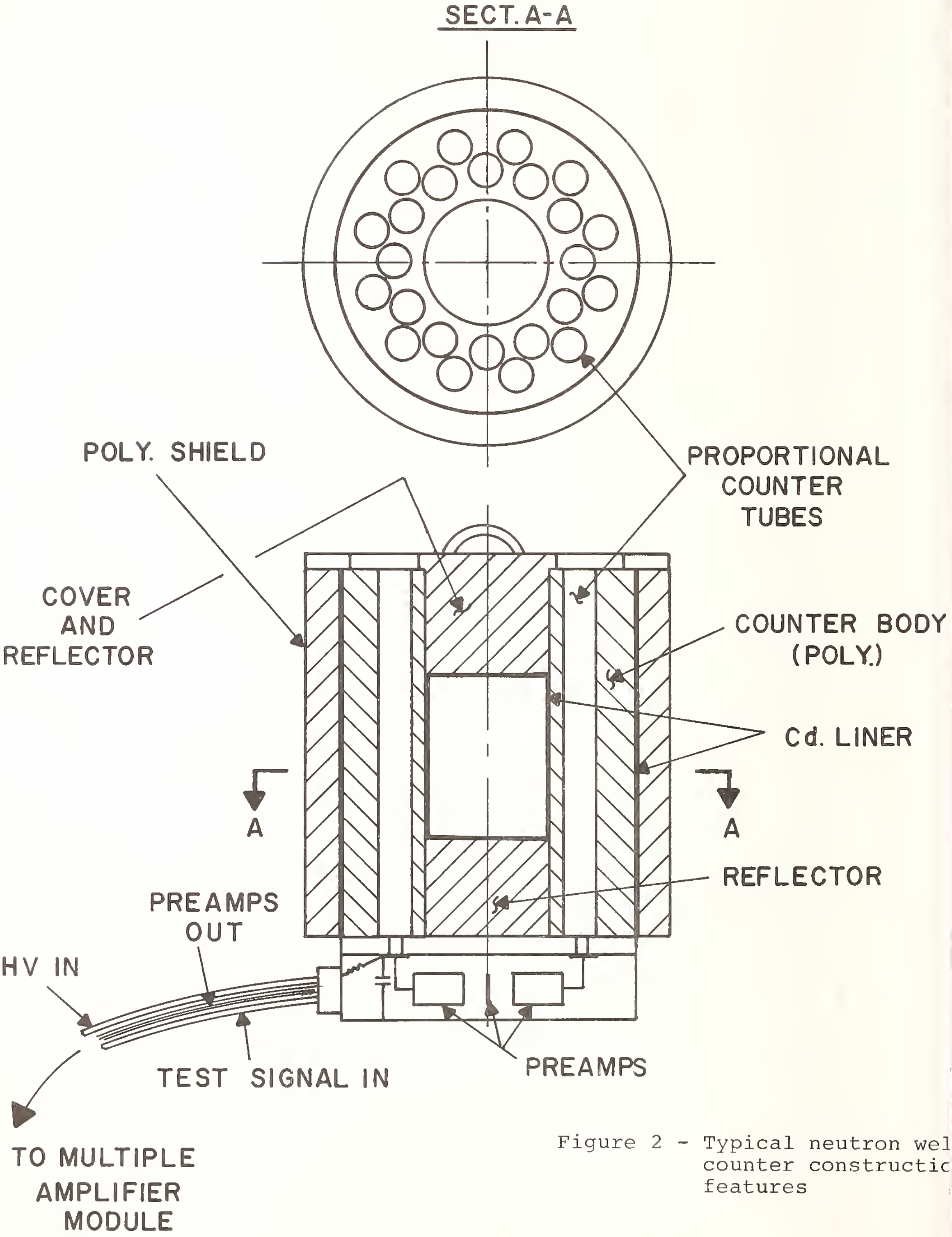


Figure 2 - Typical neutron wel
counter constructic
