Microscopic Determination of Non-Opaque Crystalline Chemical Compounds by the Immersion Method.

Thesis

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by
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Outline of Thesis

on

The Microscopic Determination of Non-Opaque Chemical Compounds by the Immersion Method.

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Microscopic Determination of Non-opaque Crystalline Chemical Compounds by the Immersion Method.

The purpose of this investigation is the identification of transparent crystalline chemical compounds by means of their refractive indices. Most chemical compounds are crystalline and nearly all of the crystalline compounds are transparent, furthermore no two chemical compounds have refractive indices that are identical, consequently by constructing a set of tables of accurate refractive indices of such compounds a means is obtained for the rapid identification of a majority of the known chemical substances. The success of such a means of identification depends upon a speedy and accurate method for the determination of the refractive indices of crystalline compounds. For this purpose several methods have been originated, but only one that combines the qualities of speed, accuracy, and simplicity. This method is due chiefly to F. Becke and is the only one used in this investigation.

History of the Immersion Method.

In 1872 Maschke, (Annalen der Physik - CXLV pp. 568-569) in separating microscopic mineral fragments, made use of a phenomena that had long been known. If a crystal is immersed in a liquid of a different refractive index and viewed under a microscope it will be seen that its borders are either dark, colored, or indefinite, depending upon whether the refractive index of the crystal is greater, less, or equal to that of the imbedding liquid. Maschke made no use of this phenomena for the determination of refractive indices, but he suggested that

just as we now have a scale of hardness so might also a series of immersion liquids be prepared for the comparison of refractive indices. He proposed for this purpose cassia oil, turpentine, poppy oil and mixtures of these and alcohol. Several attempts were made with this suggested method for determining refractive indices, but no marked success was attained until it received impetus by a publication of Schroder van der Kolk (Tabellen; Anleitung) in the year 1900. He developed the method and made use of it for the rapid determination of minerals; about three hundred being given in the order of their refractive indices, Former experimenters had made use of the dark or colored borders to indicate whether the refractive index of the crystal and the imbedded medium differed, but Schroder van der Kolk used this dark border to determine in which direction they differed. Briefly, he explained the dark band as being due to the dispersion of light, the fragments of the crystals acting as prisms. The dark band appears uniformly around the grain if it is centrally illuminated, but if illuminated obliquely the light entering the grain or fragment is so dispersed that through a microscope focused on the grain one side of the field appears shaded if the grain has the higher refractive index, while if the imbedding liquid has the higher refractive index the phenomenon is reversed, and the opposite side of the field appears shaded. Schroder van der Kolk used varied liquids and mixtures in preparing a large number of liquid media with indices

differing by a regular figure. About 1893 F. Becke, who had previous to Schroder van der Kolk measured refractive indices by oblique illumination (Sitzb. A. K. A. D. Wiss,, Wien, CII 1893, Abth.I, 358-378), discovered and refined a method of central illumination, which resulted in simpler and more rapid determinations than could be obtained by oblique illumination.

The Immersion Method Using Central Illumination.

The method as devised by Becke, using central illumination (Sitzb. A. K. A. D. Wiss., Wien, CII 1893, Abth. I 358-378) is the one employed for determining refractive indices in this investigation. In a similar manner to the method of oblique illumination the refractive index of the substance is obtained by comparison with that of liquid or solid imbedding media; the refractive index of the substance being narrowed between small limits by repeated comparison with media which more and more nearly approach its own refractive index. The phenomena exhibited by a crystal under the microscope using central illumination, however, is very different from that explained above for oblique illumination. If a crystal fragment is immersed in a liquid medium of different refractive index from its own and viewed through a microscope of medium or high power objective it exhibits characteristic phenomena. The crystal fragment, which is thinner around the edge than in the center, acts as an imperfect lens towards a beam of nearly parallel light emerging from the condenser. If the fragment has a higher refractive index than the surrounding medium it tends to focus the light above

its plane, and if the microscope is first focused on the fragment and then raised slowly above focus a bright line will appear around the inner edge of the fragment and move in towards its center. If the microscope tube is lowered below focus the fragment appears less highly illuminated than the surrounding field and if the tube is lowered still more the illuminated area moves out from the fragment. If the medium has a higher refractive index than the fragment the phenomena are reversed. On raising the microscope tube above focus the light moves away from the fragment and on lowering below focus the light moves into the fragment. In short, the light moves towards the substance of higher refractive index, when the microscope tube is raised above focus; and towards the substance of lower refractive index when the microscope tube is lowered below focus. If the fragment and the imbedding medium have the same refractive index the field of view remains uniform, there being no shifting of light on changing the focus.

