

Measurements of spectral reflectivity of manganese oxides

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Summary. An accurate and highly sensitive method for the measurement of reflectivities incorporating a photomultiplier and a direct-reading galvanometer is described. The high sensitivity of the technique permits the determination of spectral reflectivities as opposed to 'white' light reflectivities, the latter values being subject to variation according to the type of apparatus used in their determination. The absolute spectral reflectivities of pyrite determined by the method are in good agreement with those quoted by some previous workers. Spectral reflectivities in air and oil and refractive and absorption indices are given for wavelengths from 430–650 $m\mu$ for manganese oxide minerals.

THE accurate measurement of reflectivity is the most important quantitative technique available for the routine identification of opaque minerals in polished section. Significant contributions to the theory and practice of such measurements have been made by Berek (1922), Schneiderhohn (1922), Cissarz (1932), Orsel (1930), Ehrenberg and Ramdohr (1934), Moses (1936), Folinsbee (1949), Hallimond (1953, 1957), Bowie and Taylor (1958), Leonard (1960), Cameron (1961), and Gray and Millman (1962).

Unfortunately there are marked variations in the reflectivity values quoted for specific minerals by different workers, as Cameron (1961) points out, and Ramdohr (1963) has questioned the reliability of some recent results. Although older values in many cases differed by amounts greater than 2 %, presently accepted results tend to agree more closely than this, but are still sufficiently variable to cause concern. The principal reasons for variation seem to be related to differences in apparatus, experimental technique, material studied, and method of preparation of the polished surface. Recently, however, the standardization of methods has become a prime concern of committees of the Mineralogical Society and International Mineralogical Association and some

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progress has already resulted from consultation between workers in this field.

The *reflection coefficient* r for a given surface is defined as the ratio of the reflected light intensity to the incident intensity, but it is more common to express this as a percentage termed the *reflectivity* and denote it by R . The value for normal incidence on the surface is used in ore microscopy, even though this is difficult to measure by an absolute method and is only approximated to in measurements with the microscope because of convergence of light from the objective.

The procedure for measurement of reflectivity under the microscope consists in comparing the intensity of light reflected by a given surface with that obtained from a standard surface of known reflectivity under the same conditions, after taking account of a correction due to reflection at other surfaces in the optical system.

Two kinds of apparatus have been used: *Visual microphotometers*—most recently by Hallmond (1957), Murchison (1957), and Leonard (1960); and *Photoelectric microphotometers*—Bowie and Taylor (1958), Gray and Millman (1960), Cameron (1961), Jones (1962), and Nichol (1962). Because of the subjective factors involved in the former, the use of photoelectric methods is becoming more common.

It has been the practice to use a white light source but this gives values that depend on the spectral energy distribution in the source and the spectral sensitivity of the photoelectric unit employed. For example, the maximum sensitivity of the selenium barrier layer cell used by Bowie and Taylor is at $520\text{ m}\mu$, close to that of the human eye; that of the CdS cell of Gray and Millman is at $600\text{--}700\text{ m}\mu$ and that of the photomultiplier described by Jones is at $400\text{--}500\text{ m}\mu$. To overcome this difficulty measurements must be made for a restricted wavelength band using filters or a monochromator to approximate as closely as possible to truly monochromatic light (Ehrenberg and Ramdohr, 1934; Orcel and Pavlovitch, 1932; Gray and Millman, 1962).

When accurate values of reflectivity are obtained, it becomes possible to calculate the more fundamental optical constants of a mineral—the refractive index n and the absorption index K . The expression $R = 100\{(n-N)^2 + n^2K^2\}/\{(n+N)^2 + n^2K^2\}$ gives the reflectivity in terms of these constants and N , the refractive index of the surrounding medium, in the case of an isotropic, absorbing specimen. For anisotropic specimens, the reflectivities, R_1 and R_2 , of the principal directions in a given section are related in the same way to refractive indices n_1 and n_2 and absorption indices K_1 and K_2 . Thus, if the reflectivity is

determined in two media of different refractive index, the resulting equations may be solved for n and K . If r_a and r_o are the reflection coefficients in air and oil respectively, then

$$n = (N^2 - 1)/2\{N(1 + r_o)/(1 - r_o) - (1 + r_a)/(1 - r_a)\},$$

$$K^2 = \{r_a(n + 1)^2 - (n - 1)^2\}/n^2(1 - r_a),$$

where N is the refractive index of the oil.

