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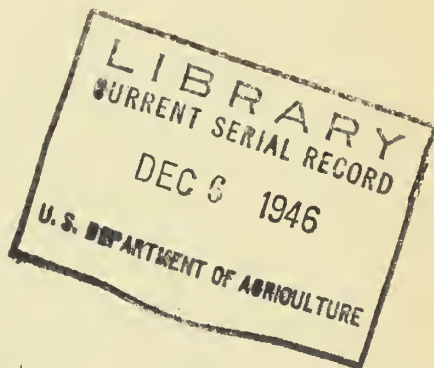
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A PHOTOELECTRIC REFRACTOMETER

By

Enoch Karrer and Rollin S. Orr



Southern Regional Research Laboratory
New Orleans, Louisiana
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By Enoch Karrer and Rollin S. Orr
Southern Regional Research Laboratory^{1/}
New Orleans 19, Louisiana

INTRODUCTION

In the course of developing means for measuring and controlling relative humidity in small spaces, in connection with research on properties of cotton fibers, we had up for consideration the scattering of light passing through a solid by a liquid condensed upon the solid. The outcome is the refractometer described below.^{2/}

HISTORICAL

Refractivity is an important optical characteristic of matter and the property of refraction has been employed in the study of molecular structure and identification of organic compounds, in routine control in the manufacture of certain products such as wine and beer, alcohol, sugar, butter, and other fats, alkalies, varnishes, glycerine, biological preparations, mineral waters, and in estimation of solids in preserves, of proteins in serums, etc. Many types and forms of refractometers have been invented. The types of instruments most frequently employed in the application of refractometric methods for fluid are: (1) That based upon the determination of the angle of total reflection. In the Abbe refractometer a thin layer of the sample liquid is held between two prisms, and the beam of light observed passes through the sample. In a modified form the critical angle of refraction is determined by noting the angle of total reflection. The beam of light observed is the reflected beam, so that opaque and translucent materials may be tested.^{3/} (2) That in which the liquid under test is itself in the shape of a prism, and the angle of refraction of a beam of light passing through it is observed.^{4/} (3) That in which the retardation of the velocity of light passing through the fluid is made manifest by interference phenomena.^{5/} (4) That in which the relative change in focal distance is observed when the medium into which an object is immersed is changed. This is an important application of the microscope.

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- ^{1/} One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.
 - ^{2/} Means for controlling humidity will be described elsewhere.
 - ^{3/} Modern instrument of this type is described in the catalog of Bausch and Lomb Optical Company.
 - ^{4/} Such an instrument is described in the catalog of the Fisher Scientific Company, Pittsburgh, Pennsylvania.
 - ^{5/} Zamin interferometer.

In all of these methods the test results are obtained by observing through a lens system -- either the direction of a beam of light, or position and number of the interference bands must be determined. Intensity of the light plays only incidental role. In all but one the determining light beams must pass through the fluid under examination.

In the method of refractometry suggested below and in the refractometer described, the variation in refractivity is observed as changes of intensity of light; and the light beam whose intensity is observed does not pass through the material in question. This means that all substances, colored, white, or black, clear or translucent, may be equally easily tested, and any device sensitive to light intensity may be employed to measure the refractivity. Therefore, use may be made of any one of several modern devices and means for controlling and recording the refractivity of industrial liquids. No recording, or even indicating refractometer, has up to now been available.

THE PRINCIPLES INVOLVED

When a ray of light at an incident angle, A , passes from a medium with index of refraction, R , into another of lower refractive index, r , at an emergent angle, a , the relationship $R \sin A = r \sin a$ obtains for all angles from $a = 0$ to $a = 90$.

When the incident angle, A , in the denser medium is increased until the emergent angle, a , becomes 90° , the ray no longer emerges into the less dense medium but is reflected at the interface. The limiting condition for this is that the angle of emergence into the less dense medium shall be 90° ; i.e., $\sin a = 1$. Then the relationship above becomes $r/R = \sin A$. Monochromatic parallel rays of light emerging from a medium of refractive index, R , and striking, at the critical angle of incidence, or at greater angle, an optically plane boundary surface in a surrounding medium of lower refractive index, r , will be totally reflected; and there will be no light transmitted. If with a given optical set-up the refractive index of the less dense medium be changed, there will not be total reflection and some light will be transmitted. The amount reflected may be measured with a photoelectric cell, and be correlated with the refractive index of the less dense medium surrounding the denser medium. Thus, to measure refractivity we may measure an intensity change instead of a retardation or a deviation of a ray of light. In an ideal set-up the light beam is monochromatic, and is composed of parallel rays; the interfacial surface is an optically smooth plane; the light beam is incident exactly at the critical angle; no other light than that critically reflected reaches the photoelectric cell. (The light which is transmitted when the refractive index of the fluid is changed, and the conditions for total reflection no longer exist, must not be allowed to return.) An outstanding characteristic of this method is that as these ideal conditions are approached very great sensitivity is obtained. Theoretically there is no limit to the sensitivity that might be attained.

