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Application of FT-IR Spectroscopy for In Situ Studies of Sphalerite with Aqueous Solutions of Potassium Ethylxanthate and with Diethyldixanthogen

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ABSTRACT

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Fourier transform infrared spectroscopy has been used by the Bureau of Mines to study, in situ, the reaction of aqueous solutions of potassium ethylxanthate with copper-activated sphalerite. The use of a transmittance technique was possible for sphalerite because, besides being the reactive mineral surface, sphalerite is also an infrared-transparent material in the region where some of the characteristic vibrational bands of xanthates occur. Bands characteristic of copper(I) ethylxanthate were evident after 5 min of reaction between aqueous KEtX solutions and activated plates. The bands continued to grow as the reaction proceeded and were also present on dried surfaces after the reaction. Diethyldixanthogen dissociated on copper-activated surfaces, and bands characteristic of copper(I) ethylxanthate were detected on the surface of dried plates. No evidence for zinc(II) ethylxanthate formation with either unactivated or activated plates was obtained.

INTRODUCTION

In situ spectroelectrochemical methods are currently being used by the Bureau of Mines to study the reactions of thio collectors with sulfide minerals. Earlier work (Walker et al., 1984; Richardson et al., 1984; Richardson and Walker, 1985) used continuous monitoring of the solution phase with a diode-array ultraviolet-visible spectrophotometer, but complete, unambiguous characterization of solutes and/or surface products at a molecular level is difficult from electronic absorption spectra alone. Although several authors have employed vibrational spectroscopy to characterize surface products on sulfide minerals after reaction with thio collectors (Greenler, 1962; Poling and Leja,

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1963; Leja et al., 1963; Yamasaki and Usui, 1965; Coleman and Powell, 1966; Coleman et al., 1967; Kongolo et al., 1984), no in situ studies of the reactions have been reported, mainly owing to the lack of adequate instrumentation capable of compensating for the strong absorption of water in the infrared region. The high energy throughput, high signal-to-noise ratio, high sensitivity, and fast data collection and manipulation provided by Fourier transform infrared (FT-IR) spectrometers have largely overcome this problem. Several studies of reactions at the solid–aqueous-solution interface using FT-IR have been recently reported (Davidson et al., 1981; Wan et al., 1984; Bewick et al., 1984; Pons et al., 1984; Habib and Bockris, 1985; Datta et al., 1985), which have shown that FT-IR can be a powerful technique for in situ studies.

We are currently exploring the use of FT-IR for in situ studies of thio collectors–sulfide-mineral interactions. Preliminary experiments had indicated that vibrational spectra of aqueous solutions of potassium ethylxanthate (KEtX) compressed between two commercially available ZnS windows could be readily obtained by transmission (synthetic ZnS is a commonly used infrared-transparent material). Natural ZnS (sphalerite) plates exhibit strong absorption between 4800 cm^{-1} and 2500 cm^{-1}, associated with electronic transitions of Fe(II) (Marfunin et al., 1968; Platonov and Marfunin, 1968), but are transparent in the region where some of the characteristic vibrational bands of thio collectors occur (1300 cm^{-1} to 950 cm^{-1}). Therefore, it appeared feasible to use a simple transmission method to follow, in situ, the reactions of metal-activated sphalerite and aqueous KEtX solutions by FT-IR, where sphalerite was both the reacting mineral and the infrared-transparent material.

EXPERIMENTAL MATERIALS AND TECHNIQUES

All the reagents were reagent grade, and water was deionized (18 MΩ). Potassium ethylxanthate (Eastman) was recrystallized three times by dissolving the solid in acetone followed by reprecipitation with petroleum ether. The final product was washed several times with diethyl ether and again immediately prior to use to remove dixanthogen. Zinc(II) ethylxanthate was synthesized as described by Ikeda and Hagihara (1965). Copper(I) ethylxanthate was prepared by precipitation from a copper(II) sulfate solution. The yellow precipitate was washed several times with diethyl ether to remove the dixanthogen formed in the reaction.

