In-Situ Internal Reflection Spectroscopy for the Study of Surfactant Adsorption Reactions Using Reactive Internal Reflection Elements

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IN-SITU INTERNAL REFLECTION SPECTROSCOPY FOR THE STUDY OF SURFACTANT

ADSORPTION REACTIONS USING REACTIVE INTERNAL REFLECTION ELEMENTS

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ABSTRACT

Infrared spectroscopy has been one of the most useful experimental techniques for the analysis of surface reactions. In particular, Fourier transform infrared (FTIR)/internal reflection spectroscopy (IRS) is most often used for in-situ studies. To date, three FTIR/IRS methods have been used for in-situ measurements. These techniques are evaluated for use in the characterization of surface reactions common to flotation systems. The method which uses mineral crystals as reactive internal reflection elements (IREs) is of particular interest because it allows surfactant adsorption densities to be calculated directly from in-situ spectral data in real time, and is the focus of this paper.

Application of in-situ FTIR/IRS with reactive IREs is demonstrated for collector adsorption reactions in each of the four major flotation systems. Also, the use of reactive IREs in the near-IR spectral region and in spectroelectrochemical research is discussed.

INTRODUCTION

Froth flotation is a process by which certain particle types are concentrated by separation from other types in a particulate suspension. Gas bubbles are used to float the hydrophobic particles to the air/water interface, while the hydrophilic particles remain in suspension. Particles to be floated are generally rendered hydrophobic by the adsorption of surfactants (collectors) from the aqueous phase. Controlling the surface chemistry of the solid/water interface is one

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of the most critical aspects to be considered for efficient flotation
separations.

Infrared spectroscopy has been one of the most useful experimen-
tal techniques for the analysis of surface reactions in flotation
systems. The utility of ex-situ transmission spectroscopy was first
demonstrated for flotation systems by French et al. (1), and subse-
quently by many other flotation chemists in following decades (2-5).
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 (6). 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) spectrome-
ters, many low-energy throughput IR experimental techniques previ-
ously 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/solu-
tion interface. The depth of penetration into the rarer medium and
the number of internal reflections within the IRE are determined by
the optical constants of the system and can be readily calculated
(7). Typically the depth of penetration and the number of internal
reflections vary between 0.1-1 μ and 10-50, respectively.

There are several reasons why in-situ IRS has been and will con-
tinue to be of such significance in flotation research. First, it
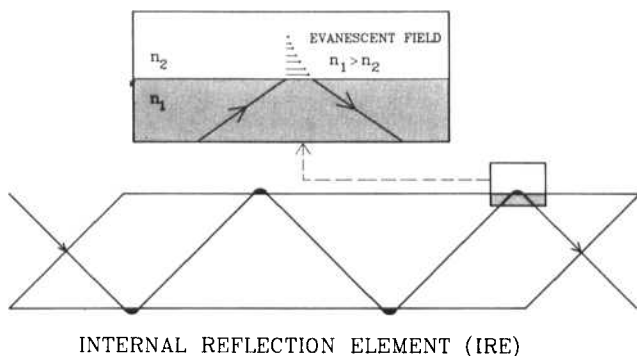

INTERNAL REFLECTION ELEMENT (IRE)

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.

confirms many conclusions based on previous ex-situ measurements.
Second, the short sampling depth (usually a fraction of the wave-
length) minimizes the strong infrared absorbance of water, a condi-
tion which had limited the use of in-situ IR spectroscopy. Finally,
from the multiple reflections at the IRE/sample interface, sensitiv-
ity is enhanced greatly over typical transmission experiments. The
sensitivity of the IRS technique is evident by the calculation of
adsorption densities from spectral data at very dilute equilibrium
collector concentrations where submonolayer coverages occur (8).
Since the 1983 review of IRS applications in flotation by Strojek
et al. (9), several new developments in in-situ IRS have occurred.
Three approaches which have been used to study flotation systems
in-situ by IRS are 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

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	$5 \times 10^{-5} - 1.5 \times 10^{-4}$ $\underline{M}$	11
Galena	Ethylxanthate Dithiophosphate	not reported	12
Chalcocite Chalcopyrite Pyrite	Thionocarbamate	$1 \times 10^{-4} - 1 \times 10^{-3}$ $\underline{M}$	13
Sphalerite	Ethylxanthate	5.2×10^{-5} $\underline{M}$	14
Chalcocite Chalcopyrite Pyrite Galena	Ethylxanthate	$1 \times 10^{-3} - 1 \times 10^{-4}$ $\underline{M}$	15

