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Procedures and computer programs to refine the double variation method

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ABSTRACT

Calibration procedures, statistical treatment of experimental data, and supporting computer programs were developed for the double variation method of measuring refractive indices to attain precision and accuracy of about ±0.0001.

INTRODUCTION

The precision and accuracy with which the refractive indices of a solid can be determined by the immersion method depend upon the precision and accuracy with which the refractive indices of the immersion oil are known. If the double variation method is to be used, the change of the oil's refractive index (n) with wavelength ($dn/d\lambda$) and with temperature (dn/dt) must also be known with comparable precision and accuracy. These data, although sometimes supplied by the manufacturer, may change as the oil ages. Indeed, sometimes after a manufacturer's supply of a given immersion oil has been exhausted, the refractive index of the replacement oil may precisely match that of its predecessor only at the wavelength 589 nm. Consequently, its printed label, if that of its predecessor, may indicate refractive indices that no longer pertain at the other wavelengths. For precise and accurate determination of the refractive indices of solids by the double variation method, therefore, it is necessary to calibrate the immersion oils to be used.

This paper describes the techniques and supporting computer programs used by the writers to calibrate immersion media and to suppress random errors when determining the refractive indices of solids by the double variation method. It also describes procedures for reducing systematic errors through use of glass standards whose refractive indices are accurately known to the fifth or sixth decimal place. Only touched upon is the use of a spindle stage (Bloss, 1981), mounted on a polarizing microscope, so as to orient anisotropic crystals so that their principal refractive indices can be measured without significant error from misorientation.

EQUIPMENT

High-accuracy refractometer

A high-accuracy Abbe refractometer, model 60/HR from Bellingham and Stanley, Ltd., has proven ideal for immersion-oil calibration. It differs from conventional types of Abbe refractometers in that (1) it does not have a built-in prism to compensate for dispersion so that it can only be used with monochromatic light sources and (2) its read-out scale is graduated in degrees and, with help of a micrometer drum, can be read to one-thousandth of a degree. The manufacturer provides four conversion tables whereby a critical-angle reading may be converted into its corresponding refractive index at each of the four wavelengths, 435.84, 546.07, 589.60, and 643.85 nm, respectively. For other wavelengths, as well as the foregoing, the conversion of critical angle α to refractive index N_L can be calculated from

$$N_L = 0.866\,025 + [N_P^2 - \sin(\alpha - 29.5°)]^{1/2} + 0.5 \sin[(\alpha - 29.5°)], \tag{1}$$

where

$$N_p = 1.860\,682 + 1.918\,32 \times 10^{-2} \times \lambda^{-2} + 1.029\,446 \times 10^{-4} \times \lambda^{-4}. \tag{2}$$

While the refractometer is in use, the temperature of the oil between its prisms must be monitored to within 0.1°C. Considering that dn/dt for Cargille oils in the 1.500–1.700 index range may equal as much as −0.0006/°C, a temperature error of 0.2°C would cause an error of approximately 0.0001 in the measured refractive index. To maintain a stable temperature for the prism box of the refractometer, room-temperature water from a reservoir is circulated through the prism box. The temperature of the immersion oil being calibrated is monitored by a chromel-alumel thermocouple inserted into a channel hollowed out in the cement surrounding the refractometer's illuminating prism.

Light source

Rather than using a monochromator to illuminate the refractometer, we use a set of three metal-vapor spectral bulbs that provide high-purity and high-intensity light at wavelengths 435.84 nm (Hg bulb with blue filter), 546.07 nm (Hg bulb with green filter), 589.60 nm (Na bulb), and 643.85 nm (Cd bulb with red filter). A heat filter placed between the bulb and the refractometer greatly reduces heat transfer to the refractometer by infrared radiation from the bulb.

Monochromator and oil cell

When employing the double variation (λ, T) method to measure the refractive indices of solid unknowns, we

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control the wavelength of illumination by means of a Schott wedge-interference filter as made by Leitz. Alternatively, any continuously variable monochromator or a series of narrow-band-pass filters with peak wavelengths at 5-nm intervals can be used. A heatable oil cell (Bloss, 1981, p. 139) changes the oil temperature and is monitored by a built-in thermocouple.