To prepare diethyldixanthogen, stoichiometric quantities of KEtX and potassium peroxydisulfate were reacted in an aqueous solution. Centrifugation was used to recover the yellow, oily product from the reaction mixture. The oil was washed with water several times to remove any unreacted material, followed by centrifugation after each washing. The neat oil was used immediately.

A Nicolet 20SX FT-IR* spectrometer was used to collect infrared spectra. A

*Reference to specific trade names does not imply endorsement by the Bureau of Mines.

combination of a deuterium triglycine sulfate (DTGS) detector and a cesium iodide beamsplitter provided a frequency range from 5000 cm^{-1} to 225 cm^{-1}. The resolution was set at 2 cm^{-1}. The instrument was continuously purged with CO_2-free, dried air. For each spectrum, 100 interferograms were collected, coadded, and signal-averaged. The single-beam spectrum resulting from the Fourier transformation of the signal-averaged interferogram was then ratioed against a single-beam spectrum of the background.

Slices of sphalerite from Santander (Spain) were cut with a diamond saw and subsequently ground and polished with a microprocessor-controlled grinding machine to a final finish with 6-μm diamond paste. To remove any organic residues, the plates were thoroughly washed with acetone. Pale yellow plates (average size 1.5 by 1.5 cm, and 0.5 to 1 mm in thickness) showing transmittance values above 50% in the 1300 cm^{-1} to 900 cm^{-1} region were selected for the studies.

The plates were activated by immersion in 25 mL of $5 \times 10^{-3} M$ $CuSO_4 \cdot 5H_2O$ solution for 30 min, at a pH adjusted to 4.5 with NaOH or H_2SO_4. This pH was chosen to ensure that the predominant copper(II) species in solution was the aqua ion and not copper hydroxo species (Ralston and Healy, 1980a,b). After activation, the plates were removed from the solution, washed several times with water, and vacuum-dried.

In situ studies were performed by compressing a small drop of a freshly prepared KEtX solution ($1 \times 10^{-3} M$) between two sphalerite plates held in a demountable variable-pathlength cell.

RESULTS AND DISCUSSION

The vibrational spectra of KEtX in a KBr pellet and in aqueous solution between ZnS windows are compared in Fig. 1. The spectrum of an aqueous solution of KEtX has previously been reported by Poling and Leja (1963). The solution spectrum in Fig. 1b is similar to theirs, but the absorption peaks at 1040 cm^{-1} and at 1111 cm^{-1} reported by these authors were found at higher energies (1045 cm^{-1} and 1118 cm^{-1}, respectively) in the present work. Instead of the broad, less intense absorption centered at 1160 cm^{-1} they reported, two peaks at 1176 cm^{-1} and 1148 cm^{-1} can be seen in the spectrum on Fig. 1b. These differences may be due to sampling technique, resolution, instrument calibration, or concentration effects. The broader bands and fewer peaks observed in the solution spectrum, when compared to the spectrum of the solid, are typical of solution spectra and can be attributed to solute–solvent interactions and to the averaging of preferred molecular orientations in a solvent medium.

The characteristic spectrum of neat diethyldixanthogen smeared between KBr windows is shown in Fig. 2. Very weak absorption bands (not shown) at 529 cm^{-1} and 378 cm^{-1}, which are absent in the spectrum of solid KEtX,