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 (7,10). Apparently, the high re-fractive 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 stu-died 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 stu-dying mineral particles in-situ under controlled potential (15). Such spectroelectrochemical 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 inti-mate contact with the "inert" IRE. Initial researchers reportedly had difficulty in achieving adequate contact with the IRE (9). Re-producible contact between experiments is very difficult, and conse-quently only qualitative measurements are possible. Also, collector contamination of the "inert" IRE cannot be ignored. Surface contam-ination can be significant, especially at the surfactant concentra-tions commonly used (see Table 1). The reactivity of an "inert" IRE is demonstrated by the in-situ spectrum of the residual contamination from a 5×10^{-3} $\underline{M}$ potassium amylxanthate solution on an "inert" german-ium IRE shown in Figure 2. The IR absorption bands from this contam-ination 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 typic-ally have a circular beam, and focussing onto the end of the flat-plate IRE geometry can be cumbersome. In recent studies, cylindrical IREs using cassegranian focussing optics which maximize energy throughput for the circular FTIR beam have become more widely used. This IRS accessory, called the CIRCLE[R] cell, has been used to inves-tigate mineral particle suspensions in-situ (16,17). Because the IRE is completely enveloped by the sample, suspensions can be used with lower solid/liquid ratios than those reported in Table 1. Neverthe-less, 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 sur-
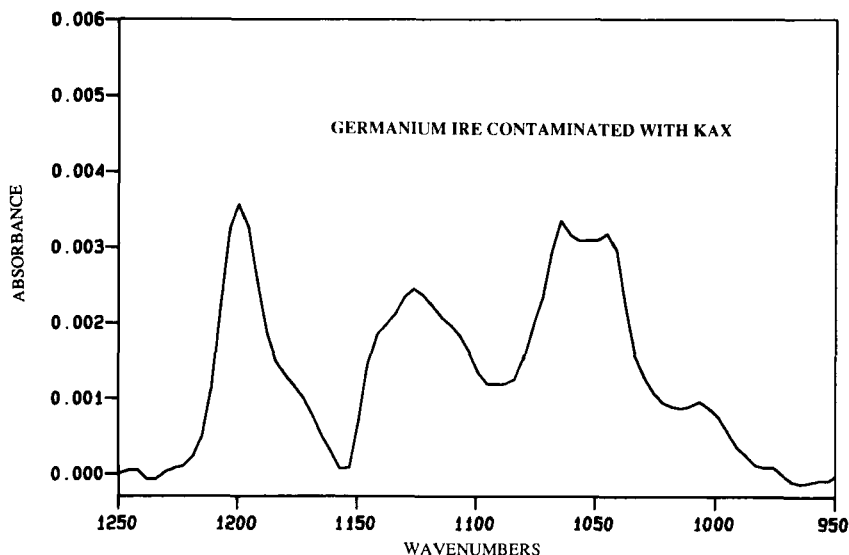
Figure 2.   In-situ FTIR/IRS spectrum of species adsorbed
            from an amylxanthate (5x10^{-3} $\underline{M}$) solution at
            the surface of an inert germanium IRE.

factant adsorption occurs directly onto the exposed mineral surface.
Shown in Table 2 are flotation systems where Method 2 has been util-
ized. Nowhere is it mentioned how the IREs were reconditioned be-
tween experiments. The aforementioned problem of Method 1, adequate
contact between mineral and IRE, is alleviated by this technique.
Reproducible 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 struc-
ture 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 (20,

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

Mineral	Collector	Concentration	Reference
Fluorite	Sodium Dodecylsulfate	1×10^{-5} - 5×10^{-3} M	18
Cassiterite	Styrene Phosphonic Acid	2.7×10^{-4} - 1.6×10^{-3} M	19