This method has not previously been much used, partly because the reduced reflectivity in oil requires a very sensitive measuring apparatus to attain the required accuracy of measurement and partly because the reflectivity of the standard in oil was difficult to determine. Cambon (1949) solved the second problem by showing how the reflectivity in oil could be determined relative to the dry standard. A transparent piece of glass of known R.I. with accurately parallel faces is placed against the specimen and between them is placed a drop of liquid of the same R.I. as the glass. Measurements are made by focusing on the section through the glass-oil assembly and comparing with a dry standard. The relationship between the true and measured reflectivity of the immersed surface depends on the reflectivity of the glass, the thickness of the glass-oil assembly, the radius of the field plane, and the solid angle of the rays from the objective. By carefully selecting the appropriate field radius and the thickness of the glass-oil assembly, the true and apparent reflectivities are the same and there is no need to correct the measured reflectivity.

The requirement for a sensitive and accurate photoelectric measuring apparatus is met by the apparatus now to be described.

Photoelectric apparatus. An eleven-stage photomultiplier (EMI 6094B) housed in a light-tight brass case fitted with a camera shutter is mounted on the vertical limb of a beam splitter replacing the normal eyepiece tube of a microscope. Power supply for the dynodes is derived from a Cintel 1892 2KV stabilized power pack through a suitable decoupled potential divider (fig. 1). Output is recorded directly by a sensitive spot galvanometer (Broadbent and Shaw, 1955) of 450 ohms internal resistance and full scale deflection of 0.94 μ A on its most sensitive scale. For stability of operating characteristics the manufacturers recommend that the current of the photomultiplier should not exceed 50–100 μ A. Linear response of the photomultiplier-galvanometer combination was checked using neutral density filters. A more rigorous check on linearity has since been carried out and details will be published by Bradshaw

and Phillips. It was found necessary to allow a warming up period of 45 min, after which a high degree of stability is obtained. The peak sensitivity of the photomultiplier lies in the range 400–500 $m\mu$ but the transmission of the Ilford 'Spectrum' filters used to provide a limited waveband varies, so that maximum output was obtained with the orange filter at 600 $m\mu$.

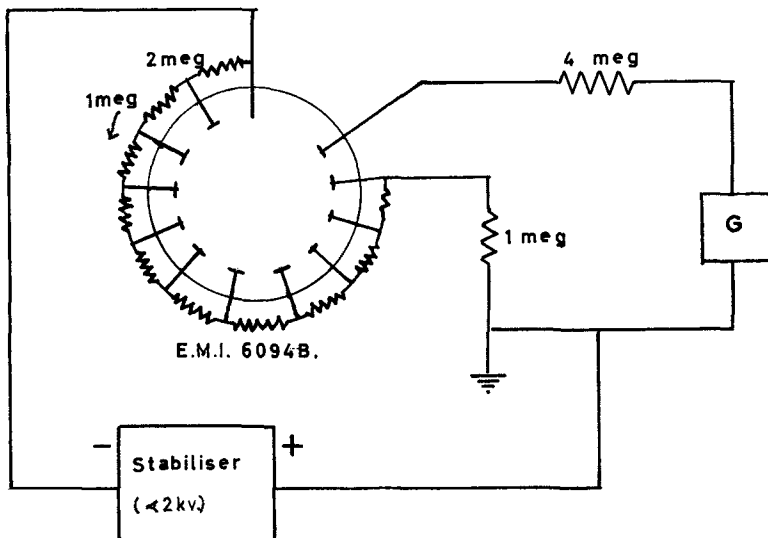


FIG. 1. Circuit diagram for reflectivity measurements.