FORM OF INSTRUMENT AND SET-UP

A very simple arrangement for a photoelectric refractometer based upon the amount of light reflected at interfaces is shown in Fig. 1. A round glass rod, R (about 12-mm diameter, and 15 cm long), is bent to U-form. At the end of one branch of the U is located a light source, L, such as a sodium arc; and above the other a photoelectric cell, P, connected in series with a galvanometer, G. When the U-rod stands in air considerable light is transmitted along the rod by multiple internal reflection out to the photoelectric cell. When the U-rod is immersed in a liquid more light will escape at the bend, and less will be transmitted internally to emerge at the end of the U on to the photo-cell. The liquid should be surrounded by a black compartment so that light will not re-enter. If the refractive index of the liquid be equal to that of the glass rod, a minimum of light will reach the photoelectric cell. The refractive index of the glass rod sets an upper limit to the range of refractive index that may be explored with this photoelectric refractometer. A more satisfactory set-up is shown in Fig. 2, where two photo-cells, P, p, are connected in opposition to the galvanometer and only differences between refractive indices of two solutions are observed. A null method may then be employed. The illumination of the comparison cell may be altered or, by use of resistors, only part of the potential from that cell may be allowed to affect the galvanometer. This arrangement eliminates the disturbing effects of fluctuation in the light source.

Another null method may be employed wherein for the second photo-cell, p, is substituted a potentiometric circuit with auxiliary e.m.f. With a barrier layer photo-cell (not of greatest sensitivity), a Leeds and Northrup potentiometer, type K, and a Leeds and Northrup galvanometer of sensitivity 0.003 $\mu\text{A}/\text{mm}$, and resistance of 470, the observations in Table I were obtained. A difference of 19.52 mv was recorded for a range of refractive index from 1.33 of water to 1.47 of carbon tetrachloride. The settings could be made to within 0.05 mv. Thus, an accuracy of about one in the third decimal place was practical. Much greater accuracy than this is obtainable. The relationship between refractive index and potential is not linear, but may be represented by a smooth curve.

Table I.

Liquid	Index of refraction at 20°C	Photo-cell potential milli-volts
Distilled water	1.3336	23.02
Acetone	1.3593	16.75
Ethyl alcohol	1.3618	16.30
ZnCl ₂ 36% solution	1.4022	10.10
Carbon tetrachloride	1.4607	3.50

The critical angle at which the light beam should strike the boundary surface is defined, as noted above, by the equation $\sin A = r/R$. The divergence of the light and curvature of the rod which determined $\sin A$ may be chosen to yield greatest sensitivity for any particular range of refractivity. Another factor which may enhance sensitivity, whenever the quantity of fluid under test is not limiting, is the length of the rod in curvature. If this is made long and of continuously changing radius of curvature, the probabilities are increased that more rays of light internally reflected will be incident at the proper angle to escape.

Also, as already noted the upper limit of the range of refractivity measured is set by the refractive index of the glass rod. Material of higher refractive index will extend the range and enhance sensitivity. By the use of liquids instead of solids for the U-rod conducting the light, a wider range is at one's disposal. For the U-rod may be used a U-tube filled with a highly refractive liquid. For example, a change from a solid glass U-rod to a soft glass U-tube filled with carbon tetrachloride increased sensitivity about 15 percent.

VARIOUS FORMS OF PRISM

This immersion form of the photoelectric refractometer was the original form in which we used it. It has certain useful applications but cannot be adjusted for critical reflection and maximum sensitivity.