21). Miller and Kellar (22) used this approach to demonstrate the
quantitative analysis of collector adsorption reactions for several
flotation systems. It was shown that the adsorption density, reac-
tion kinetics, and orientation of collectors at the surface of mine-
ral IREs can be followed in-situ and in real time. Furthermore, it
was shown for the first time that a natural mineral crystal (fluor-
apatite) could be prepared as a usable IRE on which adsorbed collec-
tor 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 **adsorp-
tion density** and thus determination of adsorption kinetics as well as
the corresponding equilibrium adsorption isotherm. Also, it is pos-
sible to determine, by frequency shifts or the appearance/disappear-
ance of absorbance bands, the **adsorption state**, i.e., whether the
collector is physically or chemically bonded at the IRE surface.
Finally, the **orientation** of adsorbed species can be deduced by com-
paring 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, Γ (mol/cm^2), of a
pyridinium-based surfactant onto a zinc selenide cylindrical IRE.
In this case, the effective number of internal reflections had to be

IN-SITU INFRARED SPECTROSCOPY WITH
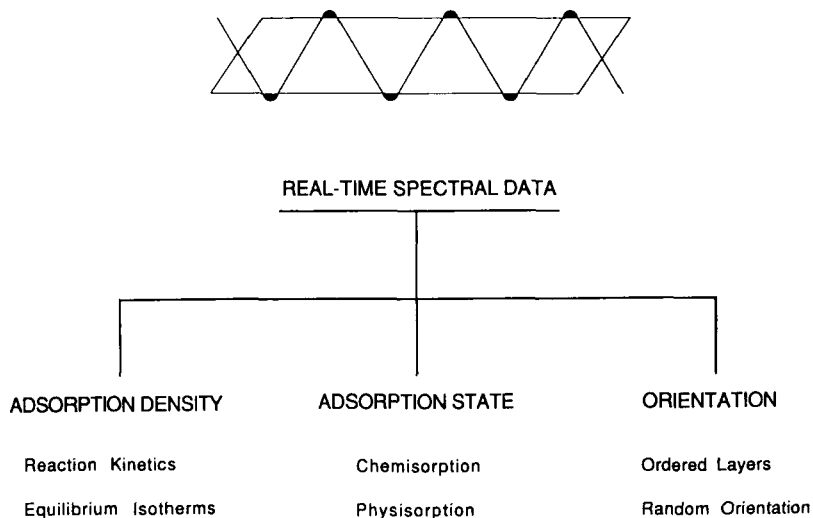
REACTIVE INTERNAL REFLECTION ELEMENTS

REAL-TIME SPECTRAL DATA

ADSORPTION DENSITY	ADSORPTION STATE	ORIENTATION
Reaction Kinetics	Chemisorption	Ordered Layers
Equilibrium Isotherms	Physisorption	Random Orientation

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

determined by a calibration procedure. Subsequently, Miller and
Kellar (22) used flat-plate prisms of fluorite and sapphire (no
calibration necessary) to calculate collector adsorption densities
according to the following equation:

$$\Gamma = (\frac{A}{\ell/t \ \cot \theta} - \varepsilon C_b d_e)/1000 \ \varepsilon \ (\frac{2d_e}{d_p}) \qquad (1)$$

where A = integrated absorbance (cm^{-1})

ℓ = IRE length

t = IRE thickness

ε = molar absorptivity of surfactant ($\ell/(cm^2 \cdot mol)$)

C_b = surfactant bulk concentration (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 (7). The absorbance,
A, for the adsorption density calculation is generally obtained by
integration of the absorbance bands of the aliphatic region of the
infrared spectrum (3,000-2,800 cm^{-1}). Other experimental details for
the calculation of adsorption densities are given elsewhere (8).

Orientation

Haller and Rice (1970) demonstrated the possibility of determin-
ing the orientation of an adsorbed layer on an IRE. Using the strong
IR absorbance band assigned to the asymmetric CH_2 stretching vibra-
tion (2925 cm^{-1}), Haller and Rice defined two limiting conditions:
molecular backbone normal to the IRE (CH_2 planes parallel to the
surface) and completely random orientation of the 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 speci-
fic 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 spec-
troscopically and the extent of ordering of the adsorbed state in-
ferred.

$$\text{Dichroic Ratio} = \frac{A_\perp}{A_\parallel} \tag{2}$$

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

The dichroic ratio for vertical orientation with CH_2 planes parallel
to the surface:

$$\frac{A_\perp}{A_\parallel} = \frac{E_{yo}^2}{E_{xo}^2} \tag{3}$$

The dichroic ratio for random orientation with CH_2 planes random to
the surface:

$$\frac{A_\perp}{A_\parallel} = \frac{E_{yo}^2}{E_{xo}^2 + E_{zo}^2} \tag{4}$$

In this paper, the in-situ FTIR/IRS technique using reactive
IREs (Method 3) has been applied to each of the four 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 flota-
tion. 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 spectroelectro-
chemical research is discussed.

