A SEMI-QUANTITATIVE MICROSCOPE TECHNIQUE FOR MEASURING THE OPTICAL ABSORPTION SPECTRA OF MINERAL AND OTHER POWDERS

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The optical absorption spectra of minerals, especially silicates, often reveal much valuable information on the siting of transition metal cations, their valence state(s), and certain aspects of the geometry of their coordination polyhedra. Such information is most readily obtained through the measurement of polarized spectra of oriented single crystals either in standard thin sections or as individual plates. However, it is often desirable to study the spectra of finely divided polycrystalline specimens of minerals, salts, or coordination complexes of transition metal ions.

Simple techniques have been used to measure the absorption spectra of powders in the near ultraviolet to the near infrared region. These techniques involve the use of mineral-oil mulls to reduce light scattering. The mull paste is spread on oil-soaked filter paper (Lee, Griswold & Kleinberg 1964), or facial tissue (Faye, 1967), mounted between CsBr discs (Asprey & Matwiyoff 1970) or between glass sides (Burns 1970). Although the spectra measured by such techniques are adequate for certain purposes, they are often poorly resolved because of light-scattering (which varies approximately with the fourth power of the wavelength) and are seldom useful for making quantitative measurements.

Petrographic microscopes, in conjunction with a Cary-14 spectrophotometer, have been used to facilitate the measurement of polarized optical absorption spectra of small crystals (mounted individually or in thin sections), or selected areas of large crystal plates (Burns 1965, 1970). In this technique, a microscope is mounted in each of the sample and reference beams of the recording spectrophotometer. The resulting spectra are generally of high quality because a concentrated light beam can be focused on a relatively small area (*e. g.*, ~200 μm in diameter with a 40 × objective) that is often free of fractures or inclusions.

Being confronted with the necessity of measuring the spectra of various kinds of mineral powders, the author combined the (mineral oil) mull technique with the microscope technique. The quality of the resulting spectra was much superior to that obtained by the other mull techniques,

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primarily because of reduced light scattering. After using the mull-microscope technique successfully for qualitative purposes it became apparent that it also had potentiality for being used in making semi-quantitative analytical and/or comparative measurements on materials that are otherwhise not amenable to such an approach. This note describes the procedure for making such measurements and gives typical results for several kinds of powdered minerals.

MICROSCOPE ASSEMBLY

Figure 1 shows the manner of mounting the relatively small Unitron MPS microscope in the light path of each of the reference and sample beams of the Cary-14 spectrophotometer.

The microscope box, or housing, was constructed of half-inch aluminum plate, painted black on the interior surfaces. Holes were drilled in the top to permit the fastening of the microscopes for use in either the visible or infrared mode of the Cary-14 spectrophotometer. To decrease the effects of stray light, the back of the box was covered with a black cloth, while the front was fitted with a "down-swinging" hinged metal door.

A groove or slot was made in the "light source" end (Fig. 1) of the microscope housing to accommodate a bar which depresses the lugs of the shutter mechanism and keeps the shutters open at all times.

It was found to be convenient to operate the spectrophotometer in the "infrared mode" in which the sample is irradiated with white light.

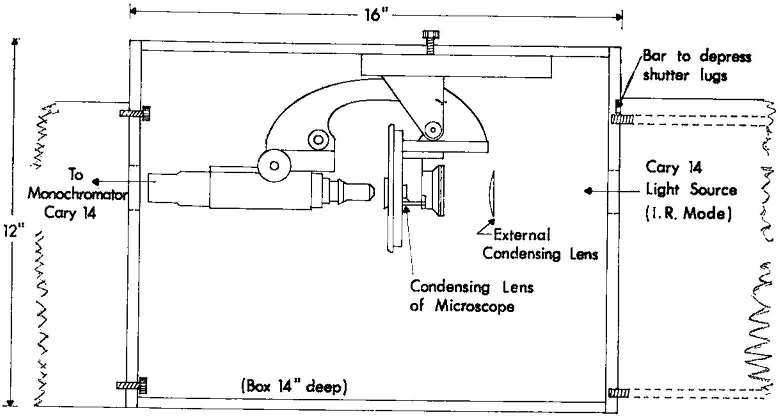

FIG. 1. Microscope assembly.

In this mode the microscopes are easily aligned in the light beams ; and spectra can be measured throughout the range 0.4 to 2.5μm.

PREPARATION OF MULLS FOR SEMI-QUANTITATIVE MEASUREMENTS

Because the consistency of a relatively thick mull is affected, in part, by the surface area of the powdered sample, it is recommended that the following procedure be used for making comparative measurements on samples of the same mineral (type) that have been ground to a similar state of subdivision by similar techniques. Because only a relatively small sample (*e.* g., $\sim$ 25 mg) is required, it is usually convenient to grind the sample by hand in a mortar for $\sim$ 5 minutes. The following technique has proved successful in the author's hands.