Some forms of prisms that may be employed for immersion purposes are shown in Fig. 3, A and B. Prism A is cut out of a thick plate of glass, about $2 \times 3 \times 1/2$ in., and has a slot sawed down $2/3$ of its length. The corners distal from the saw-cut are cut off at about 42° and polished. A simple prism such as is depicted in Fig. 3B is also useful. The angle near the apex may be chosen so that great sensitivity over any given range may be had at the extreme point. It need then be immersed only a few millimeters, and very small samples of liquids may be tested.

A further modification of the refractometer with which we have made more observations is shown in the set-up in Fig. 4. The refractor-reflector is a truncated triangular prism, or a complete triangular prism. Upon its base rests an open cylinder, constituting the cell into which the fluid under test is placed or is passed through. The light rays from the lamp, L, fall approximately perpendicularly upon one face of the prism, and approximately at the critical refraction angle on the interface between prism face and test substance. Only the reflected light irradiates the photo-cell, P, opposed against cell P_1 . Diaphragms S and S' limit the light beam. The sensitivity of the galvanometer is adjusted by means of a shunt resistance. The zero reference point of the galvanometer, G, may be set for any reference liquid such as water, as was done for the observations of Fig. 5. The maximum sensitivity available was 0.000005. However, the accuracy was dependable only to 0.00005. For this short range the calibration curve is a straight line. For such a set-up, wherein the beam of light from an incandescent lamp was narrowly restricted and carefully adjusted for the critical angle when air

is in the cell, curve 1 of Fig. 6 indicates the performance when the galvanometer sensitivity is $0.02 \mu\text{A}/\text{mm}$. Curve 2 is the corresponding curve when a sodium arc is substituted for the incandescent lamp. In curve 3 are plotted the observations when the light beam employed for curve 1 is more critically positioned. The maximum sensitivity available in the first instance became 0.0000002. The workable accuracy, however, extends only to 2 in the fifth decimal place. Mechanical disturbances, voltage fluctuations, and temperature changes preclude greater accuracy. It is probable that these factors can be controlled to yield a far greater accuracy.

Since changes in refractivity have been converted into changes in electric potential or current, it is obvious that with this refractometer one may record and control refractivity of mixtures, continuously and practically instantaneously. Also it should be noted that any light whatsoever may be used, and that there is a definite average refractive index for it. This may enhance the utility of refractometric methods in industry. Since refractivity runs in general with mass density, such a recording and controlling refractometer calibrated in terms of density may be employed for maintaining uniformity of solutions and mixtures of liquids without reference directly to optical properties.

It is of interest to point out that the phenomenon of refraction upon which this photoelectric refractometer is based may also be employed to indicate and control the level of a liquid without opening and closing any electrical contacts in, or in the neighborhood of, the liquids.

Also there exists sufficient sensitivity for detecting and controlling moisture and other vapors in the atmosphere, and in general for gases. We have also employed this form of refractometer to detect the absorption of water in a film of hygroscopic material such as glycerine. Such a film may also be employed to control moisture content of the air, or other gases.

SUMMARY

A refractometer has been devised wherein changes of intensity of light indicate changes of refractivity. The instrument is based upon the phenomenon of total and partial internal reflection of a beam of light when passing from a denser to a less dense medium at particular angles of incidence.

The responsive light beam does not pass through the substance under test. The color and transparency of the test substance, therefore, do not interfere. Average refractive index for white light (or any light) is readily measured.

The methods of use suggested are the deflection and the null methods.

This refractometer may be used in conjunction with existing electrical recording and indicating mechanisms -- making it possible to record and control continuously and instantaneously the refractivity of liquids. Accuracy in the third decimal place is easily obtained. Two in the fifth decimal place has been utilized, while a sensitivity of two in the seventh decimal place has been attained.

The phenomenon of internal reflection upon which this refractometer is based may be employed in other ways, such as for control of liquid level.

