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STANDARDS

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Bibliography on Flame Spectroscopy  
Analytical Applications  
1800-1966

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<sup>2</sup> Located at Boulder, Colorado, 80302.

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## Foreword

The National Standard Reference Data System is a government-wide effort to give to the technical community of the United States optimum access to the quantitative data of physical science, critically evaluated and compiled for convenience. This program was established in 1963 by the President's Office of Science and Technology, acting upon the recommendation of the Federal Council for Science and Technology. The National Bureau of Standards has been assigned responsibility for administering the effort. The general objective of the System is to coordinate and integrate existing data evaluation and compilation activities into a systematic, comprehensive program, supplementing and expanding technical coverage when necessary, establishing and maintaining standards for the output of the participating groups, and providing mechanisms for the dissemination of the output as required.

The NSRDS is conducted as a decentralized operation of nationwide scope with central coordination by NBS. It comprises a complex of data centers and other activities, carried on in government agencies, academic institutions, and nongovernmental laboratories. The independent operational status of existing critical data projects is maintained and encouraged. Data centers that are components of the NSRDS produce compilations of critically evaluated data, critical reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data.

The primary output of the NSRDS—compilations and critical reviews—is to be published in a new series, called the National Standard Reference Data Series, within the NBS publications program. However, it has become apparent that bibliographies, especially annotated and indexed bibliographies which are essential elements of the compilation and evaluation process, have a substantial value of their own to the technical public. Plans have therefore been made to publish a number of specialized bibliographies. Some of these will appear in the present NBS Miscellaneous Publication series or as NBS Technical Notes; others will be published and distributed through channels connected with their authors or co-sponsors.

A. V. ASTIN, *Director*

## Preface

This collection consists of 5,113 references to works on flame spectroscopy, selected with emphasis toward analytical measurements, and covers the period from about 1800 to 1966. The references are arbitrarily classified according to the following scheme:

1. Emission
  - 1.1. Early papers (1800 to 1928) (503 references)
  - 1.2. Books on analytical flame spectroscopy (14 references)
  - 1.3. Theses (60 references)
  - 1.4. Reviews (80 references)
  - 1.5. Bibliographies (20 references)
  - 1.6. Chapters in books and related material (65 references)
  - 1.7. Fundamental papers (1173 references)
  - 1.8. Instrumentation (401 references)
  - 1.9. Analytical procedures (1987 references)
  - 1.10. Less familiar flames (92 references)
2. Atomic absorption spectroscopy
  - 2.1. Atomic absorption spectroscopy (353 references)
  - 2.2. Hollow cathodes (87 references)
3. Electrical discharges having the aspect of combustion flames
  - 3.1. RF discharges (154 references)
  - 3.2. Plasma arcs (98 references)
  - 3.3. Arc-and-spark-in-flame (26 references).

In collecting the references assembled in this bibliography the author has made use of original publications and of abstracting publications such as Chemical Abstracts, Science Abstracts Section A, Biological Abstracts, Analytical Abstracts, Technical Abstract Bulletin of the Defense Documentation Center, Scientific and Technical Aerospace Reports of the National Aeronautics and Space Administration, Nuclear Science Abstracts, Current Chemical Papers (The Chemical Society, London), Metallurgical Abstracts, Ceramic Abstracts. An appreciable number of references were initially obtained from books and reviews; when possible these were verified against the original work. When the original was unavailable or written in an unfamiliar language, the reference was checked with one of the abstracting publications mentioned above.

The following libraries were used for this collection: Chemists' Club, Engineering Society, New York Academy of Medicine, Boyce Thompson Institute for Plant Research, Philips Laboratories, and New York Public Library.

The references are arranged in each section in alphabetical order by authors followed by the title of the work, always translated into English, by the complete bibliographical information, and whenever possible by the corresponding Chemical Abstract number. When it was considered necessary, brief introductory comments and subject indexes were provided at the corresponding sections.

It is the intention of the author to continue the collection of references to works on flame spectroscopy and to publish periodically supplements to the present bibliography. He will therefore appreciate receiving constructive criticism and suggestions as well as corrections of the unavoidable errors always encountered in this type of publication, and in particular he requests the authors of papers pertaining to the field covered in this bibliography to send reprints or complete references of their works.

This work was initiated through the interest, encouragement, and support of the National Bureau of Standards, Office of Standard Reference Data. It was financed jointly by the National Bureau of Standards under Contract No. CST-1343, and Philips Laboratories, a Division of North American Philips Company, Inc.

It is a pleasure to acknowledge the assistance and encouragement of S. A. Rossmassler of the National Bureau of Standards, and that of J. A. Hipple and R. C. Hughes of Philips Laboratories during the course of the work.

The capable assistance of Mrs. A. Long in assembling, organizing, and checking the references, and of Miss Mary Ruth Bateman in editing and typing the manuscript is greatly appreciated.

March 1966

R. MAVRODINEANU

## Contents

	Page
Foreword -----	iii
Preface -----	iv
Introduction -----	vii
1. Emission	
1.1. Early works -----	1
1.2. Books -----	13
1.2. Theses -----	13
1.4. Reviews -----	15
1.5. Bibliographies -----	17
1.6. Chapters in books and related material -----	18
1.7. Fundamental works -----	20
1.8. Instrumentation -----	53
1.9. Analytical procedures -----	64
1.10. Less familiar flames -----	125
2. Atomic absorption spectroscopy	
2.1. Atomic absorption spectroscopy -----	129
2.2. Hollow cathode discharge tubes -----	140
3. Electrical discharges having the aspect of combustion flames	
3.1. The radio-frequency discharge -----	145
3.2. Plasma arcs -----	150
3.3. Arc-and-spark-in-flame -----	154

## Introduction

A glance at the subject index of Section 1.9, Analytical procedures, of this bibliography will show the diverse applications of the flame photometric method. Included in this section are methods for the analysis of numerous industrial, agricultural, biological, and geochemical materials. One result of this diversity of applications is that the publications are distributed over a large number of journals, books, theses, etc.

Dr. Mavrodineanu had compiled two earlier bibliographies on flame photometry (refs. 5 and 6 in sec. 1.5), covering the period up to early 1959. The present bibliography, compiled only seven years later, contains three times as many references as the earlier collections. This striking growth of the literature of flame photometry demonstrates that it remains an active field of study. The rapid expansion of this literature is especially evident in certain areas. For example, of the 353 references on atomic absorption spectrometry included in section 2.1, less than 10 percent were published before 1959, the date of Dr. Mavrodineanu's last previous bibliography.

As was true of Dr. Mavrodineanu's earlier bibliographies, it is expected that this publication will be of considerable assistance to the many scientists actively engaged in research on, or applications of flame photometry.

M. MARGOSHES  
*Spectrochemical Analysis Section*  
*NBS Institute for Materials Research*



# Bibliography on Flame Spectroscopy

## Analytical Applications

1800-1966

R. Mavrodineanu

Flame spectroscopy, especially in its analytical applications, continues to be an active field of study. Its literature is growing steadily, and the use of flame photometry in many specialized applications calls for a comprehensive indexed bibliography. This collection consists of 5,113 references to works on flame spectroscopy, selected with emphasis toward analytical measurements. It covers the period from 1800 to 1966. Subject indexes, keyed by number to the references cited, precede most of the sections.

Key words: Flame, spectroscopy, analytical, emission, atomic absorption, electrical discharge, bibliography, indexed

## 1. Emission

### 1.1. Early Works

The 503 references assembled in this section constitute an inventory of earlier works on flame spectroscopy, published from about 1800 to 1928, when the basic contributions of Lundegårdh on analytical flame spectrophotometry were printed. An appreciable number of these papers constitute a fundamental contribution to the field of flame spectroscopy, and the limited means and often crude instrumentation available during this early period did not prevent the scientist from discovering basic phe-

nomena on the excitation processes occurring in combustion flames. Among the assembled works the reader will find a large amount of truly original and invaluable scientific information, particularly in the papers of Bunsen, Kirchhoff, Gouy, Mitscherlich, de Wetteville, Hartley, Liveing and Dewar, de Gramont, Reis, Smithells and Ingle, Eder and Valenta, Boisbaudran, Salet, *et al.* A brief index is provided to assist in the consultation of this section.

### Subject Index

Flame reaction, temperature, electrical conductivity, ionization 5, 6, 13, 14, 15, 18, 19, 20, 21, 22, 23, 36, 37, 38, 39, 40, 41, 46, 58, 59, 60, 61, 62, 68, 69, 72, 74, 95, 96, 110, 113, 122, 127, 131, 137, 138, 142, 149, 156, 157, 161, 173, 184, 185, 186, 187, 188, 189, 190, 193, 199, 202, 215, 216, 217, 218, 237, 238, 239, 241, 242, 243, 246, 247, 256, 257, 258, 261, 263, 265, 275, 276, 280, 281, 282, 283, 284, 285, 291, 293, 294, 295, 298, 307, 314, 316, 317, 323, 324, 327, 328, 329, 334, 335, 336, 337, 339, 340, 343, 361, 362, 367, 368, 369, 371, 372, 373, 377, 384, 391, 392, 393, 398, 409, 410, 412, 413, 414, 416, 419, 420, 421, 422, 423, 426, 427, 429, 431, 432, 433, 434, 435, 440, 441, 442, 444, 445, 450, 451, 453, 459, 461, 462, 469, 472, 477, 486, 488, 489, 490, 491, 492, 493, 498, 499, 501, 502, 503  
Instrumental 24, 25, 26, 27, 28, 29, 30, 53, 63, 77, 80, 81, 82, 83, 91, 97, 111, 114, 123, 129, 130, 133, 162, 165, 179, 192, 205, 216, 223, 225, 226, 248, 251, 257, 274, 278, 280, 290, 331, 332, 333, 356, 360, 374, 375, 386, 387, 397, 408, 437, 451, 452, 454, 456, 466, 487  
Aluminum 104, 174, 194, 196, 197, 204, 208, 211, 213, 245, 311, 342, 378  
Antimony 67, 71, 194, 196, 197, 204, 208, 211, 279, 311, 342, 348, 465  
Arsenic 67, 194, 197, 213, 468

Barium 10, 31, 70, 71, 75, 86, 104, 105, 119, 126, 147, 148, 150, 151, 152, 153, 168, 170, 171, 173, 175, 178, 183, 191, 192, 194, 196, 197, 204, 206, 207, 208, 209, 211, 245, 249, 266, 267, 268, 270, 273, 311, 318, 320, 326, 341, 347, 348, 353, 354, 355, 365, 370, 378, 415, 424, 436, 465, 473  
Beryllium 52, 197, 204, 211, 365  
Bismuth 42, 67, 104, 170, 173, 178, 194, 196, 197, 204, 208, 211, 311, 320, 342, 355, 378, 417, 464, 465, 473  
Boron 10, 42, 44, 107, 119, 176, 211, 236, 249, 254, 341, 348, 355, 390, 405, 424, 436, 458, 465  
Bromine 153, 355, 405  
Cadmium 67, 116, 120, 168, 173, 197, 204, 208, 211, 213, 320, 329, 330, 342, 378, 473, 474  
Calcium 10, 31, 70, 75, 86, 104, 105, 119, 124, 126, 128, 147, 148, 150, 151, 153, 167, 170, 171, 172, 173, 175, 178, 192, 194, 196, 204, 206, 207, 208, 209, 210, 211, 212, 231, 232, 233, 236, 245, 266, 267, 268, 270, 273, 299, 310, 320, 326, 342, 347, 348, 353, 354, 355, 362, 365, 370, 378, 388, 415, 436, 446, 465, 468, 473  
Carbon 1, 7, 8, 9, 43, 109, 115, 117, 121, 136, 141, 143, 160, 196, 197, 201, 202, 235, 301, 302, 303, 306, 308, 309, 338, 355, 370, 376, 384, 424, 430, 436, 438, 439, 445, 448, 475, 478, 480, 482, 483, 484, 485, 500  
Cesium 10, 15, 31, 32, 64, 66, 70, 86, 147, 150, 173, 178,

194, 195, 196, 204, 206, 207, 208, 209, 211, 212, 214, 252, 253, 268, 269, 271, 272, 273, 277, 291, 292, 294, 334, 378, 379, 380, 415, 421, 432, 433, 455, 465

**Chlorine** 3, 104, 153, 155, 325, 355, 405

**Chromium** 67, 104, 166, 170, 175, 178, 194, 196, 197, 210, 211, 310, 311, 312, 320, 341, 355, 378, 456, 464, 473

**Cobalt** 3, 10, 67, 104, 168, 173, 178, 191, 194, 196, 197, 204, 211, 310, 311, 312, 320, 342, 378, 470

**Copper** 10, 33, 42, 67, 71, 73, 98, 104, 105, 124, 147, 148, 150, 151, 153, 168, 170, 178, 194, 196, 197, 204, 208, 209, 210, 211, 212, 213, 236, 249, 260, 310, 311, 312, 320, 341, 342, 347, 348, 353, 354, 355, 365, 370, 378, 406, 407, 424, 428, 436, 443, 456, 464, 465, 473

**Cyanogen** 42, 102, 103, 196, 235, 301, 302, 303, 309, 355, 370, 384, 430, 434, 448, 476

**Fluorine** 42, 355

**Gallium** 47, 48, 49, 50, 178, 203, 204, 209, 210, 211, 212, 213, 378

**Germanium** 204

**Gold** 34, 45, 67, 104, 194, 196, 197, 204, 208, 209, 211, 213, 355, 378, 464

**Indium** 67, 73, 178, 204, 209, 210, 211, 213, 378, 381, 382, 465, 494, 495

**Iodine** 153, 355, 405

**Iridium** 67, 194, 204, 208, 211, 213, 378

**Iron** 3, 10, 67, 104, 105, 124, 155, 168, 173, 175, 178, 194, 196, 197, 204, 208, 210, 211, 212, 219, 220, 221, 224, 227, 228, 229, 230, 234, 310, 311, 312, 320, 321, 322, 345, 348, 355, 378, 456, 470, 473

**Lanthanum** 10, 70, 204, 213

**Lead** 10, 45, 67, 80, 81, 82, 173, 178, 194, 197, 204, 208, 209, 210, 211, 286, 310, 311, 342, 348, 355, 370, 378, 464, 465, 473, 481