Microscope. A Cooke, Troughton, and Simms 'Metalore' microscope was fitted with a beam splitter to allow visual examination of the specimen without disturbing the photomultiplier. The lengths of the limbs of the beam splitter were adjusted so that the image of the specimen is in focus with the photocathode and ocular simultaneously. An iris diaphragm in the beam splitter serves to eliminate stray light. Plane polarized light and a short focus, $\times 40$, 0.65 N.A. objective were used throughout the work. Particular attention was paid to the alignment of the various components of the optical system. Operation of the lamp iris controls the effective numerical aperture of the objective, so it was closed down to a constant small value to reduce the effects of oblique incidence. Neutral density filters must then be used for rough control of the light intensity, final control being obtained by adjustment of the photomultiplier gain.

Light source and stabilization. An 8-volt 48-watt tungsten filament bulb, colour temperature 3050° K, was fed from a charger. Two Lucas MT19E accumulators connected in parallel with the lamp by low-resistance connectors maintain a uniform current to the lamp because of their extremely low internal resistance. Ilford 'Spectrum' filters

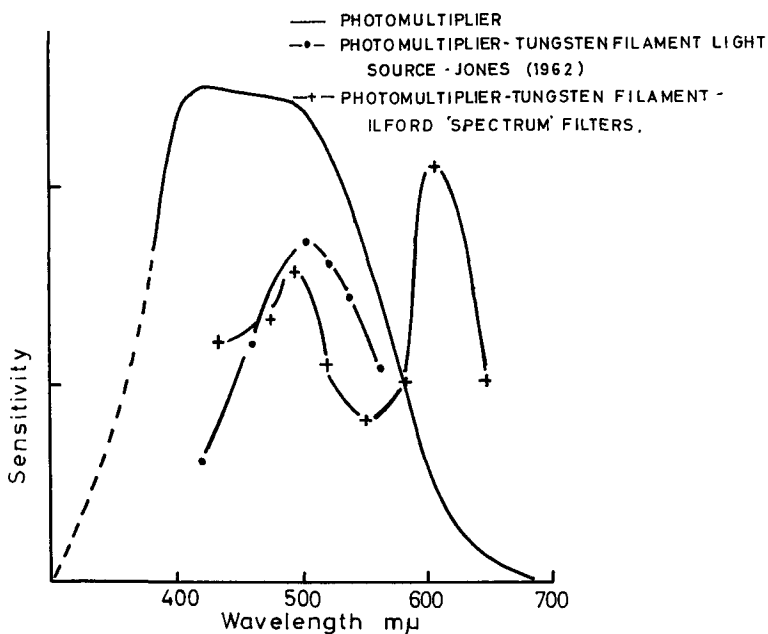


FIG. 2. Relative spectral sensitivities of photomultiplier combinations.

Nos. 601-608 with effective band widths generally of 250 $m\mu$ were mounted in a rotatable disk placed between the lamp and the entrance tube of the vertical illuminator. A monochromator or interference filters might have been preferable, but were not at the time available to us. Despite this, and the fact that the red filter in the above series is 'open ended', results obtained for pyrite agree closely with those of other workers (fig. 3).

Standards. The requirements for a suitable reflectivity standard are described by Bowie and Henry, 1964. General agreement on the most suitable standards has not yet been reached, but the mineral pyrite has been used by several workers. Hallimond (1957) described a novel method for absolute measurement of the reflectivity at quasi-normal

incidence using the microscope and gave values for the spectral reflectivity of pyrite between 470 and 670 $m\mu$, using Ilford 'Spectrum' filters and a visual photometer (fig. 3). The absolute reflectivity values for a