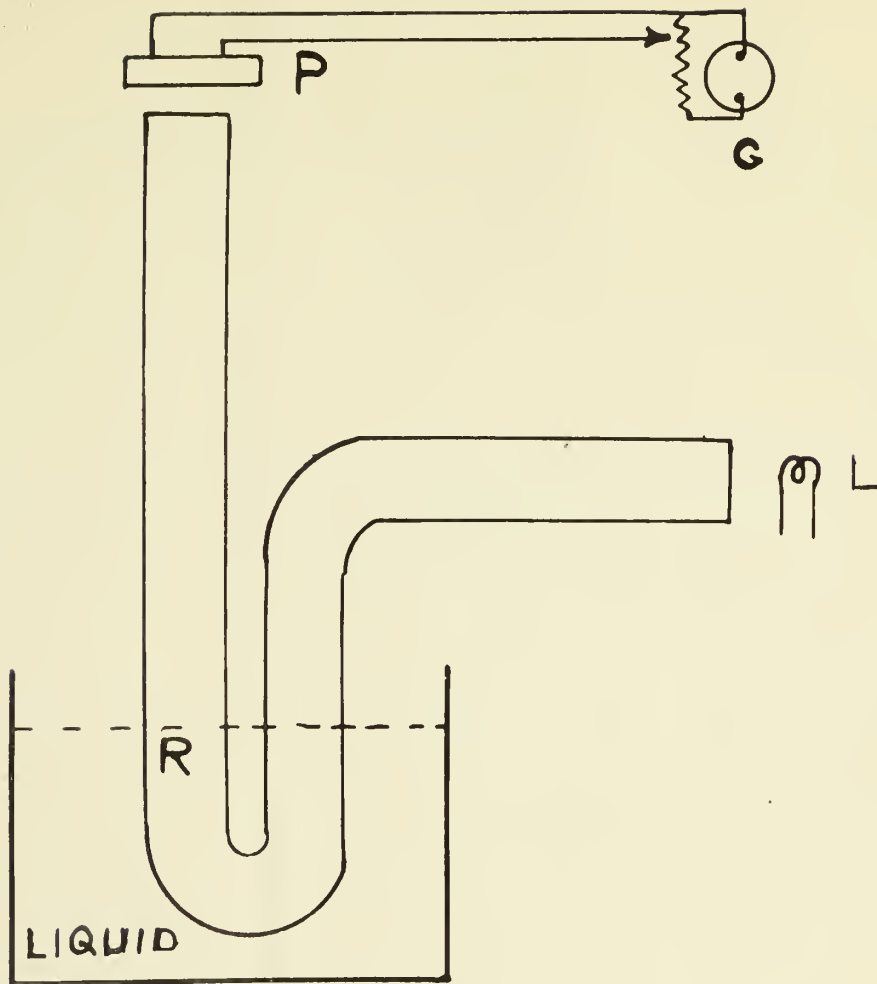


Fig. 1. A simple photoelectric refractometer; R, bent round glass rod immersed in the test liquid; P, photoelectric cell; G, galvanometer; L, light source.