Alumina/SDS

The alumina/SDS system has been used frequently as a model in-
soluble oxide/silicate flotation system for the study of collector
adsorption reactions (24-26). This system is useful for illustrating
the role of coulombic forces (i.e., surface charge of the solid de-
termined by the solution pH and the charge of the surface-active spe-
cies) 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 calcula-
tions indicate that the aggregation event could lead to vertical
bilayers called "admicelles" (27,28). Several in-situ spectroscopic
techniques have been used to study this system (22,26,29). Most of
these techniques rely on a tracer molecule to give information con-
cerning 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 (22), on the other hand,
directly examined the spectral characteristics of the adsorbed col-
lector in its surface state. These authors demonstrated that the
adsorption density and orientation of SDS on alumina can be deter-
mined in-situ. In this section, additional in-situ IRS data will be
given for the alumina/SDS system and compared with previous results
reported in the literature.

From the in-situ FTIR/IRS spectra 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
(26). It can be seen that the results from these drastically differ-
ent 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 H_2O and in
D_2O. This agreement adds credibility to previous results obtained
with D_2O as solvent (22). Deuterium oxide was used in previous in-
vestigations because it has no IR absorption bands in the aliphatic
C-H stretching region (3000-2800 cm^{-1}). It should be noted that the
IR absorbance from adsorbed collector species (circa 0.02 absorbance
units) is typically two orders of magnitude smaller than the maximum
absorbance due to the solvent (H_2O or D_2O). Therefore, in order to
analyze the IRS absorbance spectra in H_2O and calculate adsorption
densities in the region 3000-2800 cm^{-1}, the strong IR absorption by
H_2O must be taken into consideration as was done for the data pre-
sented in Table 3 and Figure 5. This analysis is detailed in a forth-
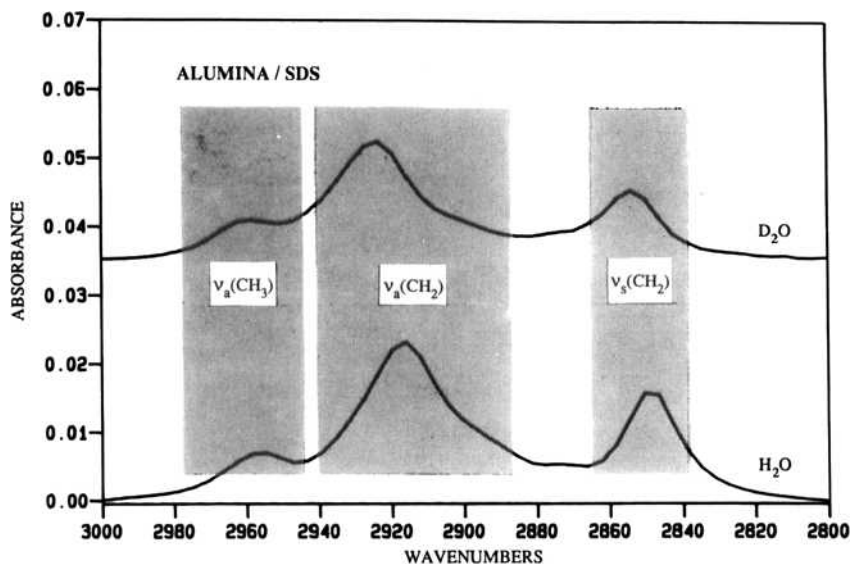coming paper (30).

Figure 4.   In-situ FTIR/IRS spectra of SDS adsorbed from H_2O and
            D_2O solutions at the surface of an alumina IRE.