features

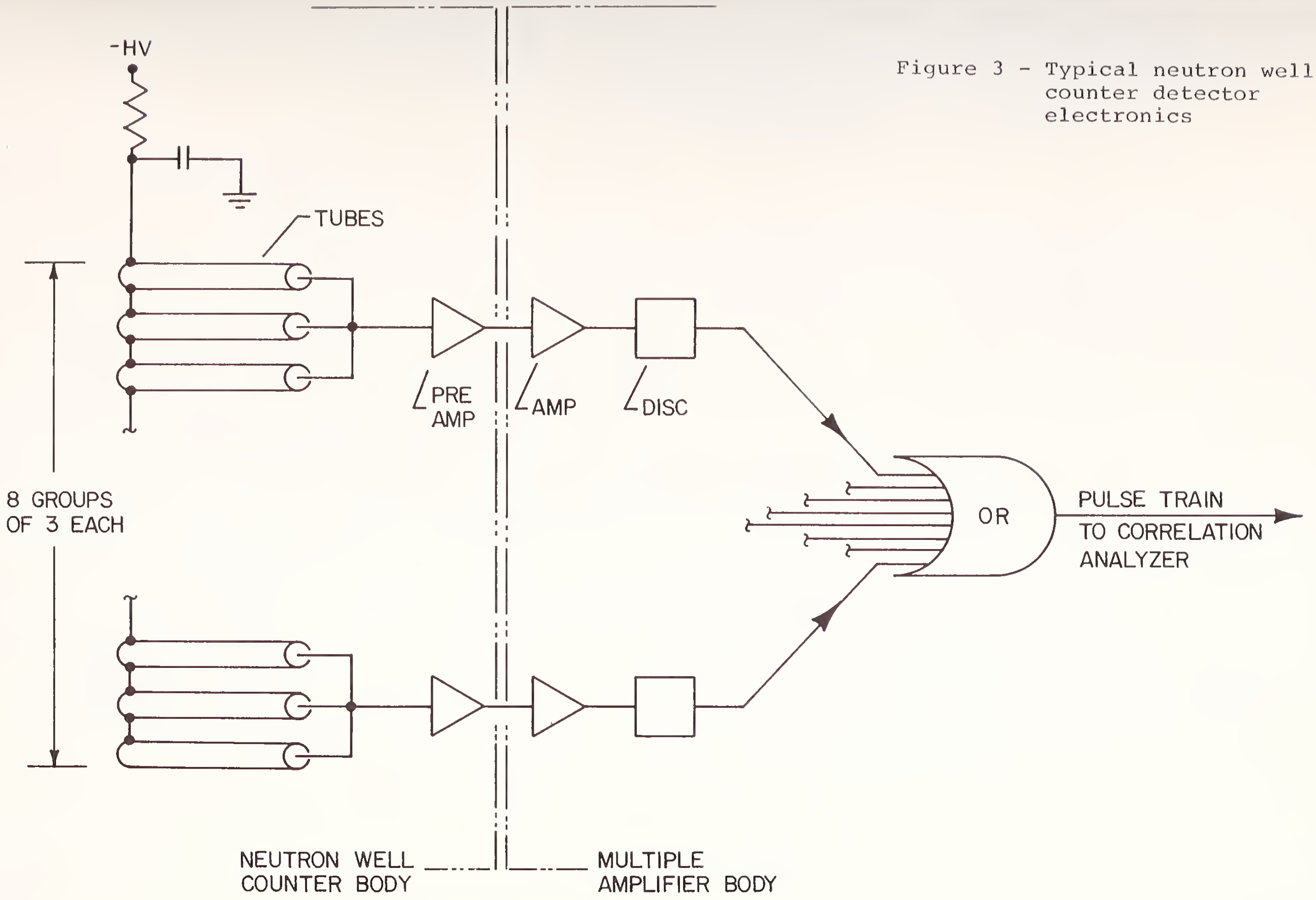


Figure 3 - Typical neutron well counter detector electronics