**Lithium** 10, 12, 31, 70, 71, 75, 86, 98, 99, 101, 119, 129, 134, 139, 140, 147, 148, 150, 151, 153, 154, 167, 168, 173, 178, 183, 194, 195, 196, 197, 204, 206, 207, 208, 209, 211, 212, 213, 214, 248, 255, 259, 261, 262, 266, 267, 268, 270, 273, 277, 292, 294, 297, 299, 300, 310, 311, 312, 319, 320, 326, 341, 354, 355, 357, 362, 370, 378, 394, 415, 428, 432, 433, 436, 448, 449, 455, 456, 460, 465, 467, 468, 471, 473, 478, 479, 497

**Magnesium** 73, 104, 118, 180, 194, 196, 197, 204, 210, 211, 213, 245, 300, 305, 310, 311, 313, 320, 326, 329, 330, 342, 344, 355, 365, 378, 465, 473, 474

**Manganese** 10, 42, 67, 76, 98, 104, 105, 168, 173, 175, 178, 194, 196, 197, 198, 204, 208, 209, 210, 211, 212, 311, 312, 320, 326, 345, 348, 355, 358, 365, 370, 378, 424, 456, 464, 465, 470, 479

**Mercury** 67, 213, 320, 329, 330, 355, 378, 395, 474

**Molybdenum** 67, 213, 244, 341, 424

**Nickel** 3, 10, 67, 104, 175, 178, 194, 196, 197, 204, 209, 210, 211, 310, 311, 312, 315, 320, 342, 378, 470

**Niobium** 104

**Nitrogen** 155, 309, 320, 383, 384, 385

**OH** 304, 384

**Osmium** 67, 146, 170, 173

**Palladium** 67, 104, 204, 208, 211, 213, 378

**Phosphorus** 67, 73, 79, 112, 182, 194, 197, 200, 326, 348, 355, 359, 369, 404, 405, 424, 496

**Platinum** 67, 168, 170, 173, 197, 348

**Potassium** 10, 30, 32, 70, 71, 75, 86, 99, 105, 119, 120, 134, 147, 148, 151, 152, 153, 163, 172, 173, 178, 194, 196, 197, 204, 206, 207, 208, 209, 210, 211, 214, 253, 255, 266, 267, 268, 270, 271, 273, 277, 291, 292, 294, 310, 311, 312, 320, 326, 334, 337, 341, 353, 354, 355, 357, 365, 370, 378, 379, 380, 389, 415, 428, 432, 433, 455, 457, 465, 467, 468, 471, 473, 497

**Radium** 157, 158, 159, 396

**Rare earths** 2, 10, 51, 70, 197, 211, 245, 264, 320

**Rhodium** 67, 211, 378

**Rubidium** 10, 31, 32, 65, 70, 86, 128, 147, 150, 164, 172, 173, 178, 194, 195, 196, 204, 206, 207, 208, 209, 211, 212, 214, 269, 271, 272, 273, 277, 291, 292, 294, 334, 378, 379, 380, 415, 432, 433, 455, 465

**Ruthenium** 211, 378

**Scandium** 84, 85

**Selenium** 42, 67, 197, 211, 355, 359, 366, 402, 405, 411, 481

**Silicon** 67, 181, 200, 326, 404, 405

**Silver** 35, 67, 173, 178, 194, 196, 197, 204, 208, 209, 210, 211, 212, 213, 311, 312, 320, 342, 365, 378, 473

**Sodium** 10, 30, 31, 32, 53, 54, 55, 70, 71, 75, 77, 86, 87, 99, 105, 111, 113, 119, 120, 128, 129, 130, 132, 133, 144, 145, 147, 148, 150, 151, 153, 155, 167, 169, 172, 173, 178, 183, 193, 194, 196, 197, 204, 206, 207, 208, 210, 211, 212, 250, 253, 259, 261, 266, 267, 270, 273, 278, 283, 284, 291, 292, 294, 296, 310, 311, 312, 317, 320, 326, 334, 341, 347, 348, 352, 353, 354, 355, 357, 362, 365, 370, 378, 394, 425, 428, 432, 433, 436, 444, 446, 447, 455, 456, 465, 467, 468, 471, 473, 478, 479, 497, 499

**Strontium** 10, 31, 56, 57, 70, 71, 75, 86, 100, 101, 104, 113, 119, 126, 128, 147, 148, 150, 151, 153, 154, 167, 168, 170, 171, 172, 173, 175, 178, 183, 191, 192, 194, 196, 197, 204, 206, 207, 208, 209, 211, 236, 245, 253, 266, 267, 268, 270, 273, 318, 320, 341, 346, 347, 348, 353, 354, 355, 357, 362, 365, 370, 378, 415, 448, 449, 465, 468, 473

**Sulfur** 4, 11, 17, 67, 106, 108, 125, 197, 211, 236, 240, 355, 359, 399, 400, 401, 405, 463

**Tantalum** 67

**Tellurium** 67, 194, 197, 211, 355, 366, 402, 424, 481

**Thallium** 10, 16, 45, 67, 70, 86, 88, 89, 90, 92, 93, 94, 113, 147, 148, 150, 151, 154, 168, 173, 178, 195, 197, 204, 208, 209, 211, 213, 259, 287, 288, 289, 311, 312, 320, 329, 330, 349, 350, 351, 357, 363, 364, 370, 378, 394, 415, 436, 465, 481

**Thorium** 10

**Tin** 17, 67, 104, 170, 173, 178, 194, 196, 197, 204, 208, 209, 211, 311, 355, 378, 403, 405, 418, 465, 470, 473

**Titanium** 67, 135, 244, 320

**Tungsten** 67, 244

**Uranium** 67, 104, 244

**Vanadium** 67

**Zinc** 67, 168, 173, 177, 196, 197, 204, 208, 211, 213, 311, 312, 315, 320, 329, 342, 348, 355, 378, 473, 474

**Zirconium** 10, 245

## A

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## 1.7. Fundamental Works

The references assembled in this section pertain to basic contributions to the field of analytical flame spectroscopy and to works on fundamental properties of combustion flame, such as flame structure and temperature, flame radiation, reactions, and ionization. Thus, the reader will find cited here the works of Lundegårdh together with a number of papers considered as substantial contributions to analytical flame spectroscopy, more than 100 references from a total of 1173 being listed in this category. The remaining works constitute a source of valuable information for the analytical flame spectroscopists interested in understanding basic flame phenomena. Although this collection was not intended to be exhaustive, it should provide nonetheless a sufficient amount of material to fulfill this purpose.

The references collected in this section are indexed under several headings to facilitate a preliminary selection.

### Subject Index

- Books** 83, 87, 88, 189, 190, 191, 192, 193, 194, 195, 196, 197, 273, 284, 333, 347, 352, 361, 386, 459, 467, 515, 524, 600, 627, 641, 694, 718, 793, 881, 887, 888, 900, 920, 1008, 1054, 1098, 1130, 1164,
- Theses** 77, 95, 227, 276, 308, 393, 439, 441, 462, 463, 468, 471, 489, 506, 605, 608, 688, 724, 725, 758, 786, 813, 872, 894, 904, 983, 998, 1122
- Reviews** 36, 48, 71, 99, 100, 101, 119, 275, 296, 297, 309, 324, 332, 345, 353, 354, 355, 357, 362, 364, 392, 403, 409, 414, 460, 522, 525, 612, 614, 616, 628, 643, 690, 691, 692, 693, 730, 744, 775, 803, 807, 808, 861, 862, 868, 901, 923, 946, 951, 962, 1012, 1031, 1032, 1033, 1042, 1043, 1074, 1124, 1150, 1153
- Flame, analytical** 6, 7, 8, 13, 31, 32, 96, 97, 135, 136, 137, 138, 141, 142, 168, 180, 280, 281, 295, 306, 336, 394, 397, 398, 399, 400, 401, 402, 403, 487, 488, 500, 501, 502, 503, 504, 507, 508, 517, 586, 621, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 667, 668, 669, 670, 671, 672, 673, 683, 684, 686, 702, 703, 704, 722, 745, 752, 789, 790, 791, 827, 829, 830, 831, 836, 849, 851, 863, 864, 865, 866, 867, 893, 931, 949, 1006, 1007, 1084, 1089, 1119, 1120, 1121, 1140, 1141, 1142, 1143, 1144, 1145, 1146, 1147, 1148, 1162, 1167, 1169
- Flame temperature** 12, 22, 34, 35, 42, 47, 62, 66, 75, 78, 103, 105, 106, 107, 109, 115, 116, 117, 118, 123, 130,

- 144, 145, 148, 185, 203, 205, 207, 208, 209, 210, 211, 212, 213, 214, 216, 240, 246, 255, 259, 260, 261, 270, 282, 294, 299, 301, 302, 310, 313, 329, 335, 337, 358, 366, 372, 373, 374, 375, 376, 379, 383, 396, 411, 415, 417, 419, 420, 421, 442, 445, 452, 453, 482, 483, 490, 501, 512, 518, 519, 520, 526, 527, 530, 539, 541, 556, 562, 571, 574, 585, 593, 595, 597, 598, 601, 602, 630, 633, 634, 636, 637, 638, 639, 642, 649, 664, 680, 695, 700, 705, 707, 708, 713, 714, 721, 723, 726, 731, 732, 733, 734, 736, 740, 741, 742, 743, 755, 757, 785, 787, 794, 795, 797, 798, 799, 800, 801, 802, 804, 805, 806, 810, 843, 845, 847, 871, 875, 879, 880, 881, 882, 883, 886, 887, 888, 889, 890, 891, 892, 895, 896, 897, 898, 905, 914, 933, 940, 945, 946, 947, 952, 953, 954, 959, 963, 967, 968, 969, 970, 974, 975, 991, 992, 997, 998, 999, 1000, 1001, 1002, 1003, 1004, 1013, 1020, 1023, 1024, 1025, 1026, 1041, 1042, 1043, 1049, 1050, 1051, 1052, 1053, 1056, 1057, 1076, 1078, 1079, 1080, 1081, 1083, 1085, 1086, 1087, 1088, 1092, 1097, 1116, 1118, 1127, 1142, 1152, 1155, 1172, 1173

- Flame geometry** 38, 39, 56, 57, 90, 98, 150, 152, 155, 184, 227, 228, 239, 247, 248, 249, 253, 262, 268, 269, 272, 314, 316, 317, 318, 319, 320, 321, 322, 324, 325, 326, 327, 328, 330, 331, 332, 385, 391, 422, 424, 436, 446, 486, 525, 528, 542, 570, 584, 603, 604, 610, 611, 614, 634, 640, 645, 646, 647, 675, 689, 699, 709, 729, 772, 848, 859, 860, 878, 884, 885, 907, 916, 917, 924, 927, 928, 932, 936, 937, 942, 943, 944, 976, 986, 993, 994, 995, 996, 1040, 1093, 1125, 1126, 1128, 1129, 1131, 1132, 1133, 1150, 1156, 1157, 1158, 1160, 1161, 1163

- Flame radiation** 1, 3, 4, 11, 23, 24, 25, 26, 27, 28, 29, 30, 33, 37, 41, 43, 44, 45, 46, 52, 53, 54, 61, 63, 67, 68, 69, 70, 72, 73, 74, 81, 84, 85, 86, 89, 94, 102, 104, 105, 106, 107, 108, 111, 112, 115, 116, 117, 118, 122, 123, 126, 127, 135, 136, 137, 138, 141, 142, 151, 153, 169, 170, 171, 172, 174, 175, 176, 178, 179, 180, 181, 182, 186, 187, 188, 198, 199, 200, 204, 215, 223, 224, 225, 226, 230, 232, 233, 234, 235, 236, 237, 238, 241, 242, 245, 256, 257, 258, 265, 266, 267, 272, 278, 290, 298, 301, 307, 339, 340, 343, 344, 346, 348, 349, 350, 356, 359, 360, 365, 367, 368, 369, 370, 371, 373, 375, 377, 378, 379, 380, 381, 382, 385, 387, 388, 389, 408, 410, 416, 423, 424, 425, 426, 427, 428, 432, 438, 442, 443, 447, 448, 449, 450, 451, 454, 455, 456, 477, 478, 479, 480, 482, 483, 484, 492, 498, 499, 507, 508, 509, 510, 511, 514, 516, 521, 523, 533, 535, 536, 537, 543, 544, 545, 546, 547, 563, 564, 567, 568, 569, 573, 583, 587, 588, 596, 599, 606, 620, 621, 622, 623, 624, 625, 651, 652, 665, 666, 676, 677, 681, 682, 687, 697, 698, 701, 704, 711, 717, 719, 720, 728, 737, 738, 739, 747, 750, 751, 756, 759, 764, 771, 774, 778, 780, 781, 782, 783, 796, 805, 806, 808, 809, 811, 812, 814, 819, 820, 821, 822, 823, 824, 825, 826, 828, 834, 835, 837, 838, 839, 840, 841, 842, 844, 853, 854, 856, 868, 869, 870,

873, 877, 899, 901, 902, 903, 909, 915, 918, 919, 920, 923, 925, 926, 948, 971, 972, 973, 977, 979, 980, 981, 982, 985, 1005, 1015, 1016, 1017, 1018, 1035, 1044, 1049, 1050, 1051, 1052, 1053, 1068, 1075, 1077, 1082, 1094, 1095, 1100, 1101, 1102, 1103, 1104, 1105, 1106, 1107, 1108, 1154, 1169

