

## INFRARED SPECTROSCOPY FOR IN-SITU CHARACTERIZATION OF SURFACE REACTIONS

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**Abstract.** Infrared spectroscopy has been one of the most useful experimental techniques for the analysis of surface reactions in flotation systems, including surface alteration and surfactant adsorption reactions. With the advent of Fourier transform infrared (FTIR) spectrometers, many low-energy throughput IR experimental techniques previously unused by flotation researchers have come into greater use. In particular, internal reflection spectroscopy (IRS) is the most often used technique for in-situ studies. To date, three IRS methods have been used for in-situ measurements. These techniques are evaluated for use in characterization of surface reactions in flotation systems. The method using mineral crystals as reactive internal reflection elements (IRE) is of particular interest because it allows surfactant adsorption densities to be calculated directly from in-situ spectral data in real time.

Application of in-situ FTIR/IRS with reactive internal reflection elements will be demonstrated for collector adsorption reactions in each of the major flotation systems. The alumina ( $\text{Al}_2\text{O}_3$ )/sodium dodecylsulfate system is used as an example for insoluble oxide/silicate flotation, while the fluorite ( $\text{CaF}_2$ )/oleate system serves as a paradigm for semisoluble salt flotation. For sulfide flotation, sphalerite (ZnS) is used as the reactive IRE with potassium amylxanthate and potassium ethylxanthate as collectors. In the case of soluble salt flotation, sylvite (KCl) is used as the IRE with n-octylamine as collector. Finally, the use of reactive IREs in the near-IR spectral region and in spectroelectrochemical research is discussed.

### INTRODUCTION

Infrared spectroscopy has been one of the most useful experimental techniques for the analysis of surface reactions in flotation systems. The utility of ex-situ transmission spectroscopy was first demonstrated by French et al. (1954) for flotation systems, and subsequently by many other flotation chemists in following decades (Eyring and Wadsworth, 1956; Poling and Leja, 1963; Fuerstenau and Miller, 1967; Lovell, Goold, and Finkelstein, 1974). These ex-situ measurements have given a wealth of information on many flotation systems.

However, ex-situ IR measurements have always been subject to the criticism that surface states may be altered during sample preparation (Ataman and Mark, 1977). In fact, any ex-situ methodology, especially the high-vacuum techniques such as Auger and x-ray photoelectron spectroscopy, suffer from the same criticism.

With the advent of Fourier transform infrared (FTIR) spectrometers, many low-energy throughput IR experimental techniques previously unused by flotation researchers have come into greater use. In particular, internal reflection spectroscopy (IRS) allows for in-situ measurements and as such has become the method of choice for infrared analysis of flotation systems. IRS involves the internal reflection of light through a crystal termed an internal reflection element (IRE). This is shown schematically in Figure 1 for a ray of light undergoing multiple internal reflections in an IRE. As is shown in Figure 1, a small portion of the light actually samples the IRE/solution interface. The depth of penetration into the rare medium and the number of internal reflections within the IRE are determined by the optical constants of the system and can be readily calculated (Harrick, 1979).

There are several reasons why in-situ IRS has been and will continue to be of such significance in flotation research. First, it confirms many conclusions based on previous ex-situ measurements.

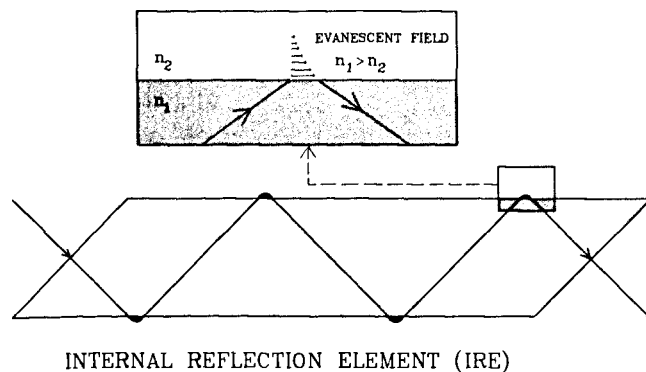


Figure 1. Schematic of light undergoing multiple internal reflections in an IRE, where  $n_1$  and  $n_2$  are the refractive indices of the IRE and sample.

Second, the short sampling depth (usually a fraction of the wavelength) minimizes the strong infrared absorbance of water, a condition which had limited the use of in-situ IR spectroscopy. Finally, from the multiple reflections at the IRE/sample interface, sensitivity is enhanced greatly over typical transmission experiments. The sensitivity of the IRS technique is evidenced by the calculation of adsorption densities from spectral data at very dilute equilibrium collector concentrations (Kellar, Cross, and Miller, 1989). Since the 1983 review of IRS applications in flotation by Strojek et al., several new developments in in-situ internal reflection spectroscopy have occurred. Three approaches have been used to study flotation systems in-situ by IRS as discussed in the following section.

#### EXPERIMENTAL TECHNIQUES

##### Method 1. Particulate Suspension with Inert IRE

By far the most common and easiest application of in-situ IRS analysis involves pressing and dewatering a particulate suspension against an "inert" IRE such as germanium. Table 1 lists the various applications of this method. As can be seen from Table 1, the mineral particles studied have always been sulfide minerals. The reason for the absence of studies involving other mineral systems (e.g., oxides and semisoluble salts) is not immediately clear. However, IRS theory predicts that the electric field of the IRS beam determines the strength of the sample IR signal (Hansen, 1973; Harrick, 1979). Apparently, the high refractive index of sulfides ( $n > 2$ ) gives rise to intense electrical fields which are ideal for this method of study.

The strength of Method 1 is that surface reactions can be studied in-situ for many particulate suspensions. Another advantage of the method is that scattering from the particles, common to many techniques such as diffuse reflectance, is absent due to the short pathlengths used. Of particular interest is the possibility of studying mineral particles in-situ under controlled potential (Leppinen, Basilio, and Yoon, 1988b). Such spectro-electrochemical experiments should help elucidate many of the unresolved questions concerning mechanisms involved in sulfide mineral flotation.

