STANDARDIZATION OF INDEX LIQUIDS

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The determination of the indices of refraction of materials in standardized immersion liquids under a petrographic microscope has become the accepted method of mineral identification; has been very generally adopted for work with ceramic materials; and is gradually coming into use by chemists in the study of crystallized chemical materials. The rapidity with which optical methods may be applied, the small amount of material required, and the ability even to differentiate two or more distinct crystalline materials of identical chemical composition gives them very wide application in scientific and commercial determinations. The two most fundamental pieces of equipment for the application of these methods are a petrographic microscope and a set of accurately calibrated immersion liquids. The importance of immersion liquids is indicated by widespread discussion of the best materials and methods suitable for the preparation of such a set of index liquids. The petrographic laboratory of the United States Geological Survey has occasion to prepare and standardize as many as 50 sets of such liquids a year, and so the experience thus gained may be of use to others who have occasion to prepare such liquids.

Immersion liquids should be as nearly colorless as possible, and chemically stable. They should have as low volatility as possible, and when two liquids are to be mixed, the components should in general have equal or nearly equal rates of volatilization. If the volatility of both components is negligibly low, equal volatilization is not so essential, but liquids of very low index are unfortunately liquids of high volatility and it is advisible that these should have nearly equal rates of volatility. Each liquid should be miscible with the liquid lying immediately above or below, and it is desirable that the entire series of liquids should be completely miscible. A moderate degree of viscosity is also highly desirable, because with a viscous liquid both the mounted grains and the coverglass are better held in place and grains may be manipulated to bring them into suitable orientation without the violent agitation that otherwise often takes place when the coverglass is slightly moved. The liquid should be inert and not dissolve or react with the substance to be immersed. It is also desirable to use as small a number of

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components as possible, since then the various properties—indices of refraction, dispersion, and change with temperature—can be graphically expressed as simple curves between a few end members. Many mineralogists may have been deterred from attempting to prepare their own set of index liquids by the impression which seems to have gained ground that an elaborate technique is involved in the preparation of materials that fulfill the foregoing requirements. The fact is that easily procurable and relatively inexpensive index media are available over a wide range of indices of refraction, and that distillation and similar elaborate processes are quite unnecessary. Elaborate lists of materials to be used as index media have been described, but in fact better and more stable sets of liquids may be prepared from a few media.

A very large proportion of all mineral determinations involves the use of index liquids lying between 1.470 and 1.740, and fortunately liquids within that range that fulfill nearly all the foregoing requirements may be prepared from three components. The liquids lying between 1.470 and 1.630 are prepared by mixing medium Government oil and monochlor-naphthalene, and are almost colorless, slightly viscous, and remarkably stable; and those between 1.630 and 1.740 by the addition of methylene iodide to monochlor-naphthalene, and are pale honey-yellow, and slightly less stable. Since liquids may be prepared within this range (1.470–1.740) from only three liquids, all of their properties may be expressed by two sets of curves.

Medium Government oil[1] is an acid-free, colorless, odorless, and tasteless oil commonly used for instrument baths, such as immer-

[1] The liquids suggested may be obtained from dealers whose names are listed below.
Medium Government oil, 1 gal. $3.50.
Standard Oil Company of Indiana, Chicago, Ill.
Leeds & Northrup Company, 4901 Stenton Avenue., Philadelphia, Pa.
Halowax Oil No. 1007 (monochlor-naphthalene), 1 gal. $5.00.
Halowax Corporation, Division of Bakelite Corporation, 247 Park Avenue, New York City.
Methylene iodide (MP) (No. 167), 100 grams $5.00.
Methylene iodide (Pract.) (No. P-167) 1 kg. $45.00.
Research Laboratory, Eastman Kodak Company, Rochester, N. Y.
Methylene Iodide, 1 lb. $20.00.
Eimer and Amend, New York, N. Y.
Methylene Iodide, 1 lb. $22.00.
Merck and Company, New York City.
Other liquids may be purchased from local dealers.

sion of resistance coils where a high degree of purity and stability is required. This oil has a viscosity at 100° F. of 95 to 100 seconds. Tests were made in this laboratory on the volatility of this liquid. A sample of 200 cc. was heated in open air at 70° C., and samples for index reading were taken every 12 hours for 276 hours. No change could be detected in the index of refraction (1.4658 at 24° C.), after cooling. The temperature was raised to 150° C. and held for 21 hours. The liquid became pale yellow in color but there was still no change in index of refraction after cooling. The remarkable stability of this liquid, together with its other favorable qualities, renders it a highly desirable index liquid. "Light" Government oil is less suitable as an index medium because it has a lower viscosity.

