

The photoelectric measurement of reflectivity.

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Summary. A simple photoelectric-cell attachment for use with an ordinary ore-microscope is described. Stabilization of the light source and accurate calibration of the photometer enable reflectivity values to be determined within an accuracy of 1 % of the measured value. The choice of a universally acceptable standard is discussed. The photometer can be used with white light or with light of different wave-lengths. Bireflection, dispersion, and dispersion of the bireflection can readily be measured.

THE accurate determination of the reflectivity¹ of minerals in polished section has been regarded for many years as a valuable aid to their identification. Reflectivity can be measured visually or photoelectrically, but it is generally agreed that the photoelectric method is capable of greater accuracy, provided the mineral grains are not unduly small. Hitherto, however, no simple, inexpensive, and yet reliable apparatus has been described to exploit this potential accuracy fully. The photoelectric method was first employed by Orcel (1927, 1928, 1930) in France, using an alkali-metal cell. A few years later Ehrenberg and Ramdohr (1934) in Germany, and Moses (1936) in the United States of America, independently conducted detailed investigations on the reflecting power of minerals using rectifying cells. More recently Folinsbee (1949) has made a contribution to the simplification of reflectivity measurements by employing a standard photographic exposure meter coupled directly to an ore-microscope; but the accuracy sacrificed by the employment of this technique more than outweighs its advantages. A further drawback of Folinsbee's method from the point of view of practical mineragraphy is that measurements cannot be made on grains less than 1 mm. across.

The apparatus described in this paper has been used for six years and during this time has proved to be not only robust and reliable but capable of measuring the relative reflectivity of ore minerals within the desired precision of plus or minus 1 % of the measured value. The photoelectric-cell characteristics have been tested periodically through-

¹ Defined as the percentage of normally incident light reflected from the surface.

out the trial interval, and, as they have not changed appreciably, the apparatus seems to be highly satisfactory in every way. Measurements can be made on grains of about 0.06 mm. in diameter using a 4-mm. objective, and 0.04 mm. with a 1.8-mm. oil-immersion objective. The accuracy of the measurements made on grains of these minimum sizes is not always within the accuracy quoted above, but simple modifications to the apparatus described, such as using a more sensitive galvanometer and a more powerful light source, could enable measurements of the required precision to be made. This, however, is not considered necessary for general use.

Description of the apparatus.

The essential components of the apparatus are an ore-microscope with a tube iris diaphragm, a selenium barrier-layer cell in a suitable holder, and a sensitive galvanometer with a relatively low internal resistance. In localities where there are large fluctuations in both mains voltage and frequency, the light source must be stabilized, but elsewhere this refinement is not essential for diagnostic purposes.

Microscope. A microscope with a cover-glass reflector unit, bloomed objectives, and external illumination is necessary for good results. That used by the writer is a standard Cooke, Troughton, and Simms ore-microscope to which an additional iris has been fitted in the tube just below the base of the ocular. The purpose of this iris is to cut out stray light reflected from minerals outside the field being examined. Use could be made of the iris diaphragm normally available on microscopes fitted with a Wright slotted ocular, and the cell could be mounted in the accessories carrier. Whatever type of housing is used for the cell it is essential for accurate work that an iris be provided as near as possible to the sensitive surface of the cell.

Cell holder. The cell holder was designed so that it could replace the ocular easily and in such a way that the sensitive surface of the cell would always take up a position in the plane of the primary image of the mineral under examination.

The construction of the cell mount shown in fig. 1 is probably more elaborate than necessary, but as this is essentially an experimental model it was necessary to make it so that the cell could be replaced easily and filters introduced below the sensitive surface.

Galvanometer. A spot galvanometer is employed with an internal resistance of 450 ohms and with a linear scale graduated from 0 to 100; it is manufactured by the Cambridge Instrument Company Limited.