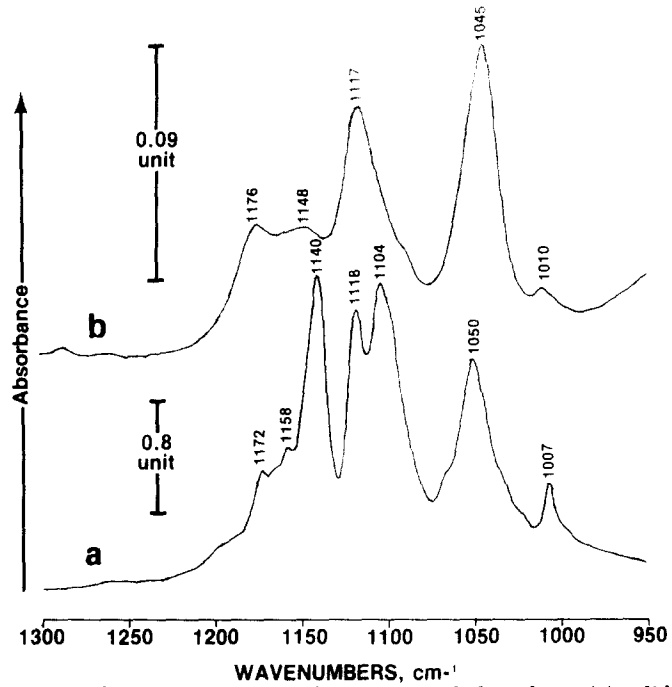

Fig. 1. Vibrational spectrum of potassium ethylxanthate: (a) solid in a KBr pellet; (b) aqueous solution between ZnS plates.

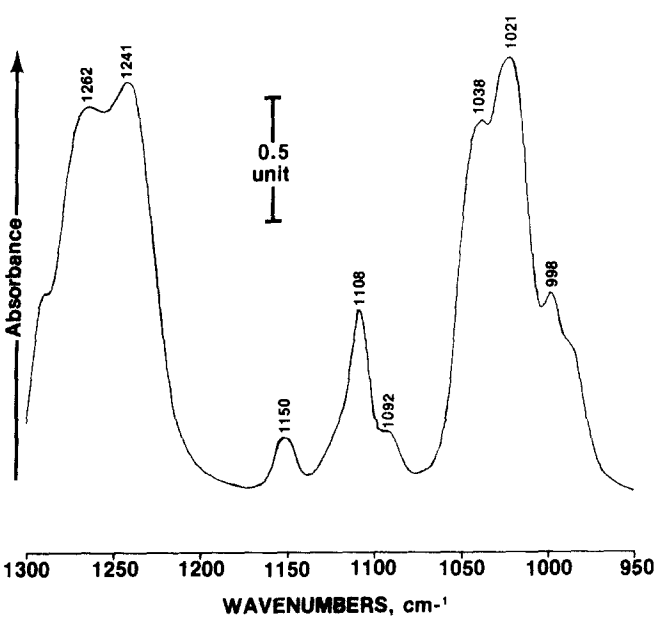

Fig. 2. Vibrational spectrum of diethyldixanthogen. Neat oil between KBr windows.

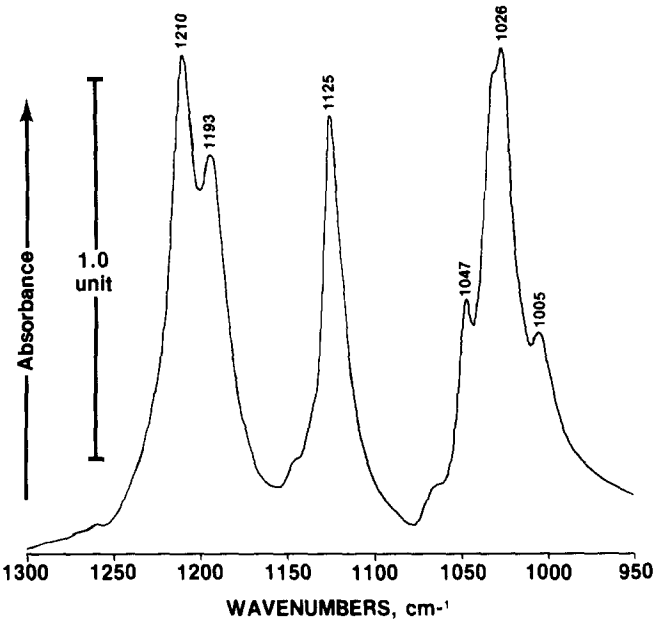

Fig. 3. Vibrational spectrum of zinc(II) ethylxanthate in a KBr pellet.

confirmed the presence of the disulfide group (S-S). Compounds containing a disulfide group are known to show stretching S-S bands in this region, as discussed by Nakamoto (1978).