Table 3.
Adsorption Density of SDS by Alumina at
pH 6.5 (26) and pH 7.3 (22; present work)

SDS Equilibrium Concentration (M)	SDS Adsorption Density (mol/cm^2)		
		In-Situ IRS	
	Reference 26	H_2O	D_2O Reference 22
1×10^{-3}	6.7×10^{-10}	4.5×10^{-10}	4.4×10^{-10}
4×10^{-3}	6.7×10^{-10}	--	5.3×10^{-10}

Using polarized light and calculated dichroic ratios, Miller and Kellar (22) 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 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_2 planes parallel to the IRE surface (31,32), 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
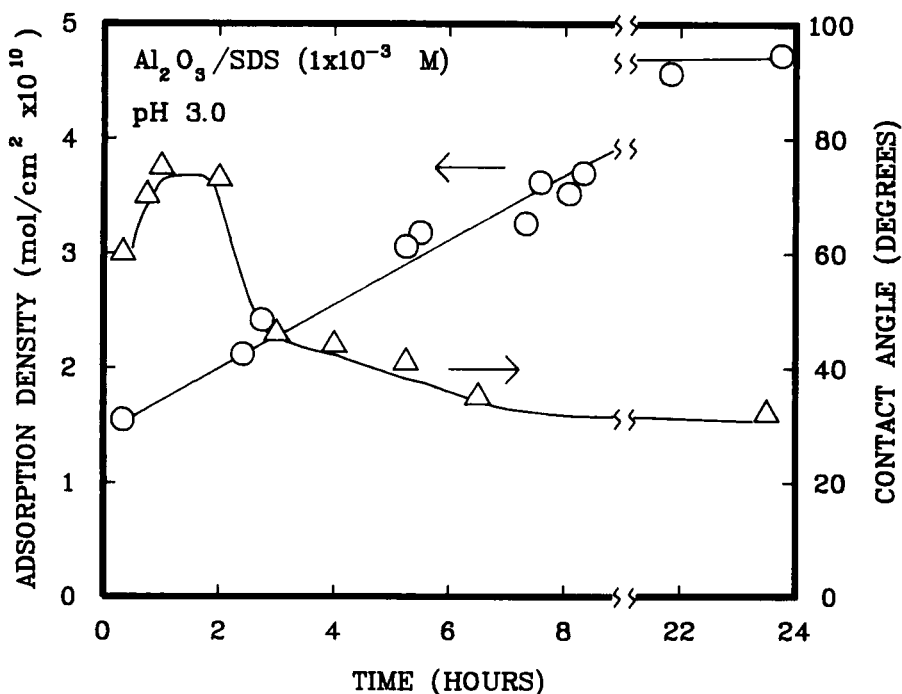

Figure 5. Adsorption density from in-situ FTIR/IRS data and contact angle at the alumina IRE surface as a function of time for 1×10^{-3} M SDS.

Table 4.
Orientation of SDS on Al_2O_3
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	$A_\perp/A_\parallel$ = 0.031/0.022
= 1.0×10^{-3} M	= 1.41

surface were compared with the time dependence of the hydrophobic
character of the alumina surface as measured by contact-angle goniom-
etry. The contact-angle experimental techniques are similar to those
described previously (33). Figure 5 displays this comparison. It
can be seen that the adsorption density of SDS on Al_2O_3 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. These results are inter-
preted as indicating that, after two hours, the randomly adsorbed SDS
(approximately equivalent to a monolayer) has maximum exposure of the
aliphatic groups and that upon further adsorption a tail-tail config-
uration 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
cm^{-1}), fluorite (CaF_2) is an ideal substrate for in-situ FTIR/IRS
study. It is well known that the semisoluble salt minerals (includ-
ing fluorite) tend to form surface and/or bulk precipitates of the
collector salt. Such surface precipitation leads to multilayer for-
mation. As expected, the in-situ spectrum of surface-precipitated
calcium oleate has been found to be quite similar to the ex-situ
spectrum of bulk precipitated calcium oleate (22).