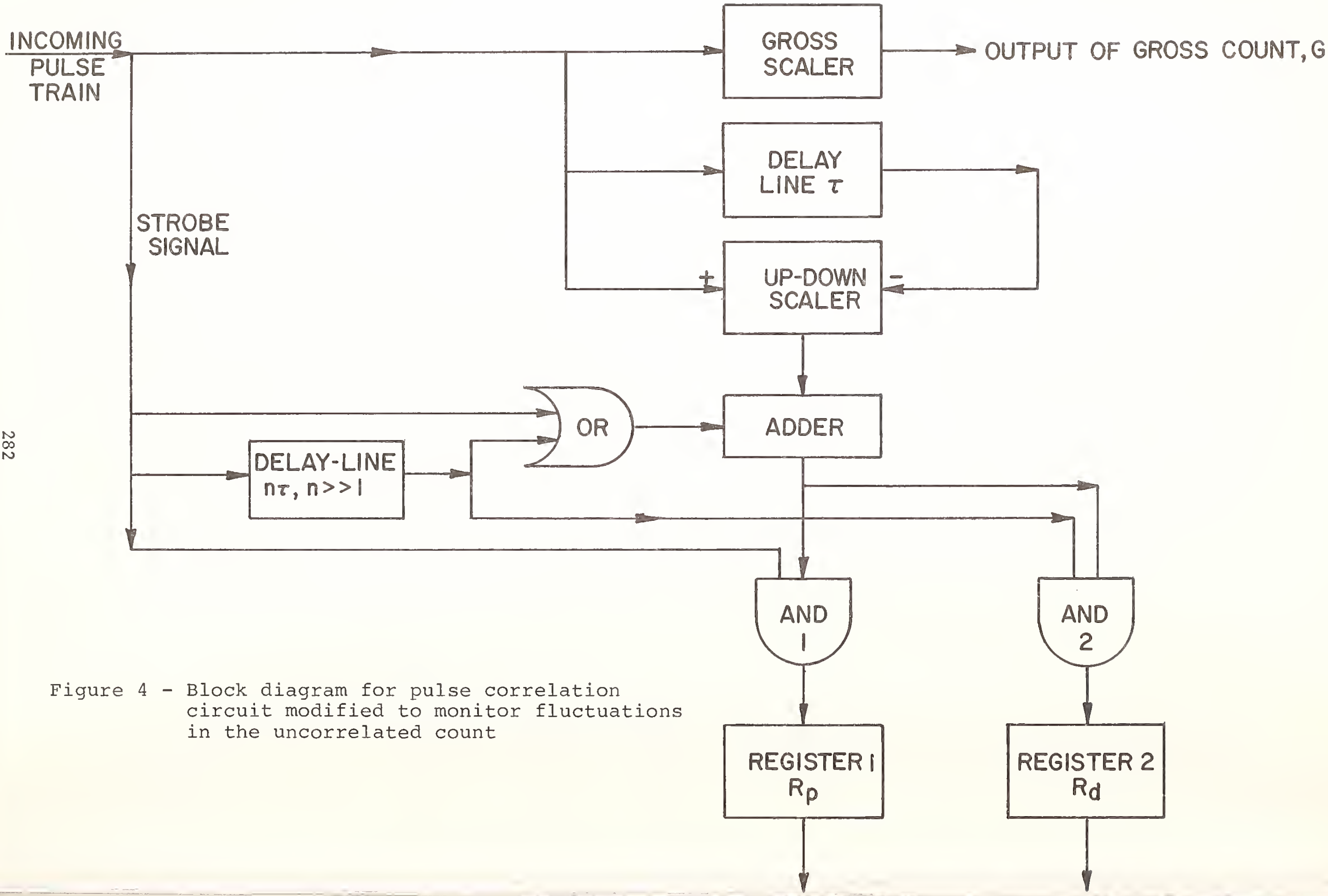
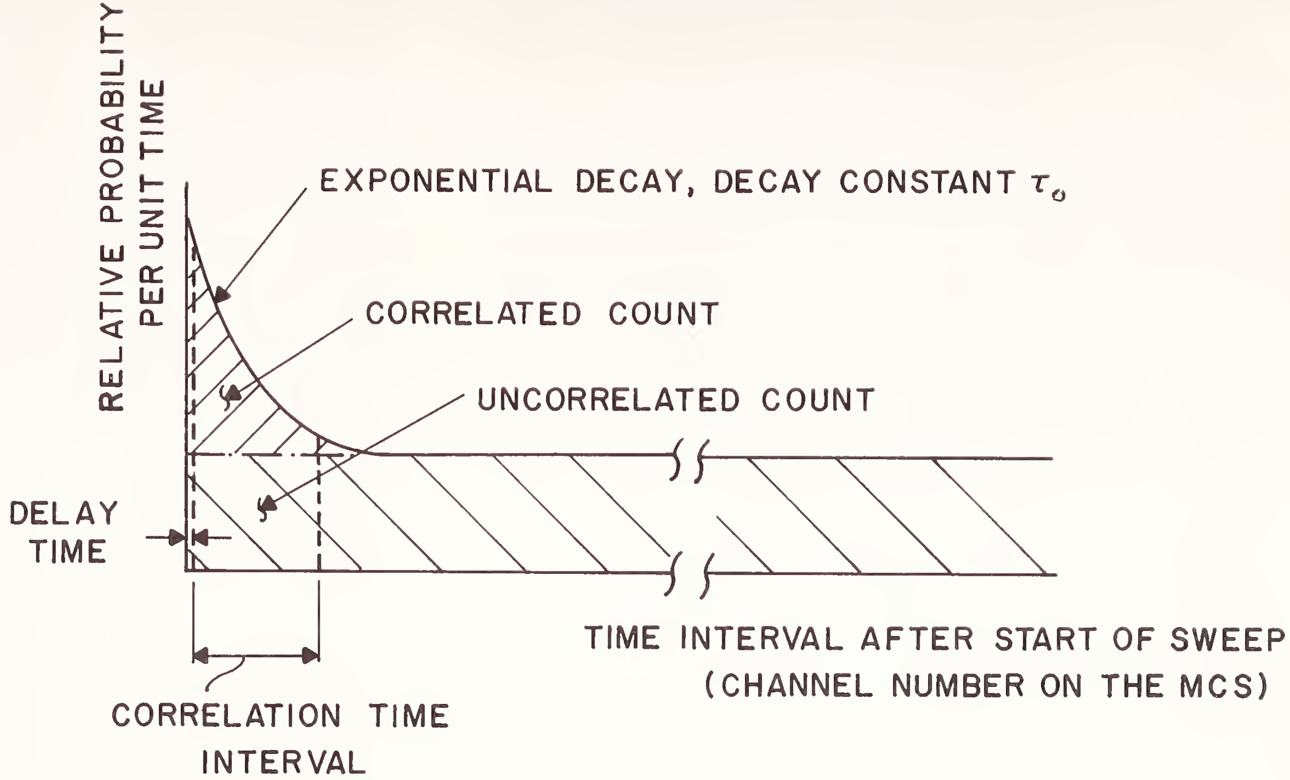