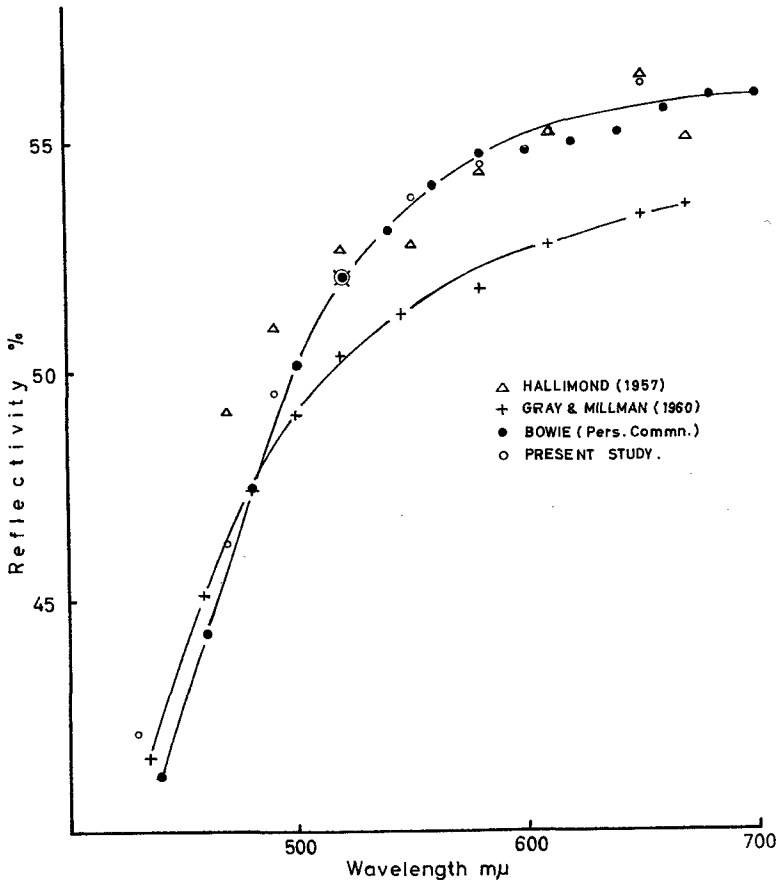


FIG. 3. Spectral reflectivity of pyrite.

specimen of pyrite from Rio Marina, Elba, using Hallimond's apparatus in conjunction with the present method (table I) are shown in fig. 3 together with data quoted by Gray and Millman (1960) and by S. H. U. Bowie (personal communication) on determinations carried out by the National Physical Laboratory, Teddington. Values obtained in the present work agree closely with the N.P.L. figures and with those of Hallimond above 500 $m\mu$. The values of Gray and Millman (1960) are

similar below 500 $m\mu$ but at longer wavelengths are markedly lower than ours.

The reflectivity of the manganese oxide minerals ranges from 10 to 40 % and it is therefore desirable to use a standard with a lower reflectivity than pyrite. For this purpose a specimen of marmatite (Fe-rich sphalerite) from Trepča, Yugoslavia, was measured by the Hallimond method. It has a white light reflectivity of 19.0 % and a spectral dispersion of 19.0 to 17.0 % (table I) at wavelengths of 430 to 650 $m\mu$. Refractive indices at 589 $m\mu$ quoted by Palache, Berman, and Frondel

TABLE I. Spectral reflectivity (%) of pyrite and marmatite

Wavelength, $m\mu$	430	470	490	520	550	580	610	650
Pyrite	42.1	46.2	49.5	52.0	53.7	54.4	55.2	56.2
Marmatite	19.0	18.8	18.3	18.0	17.8	17.6	17.3	17.0

(1944) give calculated reflectivities varying from 16.6 % for sphalerite with 0.15 % Fe to 17.9 % for sphalerite with 17.06 % Fe (Cameron, 1961). The interpolated reflectivity of the marmatite sample at this wavelength is 17.5 %. The spectral dispersion of the marmatite (fig. 4) corresponds closely with that of iron-poor sphalerite determined from refractive indices (Hallimond, 1953). The sphalerite values of Gray and Millman (1962) show a much greater spectral dispersion than the values discussed above.