Spindle stage

A spindle stage, mounted on a polarizing microscope, plus the techniques of Bloss (1981) will serve to orient anisotropic crystals so that their principal refractive indices can be measured without significant error due to misorientation. A spindle stage is even valuable if the unknown grain is isotropic. By its means one can orient the grain so that it best shows a Becke line or an oblique shadow when comparing the refractive indices of the grain and oil.

CALIBRATION PROCEDURES

Immersion oils

To calibrate the oil, we make at least 10 critical-angle measurements at each of four wavelengths (643.85, 589.60, 546.07, and 435.84 nm). The measurements at 643.85 and 435.84 nm are difficult because of the eye's reduced sensitivity to these wavelengths. Consequently, it is necessary to work in a darkened room and to prevent stray light from the light source from entering the observer's eyes. For each critical-angle measurement, the oil's temperature (t) is also determined. The FORTRAN computer program OIL (available in FORTRAN IV for both IBM main frame computer and IBM PC), written by S.C.S., converts each measured critical angle to its corresponding refractive index (n_t). OIL then corrects this index to its value at 25°C ($n_{25,\lambda}$) by inserting the values of t and n_t, plus dn/dt of the oil into the equation

$$n_{25} = n_t - (t - 25°)(dn/dt). \qquad (3)$$

Using a least-squares method, OIL next fits to the n_{25} values thus obtained for each wavelength (in nanometers) the Cauchy dispersion equation:

$$n_{25,\lambda} = c_1 + \frac{c_2}{\lambda^2} + \frac{c_3}{\lambda^4}. \qquad (4)$$

After the intercept c_1 and the regression coefficients c_2 and c_3 are obtained, the calibrated oil's refractive index for any wavelength and temperature ($n_{t,\lambda}$) can be calculated from

$$n_{t,\lambda} = c_1 + \frac{c_2}{\lambda^2} + \frac{c_3}{\lambda^4} + (t - 25)(dn/dt). \qquad (5)$$

If the Cargille oils used in our laboratory have been kept tightly closed and protected from light between each use, their Cauchy constants (c_1, c_2, c_3) have remained unchanged, within the experimental error, for at least a year.

Measuring system

The precision and accuracy with which a solid's refractive indices can be measured depend upon (1) the sensitivity of the criterion of match between the indices of grain and oil and (2) knowledge of the exact refractive index of the oil at the conditions of match. Louisnathan et al. (1978) addressed item 1. Item 2 depends upon how precisely and accurately one knows (a) the temperature and wavelength of match and (b) dn/dt of the oil, and its Cauchy constants (c_1, c_2, c_3) so that Equations 3 and 4 can serve to calculate the refractive index of the oil for the temperature and wavelength of match. Although statistical analysis of the data may reduce the effect of random experimental errors, systematic errors may also affect the determinations of the temperature and the wavelength of match. Moreover, if only a few oils are used during the double variation procedures, errors in dn/dt and the Cauchy constants for these oils will themselves become systematic errors. In our laboratory, our measuring system is calibrated by means of standard optical glasses whose refractive indices at various wavelengths are accurately known to the sixth decimal place.

To calibrate our measuring system so as to reduce systematic errors, we use 13 highly homogeneous optical glasses kindly supplied to our laboratory by the Corning Glass Company. For these 13 glasses, whose indices range from 1.51 to 1.80, the refractive indices were measured to the sixth decimal at wavelengths 435.8, 546.1, 587.6, and 632.8 nm by C. J. Parker and Al Werner (pers. comm.) of Corning through the use of the minimum deviation method and a specially designed spectrometer.