A 25-mg portion of the powdered sample is transferred to a mortar and 50 μl of a 3 : 1 mixture of toluene and a relatively low-viscosity mineral oil (*e.g.*, 200-210 cps) — preferably one having a refractive index close to that of the sample, is added. With a pestle the materials are thoroughly mixed into a paste while the toluene is exaporating. After a few minutes, when the odor of toluene can no longer be detected, a portion (the weight required will depend on the intensity of colour) is transferred to a microscope slide. With a spatula, a flattened layer is prepared ; then, with the aid of a cover-slip used as a trowel, a layer of mull is smoothed out (usually covering $\sim$ 0.5 cm^2). A cover-slip is then placed over the mull film, and, with the points of a pair of tweezers, for example, it is tapped uniformly into a position that is approximately parallel to the underlying slide so that a uniformly thick layer of mull is produced.

A micrometer, with jaws $\sim$0.5 cm in diameter, is now conveniently used to exert uniform pressure on the mull sandwiched between the glass plates, and at the same time, to measure the total thickness, (the combined thickness of slide and cover-slip having been previously measured). Care must be taken in opening the jaws of the micrometer so that the cover-slip is not jarred into a non-parallel position which could cause the formation of a wedge-shaped layer of mull.

The microscope slide is mounted on the stage and viewed with the appropriate objective lens (the author has found $\sim$ 10 × to be most useful) to ensure that the area in the field of view is free of voids or features that destroy its uniformity. The eyepiece and sub-stage mirror are then removed and the microscope is mounted as in Figure 1. With light incident on the microscopes as in Figure 1, it is convenient to align the microscope and the external condensing lens to give maximum brightness of the transmitted light by viewing the image of the mull on a piece of white paper held over the entrance port to the monochromator of the spectrophotometer.

The datum level of the spectrogram can be adjusted, not only with the balance control of the spectrophotometer, but with the focus adjustment of the reference beam microscope. Such adjustments give considerable flexibility in placing the spectrum on the chart paper, and in many cases prevent discontinuity when the trace reaches the top of the chart paper at a critical portion of the spectrum.

SOME APPLICATIONS

Although the examples given below are of limited interest they represent the type of application to which the mull-microscope technique may be put.

Comparison of lapis lazuli specimens

As part of a general study on lapis lazuli being carried out by Dr. D.D. Hogarth of the University of Ottawa, the mull-microscope technique was used to make an objective comparison of the "colour" of lapis lazuli specimens from three localities. The main absorption band of a typical lapis lazuli spectrum and the method used to measure its height above background are shown in Figure 2.

Table 1 gives the values of the absorption coefficient α (where $\alpha = \frac{\text{absorbance above background}}{\text{thickness of mull in cm}}$) for a number of mull samples of each of

TABLE 1. MULL ABSORPTION COEFFICIENT, α (CM^{-1}), OF LAPIS LAZULI SPECIMENS FROM VARIOUS LOCALITIES

	Chile	Afghanistan	Baffin Island
	73	90	24
	73	100	27
	84	100	26
	72	95	27
	67	91	25
	70	99	
Mean	73	96	26
Standard Deviation	5.8 cm^{-1}	4.6	1.3
Mean % Deviation	4.8	4.0	3.8

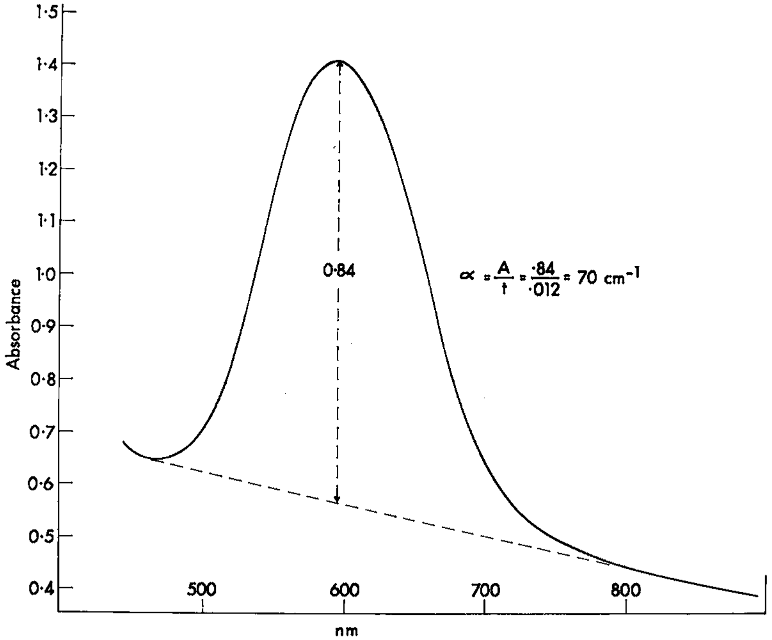

FIG. 2. Partial spectrum of mull of Chilean lapis lazuli; mull thickness 0.012 cm.

the three lapis lazuli specimens. With the mean percentage deviation being less than 5% it is evident that mull-microscope technique is useful for making semi-quantitative measurements.