Figure 4 - Block diagram for pulse correlation circuit modified to monitor fluctuations in the uncorrelated count

Figure 5 - Typical Rossi-α experiment result



An Instrument for Monitoring the Transuranic Content of Chopped Leached Hulls from Spent Nuclear Fuel Elements

by

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ABSTRACT

A leached hull monitor featuring high sensitivity for direct transuranic element analysis of various kinds of reactor fuels has been designed for the Commercial Nuclear Waste Vitrification Program (CNWVP) at Battelle-Northwest Laboratories. The instrument can detect the presence of transuranics in undissolved fuel embedded in the chopped hulls following a leaching process, or in undissolved fines or other liquid or solid effluents associated with the CNWVP chemistry. The monitor detects neutrons arising from spontaneous fission and from (α,n) reactions on oxygen in the hulls and wastes. The system is constructed using a massive external neutron shield, an internal lead gamma-ray shield between the sample and the neutron detectors, and an electronic system which records all single and coincidence neutron events which occur during a preset time interval. Both the transuranic neutron flux and the cosmic-ray produced neutron background are determined simultaneously. The system is calibrated with known sources of uranium and plutonium oxides and metals with isotopic compositions typical of each reactor fuel to be processed. The estimated detection limit of the system is 2 mg of Pu in a 10^4 second counting period.

KEYWORDS: Design of hull monitor; plutonium; nuclear fuel; nuclear waste

INTRODUCTION

Transuranic accountability requirements present many difficult problems in the analysi of effluents and solid wastes during reprocessing of spent nuclear fuels. Transuranic residuals may be embedded in the cladding material or be in the form of undissolved fuel following the leaching process due to entrapment in the hulls by the chopping process. If the concentration of these transuranics exceeds some preset allowable limit, the hulls must be releached or placed in retrievable storage instead of some less expensive waste disposal.