**Flame reactions** 2, 10, 15, 16, 17, 18, 19, 20, 21, 22, 49, 50, 51, 55, 59, 60, 79, 80, 82, 91, 92, 93, 99, 110, 113, 114, 120, 121, 122, 124, 125, 128, 129, 131, 132, 133, 139, 140, 142, 143, 147, 149, 153, 154, 173, 177, 180, 183, 186, 201, 202, 206, 215, 229, 250, 251, 252, 254, 263, 264, 271, 272, 277, 278, 279, 283, 285, 286, 287, 288, 289, 291, 292, 293, 300, 303, 304, 311, 312, 315, 323, 325, 331, 332, 334, 338, 341, 342, 350, 351, 357, 358, 363, 368, 376, 379, 382, 384, 390, 395, 404, 405, 406, 412, 417, 418, 419, 423, 426, 429, 430, 431, 432, 433, 434, 435, 437, 457, 458, 464, 465, 466, 469, 470, 473, 474, 475, 476, 481, 485, 491, 492, 493, 494, 495, 496, 497, 498, 509, 511, 513, 514, 523, 529, 531, 532, 533, 534, 535, 538, 540, 567, 568, 569, 572, 589, 590, 591, 592, 593, 594, 595, 599, 607, 609, 613, 615, 617, 618, 619, 626, 628, 629, 634, 635, 644, 648, 676, 678, 679, 685, 696, 697, 706, 711, 712, 727, 746, 753, 761, 763, 764, 766, 769, 770, 773, 776, 777, 779, 784, 788, 796, 814, 815, 816, 817, 818, 846, 855, 873, 874, 876, 877, 906, 908, 911, 913, 921, 922, 929, 930, 934, 935, 938, 939, 951, 955, 956, 957, 958, 960, 961, 962, 964, 965, 978, 990, 994, 995, 996, 1010, 1011, 1014, 1019, 1021, 1029, 1030, 1035, 1036, 1045, 1046, 1047, 1048, 1058, 1059, 1060, 1061, 1064, 1065, 1070, 1071, 1072, 1073, 1075, 1087, 1088, 1091, 1099, 1100, 1110, 1111, 1112, 1113, 1114, 1115, 1118, 1123, 1134, 1137, 1149, 1151, 1159, 1165, 1173

**Flame ionization** 5, 9, 14, 40, 58, 64, 65, 76, 133, 134, 146, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 217, 218, 219, 220, 221, 222, 231, 243, 244, 274, 303, 305, 407, 412, 413, 414, 440, 444, 461, 472, 503, 504, 505, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 565, 566, 575, 576, 577, 578, 579, 580, 581, 582, 631, 632, 650, 667, 668, 674, 710, 715, 716, 735, 748, 749, 754, 760, 762, 765, 767, 768, 792, 832, 833, 850, 852, 857, 858, 910, 911, 912, 925, 926, 941, 950, 966, 984, 987, 988, 989, 1009, 1022, 1027, 1028, 1033, 1034, 1037, 1038, 1039, 1062, 1063, 1066, 1067, 1069, 1090, 1096, 1109, 1117, 1135, 1136, 1138, 1139, 1165, 1166, 1168, 1170, 1171

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## 1. 8. Instrumentation

The 401 references on instrumentation used in analytical flame spectroscopy assembled in this section cover the field of general instrumentation, atomization, burners, spectrographs and monochromators, optical filters, photoelectric photometry, multichannel instruments, and interference spectroscopy as seen from the index. Among these, the reader will find extensive information on the process of pneumatic atomization in references 65, 67, 133, 207 to 209, 237, 258 to 263, 277, 357, and 390. The ultrasonic atomization is discussed in references 10, 31, 76, 77, 103, 193, 243, and 281, while electrical atomization is examined in references 20, 270, 348 to 353. An authoritative comparative discussion of the optical parameters of spectral instruments using prisms or grating as dispersive elements is to be found in references 166 and 167, while general information on applied optics is given in reference 182. A large number of references of more than 600 papers on photoelectric photometry is assembled in a bibliography (ref. 13) while the detailed discussion of various aspects of electronics for spectroscopists is to be found in reference 50a.

The relatively new and very promising field of interference spectroscopy is reviewed in references 38 and 256, and a detailed discussion of this subject is to be found in the basic works from references 157, 168, and 236.

### Subject Index

**General Instrumentation** 5, 6, 7, 8, 9, 11, 12, 14, 16, 18, 27, 29, 33, 36, 37, 39, 44, 45, 47, 49, 52, 53, 54, 57, 58, 59, 60, 61, 62, 68, 69, 73, 79, 80, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 99, 100, 101, 104, 109, 111, 114, 117, 120, 121, 128, 129, 134, 137, 148, 149, 150, 151, 154, 156, 159, 160, 161, 162, 163, 164, 165, 169, 171, 172, 173, 174, 175, 177, 180, 181, 183, 184, 189, 194, 198, 200, 201, 202, 203, 205, 206, 215, 217, 218, 220, 227, 233, 235, 238, 239, 242, 245, 246, 252, 254, 257, 266, 267, 271, 272, 274, 275, 276, 278, 279, 282, 285,

288, 289, 290, 291, 293, 303, 305, 307, 308, 310, 311, 314, 318, 320, 322, 323, 329, 330, 331, 332, 336, 338, 339, 341, 342, 344, 347, 354, 360, 361, 362, 363, 364, 367, 369, 370, 374, 376, 377, 378, 379, 381, 383, 384, 385, 391, 394, 396, 398, 399, 400

**Atomization** 4, 10, 17, 19, 20, 21, 24, 25, 26, 30, 31, 42, 43, 48, 55, 58a, 64, 65, 67, 74, 76, 77, 83, 84, 85, 97, 98, 102, 103, 106, 107, 113, 115, 116, 124, 130, 133, 136, 141, 143, 144, 146, 147, 153, 165, 186, 192, 193, 195, 196, 197, 204, 207, 208, 209, 216, 228, 229, 230, 237, 240, 243, 244, 247, 248, 249, 251, 253, 258, 259, 260, 261, 262, 263, 268, 269, 270, 273, 277, 280, 281, 284, 294, 295, 296, 297, 299, 301, 308, 309, 317, 324, 328, 334, 348, 349, 350, 351, 352, 353, 355, 357, 358, 359, 368, 386, 387, 388, 390, 392, 393, 395, 401

**Burners** 1, 17, 21, 22, 28, 30, 32, 34, 43, 56, 66, 70, 71, 72, 75, 78, 80, 81, 82, 97, 105, 108, 112, 113, 118, 125, 145, 147, 158, 165, 176, 178, 179, 185, 190, 194, 197, 199, 210, 221, 222, 230, 234, 241, 243, 244, 250, 264, 265, 283, 292, 295, 298, 308, 309, 313, 316, 317, 328, 334, 335, 345, 346, 365, 366, 373, 386, 387, 388, 397

**Spectrographs, Monochromators** 2, 3, 23, 138, 166, 167, 182, 212, 219, 287, 300, 326, 337, 356, 375, 380, 384

**Optical filters** 15, 35, 46, 50, 51, 86, 110, 122, 123, 131, 132, 135, 139, 140, 155, 170, 182, 187, 188, 191, 213, 214, 293, 302, 306, 312, 315, 319, 321, 325, 327, 333, 340, 343, 382, 389

**Photoelectric photometry** 13, 50a, 119, 211, 255, 394, 395a

**Multichannel instruments** 33, 36, 40, 41, 63, 126, 127, 142, 152, 223, 224, 225, 226, 231, 232, 286, 304, 371, 372

**Interference spectroscopy** 38, 157, 168, 236, 256

### A

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## 1. 9. Analytical Procedures

The 1987 references assembled in this section, of works, in which flame spectrophotometry is used as an analytical tool are distributed in the corresponding index under "Material Analyzed" and "Elements Determined." From this index, it can be seen that the largest use of the method is in the biological field, where flame spectrophotometry has become both an indispensable and reliable technique for the analysis of blood, serum, urine, tissue, bone, etc. A similar extensive use of this technique is to be found in the analysis of agricultural materials such as soils, plants, fertilizers, and in that of minerals, ores, and rocks. Further analytical applications will be found in the fields of metallurgy, petroleum, silicates, waters, and foods.

Since the primary object of this collection is to provide the analytical chemist with as much information as possible, an effort was made to be exhaustive rather than selective. Thus this section contains an appreciable number of references varying largely in quality. While many of the works assembled here constitute genuine contributions to the field of analytical flame spectroscopy, some of the printed works present only a minor interest and belong more to the individual and limited use of laboratory "cook-book recipes" rather than to a publication.

Since no critical attitude was taken in collecting the references which follow, the selection and determination of the quality of a particular work is left solely to the appreciation of the reader.

### Subject Index

**General considerations on analytical procedures** 43, 55, 63, 83, 87, 109, 111, 112, 115, 154, 178, 217, 218, 223, 224, 228, 241, 243, 244, 249, 252, 275, 286, 305, 306, 322, 351, 356, 357, 435, 436, 437, 438, 450, 455, 468, 469, 474, 477, 499, 505, 511, 521, 555, 564, 568, 599, 601, 618, 619, 624, 639, 648, 663, 666, 673, 714, 718, 746, 748, 752, 757, 800, 808, 812, 826, 833, 871, 872, 881, 886, 887, 909, 933, 948, 965, 969, 998, 1045, 1046, 1056, 1057, 1058, 1059, 1060, 1061, 1068, 1091, 1092, 1135, 1156, 1170, 1177, 1192, 1193, 1201, 1204, 1207, 1211, 1213, 1217, 1227, 1255, 1288, 1289, 1296, 1304, 1313, 1334, 1337, 1338, 1340, 1349, 1350, 1355, 1356, 1357, 1358, 1362, 1364, 1366, 1367, 1371, 1372, 1373, 1374, 1375, 1376, 1383, 1405, 1406, 1408, 1409, 1412, 1413, 1414, 1416, 1417, 1418, 1419, 1420, 1423, 1424, 1425, 1427, 1429, 1430, 1431, 1432, 1433, 1434, 1435, 1439, 1441, 1442, 1447, 1454, 1456, 1457, 1459, 1460, 1461, 1471, 1472, 1473, 1475, 1477, 1484, 1492, 1494, 1496, 1506, 1509, 1517, 1521, 1546, 1550, 1554, 1561, 1564, 1595, 1602, 1615, 1619, 1622, 1624, 1627, 1628, 1635, 1640, 1651, 1653, 1657, 1659, 1667, 1681, 1701, 1702, 1709, 1711, 1714, 1720, 1721, 1723, 1724, 1740, 1776, 1788, 1794, 1798, 1799, 1804, 1805, 1817, 1884, 1889, 1890, 1891, 1898, 1901, 1908, 1915, 1917, 1935, 1958, 1968, 1983, 1985, 1987

### Materials Analyzed

**Air** 264, 358, 480  
**Alcoholic beverages and vinegar** 174, 311, 324, 500, 622, 897, 1171, 1172, 1318, 1399, 1400, 1401, 1402, 1403, 1748, 1942

**Biological materials** 15, 17, 18, 21, 25, 27, 40, 42, 45, 46, 49, 55, 57, 59, 60, 61, 77, 78, 86, 96, 97, 100, 101, 102, 103, 104, 108, 110, 114, 115, 116, 123, 124, 127, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 146, 147, 157, 158, 160, 168, 171, 173, 181, 194, 195, 212, 213, 219, 225, 226, 231, 246, 247, 248, 252, 268, 272, 278, 280, 302, 303, 310, 312, 314, 317, 321, 331, 332, 333, 336, 346, 353, 359, 369, 371, 375, 376, 378, 415, 424, 441, 442, 448, 461, 462, 464, 466, 467, 468, 471, 491, 501, 502, 505, 506, 507, 508, 511, 516, 537, 548, 549, 551, 555, 557, 561, 572, 576, 596, 597, 598, 599, 600, 602, 607, 608, 609, 610, 611, 612, 621, 629, 630, 631, 632, 636, 652, 657, 678, 680, 705, 708, 709, 716, 723, 724, 737, 738, 740, 742, 748, 749, 750, 751, 752, 753, 792, 795, 796, 797, 799, 800, 801, 802, 803, 804, 806, 807, 817, 818, 826, 832, 833, 834, 835, 836, 837, 839, 885, 888, 889, 890, 893, 894, 903, 909, 912, 913, 917, 920, 922, 924, 926, 930, 937, 950, 951, 952, 953, 961, 965, 990, 992, 998, 999, 1001, 1013, 1014, 1019, 1020, 1023, 1027, 1033, 1035, 1038, 1042, 1048, 1049, 1055, 1062, 1065, 1077, 1078, 1079, 1080, 1085, 1092, 1106, 1114, 1115, 1130, 1131, 1159, 1167, 1178, 1194, 1195, 1200, 1203, 1209, 1210, 1214, 1215, 1219, 1221, 1224, 1225, 1226, 1227, 1235, 1243, 1251, 1252, 1253, 1254, 1257, 1258, 1262, 1263, 1266, 1268, 1270, 1272, 1275, 1276, 1277, 1285, 1286, 1289, 1290, 1291, 1295, 1299, 1302, 1306, 1308, 1325, 1328, 1329, 1348, 1351, 1378, 1379, 1388, 1389, 1392, 1394, 1404, 1407, 1410, 1411, 1440, 1458, 1463, 1464, 1465, 1468, 1469, 1470, 1478, 1479, 1480, 1484, 1490, 1501, 1502, 1508, 1509, 1510, 1520, 1523, 1524, 1530, 1531, 1535, 1549, 1568, 1569, 1570, 1575, 1579, 1580, 1581, 1582, 1601, 1603, 1605, 1606, 1607, 1608, 1609, 1610, 1611, 1624, 1632, 1650, 1651, 1652, 1658, 1663, 1664, 1668, 1671, 1674, 1676, 1684, 1686, 1687, 1688, 1694, 1699, 1703, 1704, 1707, 1709, 1713, 1714, 1715, 1716, 1718, 1737, 1738, 1747, 1751, 1753, 1755, 1760, 1775, 1776, 1778, 1789, 1791, 1792, 1793, 1795, 1796, 1797, 1799, 1800, 1801, 1807, 1808, 1809, 1814, 1820, 1830, 1841, 1847, 1853, 1857, 1859, 1861, 1872, 1873, 1878, 1879, 1880, 1884, 1892, 1911, 1918, 1919, 1920, 1921, 1928, 1931, 1932, 1933, 1934, 1937, 1938, 1940, 1941, 1943, 1947, 1979