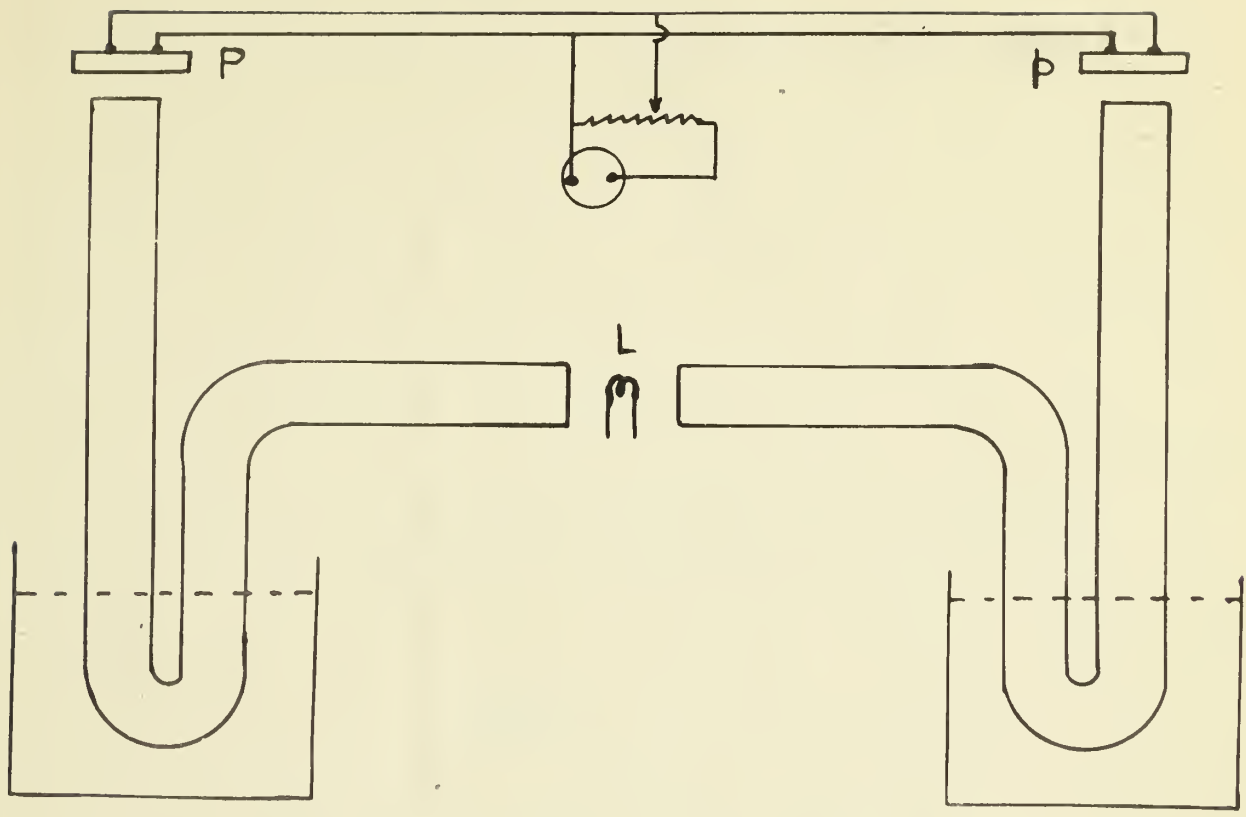


Fig. 2. A differential photoelectric refractometer. Two photoelectric cells are in opposition.

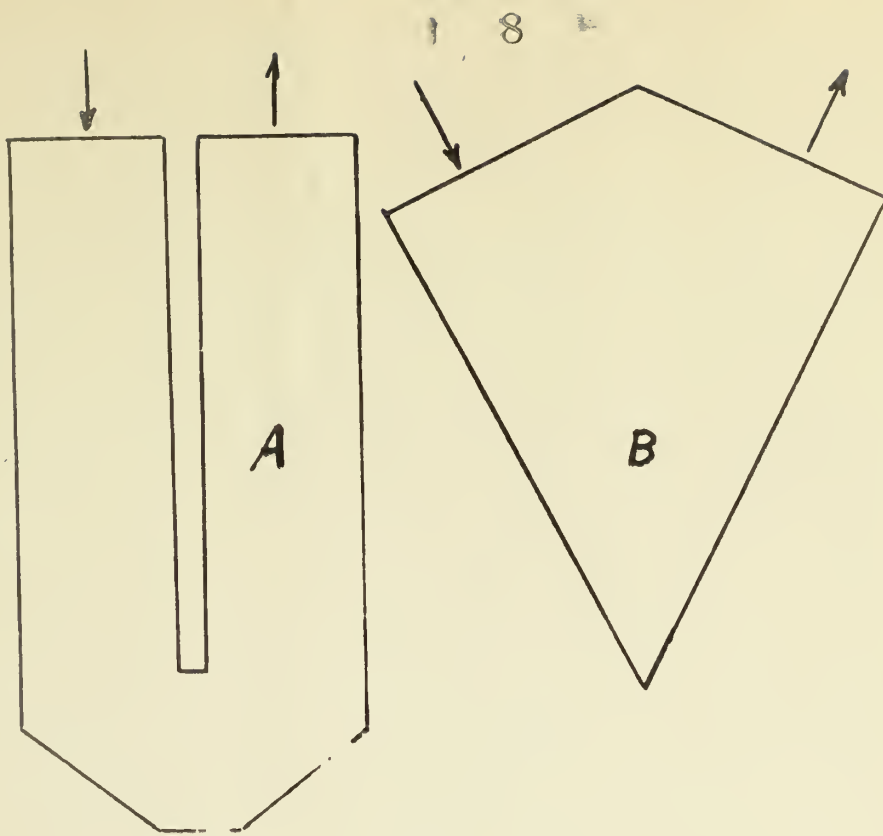


Fig. 3. Forms of prisms for the photoelectric refractometer.