There are a variety of methods to detect transuranic elements in chopped leached hulls or other wastes associated with the nuclear fuel recovery process. Active methods such as the detection of delayed neutrons from neutron-induced fission, detection of neutrons from spontaneous fission, or detection of (α,n) neutrons produced by the decay of the transuranic elements would be the most direct means of measurement. Other less direct measurement techniques, which have been considered by workers in the field, are the detection of fission or activation products which hopefully can be related to the quantity of residua fuel. These measurements are generally made using an analysis of gamma-rays emitted by fission products.[1] The latter technology does not directly determine the actual transuranic species and thus is subject to error when preferential leaching of fission products or tran uranic elements occurs in a process stream or in the chopped leached hulls. In addition, high energy fission product recoils embed themselves in the cladding in such a fashion that they may be unleachable with respect to the transuranic species, which creates an overestimate of transuranic element content. In either case, an erroneous value for the transurani content will be obtained by the indirect method.

[1] T. Gozani, "Leached Hull Monitor for Detection of Undissolved Irradiated Nuclear Fuel," INTEL-RT 2311-003, Report by I.R.T. Corp., P.O. Box 80817, San Diego, CA

This communication describes a neutron detection system for the direct measurement of e transuranic elements in the hulls of chopped leached fuel elements and some associated fluent wastes.

INSTRUMENTAL DESIGN

The most direct means of measuring the transuranic elements in chopped leached nuclear el hulls and wastes is to detect their characteristic neutron emission. Since hulls and stes are highly radioactive, the neutron detection system must be able to operate in the esence of high gamma-ray fields. Neutrons can normally best be detected by ^{3}He counters, $_3$ counters, or fission chambers. However, for this application, fission detectors are too efficient, and ^{3}He counters are too sensitive to gamma radiation. Hence, BF$_3$ counters ve been chosen.

The monitor has been designed to accept a 5-gallon can of leached hulls or other wastes ich will be highly radioactive. A 10-cm thick 800 kg lead shield is located between the mple cavity and an annular detector array as shown in Figure 1. This thickness has been perimentally determined to be an optimum trade-off between gamma-ray attenuation and loss geometry/efficiency for neutron detection, and is expected to reduce the radiation dose the BF$_3$ tubes from about 10^4 to about 7 R/hr. Also, the BF$_3$ neutron detectors are ielded from excessive external gamma radiation and from external neutron sources by a mod-ar tank ranging from 15- to 30-cm thick filled with a saturated aqueous solution of boric id. The water acts as a bulk shield for gamma radiation and is a moderator for fast neu-rons. Once thermalized, extraneous neutrons are eliminated with high efficiency by the ric acid. Neutrons emitted by the residual transuranics in the sample chamber pass rough the lead shield and enter the counter/moderator module, which consists of one hun-red 5-cm diameter, 65-cm long carbon-coated BF$_3$ proportional counters (Reuter Stokes, Inc.) rrounded by a minimum of 2.5-cm of polyethylene which acts as a thermalizer for the neu-rons. The carbon coating reduces the degradation that would normally occur from gamma-rays. e stainless steel clad tubes are filled to 90 cm Hg pressure with BF$_3$ which has been en-ched to 96% ^{10}B. All tubes are matched in gain at a common point on their plateau voltage ±3%. Plateau voltages are 1000 volts long starting at approximately 1500 volts with a ope of ∼0.3%/100 volts. All tubes use an alumina ceramic insulation for moisture protec-on and have FWHM resolutions ranging between 16.8 and 26.9%. Tube sensitivity averages 7.8 cps/NV with some as high as 60 cps/NV. All tube testing was done with a PuBe neutron urce.

Neutrons detected by the BF$_3$ tubes generate pulses which are stored in a series of ten calers, one of which records single events. The others record double, triple, quadruple, c. coincidence events as shown in Figure 2. A variable time-delay window is used to de-ne coincidence. Pulses are stored for counting periods ranging from 100 to 10,000 seconds. fter appropriate background corrections are made, the net scaler readings are used to esti-ate the quantities of transuranics remaining in the hulls.

The remaining electronics consist of eight charge sensitive preamplifiers, four preamp-ifier power supplies, two summing amplifiers, one single channel analyzer, one timer, one igh voltage power supply, and two NIM bin/power supplies, all of which are commercially vailable.

DISCUSSION

Cosmogenic background is anticipated to be the major problem in measuring neutrons emit-ed by the transuranic elements. In an experiment conducted at Los Alamos Scientific Labora-ory[2], a substantial background which was attributed to cosmic-ray initiated neutrons in a assive lead shield containing the neutron detection equipment, was reduced by a factor of 0 when the system was covered by 0.9 meter thick concrete overburden. The backgrounds for ach system will thus vary with its relationship to massive shielding in each process facil-ty.