The spectra of zinc(II) ethylxanthate and of copper(I) ethylxanthate are shown in Figs. 3 and 4, respectively. In earlier work, there was discrepancy between Shankaranarayana and Patel (1961) and Little et al. (1961) in the assignment of bands associated with C-S and C-O vibrations in metal xanthato complexes. In later research, bands in the vicinity of 1200 cm^{-1} were associated with predominantly C-O vibrations and bands in the vicinity of 1020 cm^{-1} with predominantly C-S vibrations (Hunt et al., 1971). These vibrations are strongly coupled and, therefore, assignments to purely C-S or C-O vibrations are not possible (see Coucouvanis, 1979, and pertinent references therein). Weaker bands between 500 cm^{-1} and 300 cm^{-1} (not shown) are associated with M-S stretchings (Hunt et al., 1971; Nakamoto, 1978) in metal xanthato complexes. Unfortunately, the very strong absorption of ZnS below 800 cm^{-1} prevented the use of these bands to directly confirm the presence of any metal-sulfur bond formation on the surface.

When unactivated sphalerite plates (or ZnS windows) were used, no changes in the spectrum of an aqueous KEtX solution were observed. Nor was there any indication of xanthate-related bands when plates that had been in contact with KEtX solution were washed and dried. If ZnSe windows were used instead

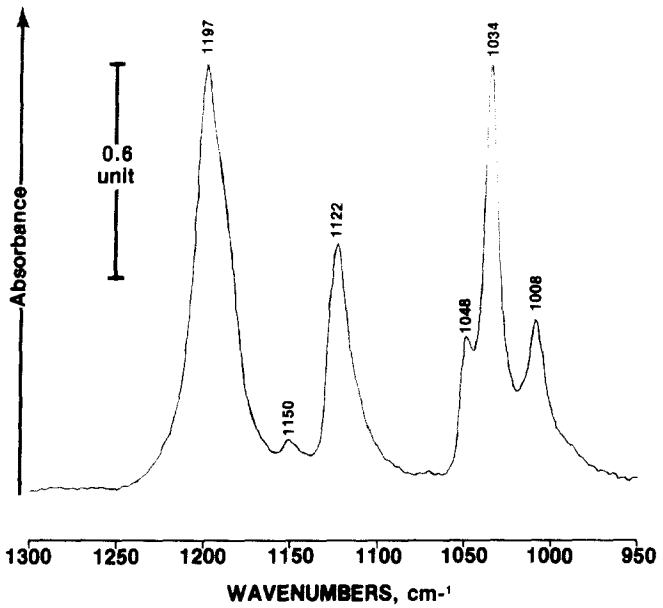

Fig. 4. Vibrational spectrum of copper(I) ethylxanthate in a KBr pellet.

of ZnS, xanthate-related bands could be observed after washing and drying, indicating that xanthate adsorbed on ZnSe without activation.

Experiments in which activated sphalerite plates were immersed in the xanthate solution, washed with water, and dried gave the spectrum shown in Fig. 5, where the peak frequencies are roughly the same as for copper(I) ethylxanthate in a KBr pellet (Fig. 4). Activated sphalerite plates were checked, prior to xanthation, for the presence of characteristic sulfate bands (1200 to 900 cm^{-1}) that would indicate the presence of a residual film from the activating copper(II) sulfate solution. This copper(II) sulfate could react with KEtX to form a copper(I) ethylxanthate precipitate on the surface. Neither FT-IR nor X-ray photoelectron spectroscopy (XPS) measurements gave any indication for the presence of sulfate groups on the surface. Based on XPS, copper on the surface was present as a copper(I) species. Perry et al. (1984) observed the presence of Cu(I) on activated sphalerite and suggested that, after activation, the surface becomes chalcocite-like. It is interesting to point out that before activation the sphalerite surface was insulating, as evidenced by the large charging effect, but the activated surface was conducting, indicating that the surface resembled a conducting copper(I) sulfide. Ralston and Healy (1980a) have presented evidence from light irradiation experiments that the band gap of ZnS narrows upon activation with copper(II).