Monochlor-naphthalene (Halowax oil No. 1007) has an index of 1.6335 at 25° C. It is almost colorless and is miscible with the liquids above and below it. A 50 cc. sample of halowax oil was exposed to open air at room temperature for 44 days and was found to have changed from 1.6335 to 1.6345 at 25° C. A change of 0.001 under conditions much more extreme than those met in actual use is almost negligible.

Liquids suitable for index media in the low ranges of indices may be prepared from the liquids suggested below:

n-Decane (1.410) is a very satisfactory low-index liquid of low volatility, which may be used in combination with kerosene to cover a range of indices from 1.410 to 1.446, or with Government oil to 1.466. It is expensive, but 10 to 25 grams are sufficient for the preparation of a set of liquids. Butyl alcohol (1.399) may be combined with either kerosene or Government oil in the same way. For the range from 1.362 to 1.404 ethyl and amyl alcohol may be combined satisfactorily. The alcohols, however, are rather volatile and amyl alcohol has a disagreeable odor. A simple mixture of water (1.333) and glycerin (1.462) may be used for the low range of indices if the minerals are sufficiently insoluble. The ethyl-amyl alcohol and water-glycerin liquids, although solvents for some minerals that have indices within that range, can be used satisfactorily if measurement with them is made rapidly. Fortunately, the minerals which have indices in the low range, are rare in occurrence and few in number—mirabilite (1.395), fluorite (1.434), and opal (1.440) being among the few common ones. Fluorite and opal are the most common, both of which are insoluble in any of the liquids suggested for use in this range.

Liquids which have indices above 1.740 are less stable. Information on the preparation of high-index media can be obtained from a paper by H. E. Merwin.[2] The United States Geological Survey Bulletin 848, Microscopic determination of non-opaque minerals, (second edition) by E. S. Larsen and Harry Berman, quotes this information.

Refractive Indices of Immersion Liquids

Name of liquid	n at 23°C.	$\frac{dn}{dt}$	Dispersion	Remarks
Medium Government Oil	1.466	0.00035	Slight	Very stable. Mixed with Halowax oil gives range from 1.470 to 1.630.
Halowax oil no. 1007 (Monochlor-naphthalene)	1.633	0.0004	Slight	Mixed with methylene iodide gives range from 1.630 to 1.740.
Methylene iodide	1.737–1.740	0.0007	Strong	Discolors on exposure to light. Metallic tin may be added to prevent this change.
Medicinal mineral oil	about 1.470		Slight	May be used instead of Covernment oil.

The values of indices of refraction (n) are for sodium D-line. The column marked dn/dt gives the change in index of refraction for each degree centigrade change in temperature. Index of refraction decreases approximately 0.00035 for 1°C., or 0.001 for 13°C., as the temperature increases.

The liquids should be kept in dropping bottles that have the combined ground stopper and dropper with glass cap. A 15 cubic centimeter bottle is the smallest that is sold by dealers, and that is larger than is required for the ordinary amount of work. It is best to keep the bottle half full, but with methylene iodide, economy suggests a smaller amount. A few grains of metallic tin should be kept in the bottles which contain methylene iodide in order that the free iodine which would darken the liquids may be taken up.

[2] Merwin, H. E., Media of high refraction for index determination with the microscope: *Jour. Washington Acad. Sci.*, vol. **3**, pp. 35–40, 1913.

The bottles should never be allowed to stand without the stopper and cap in place, and the nearly light-proof container should be kept closed as light affects methylene iodide.

Methods of Standardizing Index Liquids for Measuring Indices of Refraction

Where a few miscible liquids are to be mixed in various proportions in preparing a convenient range of index media, some accurate and easy method of measurement is necessary. Two methods of standardization have been used in this laboratory—namely, the method of minimum deviation with a hollow glass prism mounted on a one-circle goniometer, and the Abbe refractometer. With either of these methods the error of determination need not exceed $\pm .00015$. The refractometer is designed for the measurement of the indices of refraction and because of its simplicity and ease of manipulation it is very useful in measuring the low range of indices. The range of indices measurable with the standard type of instrument is 1.3000 to 1.7000. The refractometer yields quicker results than does the prism but it cannot be used for media which have indices higher than 1.7000. Liquids with high dispersion (above about 1.67) do not give clear shadow boundaries in the refractometer.