However, this method is not without its experimental problems. Since the sampling depth is short, the particulates must be in intimate contact with the "inert" IRE. Initial researchers reportedly had difficulty in achieving adequate contact with the IRE (Strojek, Mielczarski, and Nowak, 1983). Reproducible contact between experiments is very difficult, and consequently only qualitative measurements are possible. Also, collector contamination of the "inert" IRE cannot be ignored. Surface contamination can be significant, especially at the surfactant concentrations commonly used (see Table 1). The reactivity of an "inert" IRE is demonstrated by the in-situ spectrum of the residual contamination from a  $5 \times 10^{-3}$  M potassium amylxanthate solution on an "inert" germanium IRE shown in Figure 2. The IR absorption bands from this contamination of the IRE could easily be attributed to collector species adsorbed by mineral particles in the suspension adjacent the IRE.

All the IRS studies shown in Table 1 used an IRE in the shape of a flat-plate prism. This geometry readily allows for dewatering of the mineral particle suspension. However, FTIR spectrometers typically have a circular beam, and focussing onto the end of the flat-plate IRE geometry can be

Table 1.  
Flotation Studies Using In-Situ FTIR/IRS,  
Method 1. Particulate Suspension with Inert IRE

Mineral(s)	Collector(s)	Concentration	Reference
Marcasite	Ethylxanthate Dixanthogen Monothiocarbonate	$5 \times 10^{-5}$ - $1.5 \times 10^{-4}$ M	Mielczarski, 1986a
Galena	Ethylxanthate Dithiophosphate	not reported	Leppinen, 1987
Chalcocite Chalcopyrite Pyrite	Thionocarbamate	$1 \times 10^{-4}$ - $1 \times 10^{-3}$ M	Leppinen, Basilio, and Yoon, 1988a
Sphalerite	Ethylxanthate	$5.2 \times 10^{-5}$ M	Mielczarski, 1986b
Chalcocite Chalcopyrite Pyrite Galena	Ethylxanthate	$1 \times 10^{-3}$ - $1 \times 10^{-4}$ M	Leppinen, Basilio, and Yoon, 1988b

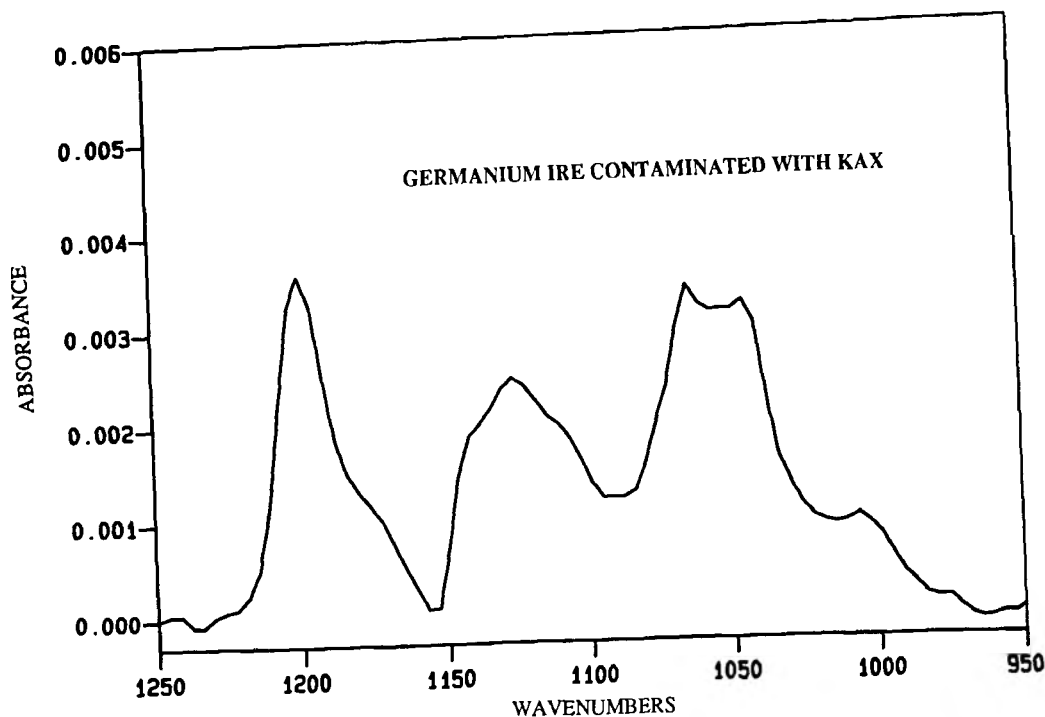


Figure 2. In-situ FTIR/IRS spectrum of species adsorbed from an amyloxanthate ( $5 \times 10^{-3}$  M) solution at the surface of an inert germanium IRE.

cumbersome. In recent studies, cylindrical IREs using cassegranian focussing optics which optimize energy throughput for the circular FTIR beam have become more widely used. This IRS accessory, called the CIRCLE<sup>®</sup> cell, has been used to investigate mineral particle suspensions in-situ (Tejedor-Tejedor and Anderson, 1987; Walker and Weissenborn, 1989). Because the IRE is completely enveloped by the sample, suspensions can be used with lower solid/liquid ratios than those reported in Table 1. Nevertheless, possible collector contamination of the "inert" IRE must still be taken into consideration.

Method 2. Coating of Inert IRE

Another method of studying adsorption reactions in-situ involves coating, usually by vacuum deposition, of the desired mineral onto an inert IRE. The coated IRE can then be placed in solution, and surfactant adsorption occurs directly onto the exposed mineral surface. Shown in Table 2 are flotation systems where Method 2 has been utilized. Nowhere is it mentioned how the IREs were reconditioned between experiments. The aforementioned problem of Method 1, adequate contact between mineral and IRE, is alleviated by this technique. Re-

Table 2.  
Flotation Studies Using In-Situ FTIR/IRS,  
Method 2. Coating of Inert IRE.