Photoelectric cell. Photoelectric cells of barrier-layer type offer several advantages over gas-filled or vacuum cells for measurements of the type described here. The most important of these are long life, robustness, compactness, and the ability to deliver an electric current without the necessity of applying an external potential. The current generated

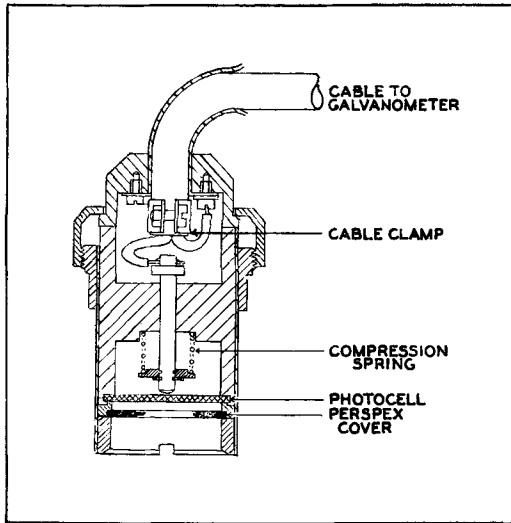


FIG. 1. Section showing construction of the cell mount.

when the sensitive surface of the cell is illuminated is directly proportional to the illumination when, as in this case, the internal resistance of the cell is high and the external load resistance is comparatively low.

Of the cells tested, the selenium barrier-layer type manufactured by Evans Electro selenium Limited delivered the greatest current for a given intensity of illumination, gave near linear response over the range of illumination used, and showed no signs of fatigue. One 'EEL' cell has been in operation for over six years and no appreciable change in its characteristics has yet been noted.

Stabilization of the light source.

One of the major problems in the use of photoelectric techniques for measuring reflectivity under an ore-microscope is the stabilization of the light source. A number of methods have been tested, including the use of a constant-voltage transformer and the use of high-capacity accumulators alone, but only one of the methods tried has produced satisfactory results. Typical readings, taken at the same time of day in

each case, are given in table I to show the effect of using unstabilized light, light stabilized by a constant-voltage transformer, and light stabilized by the method finally adopted.

TABLE I. The effect of various lighting circuits on the observed reflectivity. A pyrite standard was used and the irises adjusted to give an initial reading of 54.5 in each case.

| Time. | Unstabilized illumination. | With constant- | |
|------------|----------------------------|----------------------|--------------------------|
| | | voltage transformer. | Stabilized illumination. |
| 1500 hours | 54.5 | 54.5 | 54.5 |
| 1505 " | 53.5 | 54.0 | 54.5 |
| 1510 " | 54.0 | 54.6 | 54.5 |
| 1515 " | 54.6 | 54.0 | 54.4 |
| 1520 " | 54.2 | 53.9 | 54.5 |
| 1525 " | 53.9 | 53.9 | 54.5 |
| 1530 " | 54.0 | 54.0 | 54.5 |

The arrangement employed is shown diagrammatically in fig. 2. A constant-voltage transformer (TR), which has coarse (C) and fine (F) adjustment controls on the output current, is used to supply a partially stabilized current to a heavy-duty accumulator charger (CH). The battery (B), which is kept charged, has the requisite number of heavy-duty car-starter cells and is connected in series with a $-10, 0, +10$

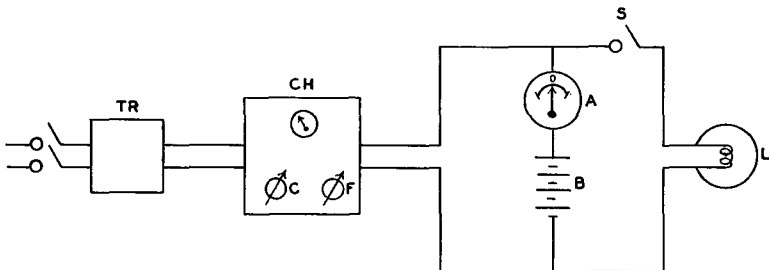


FIG. 2. Diagrammatic layout of the stabilization circuit. TR, transformer; CH, charger; C, coarse adjustment; F, fine adjustment; A, ammeter; B, battery; S, switch; L, lamp.

ammeter (A) across the charger. The lamp (L) used by the writer is a compact tungsten filament type that consumes 48 watts at 8 volts and hence requires a current of 6 amps. This is supplied by the charger, which is normally adjusted by the fine control to give an ammeter reading of zero.