Explanation of the Phenomena Observed.

The phenomena exhibited by two substances of different refractive index under the microscope depends upon the total reflection of the rays of light incident at more than the critical angle when passing from the denser to the rarer medium, and has been explained in several ways; two of which may cover all cases.

Let AB and BC, Fig. 1, be two substances in vertical

contact at B, and let BC be the substance of higher refrac-

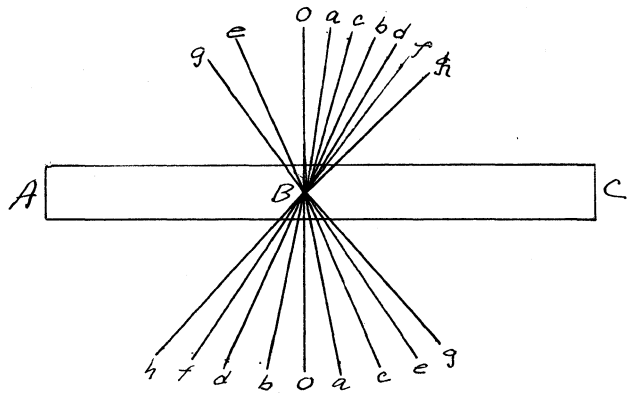


Fig I

tive index. Let o, and a to h be convergent rays of light entering from below and suppose the field of view is from above. Ray o enters along the contact of the two substances and is neither reflected nor refracted. Rays b, d, f, and h pass from the rarer to the denser medium and are refracted towards the normal and pass out on the right of o. Rays a and c pass from the denser to the rarer medium but impinge upon AB at more than the critical angle and are totally reflected emerging to the right of o. Rays e and g pass from the denser to the rarer medium and are refracted away from the normal, passing out on the left of o. Of the total number of rays passing through the contact of the two substances only two emerge on the side of the substance AB, while six emerge on the side of the substance BC, thereby giving a concentration of light over the substance with the higher refractive index. This uneven distribution of the light is caused by the total reflection of those rays that impinge upon AB at an angle greater than the critical angle. The smaller the cone of light, down to the limit of the critical

angle, entering the contact between the two substances, the clearer will the phenomenon observed be, because if the cone included only the rays from a to d, there would be four rays on side BC to none on side AB. Becke also pointed out (Tschermak's Mineralogische und Petrographiscke Mitteilungen, Vienna) that the effect is the same if the substances do not have a vertical contact, provided the rarer substance overlies the denser substance. If however the optically denser substance is above the effect is reversed, and the light will appear concentrated over the optically rarer substances. In practical work this descrepancy does not cause confusion, because the contact causing it can be detected by a shifting of the line when the focus is raised and lowered.

In the case previously explained, convergent light was necessarily used as well as a more or less vertical contact between the two substances. In all ordinary practice, parallel rays of light are used and the phenomena which are observed have been explained by G. W. Graham (Mineralogical Magazine and Journal of the Mineral Soc. of Great Britain and Ireland XV 1910, pp. 341-347). The explanation provides for the use of parallel light where the plane of contact between the two substances is inclined at all possible angles to the normal. When the plane of contact between the two substances is inclined to

