A refractometer for the determination of liquid mixtures.

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THE apparatus here described was designed in the first instance to provide a means for the rapid preparation and accurate adjustment of the liquid mixtures now commonly used for mineral determination. For this purpose refractometers of the Pulfrich type are inconvenient, not only on account of the risk of error due to the complicated centring of the prism or hemisphere and scales, but also because the transfer of a drop of liquid to the refracting surface renders the determination especially liable to errors arising from temperature variation, from contamination of the drop, and from evaporation. Further, in the preparation of liquid mixtures the frequent transference of small quantities to a refractometer is the source of much inconvenience.

The present instrument depends upon the deviation of a beam of light incident on the oblique interface between a prism of standard glass and the liquid of which the index is to be determined; the general arrangement is that of a common direct-vision spectroscope, in which the liquid occupies the place of the flint-glass prism. In order to eliminate errors in alignment, two beams are used, derived from the two opposite inclined faces of a right-angled prism placed with the hypothenuse face normal to the axis of the instrument. These beams form images on either side of the eyepiece-scale, the distance between the images being a measure of the difference in index between the prism and the liquid in which it is immersed.

Apparatus.—The instrument is shown in elevation in fig. 1. *A* is a collimator with Websky signal, *B* is a telescope provided with an eyepiece-scale graduated in 100 divisions. The collimator and telescope are supported on metal arms which are clamped by milled screws, *c*, *d*, to a plane base plate; these parts being similar in pattern to those supplied with the Hutchinson universal apparatus. It is very desirable that the lenses should be achromatic over as wide a range as possible. The tank, *C*, is supported on an adjustable table *e*, and by means of milled screws, *c*, *d*, the distance between telescope and collimator can be adjusted to accommodate tanks up to 8½ inches in length. The telescope-objective is protected from contact with the tank by a collar, *k*, the edge of which is in a plane normal to the axis; against this the tank is pressed by a similar spring-collar, *l*, on the collimator, so that normal adjustment is secured and also stray light is excluded. The standard prism *D* is placed

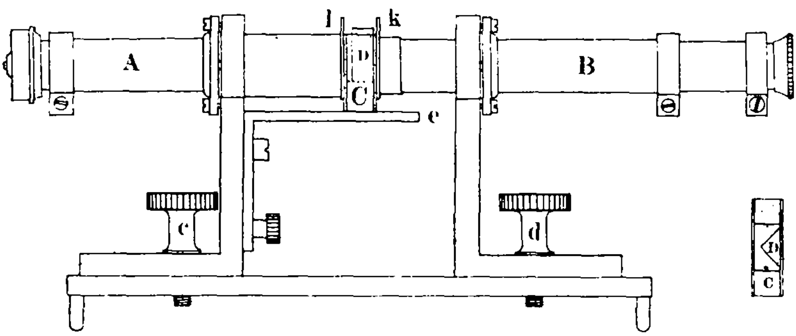

FIG. 1.—Refractometer for the determination of liquids. The inset shows a plan of the tank with prism.

in the tank with the hypothenuse side towards the telescope. In working with large tanks, where the prism is at a distance from the telescope, it is better that the prism should have a higher index than the liquid, so as to yield convergent beams which overlap on the objective.

Adjustment.—The telescope and collimator having been brought into focus for parallel rays according to the usual methods, the collimator is fixed in position by the screw *c*; the telescope is then placed so that it is in alignment, the image of the signal being at the centre of the eyepiece-scale, and is fixed by the screw *d*. The tank and prism are then placed in position and readings may be taken.

Close adjustment of alignment, of the position of the tank, or of the prism is unnecessary; provided that the two images are visible at approximately equal distances from the centre of the scale, the value of the refractive index difference measured is accurate to within one unit in the third decimal place. By using higher magnification and correcting the eyepiece-scale readings for the slight error affecting the extreme divisions, very much higher accuracy could be attained for special purposes.

For ordinary use the tank should be of sufficiently good glass to obviate disturbance of the telescope-images, but accurate parallelism between the surfaces is not required. The outer surfaces should be kept clean and free from liquid, but the presence of a large amount of suspended matter in the tank does not affect the readings, provided that sufficient light is transmitted.