The method of minimum deviation with a hollow prism is not so rapid as that with the refractometer, but it can be used for the whole range of index media with a uniform degree of accuracy. C. S. Ross has designed a very satisfactory prism which is constructed by first grinding a rough glass prism, the approximate angle being determined by a contact goniometer. The hollow prism is made by cementing two parallel sided glass slides (12 by 25 mm.) to this base with bakelite, so that they project about 10 mm. above the base. The edges of the glass prism are cemented together with bakelite. The top of the basal prism is sloped inward so there will be less tendency for the drop of index liquid to escape. A prism angle of about 45° is a convenient size. Knowing the angle of the prism, determined by accurate measurement, using the formula

$$\frac{\text{Sin } \frac{1}{2} \text{ (Prism angle} + \text{angle of deviation)}}{\text{Sin } \frac{1}{2} \text{ (Prism angle)}}$$

a table should be constructed to show the angle of minimum deviation required to give any desired index of refraction.

Monochromatic Light Source

The most satisfactory and convenient source of monochromatic light for the determination of indices of refraction of index media is a small helium gas tube. The helium gas tube, unlike the sodium flame commonly employed, may be used in an open lighted room without interference of air currents or outside sources of light. There is no appreciable radiation of heat; therefore, the position of the tube may be adjusted at close range to the goniometer signal slit. The tube lights instantaneously and maintains uniform intensity. The light given off is soft yellow-white, but on passing through the prism containing the index medium is split into seven well separated spectral lines. The yellow line, D_3, 5876Å, corresponds closely in value to the sodium line, D_2, 5890Å. The prominent red helium line, 6678Å, is relatively near in value to the lithium line, 6708Å; and the blue-green, 5016Å, and the blue-violet, 4471Å, of the helium are not far from the thallium, 5351Å, and the hydrogen, 4340Å. Thus, the helium gas tube from a single light source furnishes a light that gives principal lines almost uniformly distributed through the spectrum and includes wave lengths that may take the place of the commonly used sodium, lithium, thallium, and hydrogen sources of monochromatic light.

Spectrum of Helium
Wave lengths in Ångstrom units

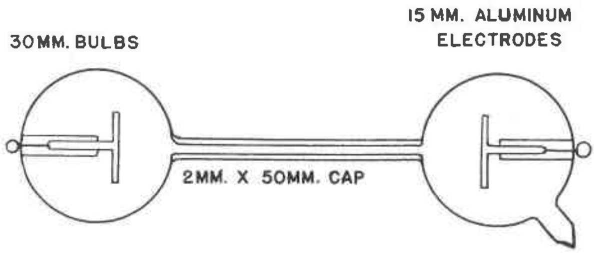
Color	*Wave length*
Blue violet	4471
Blue	4713
Pale blue-green	4922
Blue-green	5016
Yellow	5876
Red	6678
Red	7065

The helium lines may be used in the construction of a system of dispersion curves made by plotting the indices of refraction against the wave lengths of the conspicuous spectral lines in a similar way to that by R. D. Butler,[3] in which he used a hydrogen source and lithium, sodium, and thallium flames. A set of dispersion curves from which the index of refraction can be read to the fourth decimal place (±.0002) has been constructed for the liquids described in

[3] Butler, R. D., Immersion liquids of intermediate refraction (1.450–1.630): *Am. Mineralogist*, vol. **18**, pp. 386–401, 1933.

this paper and may be used to read the index of refraction of the liquids for any wave length.

The helium tube used by the Geological Survey was designed and made by P. G. Nutting.[4] As is illustrated in the accompanying sketch, the tube consists of two spherical bulbs 30 mm. in diameter connected by a straight piece of capillary tubing 50 mm. in length and 2 mm. bore. The electrodes are made of aluminum 1.5 mm.



HELIUM SPECTROMETER LAMP

thick and 15 mm. in diameter. These tubes are easily made by a skillful glass-blower and filled with helium gas at small cost. Helium gas has the advantage of withstanding a strong current for long periods of time.

The helium gas tube is best operated on a small potential transformer capable of delivering at least 20 milliamperes at 5,000 volts potential. The current is regulated by a lamp rheostat on the low voltage side of the transformer which is fed from ordinary A. C. mains. The current from a transformer connected in this way is not dangerous to handle, because the maximum current is limited by the resistance in the primary.

[4] Nutting, P. G., Luminous properties of electrically conducted helium gas: *Bureau of Standards Bull.*, vol. **4**, 1907.