Mineral	Collector	Concentration	Reference
Fluorite	Sodium Dodecylsulfate	$1 \times 10^{-5}$ - $5 \times 10^{-3}$ M	Mielczarski, Nowak, and Strojek, 1983
Cassiterite	Styrene Phosphonic Acid	$2.7 \times 10^{-4}$ - $1.6 \times 10^{-3}$ M	Kuys and Roberts, 1987

producibile mineral film thickness and coherency have limited this approach to only semiquantitative work. Given the tedious nature of coating a mineral film of appropriate composition and crystal structure onto the inert IRE, this approach has been used less often than Method 1.

### Method 3. Reactive Internal Reflection Elements

During the past several years, researchers have demonstrated the utility of fabricating the desired substrate into a reactive IRE and directly studying surface reactions in-situ at the IRE surface (Sperline, Muralidharan, and Freiser, 1987; Parry and Harris, 1988). Miller and Kellar (1988) used this approach to demonstrate the quantitative analysis of collector adsorption reactions for several flotation systems. It was shown that the adsorption density, reaction kinetics, and orientation of collectors at the surface of mineral IREs can be followed in-situ and in real time. Furthermore, it was shown for the first time that a natural mineral crystal (fluorapatite) could be prepared as a usable IRE on which adsorbed collector could be examined from its FTIR spectrum. Of course, Method 3 is limited to systems where IR transparent IRE crystals are available and appropriate care must be taken to avoid and/or correct for any impurity contamination from the system. Fortunately, the reactive IRE crystals are easily cleaned and restored for repeated use.

### REACTIVE INTERNAL REFLECTION ELEMENTS

The use of reactive internal reflection elements can provide considerable information from real-time spectral data. As shown in Figure 3, this method allows direct calculation of collector **adsorption density** and thus determination of adsorption kinetics as well as the corresponding equilibrium adsorption isotherm. Also, it is possible to determine, by frequency shifts or the appearance/disappearance of absorbance bands, the **adsorption state**, i.e., whether the collector is physically or chemically bonded at the surface. Finally, the **orientation** of adsorbed species can be deduced by comparing the spectra obtained with different states of polarized light. Generally, Methods 1 and 2 can only provide information regarding the state of the adsorbed species and thus are of limited utility.

#### Adsorption Density

In 1987, Sperline, Muralidharan, and Freiser calculated from in-situ spectral data the adsorption density,  $\Gamma$  (mol/cm<sup>2</sup>), of a pyridinium surfactant onto a zinc selenide cylindrical IRE. In this case, the effective number of internal reflections had to be determined by a calibration procedure.

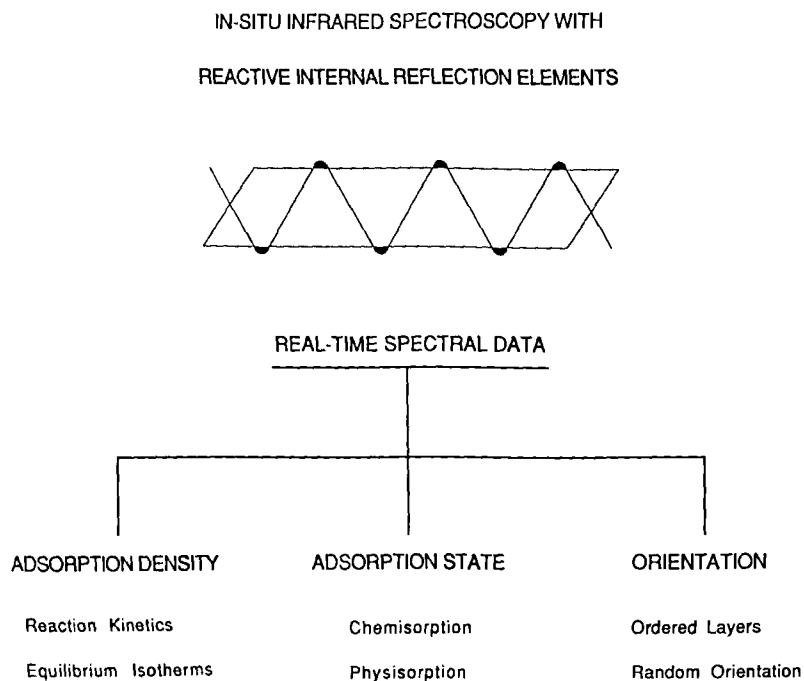


Figure 3. Utility of FTIR Internal Reflection Spectroscopy (IRS) with reactive internal reflection elements (IRE) for the analysis of surface reactions.

Subsequently, Miller and Kellar (1988) used flat-plate prisms of fluorite and sapphire (no calibration necessary) to calculate collector adsorption densities according to the following equation:

$$\Gamma = \left( \frac{A}{l/t \cot \theta} - \epsilon C_b d_e \right) / 1000 \epsilon \left( \frac{2d_e}{d_p} \right) \quad (1)$$

where  $A$  = integrated absorbance ( $\text{cm}^{-1}$ )  
 $l$  = IRE length  
 $t$  = IRE thickness  
 $\epsilon$  = molar absorptivity of surfactant ( $l/(\text{cm}^2 \cdot \text{mol})$ )  
 $C_b$  = surfactant bulk concentration ( $\text{mol}/l$ )  
 $d_p$  = depth of penetration  
 $d_e$  = effective depth.

The terms  $d_e$  and  $d_p$  are functions of the optical constants of the system and can be determined without difficulty (Harrick, 1979). The absorbance,  $A$ , for the adsorption density calculation is generally obtained by integration of the aliphatic region of the infrared spectrum ( $3,000$ - $2,800 \text{ cm}^{-1}$ ). Other experimental details for the calculation of adsorption densities are given elsewhere (Kellar, Cross, and Miller, 1989).