The in situ spectra during reaction of KEtX with copper-activated sphalerite are shown in Fig. 6. In the spectrum recorded after 5 min of placing the ethylxanthate solution between the activated plates, the presence of EtX^-

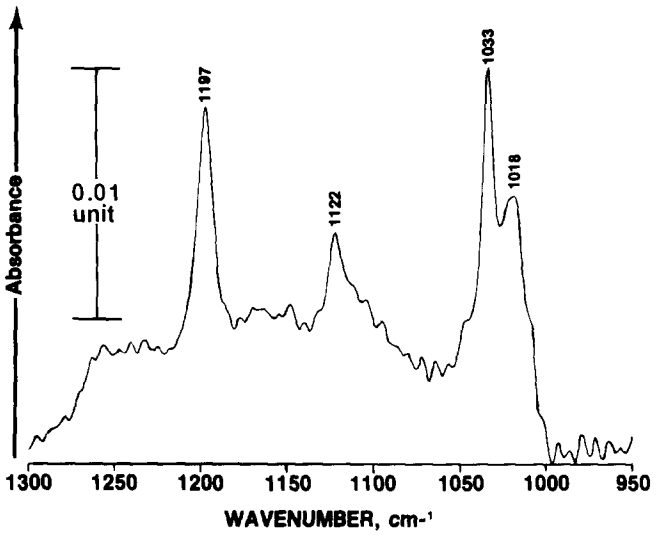

Fig. 5. Vibrational spectrum of copper-activated sphalerite plate after in contact with an aqueous solution of potassium ethylxanthate. Plate was washed and dried.

anions in solution was indicated by bands at ca. 1045 cm^{-1} and 1117 cm^{-1} (Fig. 1b). The appearance of new bands, one between 1090 cm^{-1} and 1200 cm^{-1} and another ca. 1034 cm^{-1} suggested that a metal xanthate was being formed. These two bands, which are characteristic of copper(I) ethylxanthate (Fig. 4), continued to grow in intensity as the reaction proceeded through the 45-min period while the intensities of the bands associated with EtX^- anions in solution decreased. A small absorption between 1200 cm^{-1} and 1300 cm^{-1} suggested the presence of small quantities of diethyldixanthogen, which was likely to form from reaction with oxygen (see below).

After 45 min, the plates were separated, washed, and dried. The spectrum of a dried plate (Fig. 7) again showed that the peak frequencies were those of copper(I) xanthate in a KBr pellet (Fig. 4). Although the peak frequencies in the spectra of dried samples (Figs. 5 and 7) matched those of bulk copper(I) ethylxanthate, the relative intensities of the bands at 1048 cm^{-1} and 1018 cm^{-1} had changed from almost equally intense bands in the bulk material to a relatively more intense 1018 cm^{-1} band in the spectra of dried plates. Changes in relative intensities are indicative of orientation of the adsorbed molecule in relation to the surface.

The present work has confirmed earlier work by Yamasaki and Usui (1965) and Coleman et al. (1967) in which formation of copper xanthate was also detected on sphalerite surfaces in samples removed from aqueous solutions and dried prior to recording spectra.

A smear of neat diethyldixanthogen compressed between two ZnS windows or plates of unactivated sphalerite gave the same spectrum as the one obtained

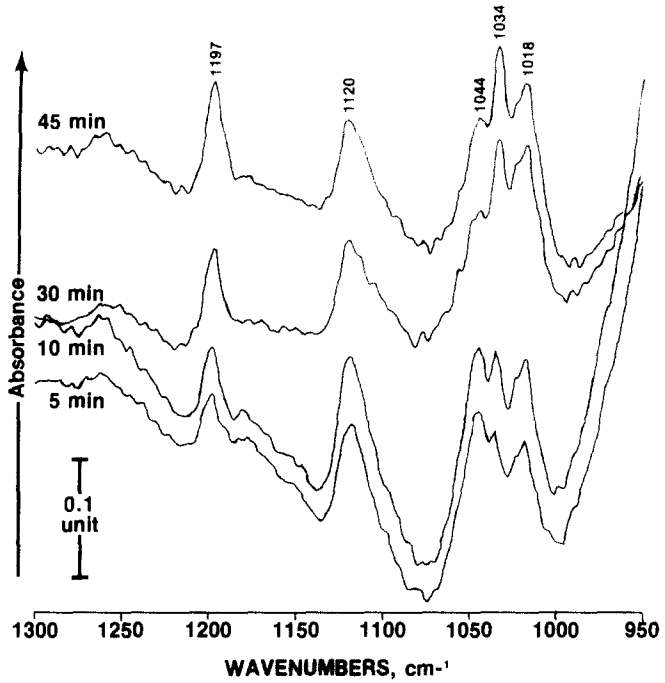

Fig. 6. Vibrational spectra during reaction of aqueous solution of potassium ethylxanthate with copper-activated sphalerite.

