SYNOPSES

The identification of sulphide minerals by infra-red spectroscopy

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THE value of infra-red spectra in identifying sulphide minerals has been assessed by surveying the spectra of some forty specimens. Spectra of finely ground samples dispersed in polyethylene discs were obtained in the region 420–90 cm^{-1} with a resolution of 3–4 cm^{-1}, using a Beckman-RIIC Fourier-Transform Interferometer. Except for minerals whose metallic conductivity obliterated vibrational features, the spectra permitted rapid recognition of sulphide minerals either alone or in mixtures.

Spectra of the following twenty-five pure, or nearly pure specimens are presented: cinnabar, galena, pyrrhotine, alabandine, sphalerite, wurtzite, realgar, orpiment, stibnite, bismuthinite, arsenopyrite, tetrahedrite, pyrargyrite, proustite, enargite,

bournonite, boulangerite, jamesonite, and plagionite. Sulphides whose metallic conductivity led to featureless, almost total, absorption of infra-red radiation included chalcosine, troilite, millerite, covelline, bornite, and pyrrhotine: only the spectrum of the last is illustrated as a typical example.

Comparison of the spectra reproduced here with those previously published show a fair measure of agreement, although there are discrepancies. Povarennykh and co-workers, for example, have reported a common sequence of broad absorption bands at 370, 280, and 180 cm^{-1} for minerals that were found here to exhibit featureless metal-like absorption. The sources of these and other discrepancies are briefly discussed.

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THE IDENTIFICATION OF SULPHIDE MINERALS BY
INFRARED SPECTROMETRY

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Although commercial infrared spectrometers that operate in the region below 400 cm^{-1} in which sulphides mostly absorb have only recently become available, there is already a considerable amount of information published on this mineral group. The fullest survey has been undertaken by Povarennykh and co-workers (1971a, 1971b, 1973, 1974), who give spectra of nearly 60 sulphides and sulphosalts, and six arsenides in the 500-60 cm^{-1} region. Liese (1974) lists absorption maxima in the 435-250 cm^{-1} region for 44 sulphides, six arsenides, two tellurides and one antimonide. Nyquist and Kagel (1971) give spectra down to 45 cm^{-1} of 17 synthetic sulphides, 11 selenides, and eight tellurides. Other workers have published data on more limited groups of compounds (Karr and Kovach, 1969; Forneris, 1969; Whitfield, 1971; Byer et al., 1973; Petzelt and Grigas, 1973; Lutz and Willich, 1974.) All these papers include powder transmission spectra, which are most directly useful for characterization. Single crystal reflection spectra have also been obtained, and although essential for fundamental vibrational assignments in complex spectra, they are inconvenient or even impossible to obtain from many natural samples.

Unfortunately, comparison of data on the same minerals published by different authors often shows substantial discrepancies which prevent confident application of these results for identification purposes. Such discrepancies may have several origins: they may arise from misidentifications or from impurities in the minerals examined, or they may reflect the real variations in composition, structure or crystallinity that can occur within the range of a single mineral species. They can also have an instrumental origin, as many spectrometers operate at close to their practical limits in this low energy region of the infrared spectrum.

To resolve some of these uncertainties, a survey of the spectra of a number of carefully purified and characterized sulphide minerals has been undertaken using a Beckman-RIIC Model FS 720 Fourier-Transform Interferometer. This instrument was found to give trustworthy results over the region 420-100 cm^{-1} with resolution of about 3-4 cm^{-1} using a single beam splitter. The region below 100 cm^{-1} was found to exhibit at most only weak absorption bands of little value for characterization purposes and was not examined in detail, although potentially accessible on the interferometer.

EXPERIMENTAL

Spectra of samples in polythene disks were recorded in the region 500-50 cm^{-1} using the above instrument fitted with a 3.5 μm polythene terephthallate beam-splitter. The output from the interferometer was recorded on punched tape at 8 μm intervals over a mirror-travel from +4 to -4 mm path difference,

and subsequently transformed on an IBM 1130 computer to an energy spectrum (intensity, I, versus frequency), which was ratioed against the spectrum of a blank disk (I_o versus frequency) to give a relative transmission spectrum (I/I_o versus frequency). The spectrum was drawn by an IBM plotter connected to the computer with the point of maximum transmission arbitrarily set at full scale. Satisfactory spectra were obtained between about 420 cm^{-1} and 90 cm^{-1}, but at higher and lower frequencies the noise level became troublesome because of the low energy transmitted by the instrument. Examination of water-vapour spectra indicated a resolution of 3-4 cm^{-1}. Spectra of samples were also recorded in the region 2000-400 cm^{-1} on a Grubb-Parsons Spectromaster prism-grating instrument, or from 2000-250 cm^{-1} on a Perkin Elmer 577 filter-grating spectrometer.