Of greater significance, however, is the in-situ spectrum of
the chemisorbed state at what appears to be equivalent to monolayer
coverage of oleate at the fluorite surface. Shown in Figure 6 are
the in-situ spectra of precipitated and chemisorbed oleate adsorbed
on a fluorite IRE. The chemisorbed spectrum is characterized by a
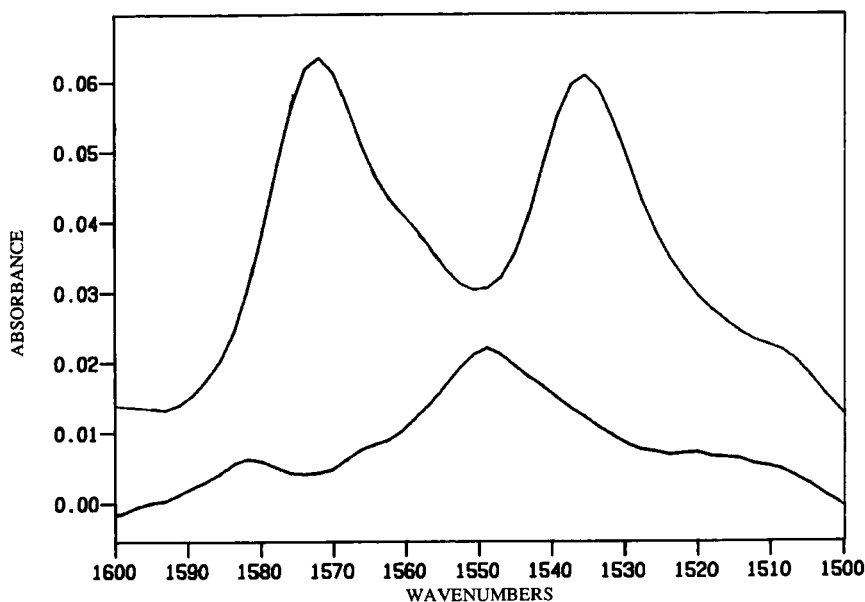single peak at 1550 cm^{-1} and the precipitated calcium oleate spectrum

Figure 6.   In-situ spectra chemisorbed and surface-precipitated
            oleate oleate adsorbed on a fluorite IRE from
            1×10^{-4} M (top) and 1×10^{-5} M (bottom) oleate
            solutions, respectively (pH = 9.5).

contains a doublet at 1574 and 1535 cm^{-1}. The peaks in this region
are due to the carboxylate stretching vibration of adsorbed oleate
(34). Furthermore, adsorption densities can be calculated from the
in-situ FTIR/IRS spectra (3050-2800 cm^{-1}) and the adsorption iso-
therms constructed as shown in Figure 7 for 25°C and 40°C. The in-
crease in adsorption density of oleate on fluorite in the chemisorbed
region (1×10^{-6}-5×10^{-5} M) further substantiates prior radiotracer and
microcalorimetric studies describing this endothermic chemisorption
reaction (35,36).

Sphalerite/Xanthate

In-situ, xanthate adsorption density measurements at the sphale-
rite, ZnS, surface have not been reported in the literature. How-
ever, the flotation behavior suggests that the adsorption potential
is small. Modest flotation of sphalerite with ethylxanthate is only
possible at KEX concentrations exceeding 1×10^{-2} M (37). Even for
amylxanthate, a concentration of 1×10^{-4} M is required to achieve ap-
preciable flotation. The sphalerite/KEX, KAX system was examined in-
situ by FTIR/IRS using a cubic, isotropic zinc sulfide single crystal
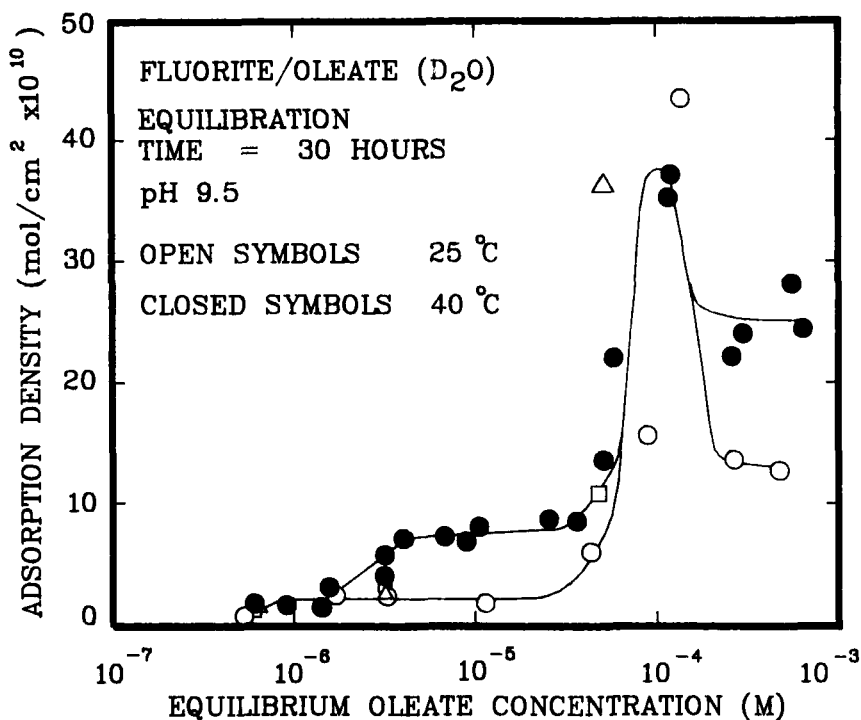
Figure 7.   Isotherms for oleate adsorption by a
             fluorite IRE at 25°C (o) and 40°C (●) as
             calculated from in-situ FTIR/IRS data.