Sample preparation. The quality of the polished surface is of major importance in reflectivity measurement. In this investigation specimens mounted in cold-setting resin were first ground by 400 and 700 grade carborundum on rotating steel laps followed by stationary cast wax-abrasive laps (Stanton, 1957). Preliminary polishing was carried out by 6-3 and $\frac{1}{4}$ -1 micron diamond paste on wood laps followed by a final polishing with magnesia on Nylon Simplex cloth.

Measurement procedure. A procedure similar to that described by Bowie and Taylor (1958) was adopted, selecting for measurement areas without polishing defects. After focusing, the reflector unit of the beam splitter is removed from the light path before taking a reading. In the case of anisotropic minerals the maximum and minimum values were obtained by measurements on a number of grains. For spectral reflectivity, readings were taken on the standard surface with each of the filters in turn, then repeated for the sample in air and oil. Cambon's (1949) curves of $\delta R/R$ (fig. 5) were used as a first check on the values of n and K .

Accuracy and precision. The method is accurate relative to certain accepted values for pyrite and marmatite. The limiting factor with regard to precision is the reading of the galvanometer. Replicate determinations of reflectivity at the 18 % reflectivity level give precisions of

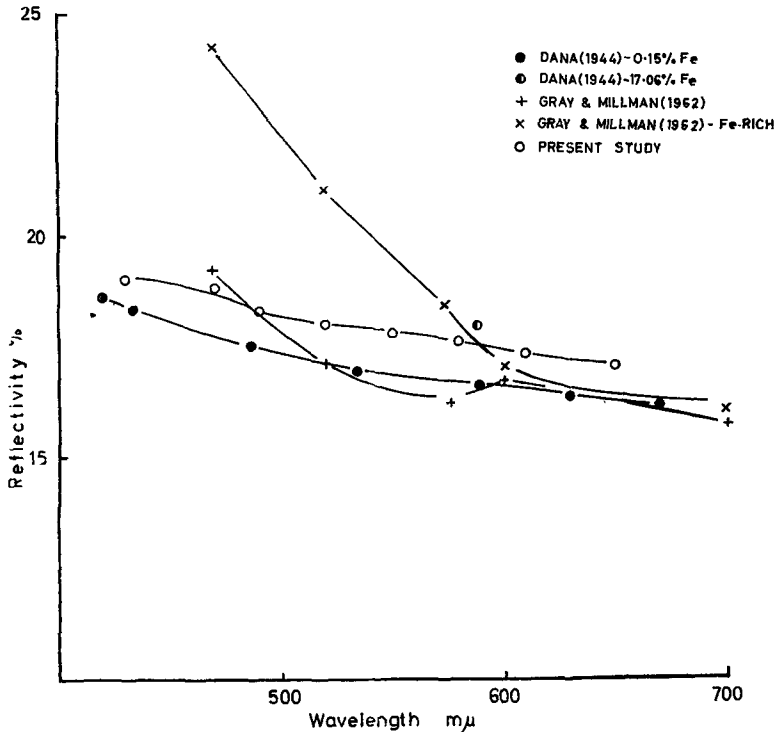


FIG. 4. Spectral reflectivity of sphalerite.

± 0.25 % at the 95 % confidence level. The precision of the values for the indices of refraction and absorption varies according to the position on the $\delta R/R$ curves. As the curves $\delta R/R = \text{constant}$ approach the horizontal, a slight difference in the $\delta R/R$ value greatly affects the determined indices.