#### Orientation

Haller and Rice (1970) demonstrated the possibility of determining the orientation of an adsorbed layer on an IRE. Using the strong IR absorbance band assigned to the asymmetric  $\text{CH}_2$  stretching vibration ( $2925 \text{ cm}^{-1}$ ), Haller and Rice defined two limiting conditions: vertical orientation of the surfactant on the IRE ( $\text{CH}_2$  planes parallel to the surface) and completely random orientation of the  $\text{CH}_2$  planes with respect to the IRE. The theoretical absorbance ratio using polarized light ( $A_{\perp}$  (perpendicular) and  $A_{\parallel}$  (parallel)) can be calculated for the two states of polarization from the optical constants of a specific system. This theoretical  $A_{\perp}/A_{\parallel}$  ratio, termed the dichroic ratio, can then be compared to the experimental  $A_{\perp}/A_{\parallel}$  ratio determined spectroscopically and the extent of ordering of the adsorbed state inferred.

$$\text{Dichroic Ratio} = \frac{A_{\perp}}{A_{\parallel}} \quad (2)$$

where the theoretical absorbances are defined in terms of the electric field vectors ( $E_o$ ) in the three spatial directions  $x$ ,  $y$ , and  $z$ .

Dichroic ratio for vertical orientation with  $\text{CH}_2$  planes parallel to the surface

$$\frac{A_{\perp}}{A_{\parallel}} = \frac{E_{y_o}^2}{E_{x_o}^2} \quad (3)$$

Dichroic ratio for random orientation with  $\text{CH}_2$  planes random to the surface

$$\frac{A_{\perp}}{A_{\parallel}} = \frac{E_{y_o}^2}{E_{x_o}^2 + E_{z_o}^2} \quad (4)$$

In this paper, the in-situ FTIR/IRS technique using reactive IREs (Method 3) has been applied to each of the major flotation systems. The alumina/sodium dodecylsulfate (SDS) system is used as an example of insoluble oxide/silicate flotation, while the fluorite/oleate system serves as an illustration of semisoluble salt flotation. For sulfide flotation, sphalerite is used as the reactive IRE with potassium amylxanthate (KAX) and potassium ethylxanthate (KEX) as collectors. In the case of soluble salt flotation, sylvite is used as the IRE with  $n$ -octylamine as collector. Finally, the use of reactive IREs in the near-IR spectral region and in spectroelectrochemical research is discussed.

#### Alumina/SDS

The alumina/SDS system has been used frequently as a model insoluble oxide/silicate flotation system for the study of collector adsorption reactions (Modi and Fuerstenau, 1960; Yoon and Salman, 1976; Chandar, Somasundaran, and Turro, 1987). This system is useful for illustrating the role of coulombic forces in adsorption processes. It is generally believed that the SDS species aggregate on the surface in vertically oriented monolayer patches called "hemimicelles," although recent thermodynamic calculations indicate that the aggregation event could lead to vertical bilayers called "admicelles" (Yeskie and Harwell, 1988; Wu et al., 1989). Several in-situ spectroscopic techniques have been used to study this system (Chandar, Somasundaran, and Turro, 1987; Miller and Kellar, 1988; Somasundaran et al., 1989). Most of these techniques rely on a tracer molecule to give information concerning its surface surroundings, from which the behavior of the adsorbed collector species may be inferred. The internal reflection FTIR technique used by Miller and Kellar (1988), on the other hand, directly examined the spectral characteristics of the adsorbed collector in its surface state. These authors demonstrated that the adsorption density and orientation of SDS on alumina can be determined in-situ. In this section, additional in-situ internal reflection spectroscopic data will be given for the alumina/SDS system in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  and compared with previous results reported in the literature.

From the in-situ FTIR/IRS spectral data similar to those shown in Figure 4, the SDS adsorption densities were calculated using Equation (1) and are compared in Table 3 to the adsorption densities measured on alumina powder by a solution depletion experimental procedure (Chandar, Somasundaran, and Turro, 1987). It can be seen that the results from these drastically different experimental techniques agree quite well at what is presumed to be equivalent monolayer coverage. One interesting point which is revealed by these FTIR/IRS experiments is the agreement between the adsorption density of SDS by alumina as determined in  $\text{H}_2\text{O}$  and in  $\text{D}_2\text{O}$ , thereby adding credibility to previous results obtained with  $\text{D}_2\text{O}$  as solvent (Miller and Kellar, 1988). Deuterium oxide was used in previous investigations (Miller and Kellar, 1988) because it has no IR absorption bands in the aliphatic C-H stretching region ( $3000$ - $2800 \text{ cm}^{-1}$ ). However, in order to analyze the IRS absorbance spectra in  $\text{H}_2\text{O}$  and cal-