as the reactive IRE.   Shown in Figure 8 is the in-situ spectrum of
amylxanthate, in the aliphatic region, 3000-2800 cm^{-1}, adsorbed on
sphalerite from a D_2O 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 (i.e., 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
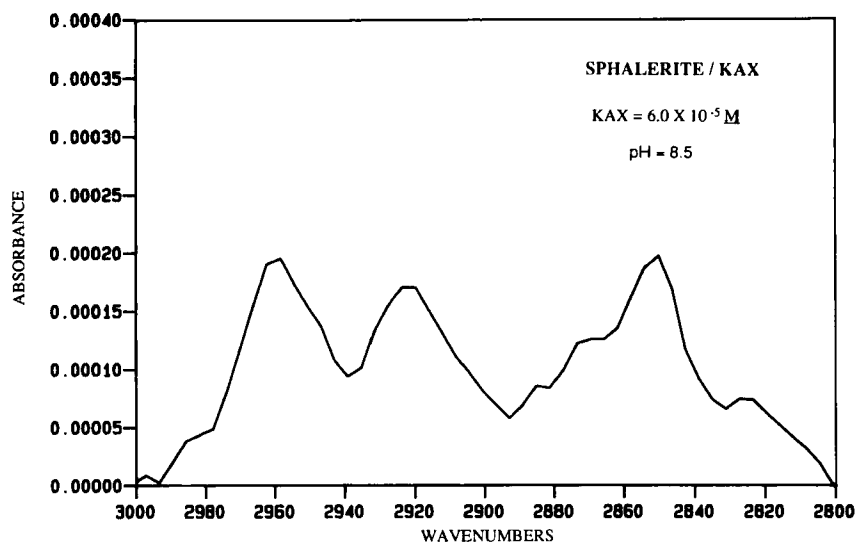changes in temperature and brine composition. As a result, little

Figure 8.   In-situ FTIR/IRS spectrum of amylxanthate
            adsorbed at the surface of a sphalerite
            IRE from 6×10^{-5} M KAX solution (pH = 8.5).

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 (mol/cm^2)
KEX	7.3×10^{-5}	not detected
KAX	6.0×10^{-5}	4.5×10^{-12}

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 IREs, and those re-
sults will be presented 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 ad-
sorbed 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 9 is the in-situ spectrum of adsorbed oc-
tylamine on KCl in the region 1650-1450 cm^{-1}. The peaks at 1608,
1581, 1514, and 1466 can be assigned to N-H, N^+-H_3, and CH_2 deforma-
tion vibrations (38). The presence of N^+-H_3 bands suggests that the
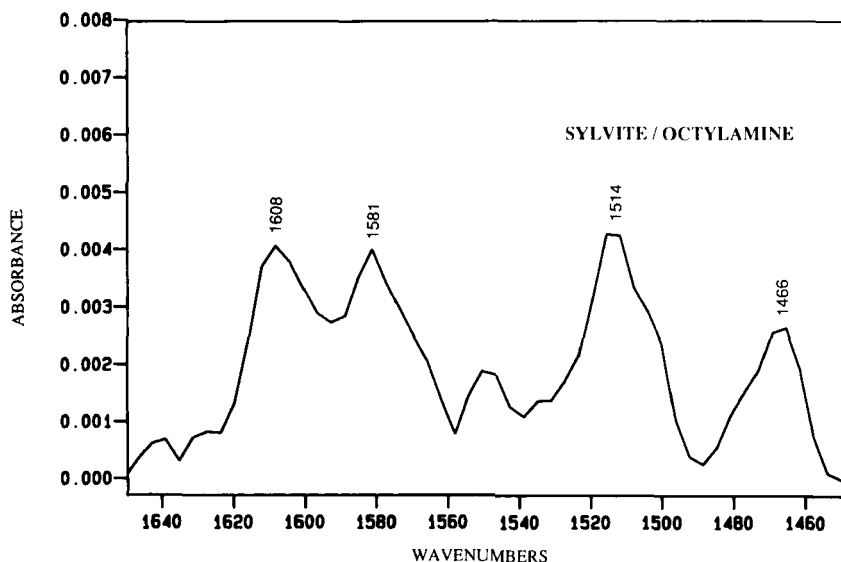surface-active species in this system is the protonated octylamine.