Samples were carefully hand-picked, freed from surface deposits by cleaning in distilled water in an ultrasonic bath for a few minutes and checked for purity by X-ray diffraction. After initial hand-grinding in an agate mortar with a few drops of propanol, about 15 milligrams were further ground to less than 2 μm with propanol in a vibratory ball mill. Because of the high refractive index of sulphide minerals, thorough grinding was essential for satisfactory spectra, which were otherwise severely affected by light scattering, producing pronounced Christiansen-filter effects.

Spectra were recorded at three concentrations: 10 mg, 2mg and 0.4 mg in polyethylene disks of 12 mm diameter. The highest concentration was first prepared by shaking 10 mg of a ground sample with 100 mg polyethylene powder for two minutes in a mechanical vibrator, without grinding balls, and subsequently compressing the powder in an evacuated mould, applying 1 tonne thrust on the 12 mm disk. The anvil used was cut at 1° from the horizontal to avoid an interference pattern arising from internal reflections in the disk. After recording the initial spectrum, the first dilution was obtained by cutting out a 70° sector from the disk, and repressing this sector in the mould between parallel faces to reform a complete circular disk of 12 mm diameter. A further 80 mg of polyethylene powder was then compressed on top using the non-parallel anvil-plunger combination. The second dilution was similarly prepared.

RESULTS

The spectra obtained for pure or nearly pure sulphide minerals are presented in Figures 1 to 10, roughly in order of increasing complexity of structure and composition.

The value of such spectra for identification purposes is obviously variable. At one extreme are spectra such as those of cinnabar (HgS), realgar (As_4S_4), orpiment (As_2S_3), chalcopyrite ($CuFeS_2$), stannite (Cu_2FeSnS_4), pyrite (FeS_2), marcasite (FeS_2), molybdenite (MoS_2), cobaltite ($CoAsS$) and enargite (Cu_3AsS_4) which show sharp well resolved absorption bands that allow easy recognition of these minerals, either alone or when associated with others. At the other extreme are sulphides whose metallic conductivity leads to featureless, almost total, absorption of infrared radiation: only one example, pyrrhotite ($Fe_{11}S_{12}$) is illustrated here (Fig. 1c), but other minerals examined that gave this type of
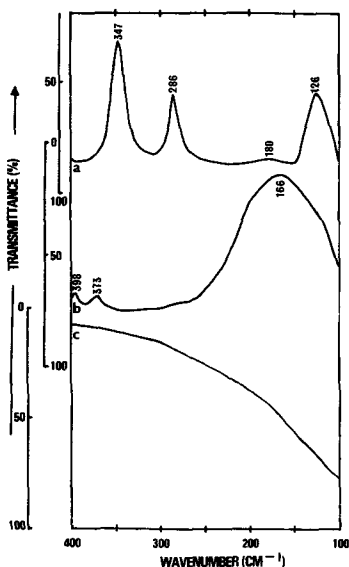
Figure 1. Far-infrared spectra of (a) cinnabar (HgS), 2 mg, (b) galena (PbS) 2 mg, and (c) pyrrhotite (Fe₁₁S₁₂) 2 mg. Bands at 398 and 373 cm⁻¹ in spectrum (b) arise from an impurity.
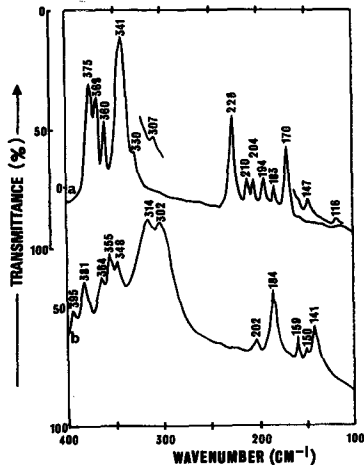
Figure 2. Far-infrared spectra of (a) alabandite (NnS) 0.4 mg, (b) sphalerite (Zn,Fe)S 0.4 mg, and (c) wurtzite (ZnS) 0.4 mg. Bands at 397 and 374 cm⁻¹ in spectrum (b) arise from an impurity.

Figure 3. Far-infrared spectra of (a) realgar (As₄S₄) 2 mg, and (b) orpiment (As₂S₃) 2 mg.