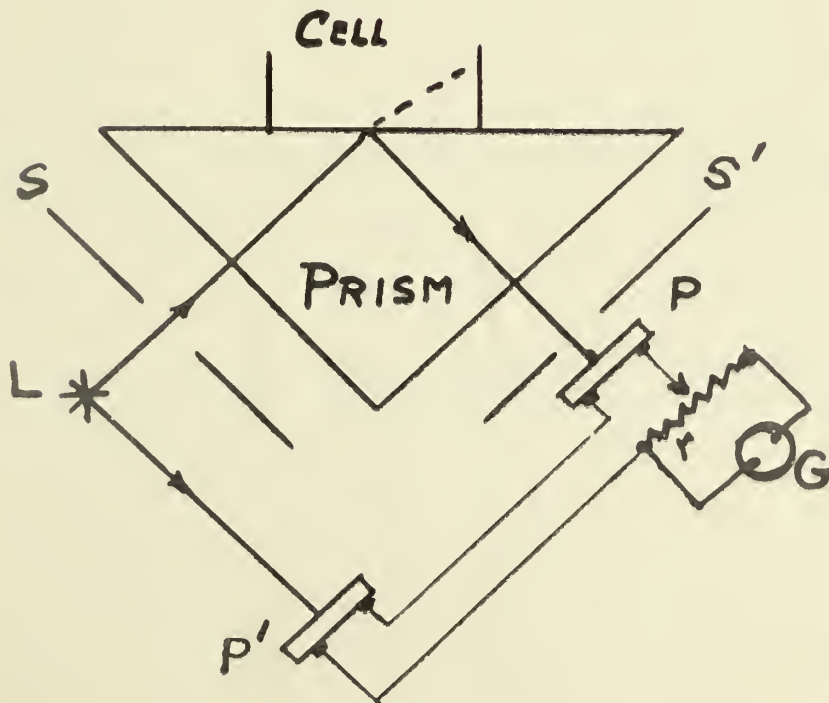


Fig. 4. A precision photoelectric refractometer.

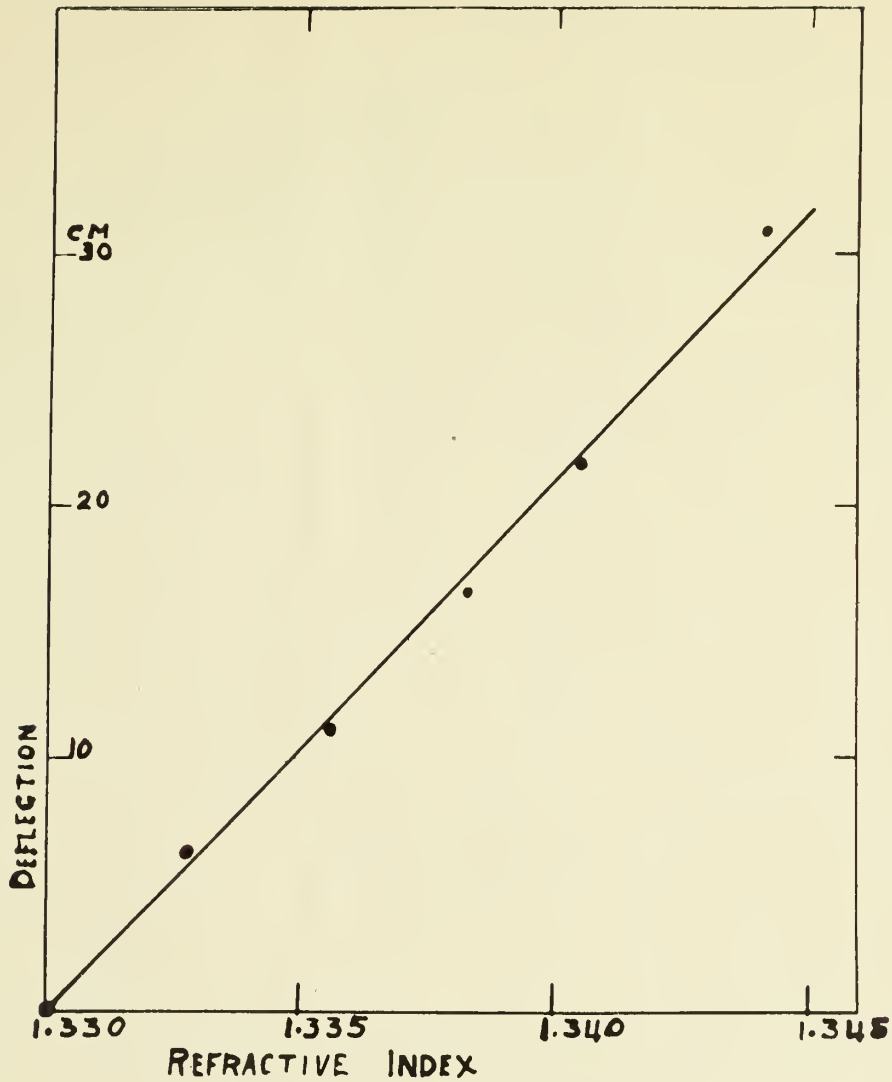


Fig. 5. Relationship between refractive index and galvanometer deflection for a series of aqueous saline solutions. Full galvanometer sensitivity utilized ($10^{-4} \mu\text{A}/\text{mm}$).