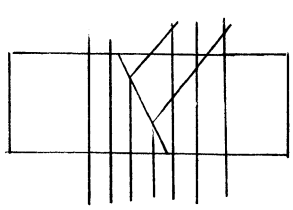


Fig II

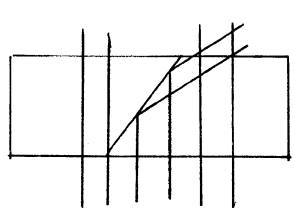


Fig III

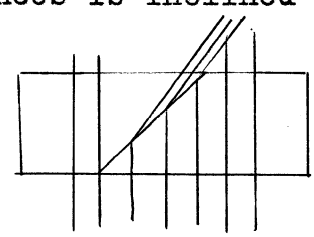


Fig IV

to the plane of the substance, two possible cases may occur;

where the substance of greater refractive index over laps the other and where the order is reversed. In the first case (Fig. 2), the rays of light on striking the contact surface, are bent towards the normal and pass out through the substance having the higher refractive index. In the second case, two conditions may arise. The rays may strike the contact surface (Fig. 3) at more than the critical angle and be totally reflected into the substance of higher refractive index, or they may strike the contact surface (Fig. 4) at less than the critical angle and be refracted away from the normal. In all cases, the light appears to be concentrated over the substance with the higher refractive index.

The appearance of the phenomena under the microscope is the same for both convergent and parallel rays of light and the following explanation will apply equally as well to both cases. If the microscope tube is focused upon the point

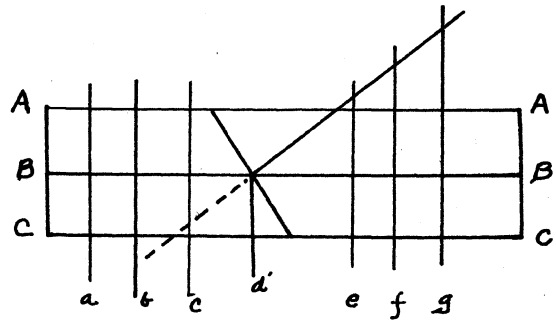


Fig. V

where the ray reaches the contact between the two substances (B Fig. 5) no bright line appears. However, on raising the tube above focus to A the rays d and e meet and cause the light to appear concentrated at that point. As the tube is raised higher above focus, the point of light concentration moves into the substance of higher refractive index, appear-

ing successively at f and g. If, on the other hand, the tube is lowered so that the focus is at C the phenomena will be reversed. The point of light concentration will appear at the intersection of ray c and the backward reflection of ray d. Under the microscope, ray d will appear not to come from the point d but rather from a point on the backward extension of the refracted portion of the ray. As the tube is lowered so that the focus is below C, more points on the intersection of the backward reflection and rays b and a will be successively illuminated and the light will appear to move away from the substance of lower refractive index.

Refractive index and Crystal form

The measurement of refractive indices of crystals by the immersion method would be comparatively simple if all crystals had only one index of refraction. A large number of crystals, however, have two principle refractive indices and a larger number have three principle refractive indices, corresponding to the principle axes of the crystal. Isotropic substances or substances having only one principle index of refraction are isometric in their crystal form. Uniaxial substances have two principle refractive indices (ω-ϵ) and are tetragonal or hexagonal in form while biaxial substances are orthorombic, monoclinic or triclinic and have three principle indices of refraction (α, β, γ). Birefringence is usually defined as the difference between γ and α. It is seldom necessary to measure all three refractive indices of anisotropic crystals because, usually all three can be obtained by measuring α and γ and

estimating β, or by measuring β and estimating α and γ making use of the birefringence as a guide. To test α and γ, the lowest and highest refractive indices, against a standard media, a crystal should be selected that shows strong birefringence. It should be turned to extinction and tested against the media then turned to the other extinction and again tested. This operation should be performed with a number of crystals as a precaution against obtaining erroneous values for γ and α. For any crystal β lies between α and γ, therefore to measure β, a crystal should be chosen which shows no appreciable birefringence so that the one refractive index obtained from such a crystal will closely approximate the value for β.

Preparation of a Series of Standard Immersion Media

In order to prepare a series of standard media, suitable for determining the index of refraction of non-opaque chemical compounds by means of the Becké method, it was necessary first to obtain substances which are miscible in all proportions with each other. The substances must also have a negligable effect on the chemical compounds whose indices of refraction are to be determined. Since oils fulfill these requirements very nicely, it was decided to use them wherever possible in preparing the solutions. Mixtures of oils possess the following characteristic properties which further enhance their value for use as immersion media:

(1) They are nearly colorless, chemically stable and without disagreeable odor.