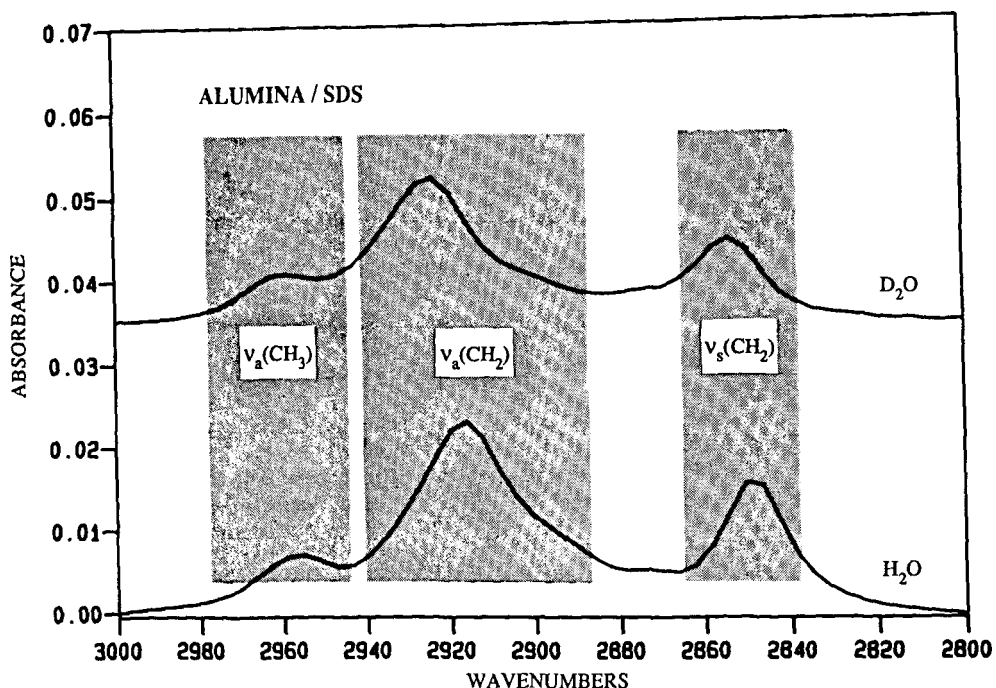


Figure 4. In-situ FTIR/IRS spectra of SDS adsorbed from H<sub>2</sub>O and D<sub>2</sub>O solutions at the surface of an alumina IRE.

Table 3.

Adsorption Density of SDS by Alumina at pH 6.5 (Chandar et al., 1987) and pH 7.3 (Miller and Kellar, 1988; present work)

SDS Equilibrium Concentration (M)	SDS Adsorption Density (mol/cm <sup>2</sup> )		
	Chandar et al. 1987	In-Situ IRS	
		H <sub>2</sub> O	D <sub>2</sub> O (Miller and Kellar, 1988)
1x10 <sup>-3</sup>	6.7x10 <sup>-10</sup>	4.5x10 <sup>-10</sup>	4.4x10 <sup>-10</sup>
4x10 <sup>-3</sup>	6.7x10 <sup>-10</sup>	--	5.3x10 <sup>-10</sup>

calculate adsorption densities, the strong IR absorption by H<sub>2</sub>O must be taken into consideration as was done for the data presented in Table 3 and Figure 5. This analysis is detailed in a forthcoming paper (Cross, Kellar, and Miller, 1989).

Using polarized light and calculated dichroic ratios, Miller and Kellar (1988) studied the orientation of SDS on alumina. Table 4 shows theoretical and in-situ experimental  $A_{\perp}/A_{\parallel}$  ratios for an adsorbed SDS film. It can be seen from the dichroic ratios reported in Table 4 that the adsorbed SDS is mostly random in orientation to the alumina IRE. This was the first attempt to determine in-situ the orientation of a self-assembled monolayer adsorbed

Table 4.

Orientation of SDS on Al<sub>2</sub>O<sub>3</sub> at pH 7.3 as Established by Dichroic Ratios According to Internal Reflection Theory

Theoretical	
Vertical Orientation	$A_{\perp}/A_{\parallel} = 4.85$
Random Orientation	$A_{\perp}/A_{\parallel} = 0.82$
Experimental	
Concentration of SDS = 1.0x10 <sup>-3</sup> M	$A_{\perp}/A_{\parallel} = 1.42$

from an aqueous solvent. Most prior IRS orientation studies have used monolayers deposited from organic solvents and examined ex-situ. While it has been found that the monolayers formed from these nonaqueous solutions were vertically oriented with CH<sub>2</sub> planes parallel to the IRE surface (Maoz and Sagiv, 1984; Tillman et al., 1988), it appears from the results presented in Table 4 that the in-situ adsorption state of SDS at the surface of alumina (adsorption from the aqueous phase) is not particularly ordered. This finding continues to receive attention in our research program at the University of Utah.

Following the determination of the equilibrium adsorption isotherm, the kinetics of the SDS adsorption process at the alumina surface were ex-

mined and then compared with the time dependence of the hydrophobic character of the alumina surface as measured by contact-angle goniometry. Figure 5 displays this comparison. It can be seen that, while the adsorption density of SDS increases linearly for the first six hours, followed by a more gradual rise thereafter, the contact angle increases rapidly to 75° after two hours then decreases significantly, achieving its equilibrium value of about 30° after approximately six hours. This is interpreted as indicating that, after two hours, the randomly adsorbed SDS (approximately equivalent to a monolayer) has maximum exposure of the dodecyl groups and that upon further adsorption a tail-tail configuration similar to an "admicelle" is established (again in random orientation) and the hydrophobicity of the surface reduced.

Fluorite/Oleate

Because of its large useful transmission range (33,000-1,100  $\text{cm}^{-1}$ ), fluorite ( $\text{CaF}_2$ ) is an ideal substrate for in-situ FTIR/IRS study. It is well known that the semisoluble salt minerals (including fluorite) tend to form surface and/or bulk precipitates of the collector salt. Such surface precipitation leads to multilayer formation, large adsorption densities in relation to most oxide and sulfide systems, and a corresponding large IR absorbance. However, it should be noted that, even for a large IR absorbance from adsorbed collector species (circa 0.02 absorbance units), the absorbance is still typically two orders of magnitude smaller than the absorbance due to the solvent ( $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ ). As expected, the in-situ spectra of surface-precipitated calcium oleate has been found to be

quite similar to the ex-situ spectra of bulk precipitated calcium oleate (Miller and Kellar, 1988).

Of greater significance, however, is the in-situ spectra of the chemisorbed state at what appears to be equivalent monolayer coverage of oleate at the fluorite surface. In this case the carboxylate region of the spectrum changes appreciably due to the nature of the chemisorbed state (Kellar, 1990). Furthermore, in this chemisorbed region, adsorption densities can be calculated from the in-situ FTIR/IRS spectra and the adsorption isotherms constructed for the chemisorbed region as shown in Figure 6 for 25°C and 40°C. The increase in adsorption density of oleate on fluorite as established in Figure 6 further substantiates prior radiotracer and microcalorimetric studies describing this endothermic chemisorption reaction (Hu, Misra, and Miller, 1986; Miller, Hu, and Jin, 1989).