Results. The white light reflectivities of the manganese oxide minerals are given in table II together with previously published values. There is a tendency for the white light values determined in the present study to be slightly higher than those reported by earlier workers. This bias is related to the fact that the photomultiplier displays maximum

TABLE II. White light reflectivities of manganese minerals

	Oreel & Pavlovitch 1932	Folinsbee 1949	Bowie & Taylor 1958	Gray & Millman 1962	Present work
Manganosite	14.4	—	—	—	15.0
Bixbyite	22.6	—	23.0	23.7	23.3
Braunite	20.4*-21.7†	20.1	17.8-19.8	19.0-19.1	21.8-22.4
Pyrolusite	29.5-39.7	33.1	30.0-41.5	—	31.2-39.6
γ -MnO ₂ -Nsutite	—	—	—	—	31.3
Pyrochroite	—	—	—	—	16.2-9.1
Manganite	15.2-17.5-21.0	19.0-31.4	14.0-20.0	14.5‡-17.5§ 22.0	15.1-17.6-21.8
Psilomelane	20.0-30.0	28.3	23.0-24.0	24.4	25.2
Groutite	—	—	—	—	12.8-21.2
Franklinite	—	18.9	—	18.5-20.0	19.0
Jacobsite	19.3	—	18.5	19.7	19.7
Hausmannite	16.4-18.9	19.6	16.0-19.0	16.7-19.1	18.0-21.5
Hetaerolite	14.7†-17.0*	—	—	16.7†-18.3*	14.3-19.1
Crednerite	29.2-37.5	—	—	—	25.0-34.0
Chalcophanite	10.6†-29.7*	18.8	10.2-26.0	13.5†-22.6*	10.7-33.6
Coronadite	27.5-32.5	—	26.0-32.0	—	28.2-34.0
Hollandite	29.6	27.3	26.0-32.5	—	27.3-34.5
Cryptomelane	—	—	—	—	28.4

* ω † ϵ ‡ b -axis§ a -axis|| c -axis

sensitivity in the blue range of the spectrum and that the manganese oxide minerals display higher reflectance in the blue relative to the red spectrum. The results, although believed to be accurate relative to one another, are therefore not strictly comparable with values quoted by

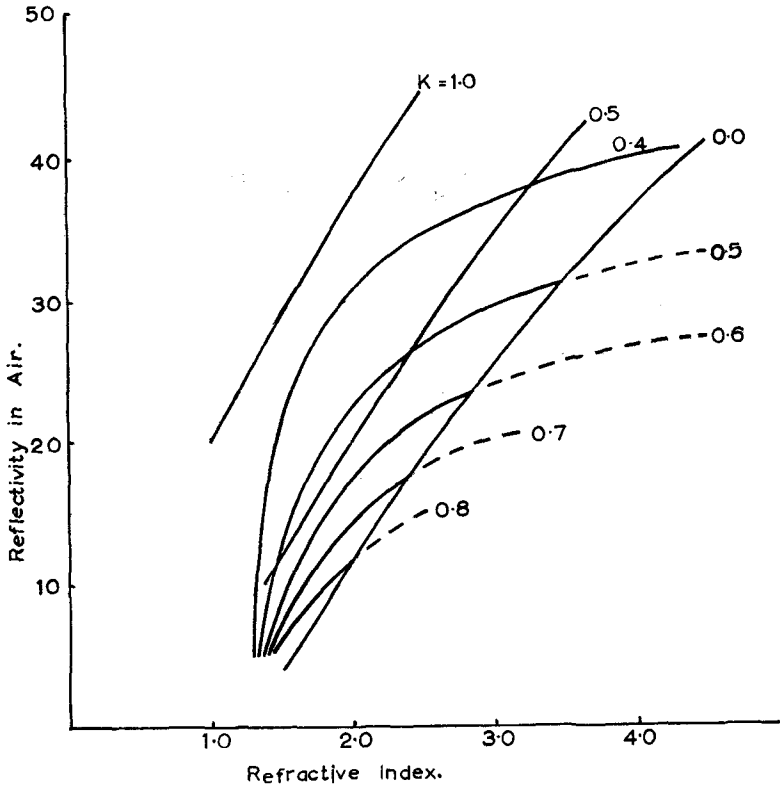


FIG. 5. Curves of $\delta R/R$ for oil of n 1.526.

previous workers but are nevertheless adequate for semi-quantitative techniques. In the cases of pyrochroite, coronadite, and hollandite it was not possible to get a perfect polished surface for examination so that the quoted reflectivities are below the true values for the minerals.