(2) They possess a low volatility and moderate viscosity.

(3) Their value for dn/dt is relatively small.

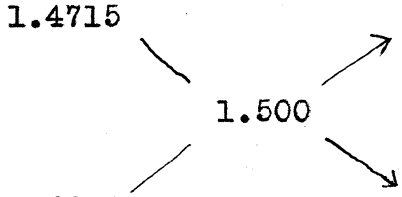
Before proceeding with the preparation of the solutions, it was necessary to know the index of refraction of the various oils which were to be used. The index of refraction of the following substances was determined at 20°C, using an Abbé refractometer which had been previously calibrated by means of a quartz plate and ∝monobromnapthalene.

Substance	$N_{20^\circ C}$
Kerosene (anhydrous)	1.4475
White Russian petroleum	1.4658
Rape seed oil	1.4730
Auto Cyl. Oil (medium)	1.5110
Olive Oil	1.4709
Oil of Eucalyptos	1.4660
Oil of Cedar	1.5170
Benzyl Alcohol	1.5404
Oil of Cloves	1.5340
Oil of Cassia	1.6044
Oil of lemon	1.4875
Oil of Lavender	1.4705
Aniline	1.5823
O-Nitro toluol	1.5459
∝ -MonoBromnapthol	1.6578

Table I

By properly mixing substances on the above list, a series of solutions having indices of refraction varying by .01 from 1.45 to 1.65 were prepared. To determine the proper amount of various compounds to use in order to ob-

tain the desired index of refraction, use was made of the method of dilution described in the U.S. Dept. of Agriculture Farmers Bulletin #42. The method is simply explained as follows: Suppose that peanut oil (n= 1.4715) and oil of Cassia (n = 1.6044) were to be used to prepare a solution having an index of refraction of 1.5000. Place the indices of refraction of the two oils to be used, at the corners of a rectangle with the desired index of refraction at the intersection of the diagonals. Subtract the smaller number from the larger number and place the result at the end of its diagonal. The results indicate the parts of each oil to be used in the mixture.



.0285 parts of peanut oil to be used

.1044 parts of oil of Cassia to be used

In this manner, solutions having the desired indices of refraction were prepared, using the mixture indicated in table II.

	Index of Refraction	Composition
1	1.45	10 cc. Kerosene 1 cc. White Russian Petroleum
2	1.46	5 cc. (White Russian Petroleum+oil of Peppermint) n = 1.464 2 cc. Solution #1
3	1.47	3 cc. Solution n = 1.464 6 cc. Rape seed oil
4	1.48	4.6 cc. Solution n= 1.464 2.6 cc. Auto Cylinder oil
5	1.49	3.5 cc. Auto Cylinder oil 4.2 cc. Rape seed oil
6	1.50	10.8 cc. Auto Cylinder oil 3.9 cc. Olive oil
7	1.51	8.8 cc. Auto Cylinder oil .3 cc. Oil of Eucalyptos

	Index of Refraction	Composition
8	1.52	8.3 cc. Oil of Cedar 2.0 cc. Benzyl Alcohol
9.	1.53	8.8 cc. Oil of Cloves 1.9 cc. Auto Cylinder Oil
10	1.54	.5 cc. Oil of Cloves 1.0 cc. Oil of Cassia 9.5 cc. Benzyl Alcohol
11	1.55	6.8 cc. Oil of Cassia 5.4 cc. Oil of lemon
12	1.56	6.0 cc. Aniline 6.0 cc. Benzyl Alcohol
13	1.57	8.3 cc. Oil of Cassia 3.4 cc. Oil of Lemon
14	1.58	5.8 cc. Oil of Cassia 4.2 cc. O- Nitro toluol
15	1.59	10.3 cc. Oil of Cassia 1.4 cc. Oil of Lemon
16	1.60	12.1 cc. Oil of Cassia .2 cc. Oil of Lemon
17	1.61	2.4 cc. Oil of Cloves 3.8 cc. α monobromnapthalene
18	1.62	1.9 cc. Oil of Lavender 7.5 cc. α monobromnapthalene
19	1.63	1.4 cc. Auto Cylinder Oil 5.9 cc. α Monobromnapthalene
20	1.64	1.2 cc. Auto Cylinder Oil 7.7 cc. α monobromnapthalene
21	1.65	2.0 cc. Auto Cylinder Oil 17.9 cc. α monobromnapthaleme