Sphalerite/Xanthate

Xanthate adsorption density measurements at the sphalerite surface have not been reported in the literature. However, the flotation behavior suggests that the adsorption potential is small. Modest flotation of sphalerite with ethylxanthate is only possible at KEX concentrations exceeding  $1 \times 10^{-2} \text{ M}$  (Clifford, 1971). Even for amylxanthate, a concentration of  $1 \times 10^{-4} \text{ M}$  is required to achieve appreciable flotation. The sphalerite/KEX, KAX system is being examined in-situ by FTIR/IRS using a zinc sulfide single crystal (cubic) as the reactive IRE. Shown in Figure 7 is the in-situ spectrum of amylxanthate, in the aliphatic region, 3000-2800  $\text{cm}^{-1}$ , adsorbed on sphalerite from a  $\text{D}_2\text{O}$

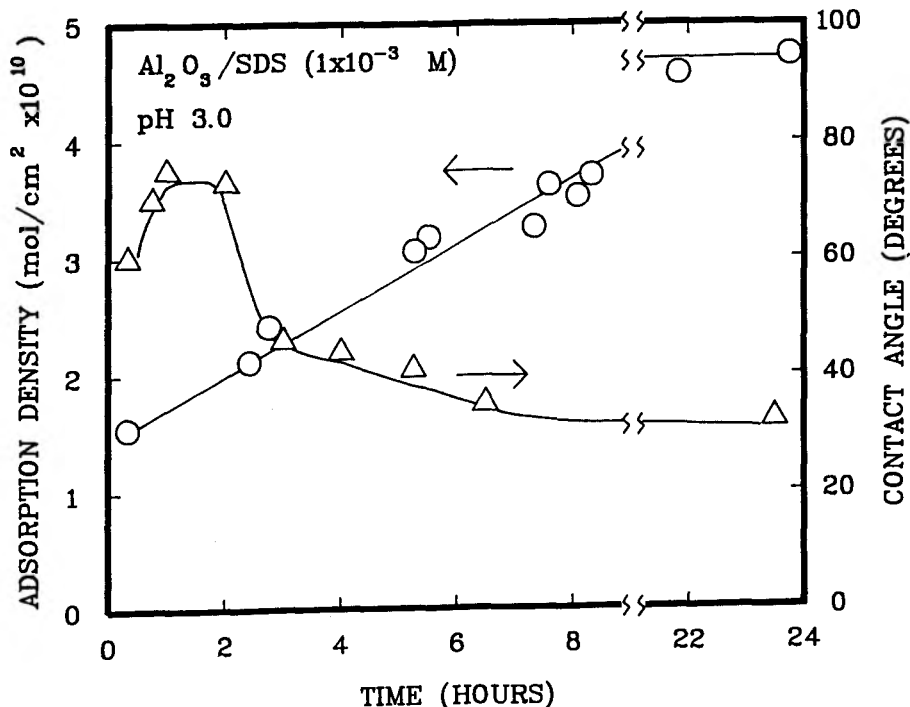


Figure 5. Adsorption density from in-situ FTIR/IRS data and contact angle at the alumina IRE surface as a function of time for  $1 \times 10^{-3} \text{ M}$  SDS.

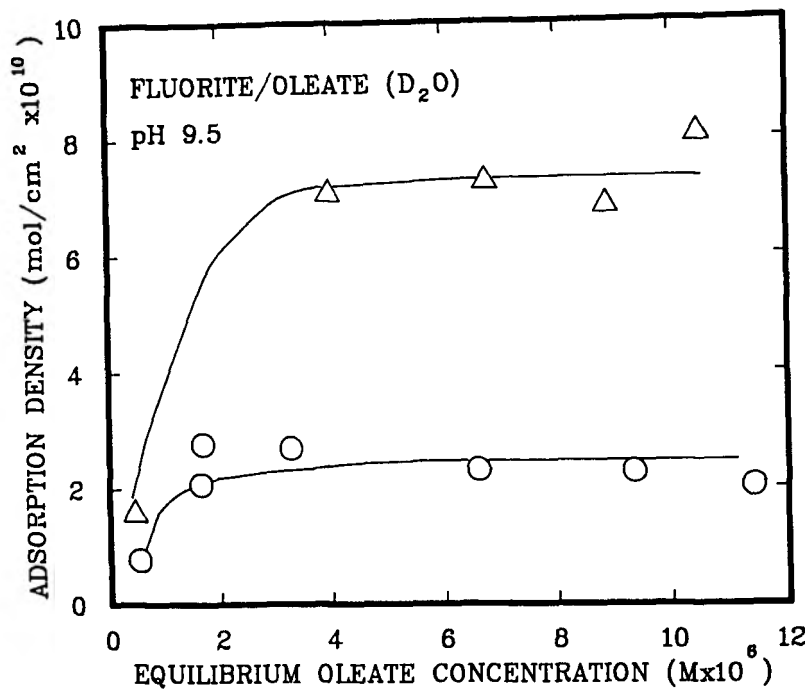


Figure 6. Isotherms for oleate adsorption by a fluorite IRE at 25°C (O) and 40°C ( $\Delta$ ) as calculated from in-situ FTIR/IRS data.