The stabilizing effect of the heavy-duty battery in this circuit results from its very low internal resistance. Any fall in the current supplied through the charger would be compensated for by current taken from

the battery; and any excess current from the charger would be diverted through the battery.

It is necessary to give the battery a charge periodically. This can be achieved simply by opening the lamp switch (S) while the charger is still operating. After charging, the battery voltage should be allowed to settle for an hour or so before it is used again for making accurate measurements. During normal use the battery and light are switched off simultaneously.

Calibration.

One of the main disadvantages of the early barrier-layer cells was the variability in sensitivity over their surface. Obviously this would have been a serious drawback to accurate measurements, and one of the first tasks of calibration was to test the response of the cell over its entire surface. To do this a disc from which a one-eighth sector had been machined out was placed beneath the cell in the holder and rotated through a complete circle; at the same time the light falling on the cell was kept constant. No variation in galvanometer reading was observed during the rotation of the disc through 360° .

The next step in the calibration of the instrument was to determine whether the response of the combined cell and galvanometer was linear. This was done in two ways. Firstly, a highly reflecting mineral was placed on the microscope stage and the field iris opened until the reading on the galvanometer was 100. Discs from which $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ sectors had been cut were then inserted in turn in the cell holder and the readings noted. The results shown in fig. 3 demonstrate that the response is linear. A second test, which checked not only the linearity of the response but also its reproducibility, was made by inserting accurately calibrated neutral density filters in front of the light source. The results of this experiment are shown in table II. The filters were calibrated by the National Physical Laboratory using a tungsten filament lamp operating at a colour temperature of 3050° K., which is the same as that of the microscope lamp employed. The percentage transmission values measured photoelectrically agree closely with those determined by the National Physical Laboratory. However, as there is some variation from cell to cell, new cells should always be tested for linearity before use.

Choice of reflectivity standard.

The choice of a reflectivity standard has been the subject of discussion for many years, but none has yet been universally accepted. This is

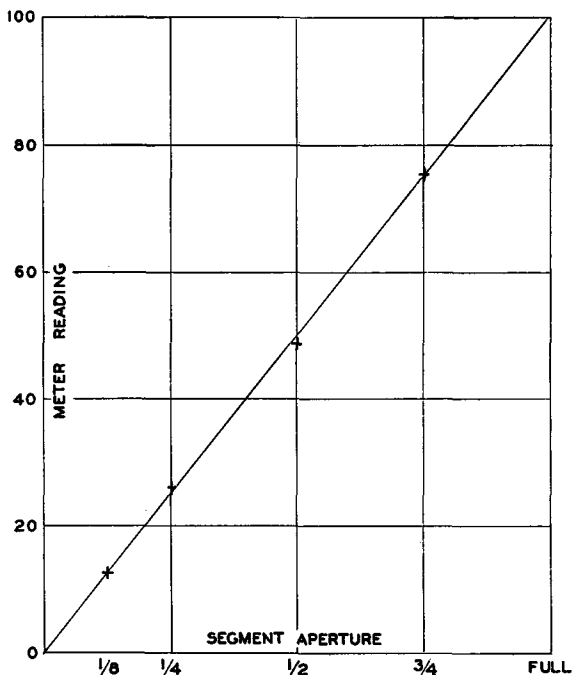


FIG. 3. Graph demonstrating the linear response of the photoelectric cell and galvanometer.

TABLE II. Calibration data on three EEL cells.

| Density* | Percentage transmission. | EEL cell No. 551. | EEL cell No. 1054(a). | EEL cell No. 1054(b). |
|----------|--------------------------|-------------------|-----------------------|-----------------------|
| 0.114 | 76.9 | 77.0 | 77.0 | 77.5 |
| 0.310 | 49.0 | 49.0 | 49.0 | 49.1 |
| 0.542 | 28.7 | 28.7 | 28.5 | 28.2 |
| 1.046 | 9.0 | 9.0 | 9.0 | 8.9 |
| 2.159 | 0.7 | 0.7 | 0.7 | 0.7 |

* Defined as the logarithm of the reciprocal of the transmission of the neutral filter used.

partly owing to the difficulty of making absolute reflectivity measurements at normal incidence and partly to the lack of an ideal substance. A good standard should have a high reflectivity with little dispersion and should be isotropic; it must be free from inclusions and flaws, should polish easily without being scratched, and should have a high resistance to tarnish.