**Catalysts** 22, 23, 1274, 1301, 1347, 1965

**Chemical compounds** 1, 8, 10, 16, 21, 32, 37, 52, 56, 91, 179, 198, 205, 206, 207, 209, 210, 211, 221, 227, 245, 261, 262, 276, 298, 335, 362, 363, 379, 449, 450, 472, 473, 476, 479, 488, 510, 546, 547, 567, 569, 603, 604, 613, 628, 642, 687, 690, 713, 719, 741, 805, 814, 815, 869, 900, 908, 916, 921, 932, 959, 960, 968, 975, 976, 979, 994, 1004, 1009, 1012, 1021, 1036, 1066, 1068, 1071, 1086, 1095, 1103, 1121, 1216, 1218, 1240, 1242, 1250, 1261, 1274, 1301, 1303, 1317, 1324, 1327, 1344, 1352, 1353, 1354, 1361, 1363, 1364, 1390, 1391, 1443, 1446, 1449, 1450, 1453, 1462, 1481, 1487, 1489, 1529, 1545, 1548, 1550, 1566, 1568, 1572, 1583, 1584, 1629, 1630, 1635, 1636, 1637, 1653, 1656, 1710, 1739, 1740, 1743, 1802, 1806, 1813, 1825, 1828, 1829, 1855, 1888, 1894, 1951, 1959, 1970, 1972, 1973, 1976, 1978

**Coals** 41, 44, 54, 85, 113, 159, 430, 470, 492, 884, 927, 942, 1043, 1141, 1142, 1297, 1444, 1445, 1540, 1638, 1641, 1642

**Dairy products** 21, 25, 164, 167, 316, 754, 919, 920, 931, 1222, 1260, 1287, 1346, 1382, 1601, 1644, 1848, 1974

**Electronic materials** 5, 6, 533

**Fertilizers** 68, 155, 176, 200, 216, 223, 224, 251, 281, 360, 439, 567, 581, 582, 583, 584, 585, 586, 587, 588, 589, 643, 644, 645, 646, 649, 653, 658, 886, 887, 1031, 1050, 1119, 1173, 1304, 1344, 1593, 1678, 1788

**Foods** 152, 273, 277, 309, 310, 327, 328, 347, 348, 416, 417, 423, 446, 502, 514, 715, 862, 863, 910, 985, 1031, 1063, 1272, 1304, 1485, 1539, 1571, 1573, 1586, 1587, 1691, 1777, 1795, 1801, 1810, 1815, 1816, 1906, 1929, 1963, 1970, 1971, 1972, 1974

**Metals, alloys, and metallurgic products** 3, 4, 14, 38, 79, 89, 90, 112, 148, 162, 220, 251, 254, 255, 256, 257,

258, 267, 294, 295, 320, 355, 368, 380, 381, 386, 389, 390, 517, 524, 527, 567, 595, 616, 625, 633, 669, 683, 691, 692, 693, 694, 695, 760, 763, 809, 813, 827, 828, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 854, 860, 861, 896, 901, 906, 928, 939, 958, 963, 964, 974, 997, 1000, 1008, 1066, 1098, 1111, 1132, 1153, 1157, 1158, 1182, 1184, 1185, 1186, 1187, 1188, 1223, 1231, 1234, 1236, 1237, 1238, 1240, 1241, 1242, 1247, 1320, 1321, 1322, 1335, 1349, 1355, 1384, 1385, 1397, 1436, 1437, 1438, 1455, 1472, 1514, 1515, 1519, 1558, 1559, 1574, 1626, 1730, 1731, 1750, 1754, 1758, 1761, 1772, 1787, 1829, 1852, 1883, 1907, 1910, 1914, 1955, 1966, 1976

**Minerals, ores, rocks** 2, 50, 73, 82, 121, 122, 141, 143, 144, 163, 182, 189, 196, 201, 204, 215, 235, 236, 239, 269, 299, 318, 319, 334, 349, 377, 406, 410, 414, 425, 426, 427, 429, 460, 487, 493, 497, 503, 518, 531, 532, 538, 540, 541, 542, 543, 544, 545, 560, 567, 605, 606, 626, 651, 674, 695, 704, 706, 717, 718, 727, 728, 731, 732, 743, 745, 824, 830, 840, 853, 864, 865, 867, 874, 878, 883, 898, 929, 937, 940, 941, 956, 962, 967, 978, 978, 988, 1003, 1007, 1011, 1016, 1017, 1018, 1022, 1025, 1026, 1045, 1046, 1064, 1072, 1073, 1105, 1112, 1133, 1150, 1180, 1181, 1189, 1208, 1232, 1248, 1279, 1292, 1320, 1336, 1345, 1359, 1360, 1364, 1368, 1369, 1370, 1377, 1381, 1386, 1387, 1405, 1447, 1483, 1511, 1513, 1516, 1543, 1547, 1551, 1552, 1553, 1555, 1556, 1557, 1560, 1562, 1563, 1565, 1622, 1642, 1662, 1670, 1677, 1685, 1690, 1730, 1731, 1734, 1735, 1746, 1749, 1758, 1782, 1785, 1819, 1823, 1839, 1864, 1875, 1896, 1897, 1922, 1924, 1967

**Organic solvents and compounds in flame spectrophotometry** 70, 161, 162, 163, 212, 227, 237, 240, 243, 244, 270, 282, 337, 338, 345, 365, 373, 385, 386, 387, 388, 389, 391, 392, 393, 394, 395, 396, 400, 403, 404, 405, 407, 408, 458, 465, 474, 477, 490, 526, 527, 528, 529, 530, 552, 553, 563, 667, 689, 694, 696, 697, 698, 699, 700, 701, 707, 728, 766, 767, 773, 951, 953, 982, 983, 1087, 1095, 1107, 1108, 1121, 1126, 1129, 1164, 1165, 1166, 1176, 1183, 1239, 1323, 1324, 1333, 1335, 1408, 1426, 1427, 1428, 1429, 1448, 1449, 1450, 1451, 1453, 1455, 1456, 1457, 1460, 1461, 1464, 1520, 1527, 1537, 1590, 1612, 1613, 1614, 1623, 1648, 1676, 1680, 1687, 1688, 1689, 1692, 1725, 1726, 1727, 1728, 1729, 1737, 1761, 1762, 1763, 1764, 1765, 1766, 1767, 1768, 1769, 1770, 1771, 1773, 1774, 1840, 1869, 1876, 1893, 1902, 1903, 1904, 1959, 1980

**Paints and varnish** 356, 1648

**Petroleum products** 33, 35, 39, 88, 156, 241, 242, 326, 345, 357, 366, 601, 662, 669, 703, 746, 747, 914, 915, 925, 1041, 1104, 1117, 1151, 1176, 1196, 1244, 1278, 1567, 1700, 1908

**Pharmaceuticals** 217, 218, 238, 447, 448, 452, 453, 454, 455, 456, 685, 710, 714, 722, 808, 957, 973, 1415, 1578, 1655, 1672, 1720, 1856, 1945

**Plants** 7, 31, 53, 64, 65, 67, 69, 74, 81, 93, 94, 95, 106, 126, 145, 166, 170, 172, 178, 181, 182, 199, 202, 208, 230, 232, 233, 234, 265, 266, 279, 283, 284, 286, 291, 293, 297, 310, 354, 364, 408, 409, 423, 431, 457, 489, 509, 511, 623, 635, 654, 655, 659, 660, 678, 681, 688, 711, 712, 715, 755, 756, 758, 784, 785, 786, 787, 788, 789, 791, 831, 842, 879, 905, 907, 910, 920, 934, 935, 936, 938, 943, 944, 945, 946, 947, 948, 972, 977, 1010, 1030, 1031, 1051, 1053, 1063, 1075, 1076, 1081, 1084, 1090, 1125, 1126, 1128, 1129, 1134, 1135, 1136, 1137, 1138, 1146, 1148, 1155, 1174, 1175, 1201, 1220, 1228, 1229, 1232, 1265, 1269, 1273, 1281, 1282, 1300, 1304, 1312, 1331, 1332, 1339, 1340, 1342, 1343, 1382, 1410, 1411, 1463, 1465, 1466, 1467, 1497, 1499, 1503, 1518, 1525, 1594, 1596, 1597, 1598, 1599, 1600, 1615, 1616, 1617, 1620, 1621, 1625, 1632, 1634, 1647, 1660, 1667, 1679, 1682, 1708, 1723, 1741, 1744, 1751, 1784, 1812, 1818, 1849, 1850, 1863, 1874, 1881, 1882, 1885, 1887, 1895, 1899, 1900, 1901, 1909, 1927, 1944, 1957, 1977

**Silicates, glass, cement, refractory materials** 9, 11, 12, 48, 72, 83, 98, 99, 107, 109, 118, 119, 120, 149, 150, 151, 165, 186, 229, 274, 305, 329, 330, 350, 351, 352, 367, 374, 383, 397, 399, 401, 402, 403, 404, 405, 407,

412, 413, 418, 419, 420, 421, 422, 432, 433, 504, 515, 534, 539, 559, 566, 567, 573, 577, 578, 579, 580, 590, 591, 592, 593, 594, 641, 661, 668, 669, 670, 671, 675, 676, 744, 757, 759, 761, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 790, 825, 841, 859, 867, 949, 959, 981, 984, 991, 995, 996, 1005, 1015, 1025, 1029, 1032, 1034, 1037, 1040, 1052, 1070, 1074, 1120, 1139, 1160, 1169, 1189, 1197, 1207, 1230, 1294, 1319, 1330, 1393, 1398, 1406, 1488, 1500, 1511, 1526, 1528, 1532, 1536, 1537, 1538, 1540, 1541, 1544, 1562, 1563, 1585, 1589, 1591, 1604, 1612, 1613, 1614, 1642, 1654, 1683, 1697, 1736, 1749, 1752, 1779, 1822, 1823, 1826, 1827, 1860, 1865, 1866, 1867, 1868, 1870, 1871, 1886, 1924, 1925, 1926, 1930, 1936, 1946, 1949, 1950, 1956, 1975, 1982, 1983, 1984, 1985, 1986

**Soils** 58, 65, 66, 75, 80, 92, 117, 154, 178, 181, 182, 203, 208, 232, 250, 251, 259, 260, 279, 285, 286, 287, 288, 290, 293, 304, 307, 308, 408, 409, 411, 463, 484, 485, 495, 511, 512, 525, 535, 550, 556, 557, 558, 623, 627, 650, 656, 658, 667, 672, 677, 679, 681, 702, 733, 736, 744, 783, 793, 794, 821, 838, 858, 875, 876, 878, 879, 904, 943, 946, 947, 948, 977, 980, 993, 1006, 1024, 1028, 1067, 1081, 1082, 1088, 1118, 1128, 1143, 1144, 1145, 1146, 1147, 1148, 1149, 1168, 1170, 1179, 1190, 1191, 1193, 1206, 1228, 1246, 1259, 1264, 1265, 1271, 1281, 1300, 1304, 1309, 1310, 1312, 1314, 1315, 1316, 1326, 1339, 1340, 1341, 1382, 1395, 1396, 1410, 1411, 1465, 1474, 1491, 1495, 1497, 1498, 1504, 1505, 1507, 1522, 1525, 1533, 1576, 1588, 1590, 1592, 1598, 1599, 1617, 1633, 1643, 1646, 1647, 1649, 1665, 1669, 1708, 1722, 1723, 1724, 1733, 1742, 1781, 1803, 1811, 1818, 1821, 1838, 1851, 1877, 1900, 1906, 1923, 1948, 1957, 1961, 1969, 1981

**Steam and boiler deposits** 20, 54, 153, 156, 169, 499, 971, 1089, 1645, 1962

**Test solutions** 19, 28, 29, 30, 47, 62, 70, 71, 76, 84, 128, 140, 142, 175, 183, 184, 187, 188, 197, 222, 228, 253, 263, 271, 275, 289, 292, 296, 323, 344, 373, 384, 388, 391, 392, 393, 394, 395, 398, 428, 434, 435, 436, 437, 438, 443, 458, 469, 475, 483, 494, 496, 498, 519, 520, 521, 522, 523, 536, 562, 564, 565, 570, 614, 615, 617, 618, 619, 634, 638, 639, 640, 648, 663, 664, 665, 666, 673, 720, 721, 735, 739, 798, 810, 812, 816, 820, 829, 856, 861, 870, 877, 882, 899, 955, 1039, 1047, 1069, 1087, 1094, 1096, 1097, 1099, 1101, 1102, 1109, 1113, 1154, 1162, 1163, 1165, 1192, 1233, 1249, 1267, 1307, 1311, 1365, 1561, 1673, 1693, 1694, 1705, 1712, 1717, 1726, 1727, 1728, 1729, 1756, 1757, 1759, 1786, 1790, 1912, 1935, 1952, 1953

**Waters** 13, 24, 26, 34, 36, 43, 51, 73, 87, 105, 125, 152, 177, 180, 181, 182, 185, 190, 191, 192, 193, 208, 261, 262, 300, 301, 310, 312, 313, 314, 315, 337, 338, 339, 340, 341, 342, 343, 361, 370, 372, 440, 444, 445, 451, 481, 482, 502, 513, 554, 557, 571, 574, 575, 637, 669, 684, 702, 725, 726, 730, 734, 811, 819, 822, 823, 825, 873, 889, 891, 902, 903, 911, 912, 986, 1056, 1057, 1058, 1059, 1060, 1061, 1083, 1093, 1116, 1122, 1123, 1124, 1161, 1176, 1198, 1205, 1245, 1257, 1259, 1268, 1280, 1293, 1410, 1411, 1458, 1563, 1482, 1486, 1512, 1534, 1542, 1577, 1618, 1645, 1661, 1695, 1696, 1698, 1732, 1773, 1774, 1780, 1783, 1824, 1833, 1834, 1835, 1836, 1837, 1842, 1843, 1844, 1845, 1846, 1854, 1862, 1900, 1905, 1913, 1916, 1954, 1962, 1963, 1964, 1965

### Elements Determined

**Aluminum** 292, 293, 325, 395, 396, 403, 406, 407, 528, 667, 733, 766, 767, 773, 928, 939, 958, 982, 983, 1169, 1223, 1339, 1341, 1380, 1612, 1614, 1657, 1869