The spectral reflectivities of the manganese minerals are given in table III. In all cases the reflectivity in the violet exceeds that in the red. The spectral values of Gray and Millman (1962) show considerably greater spectral dispersion in the manganese minerals than was found

TABLE III. Spectral dispersion of manganese minerals

<i>Mineral</i>	480 m μ	470 m μ	490 m μ	520 m μ	550 m μ	580 m μ	610 m μ	650 m μ
Manganosite	15.0	14.9	14.6	14.4	14.4	13.9	13.7	13.7
Bixbyite	22.2	22.2	22.0	22.5	22.7	22.4	21.8	21.2
Biaurite	21.7-22.8	21.5-22.5	20.6-21.7	20.7-21.7	20.4-21.4	19.8-20.7	19.4-20.2	19.0-19.7
Pyrolusite	33.3-34.0	33.8-35.0	33.2-34.5	32.7-34.0	32.7-34.0	32.4-33.7	31.9-33.3	32.0-33.2
γ -Mn ₂ O ₇ -Nautite	31.7	32.0	31.8	31.5	31.5	30.8	30.0	29.0
Pyrochroite	16.4-19.1	16.3-18.6	16.0-18.8	15.3-18.1	15.2-17.9	15.0-17.6	14.6-17.1	14.2-16.5
Manganite	14.6/17.4/21.7	15.0/17.5/21.9	14.8/17.3/21.8	14.8/17.2/21.8	14.8/17.0/21.4	14.7/17.0/20.7	14.4/16.4/20.0	13.7/15.7/19.4
Psilomelane	24.7	25.0	24.1	23.8	23.5	23.0	22.1	21.3
Groutite	12.8-21.4	12.6-20.8	12.7-20.5	12.6-20.0	12.4-20.0	12.2-20.0	12.0-19.5	11.6-18.9
Franklinite	19.2	18.9	18.8	18.6	18.4	18.2	17.8	17.1
Jacobsite	19.7	20.0	20.0	19.4	19.3	19.0	18.4	17.5
Hausmannite	18.0-21.7	18.1-21.4	17.8-21.2	17.5-20.8	17.2-20.5	16.8-19.8	16.4-19.2	15.6-18.1
Heteroite	14.3-19.0	14.2-18.6	14.0-18.2	13.6-18.0	13.4-17.5	13.2-17.2	12.8-16.7	12.2-16.0
Crednerite	24.7-35.8	24.9-36.8	24.3-36.1	24.3-36.0	23.6-35.0	23.1-34.0	22.3-32.2	21.3-30.2
Chalcofanite	10.8-33.5	10.6-32.2	10.3-30.0	10.0-28.5	9.6-27.3	9.4-25.7	9.5-24.6	9.1-23.5
Coronadite	28.2-34.4	28.3-34.2	27.2-33.3	27.2-33.3	26.7-32.3	26.0-31.5	25.0-30.0	24.7-28.7
Hollandite	27.0-33.9	27.1-33.0	26.6-33.4	26.2-32.8	25.6-32.3	25.2-32.5	24.5-30.2	24.3-29.4
Cryptomelane	27.8	28.0	27.6	27.0	26.7	26.0	25.0	23.9

in the present work. The values of Ramdohr (1950) are somewhat closer to those of the present study but cover only green, orange, and red. The spectral dispersions of three of the minerals examined in the present study were measured with the equipment used by Bowie and Henry (1964) and found to be substantially similar to those obtained in the

TABLE IV. Refractive and absorption indices of manganese minerals
G, green; *R*, red