It should be pointed out here that the background is not necessarily constant since the ajority of extraneous pulses are from temporally fluctuating cosmic particle neutron produc-ion in the massive lead shield around the central cavity. However, these events are large-

T. W. Crane and H. O. Menlove, "Application of the Shuffler System with Shielding for Small Hot Samples," LA-6788-PR (1976) ly multiple coincidence events, whereas the transuranic-produced neutrons are virtually e clusively single or double coincidence events. The multiple scaler counting system allow rather precise definition of the single and double coincidence events of cosmic origin tc inferred from the measured higher order events. In this fashion, the necessary backgrour correcting data are obtained at the same time the actual measurement is being made. Quar tative system calibration is accomplished with transuranic sources of varying size, distr bution, and chemical and isotopic composition.

The system discussed in this paper has been designed and engineered but constructior has not yet been completed so operational data are lacking. However, experiments which v conducted during the design phase determined most of the operational parameters and the tical detection limits for the transuranic elements. Although the hull monitor can be ca brated for any type of nuclear fuel, sensitivity calculations were based on a fuel where of plutonium emits 200 n/sec. The overall geometrical efficiency of all BF_3 tubes is ∿7 Using an estimated counting efficiency of 27% and knowing that the lead absorber reduces neutron flux three-fold yields a total efficiency for single neutrons of ∿7% and for dout coincidence neutrons of ∿0.6%. Background for the system is estimated to be 3 c/sec for single events and 0.04 c/sec for double coincident pulses based on mock-up experiments. background will, of course, vary as a function of overburden available to reduce the cosr ray flux, as well as temporal variations in the cosmic-ray activity. These figures yiel detection limit of ∿2 mg plutonium in a counting period of 10^4 seconds. This is at leas factor of 10 lower than that obtainable by using non-direct photon analysis of fission products to infer fissile material in the hull.

The system described in this paper will be used in the nuclear fuel recycle program it is deemed necessary to measure the transuranic content of hulls and other wastes at tl 10 nCi/g level.