**Antimony** 325, 388

**Arsenic** 388, 520

**Barium** 4, 5, 6, 12, 139, 196, 197, 198, 325, 337, 340, 345, 362, 363, 365, 384, 385, 407, 426, 439, 459, 460, 483, 484, 485, 498, 519, 533, 536, 544, 545, 617, 640, 750, 762, 810, 813, 816, 856, 857, 882, 975, 979, 982, 1032, 1097, 1104, 1233, 1239, 1339, 1353, 1354, 1396, 1414, 1434, 1435, 1439, 1454, 1457, 1548, 1554, 1633, 1639, 1925, 1950, 1952

**Beryllium** 526, 1098  
**Bismuth** 325, 388  
**Boron** 98, 198, 200, 211, 222, 240, 270, 393, 394, 595, 647, 973, 982, 1053, 1054, 1075, 1076, 1087, 1418, 1426, 1725, 1726, 1727, 1728, 1729, 1893, 1959  
**Cadmium** 665, 1109  
**Calcium** 3, 4, 5, 6, 7, 12, 21, 25, 26, 27, 28, 29, 30, 38, 45, 46, 60, 69, 73, 74, 75, 76, 77, 78, 80, 81, 84, 85, 89, 92, 93, 94, 97, 99, 101, 102, 103, 104, 105, 114, 118, 123, 125, 127, 132, 133, 137, 138, 139, 140, 144, 145, 146, 147, 151, 167, 168, 171, 172, 173, 177, 182, 185, 186, 196, 197, 199, 202, 206, 207, 213, 221, 230, 231, 233, 234, 239, 253, 259, 260, 266, 268, 277, 278, 279, 280, 283, 284, 285, 287, 289, 297, 302, 303, 309, 310, 314, 315, 320, 323, 325, 345, 348, 354, 365, 367, 370, 372, 402, 404, 405, 406, 407, 408, 409, 411, 415, 418, 423, 424, 425, 431, 433, 439, 440, 450, 451, 452, 458, 460, 461, 462, 467, 471, 476, 481, 482, 489, 491, 492, 498, 501, 512, 519, 522, 523, 533, 536, 537, 545, 549, 557, 558, 559, 561, 562, 563, 567, 603, 604, 614, 617, 621, 630, 634, 640, 641, 642, 650, 651, 654, 655, 656, 657, 667, 674, 676, 677, 681, 682, 685, 688, 691, 693, 696, 704, 705, 707, 709, 711, 712, 715, 716, 719, 720, 722, 723, 738, 747, 750, 754, 755, 756, 758, 762, 763, 766, 783, 788, 789, 795, 796, 798, 802, 803, 804, 806, 807, 810, 813, 816, 821, 932, 935, 937, 942, 844, 846, 847, 851, 856, 857, 879, 880, 882, 885, 888, 891, 894, 904, 908, 910, 917, 918, 922, 923, 924, 931, 936, 937, 943, 945, 952, 953, 958, 960, 961, 962, 963, 964, 966, 967, 975, 977, 981, 982, 986, 987, 990, 993, 997, 1000, 1006, 1010, 1025, 1029, 1032, 1038, 1039, 1048, 1055, 1063, 1064, 1065, 1074, 1077, 1078, 1079, 1080, 1081, 1085, 1088, 1090, 1094, 1096, 1097, 1101, 1103, 1104, 1110, 1113, 1115, 1116, 1118, 1127, 1130, 1133, 1134, 1155, 1167, 1169, 1174, 1178, 1185, 1190, 1191, 1196, 1208, 1210, 1215, 1219, 1221, 1222, 1224, 1226, 1233, 1236, 1239, 1240, 1241, 1254, 1262, 1263, 1265, 1268, 1270, 1271, 1277, 1281, 1282, 1302, 1306, 1309, 1312, 1314, 1315, 1320, 1329, 1331, 1332, 1333, 1339, 1342, 1343, 1347, 1351, 1352, 1353, 1354, 1361, 1380, 1382, 1385, 1388, 1389, 1390, 1392, 1395, 1400, 1411, 1414, 1440, 1442, 1452, 1457, 1461, 1464, 1466, 1467, 1468, 1470, 1472, 1474, 1476, 1486, 1488, 1492, 1497, 1498, 1499, 1501, 1502, 1503, 1506, 1508, 1509, 1510, 1522, 1524, 1525, 1528, 1530, 1531, 1534, 1536, 1554, 1558, 1559, 1574, 1577, 1580, 1581, 1586, 1587, 1595, 1596, 1597, 1600, 1601, 1603, 1605, 1606, 1607, 1608, 1613, 1618, 1620, 1625, 1626, 1631, 1636, 1639, 1640, 1644, 1646, 1648, 1655, 1658, 1660, 1669, 1676, 1682, 1689, 1693, 1694, 1697, 1704, 1708, 1716, 1717, 1719, 1723, 1730, 1733, 1735, 1743, 1747, 1748, 1749, 1751, 1752, 1759, 1762, 1767, 1774, 1784, 1792, 1793, 1795, 1799, 1800, 1803, 1807, 1808, 1809, 1811, 1812, 1814, 1815, 1817, 1828, 1837, 1839, 1840, 1841, 1843, 1846, 1848, 1849, 1855, 1856, 1877, 1887, 1892, 1894, 1895, 1898, 1901, 1903, 1904, 1905, 1906, 1916, 1923, 1925, 1927, 1932, 1933, 1935, 1940, 1941, 1945, 1946, 1747, 1948, 1950, 1952, 1953, 1955, 1956, 1957, 1964, 1970, 1971, 1972, 1975, 1976, 1978, 1980  
**Cesium** 24, 71, 139, 141, 183, 184, 187, 188, 189, 190, 191, 192, 193, 214, 341, 343, 407, 475, 536, 538, 540, 541, 542, 543, 546, 552, 553, 557, 575, 615, 617, 637, 638, 640, 684, 721, 734, 772, 813, 824, 829, 855, 859, 861, 878, 882, 927, 940, 947, 982, 1022, 1026, 1141, 1142, 1294, 1339, 1364, 1368, 1387, 1403, 1430, 1431, 1432, 1433, 1441, 1468, 1493, 1514, 1516, 1527, 1544, 1553, 1565, 1584, 1670, 1675, 1745, 1833, 1836, 1839, 1889, 1914, 1924, 1944, 1967  
**Chromium** 45, 142, 237, 253, 254, 255, 256, 257, 258, 325, 369, 407, 490, 854, 921, 982, 1397, 1408, 1472, 1907  
**Cobalt** 32, 253, 254, 255, 256, 257, 258, 407, 626, 700, 982, 1397, 1423, 1427, 1456, 1468, 1472, 1623, 1648, 1765, 1770  
**Copper** 126, 138, 161, 162, 310, 325, 380, 381, 386, 387, 390, 407, 626, 640, 650, 697, 698, 715, 716, 799, 875, 876, 896, 915, 982, 1107, 1129, 1153, 1211, 1239, 1253, 1397, 1417, 1425, 1467, 1468, 1470, 1472, 1623, 1629, 1630, 1763, 1768, 1849, 1850, 1888  
**Gallium** 163, 212, 699, 1099, 1100, 1109, 1157, 1239, 1515, 1557, 1563, 1626, 1764, 1769  
**Halogens** 264, 620, 819, 869, 1093, 1117, 1121, 1163, 1199  
**Indium** 163, 212, 267, 335, 640, 664, 699, 982, 1099, 1100, 1109, 1158, 1234, 1323, 1447, 1472, 1515, 1555, 1557, 1560, 1562, 1564, 1764, 1769  
**Iron** 126, 138, 310, 383, 387, 389, 406, 407, 490, 517, 526, 626, 633, 667, 695, 715, 716, 921, 958, 982, 1064, 1116, 1164, 1169, 1190, 1339, 1384, 1408, 1448, 1450, 1460, 1467, 1468, 1470, 1472, 1613, 1623, 1630, 1849, 1907  
**Lanthanum** 319, 692, 867, 982, 1165, 1166, 1384, 1772, 1787  
**Lead** 39, 242, 294, 295, 325, 326, 662, 914, 1041, 1151, 1278, 1567, 1648, 1700, 1888  
**Lithium** 13, 24, 84, 85, 118, 119, 121, 122, 139, 144, 179, 183, 184, 185, 187, 188, 189, 190, 191, 192, 193, 208, 229, 235, 236, 269, 299, 301, 337, 342, 345, 361, 372, 387, 397, 402, 404, 405, 407, 412, 432, 434, 472, 473, 477, 503, 510, 512, 536, 541, 543, 546, 560, 565, 566, 571, 573, 615, 617, 628, 635, 638, 640, 667, 684, 687, 717, 721, 734, 759, 772, 790, 813, 815, 816, 824, 830, 855, 859, 861, 877, 878, 882, 883, 889, 890, 891, 892, 899, 900, 902, 911, 918, 927, 929, 934, 935, 940, 941, 960, 982, 994, 996, 1000, 1012, 1014, 1025, 1032, 1040, 1070, 1071, 1103, 1123, 1139, 1189, 1190, 1217, 1218, 1240, 1256, 1303, 1320, 1324, 1335, 1339, 1345, 1349, 1359, 1360, 1368, 1387, 1401, 1430, 1431, 1432, 1433, 1443, 1466, 1472, 1482, 1486, 1512, 1516, 1519, 1532, 1547, 1551, 1554, 1555, 1558, 1566, 1626, 1637, 1642, 1659, 1705, 1706, 1750, 1756, 1759, 1782, 1804, 1818, 1829, 1831, 1834, 1835, 1839, 1842, 1858, 1860, 1868, 1870, 1871, 1876, 1911, 1912, 1924, 1939, 1944, 1950, 1954, 1967, 1975  
**Magnesium** 3, 17, 18, 42, 52, 74, 105, 125, 137, 138, 139, 145, 146, 147, 186, 187, 199, 233, 234, 239, 250, 266, 277, 280, 284, 285, 297, 310, 329, 354, 355, 375, 406, 407, 408, 409, 415, 423, 426, 433, 467, 512, 536, 537, 548, 558, 559, 563, 579, 596, 622, 623, 642, 667, 674, 681, 685, 693, 694, 706, 711, 712, 716, 750, 756, 783, 797, 804, 813, 818, 844, 846, 847, 848, 849, 850, 851, 870, 924, 936, 943, 949, 953, 972, 982, 1000, 1063, 1064, 1066, 1074, 1081, 1084, 1103, 1108, 1113, 1116, 1118, 1134, 1169, 1190, 1191, 1202, 1203, 1219, 1221, 1225, 1226, 1239, 1258, 1262, 1266, 1271, 1277, 1282, 1314, 1315, 1339, 1343, 1352, 1353, 1354, 1384, 1395, 1397, 1400, 1402, 1416, 1419, 1424, 1440, 1457, 1467, 1468, 1472, 1495, 1530, 1536, 1590, 1598, 1599, 1601, 1611, 1613, 1660, 1665, 1669, 1682, 1686, 1708, 1722, 1723, 1761, 1766, 1768, 1791, 1793, 1824, 1841, 1849, 1878, 1879, 1887, 1898, 1902, 1904, 1925, 1930, 1948, 1956  
**Manganese** 126, 250, 253, 254, 255, 256, 257, 258, 266, 284, 310, 325, 337, 338, 386, 387, 406, 407, 420, 428, 490, 512, 526, 578, 579, 580, 640, 650, 667, 697, 698, 715, 716, 783, 852, 864, 865, 906, 943, 944, 958, 982, 1064, 1190, 1191, 1232, 1265, 1314, 1315, 1408, 1467, 1468, 1470, 1472, 1497, 1536, 1565, 1630, 1648, 1700, 1763, 1768, 1849, 1850, 1907, 1960  
**Mercury** 1109  
**Molybdenum** 1153  
**Nickel** 32, 254, 255, 256, 325, 386, 407, 527, 595, 700, 982, 1397, 1423, 1467, 1468, 1472, 1623, 1765, 1770  
**Nitrogen** 108, 820  
**Organo-halogens** 486, 729, 1199  
**Oxygen** 683, 1184, 1186, 1187, 1188, 1321, 1322, 1910  
**Palladium** 529, 530, 1153, 1305, 1449  
**Phosphorus (phosphate)** 128, 227, 373, 429, 1044, 1095, 1483, 1805  
**Potassium** 1, 2, 9, 10, 11, 16, 21, 22, 34, 36, 37, 40, 41, 44, 47, 48, 50, 51, 53, 54, 56, 57, 58, 59, 61, 62, 64, 65, 66, 67, 68, 72, 73, 74, 80, 81, 82, 84, 85, 86, 90, 93, 94, 96, 100, 101, 102, 103, 104, 105, 106, 110, 113, 114, 116, 118, 119, 123, 124, 129, 130, 131, 132, 133, 134, 135, 136, 138, 139, 143, 146, 147, 149, 150,