Theoretically, the reflectivity (R) of a transparent isotropic medium at normal incidence in air can be calculated from the Fresnel equation:

$$R = \frac{(n-1)^2}{(n+1)^2} \times 100,$$

where n is the refractive index. A highly refracting mineral like diamond can therefore be used as a primary standard, the reflectivity being calculated for light of different wave-lengths from the corresponding refractive indices. Even diamond, however, has too low a reflectivity (17.2 in sodium light) for it to be an ideal standard, and complete elimination of internal reflections is a difficult matter. As will be shown below, a carefully cut diamond may be used as a primary standard with which to establish the best reflectivity value for a secondary standard for routine use. Blende has sometimes been used as a standard, but compared to diamond it has the additional disadvantage that its reflectivity depends on its iron content.

Several pure metals, namely copper, silver, rhodium, and platinum, have been examined for use as secondary standards, but none proved entirely satisfactory. A large number of mineral species have also been considered and eventually pyrite was chosen as the most suitable. Its surface does not tarnish readily and its reflectivity, which is remarkably constant from specimen to specimen, lies near the middle of the range found in ore minerals. Sections of pyrite from ten different localities give values in white light within 0.1 of each other. This, of course, does not necessarily mean that all pyrite will have the same reflectivity, and as a precaution against this eventuality material from Rio Marina, Elba, is specified as being suitable. The only demerit of pyrite is that it has a rather high dispersion over the visible light range. However, the dispersion curve is relatively flat over the region from red to green normally used in dispersion measurements.

The reflectivity of pyrite for light of different wave-lengths was measured using a primary standard of diamond, specially cut to eliminate internal reflections. The values calculated for diamond (for the mean wave-lengths of the transmission bands of the filters used) are given below, together with the corresponding values determined for pyrite:

| | Wratten 58. Green. | Wratten 22. Orange. | Wratten 25. Red. |
|---------|-----------------------|------------------------|---------------------|
| Diamond | 17.1 | 17.2 | 17.3 |
| Pyrite | 52.8 | 54.5 | 54.3 |

The reflectivity of pyrite for a tungsten filament light source operating at a colour temperature of 3050° K. was estimated to be 52.8 by the same method, assigning a value of 17.2 to diamond. Since, however, values are available (Folinsbee, 1949; Uytenbogaardt, 1951) for the reflectivities of some 200 mineral species measured relative to pyrite at 54.5, the latter value has been adopted as an interim measure until sufficient new and more accurate data are available. The values quoted above are regarded as tentative and are subject to revision in a future communication.

Use of the photometer.

Measurement of reflectivity. To obtain the reflectivity of an unknown mineral the pyrite standard is first placed on the stage, brought into focus, and a scratch-free area selected. The ocular is then replaced by the cell unit and the field and tube irises adjusted till a reading of 54.5 is obtained on the spot galvanometer. A box with a circular hole in the top and painted dead black inside is then placed immediately under the objective and the sub-stage raised until the bottom lens of the objective fits just inside the hole. A second reading is taken on the galvanometer and the zero-setting control adjusted until it reads zero. (This reading is necessary to compensate for stray light reflected mainly from the top surfaces of the lenses in the objective.) The standard is then replaced and the irises adjusted slightly to restore the reading of 54.5. Next, the unknown is placed on the stage, focused carefully, and a suitable area chosen as before. The new reading obtained when the cell has been put in position is then given directly on the galvanometer as percentage reflectivity. Once the microscope has been set up in this way, it is not necessary to take any further measurements with the standard unless the area of field controlled by the irises is changed. If great accuracy is required, readings for the standard should be obtained immediately before and after the unknown.