Observations.—Any of the usual monochromatic light-sources may be employed as the illuminant; perhaps the most suitable are the sodium and lithium flames or the mercury-vapour lamp. The latter yields brilliant yellow, green, and blue rays and also a useful fainter line in the violet. The lines may be isolated by means of Wratten screens, but they are quite easily seen together, the distance between the different colours corresponding with the dispersion-difference between the liquid and the standard prism.

If, for a given ray, the index for the liquid is exactly equal to that for the prism, the images of that colour coincide at the centre of the field, but in general two images are seen. In order to ascertain whether a given pair of images represent an index higher or lower than that of the prism, it is convenient to move the tank to one side until one of the images is extinguished; the remaining image will lie on the opposite side or on the same side of the field as the prism-face through which light is still transmitted, according as the liquid is of higher or lower index than the prism. The spectra due to the two sides of the prism may overlap to a certain extent when the deviation for a mean colour is zero, but the two sets of lines are always easily identified in the manner described.

As will be shown below, it is an important property of the right-angled prism that the refractive index difference per scale-division is the same whatever the index of the standard prism used. Hence one scale of differences only is required; in order to ascertain the index of the liquid for a given light, the scale difference between the two images is read and the corresponding refractive index difference, as obtained from a table (or from the value per scale-division), is added to or subtracted from the value for the standard prism.

Temperature control.—The temperature coefficient of refractive index for most liquids is of the order of several units in the fourth place of decimals, per degree C. Thus for D-light at 20° C., an oil with refractive index near that of orthoclase has the value 1·523, while at 25½° C. the index has fallen to 1·519. For accurate work, therefore, the temperature of the liquid must be ascertained; this is readily done by inserting a thermometer in the tank. The liquid should, of course, be stirred to secure complete mixing and evenness of temperature; local variations disturb the telescope-images, and a clear image may generally be taken as evidence of satisfactory mixing. Both for liquids and solids the temperature coefficient of refractive index is closely related to the heat expansion; the value for the prism is accordingly much lower than that for the liquid, and at ordinary temperatures no correction is required for variation in the prism. For the determination of temperature coefficients

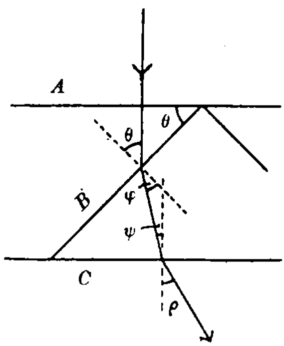

FIG. 2.

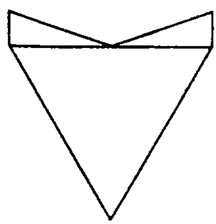

FIG. 3.

FIG. 2.—Path of ray of light through liquid (*A*–*B*) and prism (*B*–*C*).
FIG. 3.—Composite prism of fluorite and glass.

the value for the prism can easily be found by taking a series of readings with a liquid of known temperature coefficient such as aniline.[1] The co-efficient for the glass is equal to the difference between the true value for the liquid and the apparent value. In order to secure uniformity of temperature, the prism should be surrounded by freely circulating liquid. In this way the instrument affords a very certain and convenient means of obtaining temperature coefficients with sufficient accuracy for ordinary purposes.

Theory.—The path of a ray is shown in fig. 2. It is assumed that the rays are incident normally on the first surface *A* of the tank; the ray travels without deviation until it meets the interface *B* at an angle of incidence θ which is equal to the angle between *B* and the sides of the

[1] See Landolt and Börnstein, 'Tabellen'.

tank. The ray leaves B at an angle of refraction ϕ and is incident on the second side of the tank, C, at an angle ψ. The angle of emergence, ρ, is half the angle of deviation measured on the telescope-scale between the images from opposite sides of the prism.

If μ_1 = index of the first medium,

μ_2 = ,, ,, second medium,

by refraction at the interfaces,

(1) $\mu_2 = \mu_1 \sin\theta / \sin\phi$;

(2) $\sin\rho = \mu_2 \sin\psi$;

also (3) $\psi = \phi - \rho$.