152, 155, 157, 158, 159, 160, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 176, 177, 182, 183, 184, 185, 188, 189, 190, 191, 192, 193, 195, 199, 204, 205, 215, 216, 219, 225, 226, 229, 231, 232, 234, 246, 247, 253, 259, 260, 266, 269, 271, 272, 273, 274, 277, 278, 279, 280, 281, 283, 284, 285, 288, 289, 290, 291, 297, 298, 299, 300, 310, 311, 312, 316, 317, 318, 320, 321, 324, 325, 330, 331, 332, 333, 334, 336, 337, 339, 344, 345, 347, 349, 350, 351, 352, 353, 354, 359, 360, 367, 372, 374, 378, 379, 397, 402, 404, 405, 407, 409, 410, 411, 412, 414, 415, 416, 417, 421, 432, 443, 444, 445, 446, 447, 450, 451, 453, 454, 464, 471, 487, 488, 493, 494, 495, 496, 500, 504, 506, 507, 508, 510, 512, 515, 516, 518, 519, 524, 525, 534, 535, 536, 537, 541, 543, 546, 547, 556, 557, 558, 559, 569, 570, 572, 573, 574, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 597, 602, 605, 607, 608, 615, 617, 621, 627, 629, 631, 632, 635, 636, 637, 638, 640, 642, 643, 644, 645, 646, 649, 650, 652, 658, 659, 660, 661, 667, 668, 669, 670, 671, 672, 675, 680, 684, 685, 686, 687, 702, 704, 705, 707, 708, 712, 715, 716, 717, 719, 720, 721, 724, 727, 730, 731, 732, 735, 736, 737, 738, 740, 742, 744, 745, 747, 751, 753, 754, 755, 759, 760, 763, 766, 768, 769, 770, 771, 776, 777, 778, 779, 783, 789, 791, 793, 794, 795, 796, 798, 802, 804, 806, 807, 813, 814, 821, 825, 829, 834, 836, 838, 839, 840, 841, 842, 855, 858, 859, 860, 861, 866, 870, 874, 877, 882, 884, 885, 888, 889, 890, 891, 894, 895, 897, 898, 899, 900, 907, 917, 918, 919, 922, 923, 925, 927, 930, 931, 932, 936, 938, 940, 941, 942, 950, 951, 952, 953, 954, 957, 959, 960, 963, 964, 966, 967, 971, 976, 978, 980, 982, 984, 985, 986, 991, 992, 996, 999, 1001, 1005, 1006, 1007, 1010, 1011, 1015, 1016, 1017, 1018, 1019, 1022, 1023, 1024, 1025, 1028, 1029, 1030, 1031, 1032, 1033, 1034, 1035, 1036, 1037, 1042, 1043, 1049, 1050, 1051, 1052, 1062, 1063, 1064, 1065, 1069, 1072, 1073, 1081, 1082, 1086, 1088, 1103, 1105, 1106, 1110, 1113, 1114, 1118, 1119, 1120, 1122, 1124, 1126, 1128, 1131, 1134, 1136, 1137, 1138, 1139, 1143, 1144, 1145, 1146, 1147, 1148, 1149, 1150, 1154, 1159, 1160, 1161, 1168, 1169, 1171, 1172, 1173, 1174, 1175, 1178, 1179, 1180, 1181, 1183, 1185, 1190, 1191, 1194, 1195, 1197, 1198, 1200, 1209, 1214, 1216, 1217, 1218, 1220, 1221, 1222, 1228, 1229, 1230, 1235, 1239, 1240, 1242, 1243, 1246, 1249, 1251, 1252, 1257, 1260, 1261, 1262, 1263, 1264, 1265, 1269, 1270, 1271, 1272, 1273, 1274, 1275, 1276, 1277, 1279, 1280, 1281, 1282, 1283, 1284, 1285, 1286, 1287, 1290, 1291, 1292, 1299, 1300, 1302, 1307, 1308, 1309, 1314, 1315, 1316, 1317, 1318, 1319, 1320, 1325, 1326, 1328, 1330, 1332, 1336, 1339, 1343, 1344, 1345, 1346, 1347, 1348, 1350, 1363, 1370, 1378, 1379, 1381, 1385, 1386, 1393, 1394, 1395, 1398, 1399, 1400, 1404, 1407, 1410, 1415, 1428, 1430, 1431, 1432, 1433, 1436, 1437, 1438, 1441, 1442, 1443, 1444, 1445, 1446, 1466, 1467, 1470, 1472, 1474, 1478, 1479, 1480, 1486, 1487, 1488, 1490, 1491, 1496, 1497, 1500, 1504, 1505, 1506, 1511, 1513, 1514, 1516, 1522, 1523, 1524, 1526, 1528, 1529, 1532, 1533, 1535, 1536, 1537, 1538, 1539, 1540, 1541, 1542, 1546, 1547, 1548, 1549, 1552, 1554, 1559, 1561, 1565, 1566, 1568, 1571, 1572, 1573, 1574, 1576, 1577, 1579, 1582, 1584, 1585, 1586, 1592, 1593, 1596, 1597, 1600, 1601, 1603, 1604, 1609, 1610, 1613, 1616, 1617, 1618, 1621, 1626, 1632, 1634, 1637, 1638, 1641, 1642, 1643, 1644, 1645, 1646, 1649, 1650, 1652, 1654, 1656, 1659, 1660, 1661, 1662, 1663, 1664, 1674, 1675, 1676, 1677, 1678, 1682, 1684, 1687, 1688, 1689, 1690, 1691, 1694, 1697, 1699, 1703, 1704, 1707, 1708, 1713, 1714, 1715, 1716, 1717, 1723, 1733, 1736, 1739, 1740, 1744, 1747, 1748, 1753, 1756, 1757, 1759, 1773, 1779, 1783, 1789, 1795, 1796, 1797, 1799, 1801, 1803, 1804, 1806, 1807, 1810, 1811, 1812, 1815, 1816, 1817, 1818, 1821, 1822, 1827, 1829, 1831, 1838, 1839, 1841, 1845, 1848, 1849, 1851, 1853, 1854, 1856, 1857, 1859, 1860, 1863, 1865, 1867, 1868, 1870, 1871, 1872, 1873, 1874, 1875, 1885, 1886, 1887, 1894, 1895, 1896, 1898, 1901, 1905, 1909, 1911, 1918, 1919, 1920, 1921, 1922, 1924, 1925, 1926, 1928, 1929, 1932, 1934, 1936, 1937, 1938, 1939, 1941, 1942, 1943, 1946, 1947, 1948, 1949, 1950, 1957, 1961,

1963, 1964, 1965, 1966, 1969, 1970, 1972, 1973, 1974, 1975, 1976, 1977, 1978, 1979, 1981, 1982, 1986, 1987  
**Rare earths** 319, 465, 478, 970, 1002, 1162, 1298, 1311, 1337, 1365, 1367, 1371, 1451, 1459, 1545, 1550, 1680, 1692, 1785  
**Rhodium** 529, 530, 921  
**Rubidium** 16, 71, 139, 144, 180, 181, 182, 184, 187, 188, 189, 190, 191, 192, 193, 315, 341, 343, 407, 410, 466, 475, 493, 497, 532, 536, 539, 541, 543, 546, 610, 617, 638, 640, 667, 672, 678, 684, 713, 721, 734, 743, 772, 787, 813, 824, 829, 855, 859, 861, 877, 878, 882, 927, 940, 947, 982, 1003, 1008, 1013, 1021, 1022, 1025, 1142, 1220, 1339, 1363, 1364, 1387, 1403, 1430, 1431, 1432, 1433, 1441, 1465, 1467, 1468, 1470, 1493, 1514, 1516, 1527, 1543, 1544, 1547, 1548, 1553, 1565, 1584, 1670, 1673, 1675, 1685, 1734, 1740, 1741, 1831, 1833, 1836, 1839, 1850, 1864, 1875, 1889, 1924, 1944, 1967  
**Scandium** 1311, 1692  
**Silver** 325, 392, 613, 625, 640, 896, 1153, 1234, 1239, 1420, 1425, 1455, 1468, 1470, 1481, 1515  
**Sodium** 1, 8, 9, 10, 11, 14, 15, 16, 20, 21, 22, 23, 34, 35, 36, 37, 40, 41, 44, 47, 48, 50, 51, 53, 54, 57, 59, 61, 62, 64, 66, 70, 72, 73, 74, 82, 84, 85, 86, 88, 90, 93, 94, 97, 100, 102, 103, 104, 105, 106, 110, 113, 114, 117, 118, 119, 123, 124, 129, 131, 132, 133, 134, 135, 138, 139, 140, 143, 146, 147, 148, 149, 150, 152, 153, 156, 158, 160, 164, 165, 167, 169, 171, 173, 175, 177, 182, 183, 184, 185, 187, 188, 189, 190, 191, 192, 193, 194, 195, 199, 203, 205, 209, 210, 215, 220, 225, 226, 229, 231, 232, 234, 238, 245, 246, 253, 259, 260, 266, 269, 271, 272, 273, 274, 276, 278, 279, 280, 283, 285, 288, 289, 297, 298, 299, 300, 310, 316, 317, 320, 321, 324, 325, 327, 328, 331, 333, 334, 335, 336, 344, 346, 347, 350, 351, 352, 354, 359, 365, 366, 367, 368, 371, 372, 374, 377, 378, 379, 387, 397, 402, 404, 405, 406, 407, 411, 412, 413, 414, 415, 421, 422, 432, 440, 441, 442, 444, 445, 446, 447, 449, 450, 451, 453, 454, 459, 464, 470, 471, 479, 480, 487, 491, 493, 494, 504, 506, 507, 508, 510, 512, 514, 515, 516, 519, 524, 534, 536, 537, 541, 543, 546, 547, 550, 551, 554, 558, 559, 566, 572, 573, 574, 576, 577, 578, 579, 580, 590, 597, 602, 605, 607, 608, 609, 611, 612, 616, 617, 619, 621, 627, 629, 631, 632, 635, 636, 637, 640, 642, 653, 661, 667, 668, 669, 670, 671, 672, 675, 684, 685, 702, 704, 707, 708, 710, 716, 717, 719, 720, 721, 724, 727, 730, 735, 738, 740, 741, 742, 744, 745, 747, 751, 753, 754, 755, 759, 761, 763, 764, 765, 766, 768, 769, 770, 771, 774, 775, 776, 777, 778, 779, 780, 783, 784, 785, 786, 789, 791, 795, 796, 798, 801, 802, 804, 805, 806, 807, 813, 817, 821, 825, 827, 828, 829, 834, 836, 839, 842, 843, 845, 855, 859, 860, 861, 862, 863, 866, 873, 874, 877, 882, 884, 885, 888, 889, 890, 891, 892, 893, 895, 897, 898, 899, 900, 905, 913, 916, 917, 919, 922, 923, 925, 926, 927, 931, 932, 940, 941, 942, 951, 952, 953, 955, 959, 960, 963, 964, 966, 967, 968, 971, 974, 976, 978, 982, 984, 985, 986, 988, 991, 992, 996, 999, 1000, 1001, 1004, 1005, 1009, 1010, 1011, 1015, 1017, 1019, 1020, 1023, 1025, 1027, 1029, 1032, 1033, 1034, 1035, 1036, 1037, 1042, 1043, 1049, 1052, 1064, 1065, 1089, 1093, 1103, 1105, 1110, 1111, 1112, 1113, 1114, 1116, 1118, 1120, 1122, 1132, 1137, 1139, 1140, 1143, 1144, 1150, 1159, 1160, 1161, 1169, 1171, 1172, 1178, 1182, 1183, 1185, 1190, 1191, 1194, 1195, 1197, 1198, 1200, 1209, 1214, 1216, 1218, 1221, 1222, 1228, 1230, 1235, 1237, 1238, 1240, 1244, 1250, 1251, 1252, 1257, 1259, 1260, 1262, 1263, 1264, 1265, 1269, 1270, 1271, 1272, 1275, 1276, 1277, 1279, 1280, 1281, 1283, 1284, 1285, 1286, 1287, 1290, 1292, 1295, 1297, 1299, 1300, 1301, 1302, 1307, 1308, 1310, 1314, 1315, 1317, 1318, 1319, 1320, 1327, 1330, 1332, 1339, 1343, 1345, 1346, 1347, 1348, 1363, 1370, 1381, 1385, 1386, 1393, 1394, 1395, 1938, 1399, 1400, 1404, 1405, 1407, 1410, 1415, 1427, 1428, 1430, 1431, 1432, 1433, 1436, 1437, 1438, 1442, 1444, 1445, 1446, 1472, 1474, 1478, 1479, 1485, 1486, 1488, 1489, 1497, 1499, 1500, 1506, 1511, 1513, 1514, 1516, 1524, 1526, 1528, 1529, 1532, 1536, 1537, 1538, 1539, 1540, 1541, 1542, 1546, 1548, 1549, 1552, 1554, 1559, 1561, 1565, 1566, 1568, 1571, 1572, 1573, 1574, 1576, 1577, 1579, 1582, 1584, 1585, 1586, 1592, 1593, 1596, 1597, 1600, 1601, 1603, 1604, 1609, 1610, 1613, 1616, 1617, 1618, 1621, 1626, 1632, 1634, 1637, 1638, 1641, 1642, 1643, 1644, 1645, 1646, 1649, 1650, 1652, 1654, 1656, 1659, 1660, 1661, 1662, 1663, 1664, 1674, 1675, 1676, 1677, 1678, 1682, 1684, 1687, 1688, 1689, 1690, 1691, 1694, 1697, 1699, 1703, 1704, 1707, 1708, 1713, 1714, 1715, 1716, 1717, 1723, 1733, 1736, 1739, 1740, 1744, 1747, 1748, 1753, 1756, 1757, 1759, 1773, 1779, 1783, 1789, 1795, 1796, 1797, 1799, 1801, 1803, 1804, 1806, 1807, 1810, 1811, 1812, 1815, 1816, 1817, 1818, 1821, 1822, 1827, 1829, 1831, 1838, 1839, 1841, 1845, 1848, 1849, 1851, 1853, 1854, 1856, 1857, 1859, 1860, 1863, 1865, 1867, 1868, 1870, 1871, 1872, 1873, 1874, 1875, 1885, 1886, 1887, 1894, 1895, 1896, 1898, 1901, 1905, 1909, 1911, 1918, 1919, 1920, 1921, 1922, 1924, 1925, 1926, 1928, 1929, 1932, 1934, 1936, 1937, 1938, 1939, 1941, 1942, 1943, 1946, 1947, 1948, 1949, 1950, 1957, 1961,

1575, 1577, 1579, 1585, 1586, 1588, 1589, 1596, 1601, 1603, 1604, 1609, 1610, 1618, 1626, 1632, 1634, 1637, 1638, 1641, 1642, 1644, 1645, 1646, 1647, 1650, 1654, 1655, 1656, 1659, 1660, 1661, 1662, 1663, 1664, 1675, 1676, 1679, 1684, 1689, 1690, 1691, 1694, 1697, 1699, 1703, 1704, 1707, 1708, 1714, 1716, 1717, 1718, 1723, 1732, 1736, 1738, 1744, 1748, 1753, 1756, 1757, 1759, 1760, 1773, 1777, 1779, 1783, 1789, 1795, 1796, 1797, 1799, 1801, 1802, 1803, 1804, 1806, 1807, 1810, 1811, 1812, 1813, 1815, 1816, 1817, 1822, 1825, 1827, 1829, 1830, 1831, 1839, 1841, 1843, 1844, 1847, 1848, 1853, 1854, 1855, 1856, 1857, 1859, 1860, 1865, 1867, 1868, 1870, 1871, 1872, 1873, 1875, 1881, 1882, 1883, 1886, 1894, 1896, 1897, 1898, 1900, 1905, 1918, 1919, 1920, 1921, 1922, 1924, 1925, 1926, 1928, 1929, 1932, 1934, 1936, 1937, 1938, 1939, 1942, 1943, 1945, 1946, 1947, 1948, 1949, 1950, 1951, 1962, 1963, 1964, 1965, 1966, 1970, 1972, 1973, 1975, 1976, 1978, 1979, 1982, 1987