Figure 4. Far-infrared spectra of (a) stibnite (Sb₂S₃) 2 mg, and (b) bismuthinite (Bi₂S₃) 2 mg.
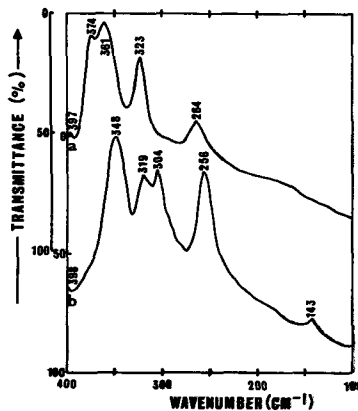
Figure 5. Far-infrared spectra of (a) chalcopyrite (CuFeS₂) 2 mg, and (b) stannite (Cu₂FeSnS₄) 2 mg.

spectrum include chalcocite (Cu₂S), troilite (FeS), millerite (NiS), covellite (CuS) and bornite (Cu₅FeS₄). Between these extremes are spectra exhibiting one/more broad bands, which, although often characteristic, might prove difficult to recognise in mixtures.

Some practical assessment of the value of infrared spectra for characterising sulphides was possible in the course of the present survey, since many of the minerals drawn from museum collections proved, as is not unusual, either not to correspond with their labels, or to contain significant proportions of other minerals. Examples of faulty labels and actual
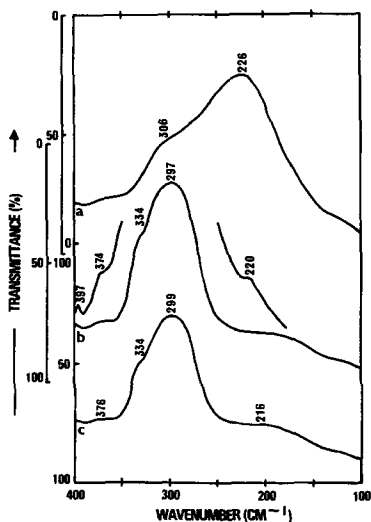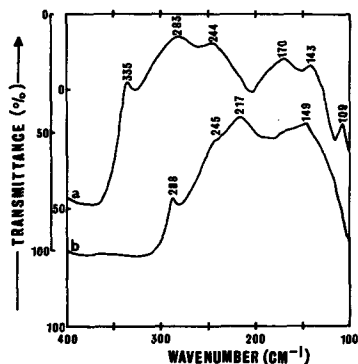
compositions include: realgar, actually crocoite; jamesonite, actually galena; marcasite, actually pyrite; argentite, actually mixed galena and sphalerite; argentite, principally stephanite; stephanite, principally argentite; tetrahedrite, actually chalcocite; greenockite, actually prehnite; stannite, actually arsenopyrite. All these mis-labellings were obvious from the spectra, where authentic spectra were available for comparison. In the spectra published here, small amounts of pyrite can be recognised in the tetrahedrite and boulangerite spectra (bands near 418 and 349 cm^{-1} in Figs 8 and 10a). Galena and sphalerite appear to contain two impurities in common, one giving sharp weak features at 373, 398, 600 and 630 cm^{-1} and the other slightly broader bands at 463 and 513 cm^{-1}, neither of/was which detected by X-ray diffraction.

Comparison of the spectra reproduced here with those previously published show a fair measure of agreement, although there are discrepancies. Data reported by Liese (1974) for proustite is consistent more with pyrargyrite, and his results for chalcocite and boulangerite do not agree well with ours. Some of the spectra by Povarennykh and coworkers obviously incorporate erroneous features of instrumental origin; for example, their spectra of minerals such as pyrrhotite and chalcocite that give featureless metal-like absorption all show a common sequence of bands at 370, 280 and 180 cm^{-1}, which must be of instrumental origin. Bands near these positions sometimes appear as additional bands in other of their spectra, and occasionally they fail to report bands noted by ourselves and others. As an example, our spectrum of realgar is essentially identical with that of Forneris (1969) and Whitfield (1971), but Povarennykh et al., (1971b) did not find the band at 194 cm^{-1}, whereas Povarennykh (1974) reports several additional bands between 250 and 300 cm^{-1}, but still none at 194 cm^{-1}. These discrepancies are probably of instrumental origin, but in other instances differences in spectra could reflect real differences in composition, structure or crystallinity, as is true for other mineral species.