	Palache, Berman, and Frondel, 1944		Present study			
	ω	ϵ	ω	ϵ	K_{ω}	K_{ϵ}
Manganosite	$\left\{ \begin{array}{l} G \text{ 2.16} \\ R \text{ 2.16} \end{array} \right.$		2.17		0.05	
Bixbyite	Not reported		2.45		0.15	
Braunite	Not reported		2.60	2.50	0.00	0.00
γ -MnO ₂ (nsutite)	Not reported		3.35		0.00	
Pyrochroite	1.723	1.681	1.65	1.60	0.50	0.50
Manganite	$a = 2.25$		2.05		0.05	
	$b = 2.25$		1.90		0.05	
	$c = 2.53$		2.50		0.05	
Psilomelane	Not reported		2.40		0.20	
Groutite	Not reported		2.40	1.80	0.10	0.10
Franklinite	$R \text{ 2.36}$		2.30		0.05	
Jacobsite	2.30		2.30		0.10	
Hausmannite	2.45	2.15	2.40	2.15	0.10	0.15
Hetaerolite	2.35	2.10	2.30	2.07	0.10	0.10
Crednerite	Not reported		3.25	2.40	0.20	0.10
Chalcophanite	$\gg 2.72$	2.72	2.70	1.75	0.10	0.10
Coronadite	Not reported		3.25	2.95	0.20	0.15
Hollandite	Not reported		3.30	2.90	0.05	0.05
Cryptomelane	Not reported		2.60		0.30	

present method. These, together with the close correspondence between theoretical and measured values obtained for sphalerite, indicate that present spectral dispersion values are reliable.

The indices of refraction and absorption of the manganese minerals in 'white' light together with values quoted by Palache, Berman, and Frondel (1944) are given in table IV. Although there is good agreement in the majority of cases, several differences do occur that are well outside the limits of error of the method and so are considered significant. For instance, the refractive indices of manganite parallel to a and b are 2.05 and 1.90 respectively, whereas published data quote values of 2.25; the determined value of 2.50 parallel to c is in close agreement with the published value of 2.53. The refractive indices of chalcophanite determined in the present study are ϵ 1.75 and ω 2.70, whereas Palache, Berman, and Frondel (1944) give 2.72 for ϵ and > 2.72 for ω . Refractive and absorp-

tion index values are given in table IV for nine manganese minerals not previously recorded: bixbyite, groutite, braunite, coronadite, cryptomelane, psilomelane, hollandite, γ - MnO_2 (nsutite), and crednerite.

The indices of refraction and absorption in monochromatic light show a slight reduction in value from blue to red but this variation only slightly exceeds the reproducibility of the method in the case of the manganese minerals. The results show good agreement with the few values collected by Larsen and Berman (1934), whilst figures deduced from Ramdohr's (1950) reflectivity data in green, orange, and red light appear somewhat low. The index of refraction of the oil used by Ramdohr is not known so the curves of $\delta R/R$ will differ according to the extent the index of refraction of the oil differs from 1.526. The refractive indices determined over the wavelength range 430–640 $m\mu$ for sphalerite correspond to accepted values.

This method for the determination of indices of refraction and absorption would appear to be an acceptable and simple alternative to the classical methods for the determination of n in materials of high refractive index, provided that reflectivity measurements are made with care on well-polished surfaces.

Discussion.

Attention has been drawn to the importance of standardization of equipment and analytical techniques and procedures in the determination of reflectivity. The use of a variety of types of apparatus and analytical techniques has given rise to variations among quoted reflectivities for a given mineral, related to the particular method used in their determination. These reflectivity determinations are doubtless of considerable value in general work and for this purpose established methods are adequate. However, with the extension of reflectivity measurement into more critical fields there is a need for standardized procedures together with improved sensitivity and accuracy. The adoption of the determination of spectral reflectivity as a significant physical parameter in mineral identification has been hindered by the limited sensitivity of available determinative methods (Bowie and Taylor, 1958). The analytical method described in the present paper offers the advantages of increased accuracy and sensitivity. The application of the method to the determination of the indices of refraction and absorption by the measurement of reflectivity in different media has been demonstrated, and it is suggested that the method provides the required degree of accuracy and sensitivity essential to a reliable assessment of the value of critical reflectivity

measurements with reference to crystal orientation and the members of solid-solution series together with other known sources of variation of reflectivity.

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