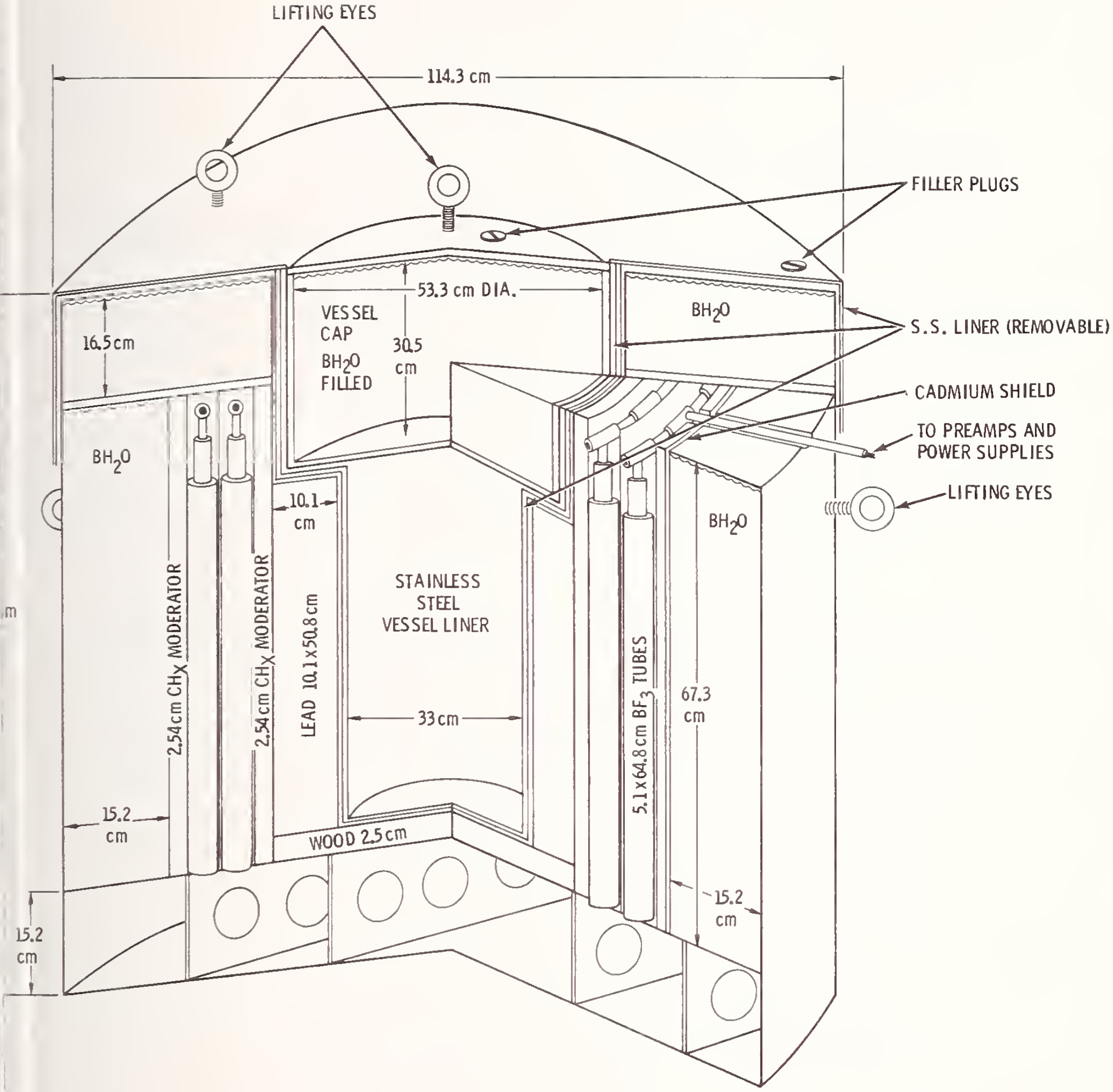
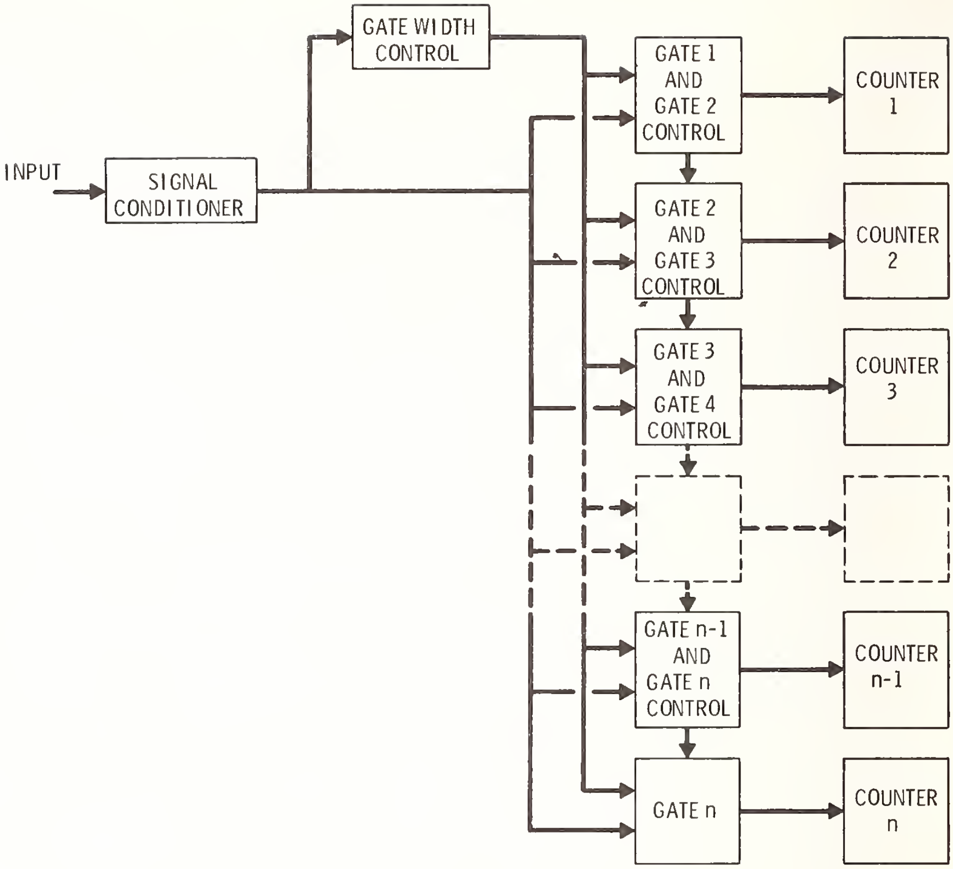