Semi-quantitative analysis of nickel-bearing serpentines

That the mull-microscope technique has semi-quantitative analytical potential is indicated by the results in Table 2. Here the absorption co-

TABLE 2. MULL ABSORPTION COEFFICIENTS AND NICKEL CONTENTS OF NICKEL-BEARING SERPENTINES *

Description		α (cm^{-1})	% Ni (Chem.)
"Garnierite"	Sample 1	38 (5)	38.0
from New Caledonia	Sample 2	32 (4)	34.5
"Chrysoprase Earth"	Sample 1	14 (3)	16.2
from Hohenstein, Saxony, Germany	Sample 2	12 (3)	12.4

NOTE : Numbers in brackets indicate the number of replicate determinations.

* See Faust (1966) for an account of nomenclature of hydrous nickel-magnesium silicates.

efficients of mulls of four specimens of nickel-serpentines are presented together with the nickel content of the mineral powders. By coincidence there is approximately a one-to-one relationship between these two parameters. The important point, however, is that having established such a relationship it is possible to analyze, semi-quantitatively, and non-destructively, small samples of unknowns of a similar kind for their nickel content.

It is worth noting that, if necessary, the mineral powder can be recovered by washing out the oil with a solvent such as toluene, followed by filtration.

Figure 3 shows that the quality of the spectrum (B) of a mull of "garnierite" (*x*-ray analysis showed this to be a mixture of chrysotile + minor lizardite) is as good as that of a single crystal of annabergite ($Ni_3(AsO_4)_2 . 8H_2O$). In both of these spectra the three principal spin-allowed absorption bands, associated with the ${}^3A_2 \rightarrow {}^3T_2(F)$, ${}^3A_2 \rightarrow$

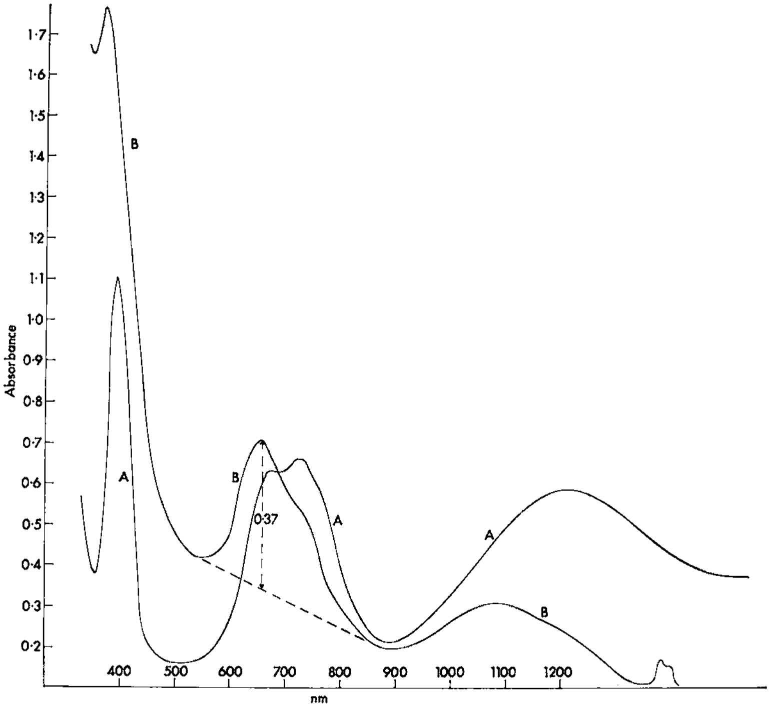

FIG. 3. A - Unpolarized spectrum of an a (010) cleavage tablet of annabergite; thickness 0.015 cm. B - Spectrum of mull of "garnierite"; thickness 0.010 cm.

$^3T_1(F)$, $^3A_2 \rightarrow {}^3T_1(P)$ transitions, are clearly resolved, in order of increasing energy.

The height of the absorption envelope associated with the $^3A_2 \rightarrow {}^3T_1(F)$ transition is the one used to calculate the absorption coefficients of the nickel-serpentine mulls. The manner in which the absorbance, above background, was arbitrarily measured is indicated in spectrum B of Figure 3.

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Manuscript received June 1970.

A TELLURIUM-BEARING CANFIELDITE, FROM REVELSTOKE, B.C.

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Canfieldite [$Ag_8(Sn,Ge)S_6$], with Sn > Ge is a rare sulphosalt mineral which is often formulated as the pure end-member of the canfieldite-argyrodite series. Until Perichaud *et al.* (1966) reported the first occurrence of the pure Sn end-member from the Massiac region, France, there was no evidence that this occurs naturally.

The purpose of this paper is to report the first occurrence of a tellurium-bearing canfieldite. The mineral was identified during a mineralogical investigation of a lead-zinc-silver ore submitted to the Mineral Processing Division of the Mines Branch for beneficiation tests by Stannex

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