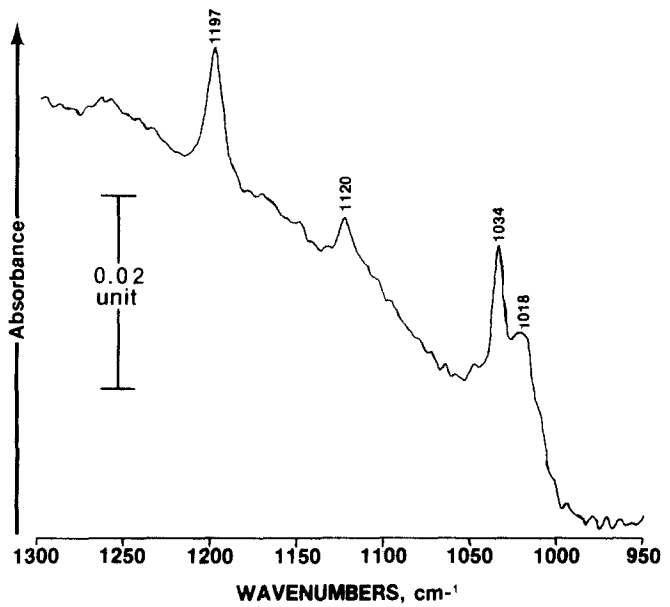

Fig. 7. Vibrational spectrum of a copper-activated sphalerite plate after undergoing in situ reaction.

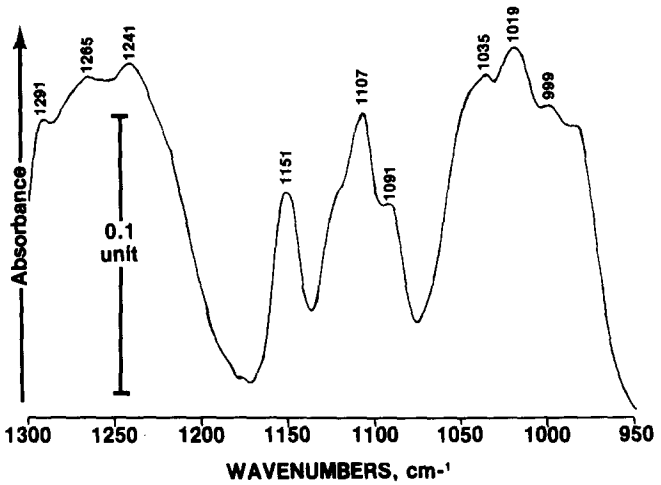

Fig. 8. Vibrational spectrum of a smear of neat diethyldixanthogen between two copper-activated sphalerite plates (after 5 min).

with KBr windows (Fig. 2), suggesting that no reaction occurred with ZnS. The spectrum shown in Fig. 8 was taken 5 min after the dixanthogen was pressed between the activated sphalerite plates. A slight shift towards lower energy and broading of the peaks between 1040 and 1015 cm^{-1} was observed with the activated plates, but no further substantial changes were observed throughout a 45-min period. After the plates were separated and washed with diethyl ether, the spectrum in Fig. 9 revealed that copper(I) ethylxanthate was present, as indicated by the weak bands at 1197 cm^{-1}, 1122 cm^{-1}, and 1035 cm^{-1}. Bands above 1200 cm^{-1} and at 1144 cm^{-1}, 1107 cm^{-1}, and 1022 cm^{-1} can be associated with the presence of the dixanthogen. After extensive rinsing with diethyl ether, no dixanthogen bands were observed, but copper(I) ethylxanthate peaks remained. Leja et al. (1963) and Poling and Leja (1963) reported that diethyldixanthogen dissociates upon adsorption onto copper films and identified the chemisorbed species as copper(I) ethylxanthate. This reaction occurred on both nonoxidized and oxidized films and on copper films which were previously sulfidized.