For best results specimens must be well polished. The criterion of a good polish is that the surface should be flat and without visible scratches at the magnification employed. The surface should be cleaned with benzene and a lens tissue before the measurement is made. (Buffing on a chamois leather pad tends to scratch soft minerals, though it is suitable for hard ones.) There is little evidence that the method of polishing has any effect on reflectivity values, but this is being investigated more fully. Tests carried out on five minerals polished with aluminium oxide and with magnesium oxide on lead laps and with

aluminium oxide on a cloth lap showed no appreciable difference in reflectivity provided the specimens were equally well polished by the three methods. Results of this experiment are given in table III:

TABLE III. Reflectivity values obtained after different polishing techniques.

| Mineral species. | Al ₂ O ₃ | MgO | Al ₂ O ₃ |
|------------------|--------------------------------|-----------|--------------------------------|
| | Lead lap. | Lead lap. | Cloth lap. |
| Pyrite | 54.5 | 54.5 | 54.5 |
| Davidite | 17.2 | 17.2 | 17.2 |
| Uraninite | 16.8 | 16.9 | 16.8 |
| Blende | 17.5 | — | 17.4 |
| Tetrahedrite | 30.7 | 30.7 | 30.8 |

Bireflection. The polished surfaces of isotropic minerals give one reflectivity value in the same way as such minerals have one refractive index in transmitted light. Similarly, most sections of anisotropic minerals have two principal directions which differ in their reflecting power for rays vibrating along them. It is a simple matter to measure the maximum and minimum reflectivity in any section by rotating the stage until these values are observed. The difference between the two values gives a measure of the bireflection of the section. Any particular section may not exhibit the maximum bireflection of the mineral, just as in any thin section the maximum birefringence may not be observed; but if a number of grains of the same mineral are examined (and this can be done very quickly) the maximum and minimum values can usually be determined without much effort. Where crystallographic directions can be observed, it is always useful to note the relationship between these and the principal directions. The numerical value of the bireflection is a valuable aid in mineral identification.

Dispersion. The reflectivity of most minerals varies with the wavelength of the incident light and unless its spectral composition is defined there is little point in employing precise photometric methods for measuring the reflectivity. Unfortunately the use of a monochromator or of filters that transmit a narrow spectral band cuts down the intensity of the illumination so drastically that either a very powerful light source must be employed or the output from the electric cell must be amplified. The first alternative introduces stabilization difficulties, as the heavier the current required the less easy it is to obtain satisfactory stabilization of the light source. The second alternative makes the whole apparatus rather complicated for general use.

It is recommended that for normal diagnostic purposes a compact

tungsten filament lamp operating at a colour temperature of 3050° K. be employed and that the Wratten filters be used to give a measure of dispersion of the reflectivity. It is usually sufficient to note whether the reflectivity increases or decreases with increase in the wave-length of the incident light.

TABLE IV. Selected minerals arranged in order of increasing reflectivity. The values are for measurements in air relative to a pyrite standard of 54.5.