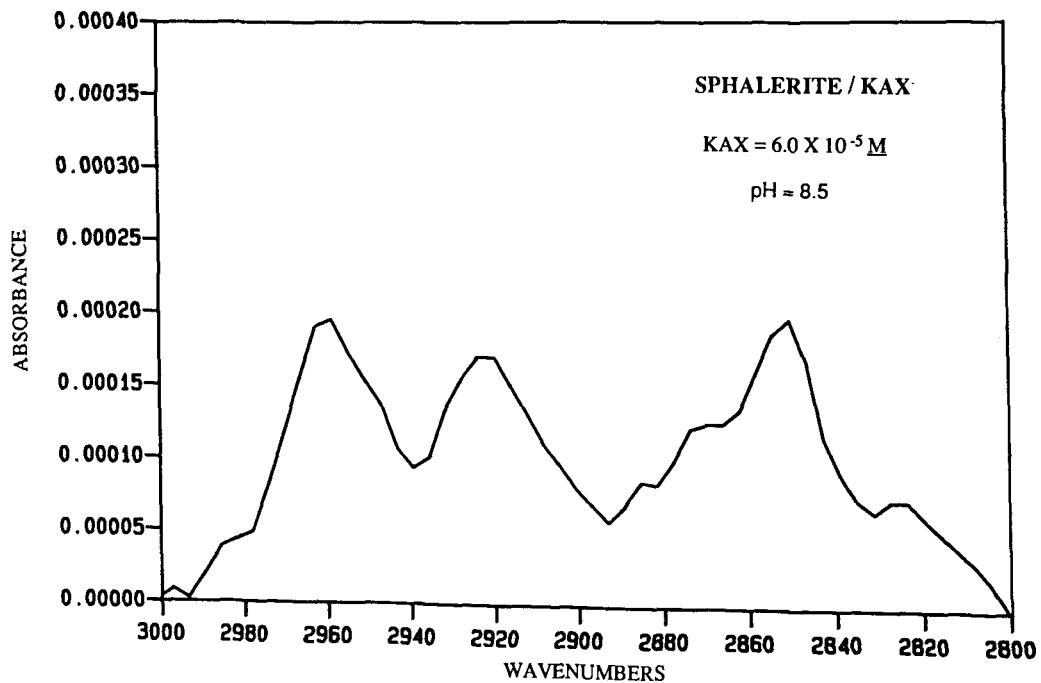


Figure 7. In-situ FTIR/IRS spectrum of amyloxanthate adsorbed at the surface of a sphalerite IRE from  $6 \times 10^{-5} M$  KAX solution (pH = 8.5).



solution. From this spectrum, the adsorption density was calculated from Equation (1) and was found, as expected, to be significantly less than an equivalent monolayer. Furthermore, in another experiment with KEX, no adsorption of ethylxanthate could be detected, as shown in Table 5. Under the conditions specified in Table 5, the surfaces were found to be hydrophilic. No contact angle was observed in either case.

Sylvite/Octylamine

The flotation chemistry of soluble salt minerals has intrigued researchers for many years. Detailed surface chemistry study has been difficult due to the sensitivity of the salt/brine interface to changes in temperature and brine composition. As a result, little information is available regarding collector adsorption density in soluble salt flotation systems. At the present time in-situ FTIR/IRS experiments are in progress using soluble salt internal reflection elements and it is intended to present the results of this research at the XVII International Mineral Processing Congress in Dresden, East Germany in September of 1991. Preliminary in-situ FTIR/IRS results for the sylvite/octylamine system suggest that for flotation to occur, multilayers of octylamine must be adsorbed at the sylvite/IRE surface.

Besides the adsorption density of octylamine, also of interest in soluble salt flotation is the adsorption state of the collector species. Shown in Figure 8 is the in-situ spectrum of adsorbed octylamine on KCl in the region 1650-1450  $\text{cm}^{-1}$ . The peaks at 1608, 1581, 1514, and 1466 can be assigned to N-H,  $\text{N}^+\text{-H}_2$ , and  $\text{CH}_2$  deformation vibrations (Leja, 1982). The presence of  $\text{N}^+\text{-H}_2$  bands suggests that the surface-active species in this system is the protonated octylamine.

Near-Infrared

One limitation in the use of reactive IREs is that not all mineral crystals are infrared-transparent in the most commonly used region, the mid-infrared (4,000-500  $\text{cm}^{-1}$ ). Shown in Figure 9 are the transmission spectra of several single-crystal

mineral IREs that have been used in the mid-infrared region. Miller and Kellar (1988) have proposed using FTIR/IRS in the near-infrared (15,000-4,000  $\text{cm}^{-1}$ ) for studying collector adsorption reactions and thus extending the utility of the reactive IRE method. Preliminary experiments have demonstrated that such FTIR/IRS measurements are possible in the near-infrared (Miller and Kellar, 1988).

The absorbance bands in the near-infrared are combination and overtone bands of the fundamental mid-infrared bands. These bands are much weaker than those found in the mid-IR. Typical intensity changes for a fundamental band and its overtones can be seen in Table 6 (Murray and Williams, 1987). The weak absorbance present in the near-IR, compared to the mid-IR, can be overcome somewhat by higher energy sources and more sensitive detectors that are available for this region of the electromagnetic spectrum.

Spectroelectrochemistry

In-situ spectroelectrochemistry for the study of flotation systems has been confined to sulfide mineral particulate suspensions and electrodes pressed against an "inert" IRE (Method 1). No spectroelectrochemical studies on sulfide minerals using reactive IREs (Method 3) have been reported. This is most likely because of the lack of commercially available single crystals and/or natural sulfide minerals with sufficient optical quality.

Recently it has been shown that in certain situations electrochemical effects can be of significance in nonsulfide mineral flotation systems (Cross, Wan, and Miller, 1988). The use of reactive internal reflection elements for the investigation of these electrochemical effects is ideal since a number of nonsulfide minerals are transparent in the mid-IR region. Spectroelectrochemistry using FTIR/IRS with reactive internal reflection elements yields essentially the same information that was presented in Figure 3 but allows for the detailed analysis of electrochemical surface reactions. Of course, the use of near-IR radiation would allow many mineral flotation systems in which electrochemical effects are important to be studied in-situ with reactive internal reflection elements.

Table 5.  
Xanthate Adsorption at the  
Surface of a Sphalerite IRE (pH 8.5)  
as Calculated from In-Situ FTIR/IRS Data.

Collector	Concentration (M)	Adsorption Density ( $\text{mol}/\text{cm}^2$ )
KEX	$7.3 \times 10^{-5}$	not detected
KAX	$6.0 \times 10^{-5}$	$4.5 \times 10^{-12}$

Table 6.  
Relative Intensity for Different  
Overtones in the Near-Infrared.