Substituting in (2), $\mu_2(\sin\theta\cos\phi - \cos\theta\sin\phi) = \sin\rho$,

and from (1) this becomes

$$\sin\theta\sqrt{\mu_2^2 - \mu_1^2\sin^2\theta} - \mu_1\cos\theta\sin\theta = \sin\rho.$$

When $\theta = 45°$ (right-angled prism), this reduces to

$$\mu_2^2 - \mu_1^2 = 2(\sin^2\rho + \mu_1\sin\rho);$$

putting $\Delta = \mu_2 - \mu_1$ (the difference between prism and liquid) this can be written

$$\frac{\Delta}{\sin\rho} = \frac{2\sin\rho}{\mu_1+\mu_2} + \frac{2\mu_1}{\mu_1+\mu_2}.$$

Hence when ρ is small, $\sin\rho \approx \Delta$.

Considering terms of second order, to determine the error,

$$\Delta = \frac{2\sin^2\rho}{\mu_1+\mu_2} + \left(1 - \frac{\Delta}{\mu_1+\mu_2}\right)\sin\rho$$

$$= \sin\rho - \frac{\Delta\sin\rho}{\mu_1+\mu_2} + \frac{2\sin^2\rho}{\mu_1+\mu_2};$$

the approximate error is thus $\dfrac{\Delta^2}{\mu_1+\mu_2}\cdot(\sin\rho \approx \Delta)$.

A second error arises from the fact that the telescope-scale measures $\tan\rho$. If d is the scale-reading,

$$\sin\rho = d\cos\rho = d\left(1 - \frac{\rho^2}{2!} + \text{etc.}\right);$$

the error is $\dfrac{d\rho^2}{2}$, and since d, ρ, and Δ are nearly equal small quantities, this is of third order and is negligible in comparison with the first error.

In the present instrument the scale covers a difference in index of $\Delta = 0{\cdot}040$. The extreme error is thus about 0·0005, and the deviation ρ is about $2\frac{1}{2}°$. For a difference of index = 0·080 the error is only about 0·0003.

The full mathematical investigation of a somewhat similar arrangement in which the hypothenuse of the prism is placed parallel with the axis of the instrument has recently been discussed by Fabry,[1] and by Uhler,[2] who deals with the general case in which the prism angle may have any value. The apparatus, designed by the former writer, consis's of a tank and prism mounted on a goniometer, the deviation being measured on the divided circle; it was intended for the accurate determination of inviolable lenses by the method of immersion.

Standard prisms.—The prisms should be standardized by accurate determination of the refractive indices on the goniometer. To cover the range of liquids commonly used, from 1·47 to 1·74, it is convenient to keep four prisms having indices 1·51, 1·58, 1·65, and 1·72 respectively; the ranges of these overlap so as, if desired, to avoid the use of the extreme ends of the scale, and also to allow some latitude in the choice of glass. The value of the scale-division should be ascertained after the instrument has been permanently adjusted; this is best done by taking readings for a liquid, the index of which lies within the overlapping range, using each of the two prisms concerned. The observed scale-readings having been increased by the error $\frac{\Delta^2}{\mu_1 + \mu_2}$ (i. e. by about one division for this instrument), the value per division is simply found by dividing the difference of index between the two prisms by the sum of the two corrected readings.

For aqueous solutions and organic liquids a prism of fluorite (1·434) is useful; this covers the range down to 1·40. For indices below this value no suitable prism substance is at present available, but the fluorite prism could readily be adapted for the range from 1·40 to 1·33 by cementing acute-angled rectifying prisms of high-index glass to the hypothenuse face in the manner indicated in fig. 3.

The apparatus lends itself readily to various uses, both for determinations and for demonstration; for some purposes it is useful to prepare graphs showing the relation of the reading to the index of the liquid. It will be unnecessary in the present paper to discuss the details of such arrangements, which will readily suggest themselves as occasion arises in the use of the instrument.

[1] Ch. Fabry, Journ. de Phys., 1919, vol. 9, p. 11; Abstract in Amer. Journ. Sci., 1920, vol. 49, p. 148.

[2] H. S. Uhler, Amer. Journ. Sci., 1920, vol. 49, p. 143.