**Strontium** 4, 5, 6, 12, 19, 25, 26, 27, 46, 73, 107, 125, 139, 144, 196, 197, 201, 202, 310, 313, 325, 337, 372, 398, 399, 400, 401, 402, 404, 405, 406, 407, 419, 427, 459, 460, 497, 498, 502, 512, 531, 532, 533, 536, 545, 557, 591, 592, 593, 640, 651, 667, 674, 690, 719, 728, 749, 750, 762, 810, 813, 816, 822, 823, 853, 856, 857, 903, 912, 918, 920, 941, 946, 956, 975, 982, 995, 996, 1025, 1032, 1047, 1083, 1094, 1096, 1097, 1101, 1102, 1113, 1118, 1190, 1191, 1205, 1233, 1239, 1268, 1293, 1312, 1314, 1315, 1339, 1352, 1353, 1354, 1369, 1390, 1391, 1401, 1414, 1421, 1422, 1439, 1457, 1458, 1462, 1463, 1467, 1486, 1548, 1554, 1558, 1559, 1594, 1607, 1608, 1639, 1695, 1696, 1698, 1735, 1746, 1774, 1780, 1790, 1818, 1819, 1820, 1823, 1826, 1837, 1839, 1843, 1880, 1892, 1940, 1952

**Sulfur (sulfate)** 31, 261, 262, 263, 358, 362, 363, 364, 792, 1267, 1520, 1666, 1668, 1755, 1898

**Tellurium** 391

**Thallium** 163, 212, 594, 640, 699, 982, 1099, 1100, 1109, 1377, 1453, 1515, 1554, 1555, 1557, 1560, 1712, 1737, 1764, 1769, 1931

**Tin** 325, 1786

**Titanium** 295, 296

**Vanadium** 255, 701, 982, 1212, 1623, 1731, 1771

**Yttrium** 282, 319, 1298, 1311, 1583

**Zinc** 325, 1109

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## 1. 10. Less Familiar Flames

The 92 references assembled in this section pertain to works on various combustion flames, some of which have already been considered as possible excitation sources in analytical flame spectroscopy, while others have not yet been studied for this purpose. Among these last flames the carbon subnitride, the nitrogen trifluoride, and perhaps the metal powder flames might well prove of practical interest. The reader will find a description of the properties of these flames in the works indexed under the corresponding fuel or oxidant gas.

### Subject Index

General papers 40, 57  
 Carbon subnitride 1, 3, 21, 42, 50  
 Chlorine 7, 74  
 Chlorine trifluoride 73  
 Converter flames (Thomas, Bessemer, etc.) 13, 35, 36, 37, 47, 48, 88, 89  
 Cyanogen 5, 14, 15, 17, 20, 22, 32, 38, 39, 44, 45, 46, 56, 63, 64, 66, 70, 77, 80, 82, 83, 84, 85, 86, 87  
 Fluorine 2, 6, 10, 11, 18, 19, 23, 28, 29, 43, 49, 53, 61, 62, 74, 76, 90, 91  
 Metal powder flames 27, 30, 41  
 Ozone 16, 67, 68, 69, 78, 79, 81  
 Perchloric acid 24  
 Perchloryl fluoride 8, 31, 52, 59, 60, 71, 72  
 Nitrogen oxide 4, 9, 12, 25, 26, 32, 33, 34, 51, 54, 55, 56, 57, 58, 62, 92  
 Nitrogen trifluoride 65, 75

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## 2. Atomic Absorption Spectroscopy

### 2.1. Atomic Absorption Spectroscopy

The 353 references of works on atomic absorption spectroscopy assembled in this section are indexed under various headings; the reader will find thus several early contributions of historical interest in the "Earlier Works" group. This is followed by "Books and Periodical Publications," and to the works mentioned there one should add a book by J. W. Robinson, *Atomic Absorption Spectroscopy*, published in the spring of 1966 by Marcel Dekker, New York. The fundamental contributions of Walsh and associates are indexed under "Theoretical and General Papers," where the reader will also find the works of Alkemade and associates together with a number of papers in which the basic properties of the atomic absorption principle are discussed.

The numerous contributions to analytical applications of the atomic absorption method are indexed under "Materials Analyzed" and "Elements Determined," and as can be seen, the method seems to find thus far the widest use in the analysis of biological materials (48 papers) and of metals and alloys (47 papers), the elements determined more often being, in decreasing order, Mg, Cu, Zn, Ca, Hg, Na, Pb, Fe, Ag, Mn, Ni, K, Au, Co, Cr, Cd, etc.

NOTE ADDED TO THE PAGE PROOF. A further contribution to the field of atomic absorption in the form of a book, "Atomic Absorption Spectroscopy" by J. Ramírez-Muñoz, is expected to be available in 1967; this work will be published by the Elsevier Publishing Company, New York.

#### Subject Index

**Earlier papers** 15, 92, 113, 134, 189, 201, 205, 239, 260, 333, 341,  
**Books and periodical publications** 16, 17, 80, 141, 220  
**Theses** 49, 116, 120, 157, 202, 275, 299  
**Reviews and articles in books** 42, 66, 67, 74, 89, 91, 101, 104, 105, 106, 115, 122, 124, 142, 144, 166, 171, 174, 182, 185, 186, 188, 195, 218, 224, 225, 230, 234, 242, 245, 247, 248, 249, 256, 263, 264, 267, 268, 270, 283, 291, 316, 328, 329, 331, 352  
**Theoretical and general papers** 2, 3, 5, 11, 12, 19, 26, 53, 62, 65, 69, 81, 95, 96, 97, 117, 125, 146, 147, 163, 170, 176, 177, 191, 192, 193, 194, 198, 203, 208, 209, 214, 215, 222, 223, 233, 236, 241, 250, 251, 252, 255, 257, 259, 265, 266, 271, 277, 282, 285, 294, 297, 300, 305, 306, 307, 308, 309, 310, 311, 312, 337, 338, 339, 340, 348  
**Instrumental** 2, 3, 33, 34, 37, 40, 43, 44, 46, 52, 56, 76, 78, 86, 99, 109, 111, 127, 128, 131, 136, 137, 139, 145, 153, 154, 155, 158, 159, 160, 161, 162, 164, 170, 175, 180, 183, 184, 190, 196, 197, 206, 207, 208, 209, 226, 240, 257, 259, 261, 269, 272, 277, 288, 289, 295, 296, 305, 313, 314, 332, 337, 341, 342, 343  
**Organic solvents in atomic absorption spectroscopy** 9, 173, 232, 233, 244

#### Materials Analyzed

**Beer, wine** 93, 349  
**Biological materials** 28, 29, 30, 47, 50, 64, 69, 70, 71, 94, 100, 119, 121, 123, 126, 129, 132, 133, 136, 143, 154, 155, 169, 187, 200, 210, 219, 231, 253, 267, 273, 276, 279, 301, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 329, 331, 353  
**Butter** 330  
**Cement and related materials** 167, 254, 292  
**Chemical reagents** 1, 35, 138, 140, 197, 221, 228, 295, 317  
**Coal** 23, 75, 216  
**Fertilizers** 8, 10, 100, 178, 268, 295  
**Gasoline** 55, 246, 295  
**Isotope analysis** 110, 112, 217, 345, 346, 347  
**Lubricating oils** 41, 118  
**Metals and alloys** 13, 14, 18, 21, 22, 24, 36, 46, 77, 79, 81, 89, 97, 98, 101, 102, 103, 108, 114, 135, 139, 150, 151, 152, 168, 179, 199, 211, 212, 213, 215, 227, 234, 262, 274, 278, 283, 286, 287, 290, 295, 302, 303, 304, 334, 335, 336  
**Ores and rocks** 13, 27, 54, 90, 107, 156, 227, 235, 237, 238, 258, 280, 295, 298  
**Plants** 8, 10, 38, 39, 57, 58, 59, 130, 131, 143, 235, 268, 284, 344  
**Soils** 8, 10, 58, 60, 64, 100, 131, 268, 284, 298  
**Test solutions** 4, 6, 7, 25, 48, 61, 63, 68, 72, 73, 82, 83, 85, 88, 122, 127, 148, 158, 161, 172, 173, 175, 184, 196, 229, 243, 271, 281, 293, 346, 347, 350, 351  
**Water** 45, 315  
**Waters: marine** 32, 84, 181  
**Waters: industrial** 31

#### Elements Determined

**Aluminum** 13, 48, 73, 92, 175, 212, 213, 271  
**Antimony** 154  
**Barium** 32, 96, 175, 271  
**Beryllium** 271  
**Bismuth** 154, 327  
**Cadmium** 31, 77, 154, 196, 215, 227, 295, 327, 351  
**Calcium** 32, 45, 47, 58, 59, 60, 71, 75, 77, 93, 130, 131, 155, 158, 187, 210, 216, 219, 292, 293, 295, 319, 321, 322, 325, 353  
**Cesium** 175, 232  
**Chromium** 41, 87, 152, 175, 295, 315, 317, 318  
**Cobalt** 7, 32, 77, 117, 124, 179, 274, 295, 315  
**Copper** 8, 27, 28, 29, 31, 32, 35, 36, 38, 41, 45, 58, 84, 93, 98, 122, 124, 126, 127, 138, 149, 151, 155, 158, 161, 178, 181, 231, 253, 262, 274, 278, 280, 295, 304, 315, 317, 330, 336, 349, 351  
**Gallium** 92  
**Gold** 107, 108, 114, 149, 155, 172, 281, 295, 350, 351  
**Indium** 92, 175  
**Iron** 6, 13, 21, 31, 32, 35, 36, 38, 41, 45, 58, 75, 84, 93, 161, 178, 197, 215, 216, 262, 278, 315  
**Lead** 30, 31, 35, 36, 41, 55, 77, 79, 124, 146, 154, 155, 175, 215, 246, 262, 279, 295, 326, 327, 349, 351  
**Lithium** 32, 112, 175, 346, 347  
**Magnesium** 4, 14, 22, 32, 45, 47, 50, 53, 57, 58, 60, 69, 70, 71, 75, 77, 90, 119, 122, 123, 124, 129, 131, 133, 135, 136, 140, 143, 154, 155, 165, 167, 168, 173, 178, 187, 199, 215, 216, 274, 276, 286, 290, 292, 295, 301, 303, 319, 320, 323, 325, 336, 344  
**Manganese** 6, 24, 32, 35, 36, 38, 84, 124, 154, 155, 175, 178, 215, 231, 274, 287, 292, 295, 315  
**Mercury** 20, 51, 86, 113, 134, 154, 155, 156, 169, 200, 201, 204, 205, 217, 228, 229, 239, 258, 298, 327, 333, 341, 342, 343

Molybdenum 61, 63  
 Nickel 7, 31, 32, 35, 36, 84, 150, 154, 215, 244, 273, 274, 295, 315, 327, 351  
 Niobium 85  
 Palladium 83, 107, 108, 172, 278, 281, 350  
 Platinum 107, 108, 172, 281, 295, 350  
 Potassium 45, 58, 60, 75, 93, 121, 122, 175, 184, 216, 231, 232, 292, 293, 324  
 Rare earths 203, 266, 348  
 Rhenium 85  
 Rhodium 107, 108, 172, 281, 295, 350  
 Rubidium 32, 215, 232, 284  
 Scandium 85  
 Selenium 235  
 Silver 25, 26, 41, 54, 77, 98, 107, 108, 114, 148, 172, 237, 238, 262, 278, 295, 334, 335, 336, 351  
 Sodium 32, 36, 39, 45, 58, 60, 72, 75, 77, 93, 121, 122, 184, 216, 221, 232, 233, 243, 254, 292, 300, 324, 333  
 Strontium 23, 32, 61, 64, 68, 154, 175  
 Thallium 92, 154, 175  
 Tin 1  
 Titanium 85, 175, 271  
 Thorium 155  
 Uranium 110, 135, 290  
 Vanadium 85, 271  
 Yttrium 85  
 Zinc 10, 27, 31, 32, 35, 36, 38, 57, 58, 77, 82, 84, 88, 94, 100, 102, 103, 129, 132, 154, 155, 178, 211, 212, 214, 231, 253, 262, 295, 302, 317, 327, 336, 349

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## 2.2. Hollow Cathode Discharge Tubes

The emission sources producing narrow lines which can be used in the atomic absorption procedure are in general of the low pressure discharge type, such as hollow cathode lamps or metal vapor discharge tubes. Since discharge lamps constitute an indispensable element of the atomic absorption procedure discussed foregoing, it was considered desirable to provide the interested worker with some information on those lamps. The 87 references covering the subject are assembled in this section and are indexed under various headings. The general properties of electrical discharges in gases are lucidly discussed by Penning in a brief monograph (ref. 57), and this work will constitute an excellent introduction for the understanding of the phenomena occurring in hollow cathode discharges. A detailed discussion of hollow cathode geometry will be found in references 84 and 87, and in this last reference the characteristics of a nearly spherical hollow cathode of original design are examined. The description of various types of hollow cathode tubes is given in the 34 papers indexed in "Instrumental," while specific discharge tubes used in conjunction with the atomic absorption instrumentation are described in references 13, 31, 47, 66, 78, and 81.

A certain number of papers on analytical applications of hollow cathode tubes are also indexed in this section, although the discharge tubes have not been used in conjunction with an atomic absorption procedure. These references are included here since they should constitute a source of useful information on the general properties and handling procedures of discharge tubes.