Table II

After these solutions were prepared, they were carefully corrected by reading the value of n with an Abbé refractometer and varying the proportions of the components until the desired value of n was obtained. Where the proportions as shown in table II were accurately measured, there was only slight adjusting necessary to make the solutions have the desired value of n. The solutions were then stored in glass dropping bottles that are fitted with ground glass stoppers and ground glass covers. The bottles were then packed in a dark place so that no action of the sunlight could decompose the solutions.

For fairly accurate work, the standard media should have

a range of index of refraction of from 1.40 to 2.72 varying by increments of .01 units. Liquid media, already described, may be used for values of n up to 1.87 but above this value solid media must be used. These solid media may be conveniently made from mixtures of piperine and the tri-iodides of arsenic and antimony or from mixtures of sulphur and selenium. For correcting the solid media, the value of n may be determined by the method of minimum deviation using a hollow prism mounted on a reflecting goiniometer. Such a hollow prism was made by grinding a prism with about a 30° angle from a piece of plate glass and then beveling one of the edges over which petrographic slides were cemented. The small cavity in the end of the prism serves very conveniently for the purpose at hand. The fig 6. will illustrate this method of preparation.

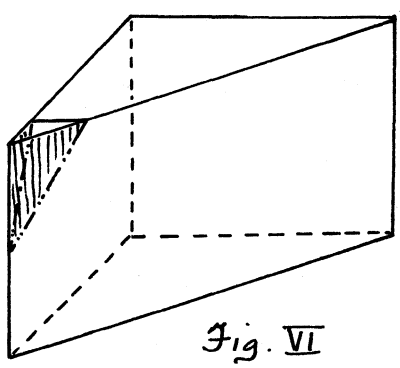


Fig. VI

However, the time available for this work necessitated the use of only liquid media whose index of refraction could be quickly determined by means of the Abbé refractometer.

Determination of the refractive index.

The index of refraction of chemical compounds belonging to the isometric system was determined according to the method which

was devised by Becke. This method made use of the standard immersion media which have already been described. This investigation covered only those chemical compounds which crystallize in the isometric system because only isometric compounds are isotropic. Compounds that crystallize in other than the isometric system have different indices of refraction depending on which axis of the crystal is orientated with the axis of the microscope. By limiting the scope of this study to isometric compounds, no birefringence was encountered and consequently no special precautions were necessary to be certain that the crystal was properly orientated, because the index of refraction was the same in all directions.

In order to determine the index of refraction of the crystalline compound, some of it was powdered to a size that would pass a 40-mess sieve and placed on an ordinary petrographic microscope slide then covered with a drop of the immersion media whose index of refraction was known. The media and crystals immersed in it were then examined with a petrographic microscope using an objective of high power. The condenser system was raised and the lower diaphragm closed. After a few trials, the microscope was so adjusted that an individual crystal of the sample was clearly in focus. Then by the method, previously described, it was determined whether the sample had a lower or higher index of refraction than that of the immersion media. Portions of the sample were examined in each of the standard media in turn until a point was reached where one media had a lower index of refraction than that of the sample and the next media in the series had a higher

index of refraction than that of the sample. The index of refraction of the sample was then said to be determined, within the limit of error of this method, because we could say that the sample had an index of refraction between two values, which values varied by only .01 units. If, by chance, the media and the sample had the same index of refraction, the line of contact between the sample and media would disappear. By the use of this method of central illumination, the indices of refraction of the following chemical compounds were determined.

Substance	N at 20° C
$Ba(NO_3)_2$	1.56
K Cl	1.49
Na Cl	1.54
K Br	1.56
Potash Alum	1.46
$Ca Cl_2$	1.52
$NH_4 Cl$	1.64

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