| Mineral species. | Reflectivity in white light (3050° K.) | | Reflectivity in orange light (Wratten 22 filter). | | Folinsbee's 'best values'. |
|------------------|--|-------|---|-------|----------------------------|
| | Range. | Mean. | Range. | Mean. | |
| Cassiterite | 11.2-12.8 | 12.0 | 11.0-12.5 | 11.7 | 12.9 |
| Covellite | 7.0-22.0 | 14.5 | 5.0-20.0 | 12.5 | 9.5-15.1 |
| Goethite | 16.1-18.5 | 17.3 | 14.8-17.0 | 15.9 | 16.1 |
| Blende | — | 17.5 | — | 16.9 | 17.8 |
| Ilmenite | 17.8-21.1 | 19.4 | 17.3-20.2 | 18.7 | 19.4 |
| Magnetite | — | 21.1 | — | 20.9 | 21.1 |
| Alabandite | — | 23.4 | — | 22.0 | 23.9 |
| Cuprite | — | 27.1 | — | 24.3 | 27.7 |
| Hematite | 25.0-30.0 | 27.5 | 24.0-27.2 | 25.6 | 27.2 |
| Tetrahedrite | — | 30.7 | — | 29.4 | 31.2 |
| Bourbonite | 36.0-38.2 | 37.1 | 34.0-35.0 | 34.5 | 35.5 |
| Pyrrhotine | 38.0-45.2 | 41.6 | 39.7-44.5 | 42.1 | 39.9 |
| Galena | — | 43.2 | — | 41.7 | 42.4 |
| Chalcopyrite | 42.0-46.1 | 44.0 | 41.0-44.8 | 42.9 | 43.2 |
| Linnæite | — | 49.5 | — | 49.2 | 47.4 |
| Arsenopyrite | 51.7-55.7 | 53.7 | 51.3-54.0 | 52.6 | 52.4 |
| Niccolite | 52.0-58.3 | 55.1 | 54.0-61.0 | 57.5 | 52.6 |
| Altaite | — | 65.5 | — | 62.2 | 63.2 |
| Gold | — | 74.0 | — | 80.6 | 73.4 |
| Antimony | 72.0-77.1 | 74.5 | 70.5-74.1 | 72.3 | 74.4 |

Dispersion of bireflection. The reflectivities corresponding to the two principal directions in the surface of an anisotropic mineral often vary independently with the wave-length of the light employed. This property is termed 'dispersion of the bireflection'; it can readily be measured with the apparatus described here, and may in some instances be of considerable diagnostic value.

Results. Table IV lists some typical measurements for white light and for orange light (Wratten 22 filter). They are compared with values given by Folinsbee (1949) for white light to illustrate the measure of agreement obtained with two quite dissimilar electric cell photometers. The ranges given for anisotropic minerals were measured on randomly oriented sections and indicate the degree of bireflection, though the

extremes recorded are not necessarily maximum and minimum values for the species.

Conclusions.

Provided precautions are taken in calibration, apparatus of the type described can be relied on to measure the reflectivity of ore minerals relative to a standard with a precision of better than 1 %. Reflectivities of 50 and over can normally be measured to a precision of ± 0.2 . This degree of precision is much better than can be obtained by visual methods, which are limited by the inability of most observers to detect a difference of less than about 2 % in the intensity of two adjacent areas (Hallimond, 1953). The apparatus is inexpensive, can be used with any ore microscope, does not suffer from fatigue, and can be operated with little manipulative skill.

When the apparatus is used in conjunction with a micro-indentation hardness tester fitted to the same microscope (Bowie and Taylor, 1957), the two constants thus determinable with a high degree of precision enable ore minerals for which the necessary data are available to be identified in much less time than has hitherto been possible.

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References.

- BOWIE (S. H. U.) and TAYLOR (K.), 1957. *Nature*, vol. 179, p. 628.
 EHRENBERG (H.) and RAMDOHR (P.), 1934. In SCHNEIDERHÖHN (H.) and RAMDOHR (P.), 1934, *Lehrbuch der Erzmikroskopie*, Berlin, vol. 1, part 1, p. 165.
 FOLINSBEE (R. E.), 1949. *Econ. Geol.*, vol. 44, p. 425.
 HALLIMOND (A. F.), 1953. *Manual of the Polarizing Microscope*, 2nd edn, York, p. 135. [M.A. 12-233.]
 MOSES (J. H.), 1936. Thesis, Univ. of Harvard. Cited by SHORT (M. N.), 1940, *Microscopic Determination of the Ore Minerals*, 2nd edn (U.S.G.S. Bulletin 914), Washington, p. 89. [M.A. 8-185.]
 ORCEL (J.), 1927. *Compt. Rend. Acad. Sci. Paris*, vol. 185, p. 1055.
 ——— 1928. *Ibid.*, vol. 187, p. 1141.
 ——— 1930. *Bull. Soc. franç. Min.*, vol. 53, p. 301 [M.A. 4-444.]
 UYTENBOGAARDT (W.), 1951. *Tables for the Microscopic Identification of Ore Minerals*, Princeton and London. [M.A. 12-6.]