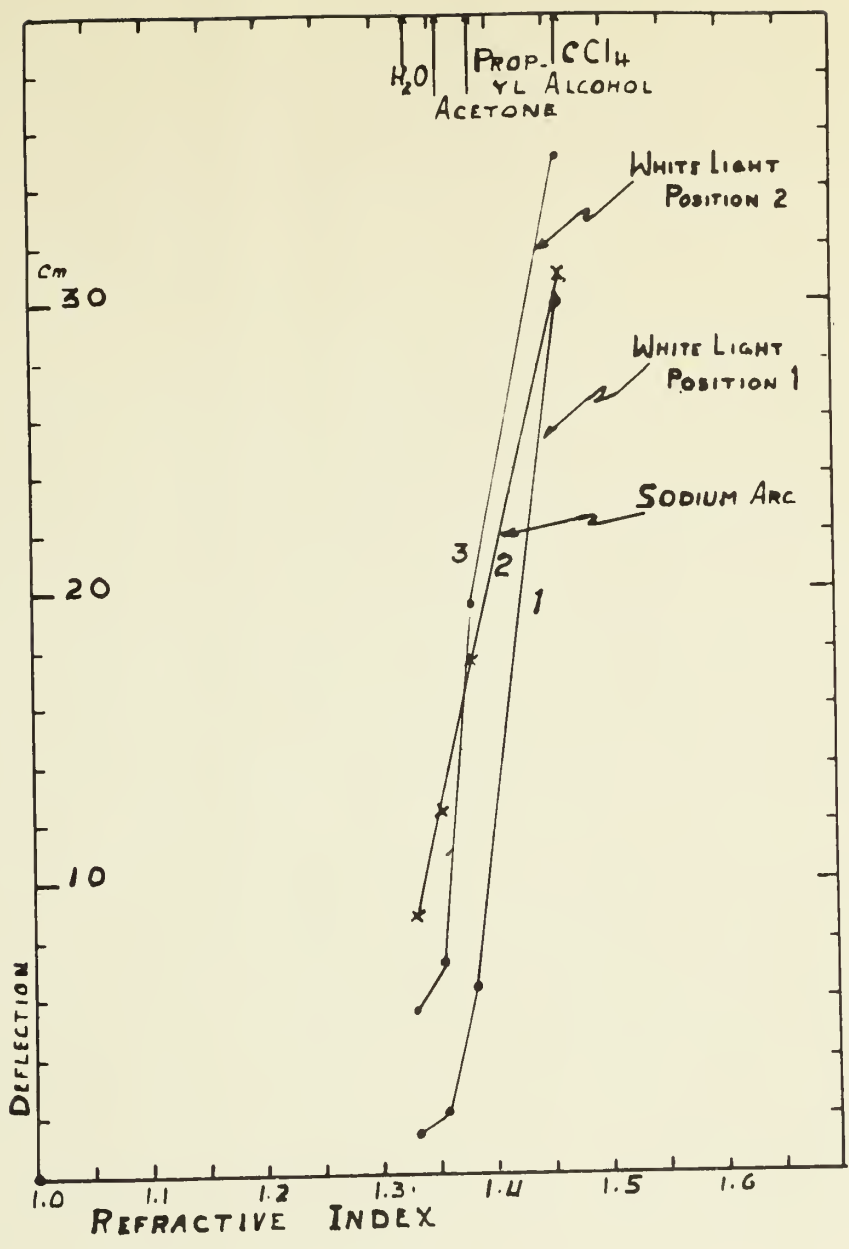


Fig. 6. Relationship between refractive index and galvanometer deflection for carbon tetrachloride, propyl alcohol, acetone, and water, when the incandescent tungsten lamp is placed in two positions, curves 1 and 3; and when the light source is sodium arc, curve 2. Galvanometer sensitivity utilized--0.02 μ A/mm.