### Subject Index

- Discharge parameters and mechanism 25, 44, 50, 53, 56, 57, 60, 66, 67, 76, 77, 83, 84, 87  
 Instrumental 3, 5, 6, 9, 10, 11, 16, 18, 19, 24, 28, 29, 38, 39, 40, 41, 42, 43, 45, 46, 51, 54, 62, 65, 68, 69, 70, 72, 73, 74, 79, 80, 82, 85  
 Discharge tubes for atomic absorption 13, 31, 47, 66, 78, 81  
 Analytical applications 1, 2, 4, 7, 8, 9, 10, 12, 14, 15, 17, 19, 20, 21, 22, 23, 27, 28, 29, 30, 32, 33, 34, 35, 36, 37, 39, 40, 41, 42, 43, 45, 48, 49, 51, 52, 55, 58, 59, 61, 63, 64, 65, 68, 70, 71, 74, 75, 85, 86

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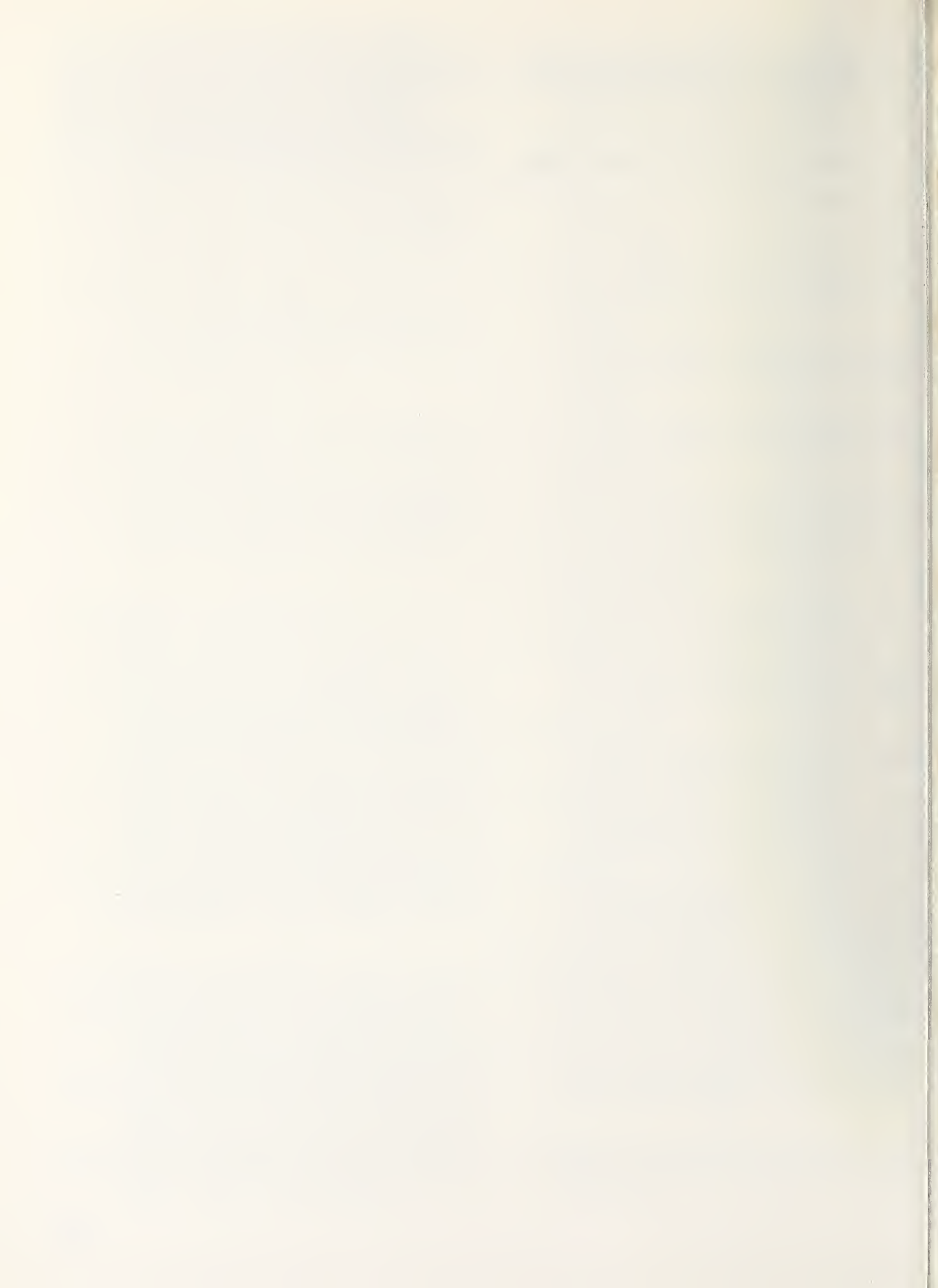
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### 3. Electrical Discharges Having the Aspect of Combustion Flames

#### 3.1. The Radio-Frequency Discharge

The references collected in this section pertain to works on radio-frequency (RF) discharges which can be used as excitation sources in analytical spectroscopy. Although these sources draw the energy from an electrical field rather than from a combustion reaction, they are assembled here since the aspect of the discharge is quite similar to that of a combustion flame. Furthermore the methods used in supplying a combustion flame with the analytical sample solution can also be used to supply the RF discharge. The RF discharge can be produced in closed vessels at various pressures or in the open at atmospheric pressures and in a variety of gases.

Excitation of the spectral emission of gases under low pressure by the action of radio-frequency fields has a long history, dating approximately from the invention of the Tesla coil. One of the earliest published studies concerning the RF excitation of gases was made by J. J. Thompson (130). The use of this discharge to produce spectral excitation of various solid or gaseous chemical species followed later through the works of Dunoyer (39-41), Bloch and Bloch (12), Vaudet (140), and Winans (148). Excitation by the Tesla coil was adapted to practical spectrochemical analysis by Gerlach and Schweitzer in 1931 (55). Further extensions of the technique were made in 1933 by Potapenko (103) and Goroncy and Urban (57), employing tube-driven, undamped oscillators. In 1941 Fenner (45) used an electrodeless discharge tube for the quantitative determination of traces of Cd in Se and of Hg in various gases. The sample in the evacuated tube was excited by a high-frequency generator producing a wavelength of 6 m.

The application of RF excitation to gases at low pressure, and to relatively volatile solids, was given further impetus by the work of Meggers (82) on monochromatic emissions as an ultimate standard of length. Further contributions have been made by Gatterer (50-53), who succeeded in exciting and determining the halogens, S, and Se in various samples containing as little as 0.001 percent. He used for this purpose a generator producing a discharge of 40 to 100 MHz with an output at the sample tube of 600 W. A similar discharge has been used by Tomkins and Fred (132) for the determination of D<sub>2</sub> in heavy water.

The method continues to be refined, adapted, and applied, as evidenced by the work of Zelickoff et al. (150) on the excitation of the vapors

of Pb, In, Ga, Sb, Bi, Hg, Cd, Tl, Zn, Ca, and Ba. Keller and Smith (67) used a 40-MHz discharge to excite and determine Cl, Br, and I at the level of 0.001 percent. A similar discharge was employed by Broida and Morgan (18) to analyze hydrogen-deuterium mixtures in the presence of air by exciting the gaseous sample contained in an electrodeless tube with a 150-MHz oscillator.

Corliss et al. (27) have succeeded in exciting the volatile halides of relatively involatile metals such as Be, Ti, Fe, Ni, Cu, Mo, U; and Tomkins and Fred (133) produced the spectra of rare earths and some heavy metals present as vapors of the halides. The need in optical pumping experiments for intense spectral lines free of self-reversal occasions continued interest in electrodeless RF discharge tubes with alkali metal fillings (10, 54). Electrodeless discharges for the analysis of gases have been extensively explored and exploited by Gatterer and Frodl (53), White (146), White and Lovelace (147), Ishida (63), Frisch and Schreider (48), and Stolov (125).

More recently, Chakrabarti et al. (23, 24) have studied the emission spectra of N<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, and that of mixtures of A-CO<sub>2</sub> excited in RF fields. An excellent review paper on RF discharges in gases has been published by Morgan (99), and covers this field up to 1953 with 70 references.

Radio-frequency discharges of flamelike appearance occurring at atmospheric pressure can also be produced by using a suitable portion of an RF circuit (60). Asami and Hori have described the spectrum produced by the discharge in air (2). A description of the excitation of samples in solution by an RF discharge was made in 1954 (79). Fundamental contributions to the field of RF discharges were made by Grigorovici and Cristescu who investigated the conditions for the production of the discharge, its temperature, and various electrical parameters, in several publications (28 to 35, 58, 59). Further experimental developments of the method have been made by Bădărău et al. (7), who introduced the sample solution, as an aspirated aerosol, into the discharge in air and excited lines of the elements: Al, Ba, Be, B, Ce, Cs, Fe, Pb, K, Sn, V, and Zn. Korolev and Zheenbaev (70-72) have investigated the sensitivity of excitation of the elements Na, K, and Li. Using excitation sources similar to the one described by Scholz (121), Yamamoto and Murayama have examined the excitation of Ca

and Mg (149), and Dunnken et al. (37, 38) that of Ca, Sr, Ba, Mn, and Cr. In both cases nitrogen and air were used as carrier gases. Zheenbaev (151-153) has demonstrated an improved sensitivity, obtained by hydrodynamic compression of the discharge, in the detection of a number of elements.

Apparatus designed specifically for the production of the RF brush discharge, for which the designation "Electronic Torch" has been generally applied, was developed by Cobine and Wilbur (25, 26); this source is magnetron-powered. A similar magnetron-driven apparatus has been described by Schmidt (120). Scholz (121) has described a "Hochfrequenz-Plasma-Flamme," powered by a triode oscillator tube, and employing a tubular-shaped "burner" through which a gas stream is passed for localizing and stabilizing the discharge.

The 154 references are distributed in the index under "Discharges in Closed Vessels at Various Pressures" and "Discharges at Atmospheric Pressure."

### Subject Index

Discharges in closed vessels at various pressures 1, 3, 9, 10, 12, 13, 14, 17, 18, 19, 27, 36, 39, 40, 41, 42, 43, 45, 46, 48, 49, 50, 51, 52, 53, 54, 57, 63, 65, 67, 68, 69, 77, 78, 82, 83, 85, 86, 87, 88, 89, 90, 91, 92, 93, 95, 99, 108, 110, 116, 117, 118, 119, 123, 124, 125, 126, 127, 128, 130, 132, 133, 134, 136, 137, 138, 139, 140, 142, 143, 146, 147, 148, 150, 154

Discharges at atmospheric pressure 2, 4, 5, 6, 7, 8, 11, 15, 16, 20, 21, 22, 23, 24, 25, 26, 28, 29, 30, 31, 32, 33, 34, 35, 37, 38, 44, 47, 55, 56, 58, 59, 60, 61, 62, 64, 66, 70, 71, 72, 73, 74, 75, 76, 79, 80, 81, 84, 94, 96, 97, 98, 100, 101, 102, 103, 104, 105, 106, 107, 109, 111, 112, 113, 114, 115, 120, 121, 122, 129, 131, 135, 141, 144, 145, 149, 151, 152, 153

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## 3. 2. Plasma Arcs

Another excitation source which takes its energy from an electrical discharge and has a shape similar to that of a combustion flame is the plasma arc. This source is produced when an electric arc is forced to pass through a narrow hole made in an appropriate material cooled with water. An inert gas is used in the process, and the same gas can be employed in conjunction with a pneumatic atomizer to introduce into the plasma arc the analytical sample solution. Although this type of discharge was known since 1922 (19, 20), and some of its

spectroscopic properties were investigated earlier (19, 46), its use as an excitation source in analytical spectroscopy was studied only during the last years, major contributions to this field originating from the Spectrochemical Section of the National Bureau of Standards (48 to 51, 74). A discussion of the characteristics of the plasma jet spectroscopic source was given in 1958 (49) and published in 1959 (50). A similar study was published in USSR (34 to 36 and 84 to 86) in 1959.

The reader will find in this section, in addi-

tion to works on plasma arcs, several works on the atomic hydrogen flame (6, 7, 12, 17, 26, 38, 39, 75) together with laser excitation (13, 14, 32) sources, since these sources are also plasma generators.

## Subject Index

- Characteristics of the discharge** 2, 3, 4, 5, 6, 7, 8, 9, 15, 17, 18, 19, 20, 23, 25, 26, 27, 30, 31, 33, 38, 39, 40, 41, 43, 44, 46, 47, 54, 57, 61, 62, 63, 64, 65, 66, 67, 68, 71, 75, 77, 82, 83, 88, 90, 91, 93, 94
- Instrumental** 11, 12, 13, 14, 19, 20, 21, 22, 23, 24, 26, 28, 38, 44, 45, 46, 48, 49, 50, 51, 55, 57, 59, 60, 66, 71, 72, 73, 74, 76, 77, 80, 81, 84, 85, 86, 88, 92, 93, 95, 96, 97, 98
- Analytical applications** 1, 10, 16, 19, 24, 29, 32, 34, 35, 36, 37, 42, 48, 49, 50, 51, 52, 53, 56, 58, 59, 60, 69, 70, 72, 74, 76, 78, 79, 84, 85, 86, 87, 88, 89, 92, 98

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### 3. 3. Arc-and-Spark-in-Flame

The capabilities of a combustion flame to produce radiations from chemical species which are difficult to excite can be increased by the superposition of an electrical discharge such as an arc or a spark. Early spectroscopic observations with a spark-in-flame source were described in 1922 by Greinacher (ref. 4), while Roche (ref. 20) examined the possibilities of using the spark-in-flame as an excitation source in analytical spectroscopy, and investigated its application to the determination of Fe, Mn, Cr, Ca, Sr, Ba, and Zn. An arc-in-flame was used by Southgate in an attempt to increase the temperature of a combustion flame (ref. 24). Further use of spark-in-flame arrangements as excitation sources in analytical spectroscopy was described also by Hultgren (ref. 5), and a detailed discussion of the instrumentation and results which can be obtained with such a source was given by Straub in his doctoral thesis (ref. 25).

More recently, Lawton and associates have described an interesting arc-in-flame source (ref. 11) which has not yet been used as a spectral analytical excitation source (see also refs. 9, 10, and 13). Further information on the properties of spark-in-flame sources will be found in the 26 references assembled in this section.

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