The reactivity of copper-activated sphalerite surfaces is dominated more by the Cu(I) sulfide-like surface than by a ZnS surface, as shown by the reaction with KEtX and with diethyldixanthogen. Stabilization of copper(I) by saturated alkyl xanthato ligands is well known (Coucouvanis, 1970, 1979; Eisenberg, 1970); therefore, the formation of copper(I) ethylxanthate rather than a Cu(II)-xanthato species is highly favored. The structure of copper(I) ethylxanthate is unknown because of the difficulty in obtaining crystals adequate for crystallographic determinations. This difficulty is mainly due to the lack of a suitable solvent for recrystallization; for example, pyridine 'dissolves' copper(I) ethylxanthate but results in decomposition to monoclinic γ-sulfur

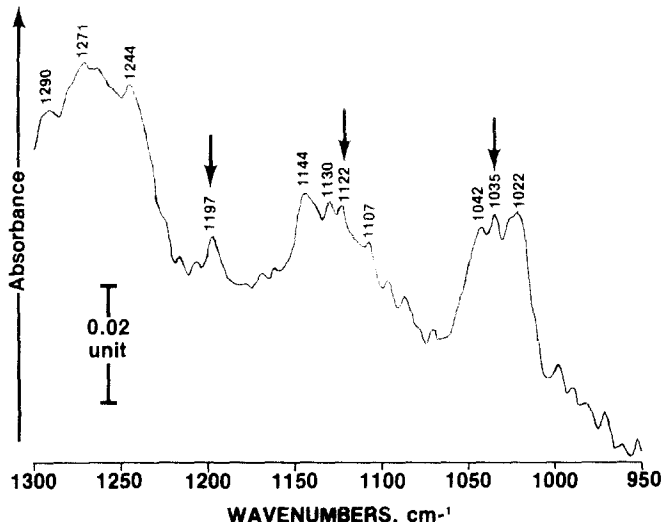

Fig. 9. Vibrational spectrum of a copper-activated sphalerite plate after 45-min contact with a smear of neat diethyldixanthogen. The plate was washed with diethyl ether. Arrows indicate characteristic vibrational bands of copper(I) ethylxanthate.

(Watanabe, 1974). The redox reaction of KEtX with a copper(II) salt in solution to produce copper(I) ethylxanthate and diethyldixanthogen is well known (Little and Leja, 1957; Coucouvanis, 1970; Rao, 1971). It is possible that the formation of the copper(I) ethylxanthate on the surface involves direct coordination with copper(I), without an accompanying redox reaction. Any dixanthogen observed in the reaction of KEtX with copper-activated sphalerite is likely to proceed from reaction with oxygen. The relatively large amounts of dixanthogen found by Coleman et al. (1967) on copper-activated, xanthated sphalerite surfaces and in nonaqueous extracts from these surfaces was probably caused by exposure to oxygen during their 2-h xanthation period rather than by reaction with the activated surface.

CONCLUSION

FT-IR has been used to study, in situ, the reaction of aqueous solutions of potassium ethylxanthate with copper-activated sphalerite. The use of a transmittance technique was possible for sphalerite because, besides being the reactive mineral surface, it is also an infrared-transparent material in the region where some of the characteristic vibrational bands of xanthates occur.

No evidence for a residual film of the activating copper(II) solution was found by FT-IR or by XPS measurements. The latter established that copper was present as copper(I) and that activated surfaces resemble more a copper(I) sulfide than zinc sulfide. During in situ reaction of copper-activated sphalerite with aqueous potassium xanthate solutions, the formation and continuous

growth of copper(I) ethylxanthate bands were observed. These bands were also present on dried plates.

When diethyldixanthogen was reacted with copper-activated plates, dissociation of the dixanthogen occurred, as inferred from the presence of copper(I)-ethylxanthate bands.

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