In determining the refractive indices of an unknown solid, we first select that Corning glass whose refractive index n_D is closest to the refractive index to be measured for the solid. We next select the three calibrated oils whose refractive indices are slightly higher, almost equal and slightly lower than that for the Corning glass selected. Using these oils, successively, we measure the Corning glass by the double variation method. For each match between glass and oil, essentially determined as discussed by Louisnathan et al. (1978), the wavelength (λ) and temperature (T) is recorded. Approximately 100 to 150 readings, evenly distributed over the visible range (486–656 nm), are made within the 20–30°C temperature range. These (λ, t) data are then processed by the FORTRAN program SOLID (available in FORTRAN IV for both IBM main frame computer and IBM PC), which, through least-squares regression methods, determines the values for the Cauchy constants c_1, c_2, and c_3 by fitting Equation 4 to the data. SOLID similarly determines values for the constants a_0 and a_1 in the linearized Sellmeier equation (Louisnathan et al., 1978; Bloss, 1981),

$$y = a_0 + a_1 x, \qquad (6)$$

where x equals λ^{-2}, y equals $(n_\lambda^2 - 1)^{-1}$, and n_λ equals the refractive index at wavelength λ. The resultant constants we call observed Cauchy and Sellmeier constants and symbolize them as $c_{1,\mathrm{obs}}$, $c_{2,\mathrm{obs}}$, $c_{3,\mathrm{obs}}$ and as $a_{0,\mathrm{obs}}$ and $a_{1,\mathrm{obs}}$, respectively. Similarly, we fit the refractive indices measured at the four wavelengths by Parker and Werner to Equations 4 and 6 to obtain constants that we symbolize as $c_{1,\mathrm{cal}}$, $c_{2,\mathrm{cal}}$, $c_{3,\mathrm{cal}}$, $a_{0,\mathrm{cal}}$, and $a_{1,\mathrm{cal}}$ where the subscript "cal" indicates that the constant was calculated from the minimum deviation data of Parker and Werner. Equation 4 and the two sets of Cauchy constants for the Corning glass standard—$c_{1,\mathrm{obs}}$, $c_{2,\mathrm{obs}}$, $c_{3,\mathrm{obs}}$ and $c_{1,\mathrm{cal}}$, $c_{2,\mathrm{cal}}$, $c_{3,\mathrm{cal}}$—permit n_{obs} and n_{cal} to be calculated at any wavelength λ. The correction value Δn_λ can thus be determined for any wavelength λ since

$$\Delta n_\lambda = n_{\mathrm{obs}} - n_{\mathrm{cal}}. \tag{7}$$

Similarly, for this Corning glass standard, Equation 6 and the two sets of linearized Sellmeier constants—$a_{0,\mathrm{obs}}$, $a_{1,\mathrm{obs}}$ and $a_{0,\mathrm{cal}}$, $a_{1,\mathrm{cal}}$—also permit n_{obs} and n_{cal} to be determined for any wavelength λ. The correction value Δn_λ can thus be again calculated for any wavelength λ by use of Equation 7.

When an unknown solid is measured, then n_{25}, its refractive index at 25°C for the wavelength at which a match occurred, can be calculated from n_t, the refractive index of the oil for the wavelength of match, and t, the temperature of match. Thus by inserting n_t, t, and dn/dt into Equation 3, we obtain n_{25}. (It should be pointed out that, since the temperature range for the data collection is held within ±5°C of 25°C, the effect of temperature variation on the refractive indices of the solid measured can be ignored.) Systematic error in this value is reduced by subtracting from it Δn_λ as calculated (Eq. 7) for the same wavelength as that of the match. Thus, $n_{25,\mathrm{corrected}} = n_{25} - \Delta n_\lambda$. Each match observed by the double variation method within the 20–30°C range for the unknown thus results in a wavelength of match λ and a corresponding corrected refractive index of match $n_{25,\mathrm{corrected}}$. Typically, 30 or more such matches for a principal refractive index are obtained over the wavelength range 486 to 656 nm. These pairs of data are then analyzed by the computer, and either Equation 4 or 6 is fitted to the data pairs by the method of least squares. In actuality, to the program SOLID we merely submit the λ and t values for the 30 or so matches, as well as dn/dt and n_{25} for the oil. The program then applies the temperature correction (Eq. 3) and the correction for systematic error based on the appropriate Corning glass standard (Eq. 7). SOLID then fits a Cauchy equation (Eq. 4) and a linearized Sellmeier equation (Eq. 6) to the (λ, $n_{25,\mathrm{corrected}}$) data pairs to obtain the constants c_1, c_2, c_3 and a_0, a_1 that will permit the unknown's refractive index to be calculated for any wavelength within the visible range (and perhaps slightly beyond).

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