In conclusion, it appears that infrared spectra in the region 400-100 cm^{-1} permit a rapid check on the purity and authenticity of sulphide minerals, except where metallic conductivity obliterates all vibrational features. Differences in sensitivity to impurities between X-ray diffraction and infrared absorption spectra justify the application of both techniques. Further research may show that spectra can reflect compositional and structural variations within sulphide species.
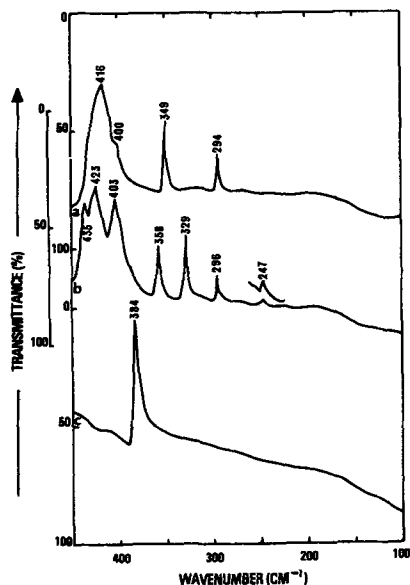

Figure 6. Far-infrared spectra of (a) pyrite (FeS$_2$) 0.4 mg, (b) marcasite (FeS$_2$) 0.4 mg, and (c) molybdenite (MoS$_2$) 2 mg. Molybdenite has also a weak absorption band at 467 cm^{-1}.

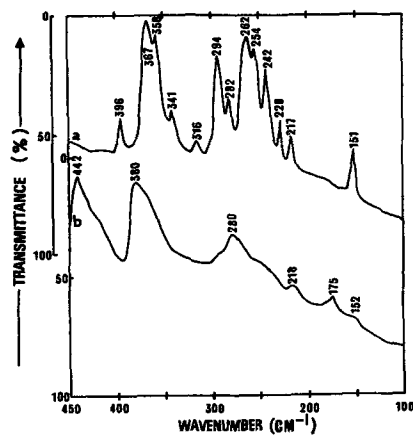Figure 7. Far-infrared spectra of (a) cobaltite (CoAsS) 2 mg, and (b) arsenopyrite (FeAsS) 2 mg.

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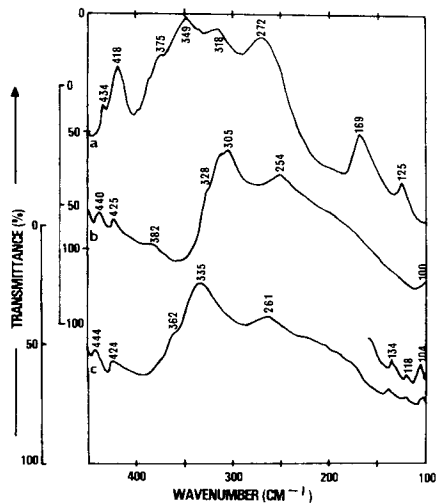
Figure 8. Far-infrared spectra of (a) tetrahedrite ($(Cu,Fe)_{12}Sb_4S_{13}$) 10 mg, (b) pyrargyrite (Ag_3SbS_3) 2 mg, and (c) proustite (Ag_3AsS_3) 2 mg. Bands at 418 and 349 cm^{-1} in spectrum (a) are from a pyrite impurity. Weak features near 425 and 440 cm^{-1} in spectra (b) and (c) are of instrumental origin.
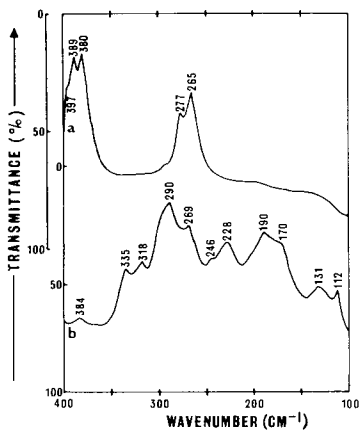

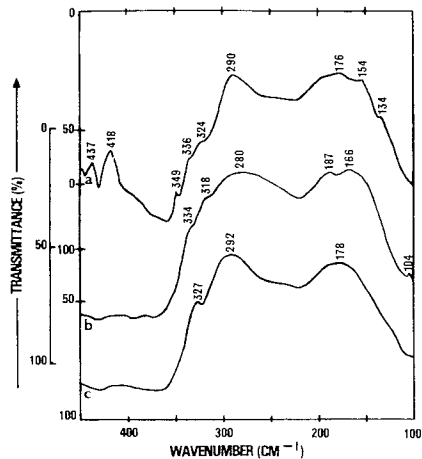Figure 9. Far-infrared spectra of (a) enargite (Cu_3AsS_4) 2 mg, and (b) bournonite (PbCuSbS$_3$) 2 mg.

Figure 10. Far-infrared spectra of (a) boulangerite ($Pb_5Sb_4S_{11}$) 2 mg, (b) jamesonite ($Pb_4Sb_6S_{13}$) 2 mg and (c) plagionite ($Pb_5Sb_8S_{17}$) 2 mg. Bands at 418 and 349 cm^{-1} in spectrum (a) are from a pyrite impurity.