FIGURE 1. SCHEMATIC OF MONITOR FOR TRANSURANIC ELEMENT ANALYSIS OF NUCLEAR FUEL HULLS AND WASTES



INITIAL CONDITIONS:	GATE 1 OPEN, ALL OTHER GATES CLOSED
FIRST PULSE:	COUNTS IN COUNTER 1, TRIGGERS GATE WIDTH CONTROL, CLOSES GATE 1, AND OPENS GATE 2
SECOND PULSE: (WITHIN GATE TIME)	COUNTS IN COUNTER 2, CLOSES GATE 2 AND OPENS GATE 3
THIRD PULSE: (WITHIN GATE TIME)	COUNTS IN COUNTER 3, CLOSES GATE 3 AND OPENS NEXT GATE
nth PULSE: (WITHIN GATE TIME)	COUNTS IN COUNTER n
ADDITIONAL PULSES: (WITHIN GATE TIME)	COUNT IN COUNTER n

AT THE END OF GATE TIME, INITIAL CONDITIONS ARE RE-ESTABLISHED

FIGURE 2. BLOCK DIAGRAM OF COINCIDENCE ELECTRONIC UNIT

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STRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bliography or literature survey, mention it here.)*

This book contains proceedings of the American Nuclear Society's (co-sponsored y the National Bureau of Standards) topical meeting entitled, "Analytical Methods for afeguards and Accountability Measurements of Special Nuclear Materials." The meeting as held in Williamsburg, Va. on May 15-17, 1978. The two objectives of the meeting ere to discuss the latest techniques for chemical analysis of special nuclear materials nd to strengthen lines of communication among scientists working in this field.

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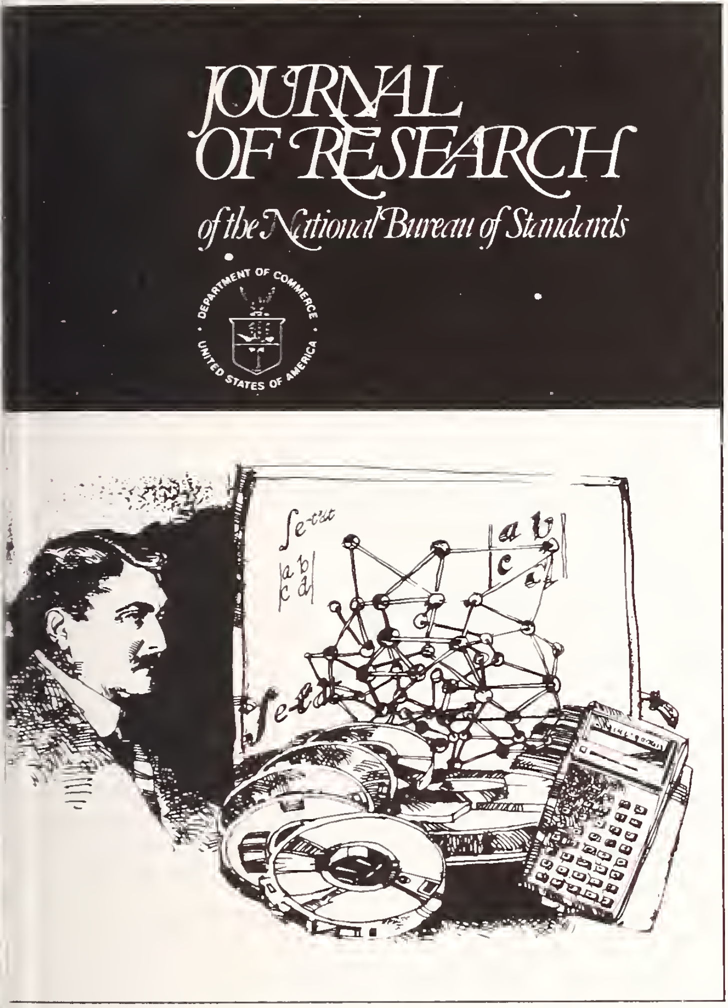

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