Figure 9.   In-situ FTIR/IRS spectrum of octylamine adsorbed
            at the surface of a sylvite IRE from a
            $5x10^{-3}$ $\underline{M}$ R_8NH_3Cl solution (pH = 4.3).

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 cm^{-1}). Shown in Figure 10 are the transmission spectra of several single-crystal mineral IREs that have been used in the mid-infrared region. As can be noted from Figure 3, the oxide IREs tend to absorb IR radiation at lower wavenumbers than the other crystal types. In fact, many minerals are not transparent in any region of the mid-infrared. Miller and Kellar (22) have proposed using FTIR/IRS in the near-infrared (15,000-4,000 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 for the mid-infrared opaque mineral calcite, $CaCO_3$ (39).

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 (40). The weak absorbance present in the near-IR, compared to the
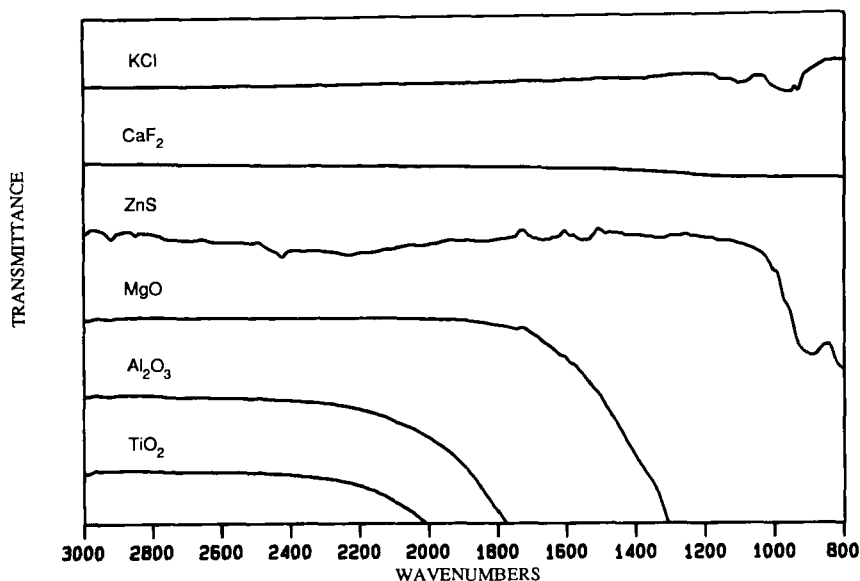

Figure 10.   Transmission spectra of selected mineral IREs.

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

Overtone	Relative Absorbance
Fundamental	100
First	9
Second	0.3
Third	0.01

mid-IR, can be overcome somewhat by higher energy sources and more
sensitive detectors that are available for this region of the elec-
tromagnetic spectrum.

Spectroelectrochemistry

    In-situ spectroelectrochemistry for the study of flotation sys-
tems has been confined to sulfide mineral particulate suspensions and
electrodes pressed against an "inert" IRE (Method 1). No spectro-
electrochemical 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 electro-
chemical effects can be of significance in nonsulfide mineral flota-
tion systems (41). The use of reactive IREs for the investigation of
these electrochemical effects is ideal since a number of nonsulfide
minerals are transparent in the mid-IR region. Spectroelectrochemis-
try using FTIR/IRS with reactive IREs yields essentially the same in-
formation 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 IREs.

SUMMARY

    The use of infrared spectroscopy for the in-situ characteriza-
tion of surface reactions has been reviewed. In general, FTIR/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 IREs.
Figure 3 summarizes the advantages of in-situ FTIR/IRS using reactive
IREs.

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 (Al_2O_3)/sodium dodecylsulfate system was used as an example for insoluble oxide/silicate flotation, while the fluorite (CaF_2)/oleate system was used for semisoluble salt flotation. In the case of sulfide flotation, sphalerite (ZnS) was used as the reactive IRE with potassium amylxanthate and potassium ethylxanthate as collectors. As an example of soluble salt flotation, sylvite (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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