Overtone	Relative Absorbance
Fundamental	100
First	9
Second	0.3
Third	0.01

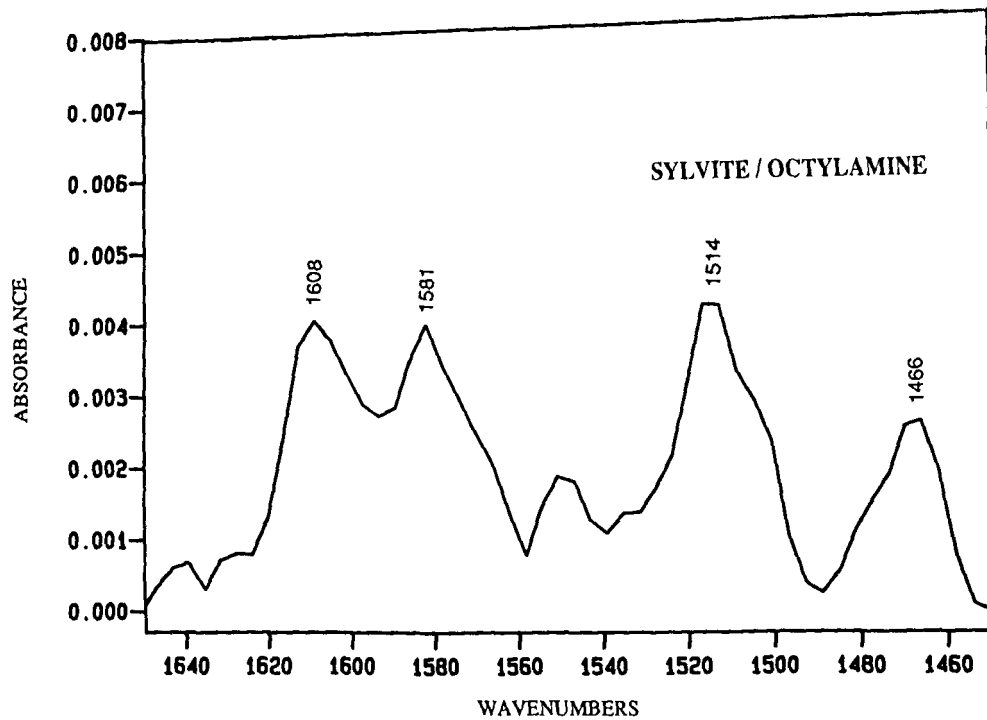


Figure 8. In-situ FTIR/IRS spectrum of octylamine adsorbed at the surface of a sylvite IRE from a  $5 \times 10^{-3}$  M  $R_8NH_3Cl$  solution (pH = 4.3).

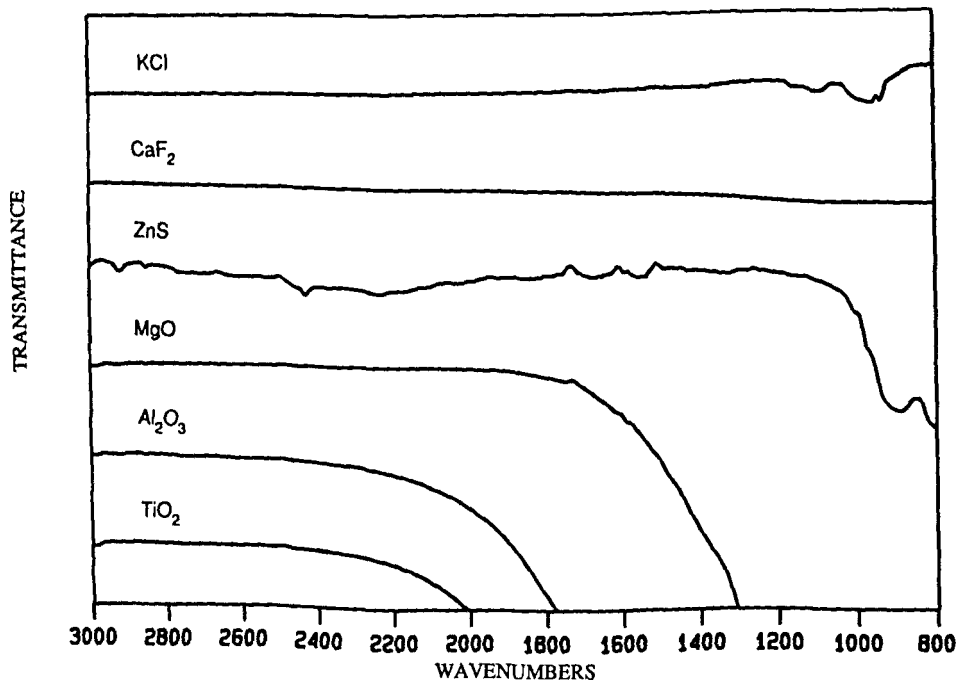


Figure 9. Transmission spectra of selected mineral IREs.

## SUMMARY

The use of infrared spectroscopy for the in-situ characterization of surface reactions has been reviewed. In general, FTIR internal reflection spectroscopy (IRS) is the only available experimental technique for the in-situ infrared study of surfaces. Three methods for in-situ FTIR/IRS have been discussed. The preferred method involves the use of reactive internal reflection elements. Figure 3 summarizes the advantages of in-situ FTIR/IRS using reactive internal reflection elements.

As is evident from Figure 3, the use of reactive IREs for the in-situ study of adsorption reactions allows for quantitative measure of the adsorption density and the extent of orientation of surfactants at the reactive IRE surface. Examples from each of the major flotation systems have been presented. The alumina ( $\text{Al}_2\text{O}_3$ )/sodium dodecylsulfate system was used as an example for insoluble oxide/silicate flotation, while the fluorite ( $\text{CaF}_2$ )/oleate system was used for semisoluble salt flotation. In the case of sulfide flotation, sphalerite ( $\text{ZnS}$ ) was used as the reactive IRE with potassium amylxanthate and potassium ethylxanthate as collectors. As an example of soluble salt flotation, sylvite ( $\text{KCl}$ ) was used as the IRE with n-octylamine as collector.

Finally, the use of reactive IREs in the near-IR spectral region and for spectroelectrochemical research was discussed.

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