



At the solid/liquid interface: FTIR/ATR — the tool of choice

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Abstract

For the last 7 years, we have been researching various aspects of the Bayer process. Predominant among these has been the surface chemistry of Bayer process solids. To this end, we have been using Fourier transform infrared (FTIR) attenuated total reflection (ATR) spectroscopy for in situ studies of the surfaces of the Bayer process solids sodium oxalate and aluminium trihydroxide under extreme (high ionic strength, high pH), Bayer-like conditions. FTIR/ATR is one of the few techniques currently available to scientists wishing to explore solid/liquid interfacial phenomena in situ. Using this investigative technique, information regarding the nature of adsorbed species can be readily acquired, with details concerning adsorbate orientation and adsorption/desorption equilibria, speciation, mechanisms and kinetics obtainable. Not surprisingly, FTIR/ATR has become one of the tools of choice for those wishing to explore the solid/liquid interface, and the body of literature available on the subject has been steadily growing over the last 10–15 years. This review addresses the current state of knowledge in the area of FTIR/ATR with respect to interfacial spectroscopy, as well as introducing some of the more fundamental theoretical and practical aspects of the technique. Particular emphasis is placed upon *applied interfacial research*. In writing this review, we draw on a considerable amount of expertise in the use of FTIR/ATR in interfacial studies (in particular, the practical considerations involved), as well as a large and comprehensive literature database focussing primarily on the investigation of interfacial processes using the FTIR/ATR technique. © 2001 Elsevier Science B.V. All rights reserved.

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1. Overview

Solid/liquid interfacial phenomena play an important role in many aspects of day-to-day life. As such, adsorption processes occurring at the solid/liquid (and solid–aqueous) interface are of great interest to scientists working in a diverse number of fields. Said phenomena are fundamental to processes such as dissolution, detergency, corrosion (and corrosion inhibition), adhesion, flotation, chromatography, and hydrometallurgy (to name a few). More importantly, interfacial phenomena govern some of the more fundamental aspects upon which these processes rely. These include adsorption/desorption equilibria, speciation, kinetics and mechanisms and, for obvious reasons, have been important areas of scientific research for many years. Many industrial processes rely heavily, if not entirely, on such interfacial phenomena, with extremely small changes in process conditions having the potential to dramatically reduce (or completely halt) production.

The chemistry of surfaces, and processes occurring thereon, in liquid environments is thus of great interest to academic and industrial researchers alike and, not surprisingly, a great deal of work has been reported in the area. Over the last 10–15 years, a substantial amount of literature concerning the use of Fourier transform infrared (FTIR) attenuated total reflectance (ATR) spectroscopy for the in situ investigation of interfacial phenomena has been published. Again, this is of little surprise given the efficacy of the FTIR/ATR technique and its ability to

provide such interfacial information from an in situ point of view. To that end, we have been using FTIR/ATR for a number of years in an attempt to further our understanding of the chemistry of the Bayer process or, more particularly, our understanding of the *surface chemistry of Bayer process solids* [1]. Such solids exist in extreme environments (high pH, high ionic strength), where the chemistry of their respective surfaces plays a crucial role in the overall refining process.

Using FTIR/ATR, we have been able to detect [2] and quantify [3] adsorbed surface-active species on the surfaces of sodium oxalate and aluminium trihydroxide (or gibbsite) in situ, in synthetic Bayer liquors of pH 12–13 and sodium ion concentration of greater than 5 M. Using the interfacial spectra obtained, we have then been able to postulate as to the nature of the adsorbed species, as well as observing the effects of increasing surfactant solution concentration on the adsorption process. Having demonstrated the usefulness of the technique under Bayer process conditions, we are currently continuing our studies in the area, the ultimate aim being the development of an FTIR/ATR based at-line or on-line Bayer process predictive tool. Such a tool could potentially offer substantial savings to alumina refiners worldwide.

Throughout the course of our studies, a large and comprehensive database of FTIR/ATR related literature has been compiled. The papers collected have focussed primarily on the investigation of interfacial processes and, more particularly, interfacial processes occurring in aqueous systems. At the same time, we have gained a considerable amount of practical expertise in the use of FTIR/ATR in such interfacial studies and, in particular, some of the practical considerations involved. This review will thus address the current state of knowledge in the area, as well as introducing some of the more fundamental theoretical and practical aspects of interfacial spectroscopy using FTIR/ATR. Particular emphasis will be placed upon *applied interfacial research*. A number of reviews have previously been published in similar areas [4–6], however, the most recent of these is now 5 years old. As such, an updated review of the area was considered warranted. Interfacial biological and biomedical research using FTIR/ATR will not be covered in any detail, as the topic has been extensively reviewed in recent years [7–11].

2. Surface analytical techniques

Traditional surface analytical techniques require the solid to be removed from solution, washed and subjected to ultra-high vacuum prior to analysis [12]. This has the undesirable consequence of completely changing the surface characteristics of the solid under investigation. While such ex situ methods can provide some insight as to the nature of a surface, the surface (as investigated) is often quite different to the original surface of interest. It is obviously more desirable to probe a surface in situ, in order to gain an accurate picture of said surface, and the nature of interactions occurring thereon.

A number of traditional ex situ techniques are available for the examination of surfaces. These include X-ray (XPES) and ultraviolet (UVPES) photoelectron

spectroscopy, electron energy loss spectroscopy (EELS), Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), field emission microscopy (FEM), field ionisation microscopy (FIM), scanning tunnelling microscopy (STM), and atomic force microscopy (AFM). Unfortunately, most of these techniques require the use of ultra-high vacuum, which, as touched on above, has the undesirable consequence of completely changing the surface characteristics of the surface under examination. AFM has recently been used to examine the surfaces of solids in solution in situ, however, a discussion of this technique is beyond the scope of this review.

Other *ex situ* techniques include dispersive and Fourier transform infrared transmission and emission spectroscopies, diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy, and dispersive and Fourier transform Raman spectroscopy. Again, these investigative techniques are limited by the fact that solids must be dried prior to analysis (although not subjected to ultra-high vacuum), altering the nature of the surface and/or adsorbed layer. Transmission and DRIFT spectroscopies, which generally involve dispersal in an infrared transparent medium (KBr for example), also experience difficulties arising from water absorption or undesired reactions with the infrared transparent medium. Photoacoustic spectroscopy (PAS) is another technique capable of surface investigation, however, it is not suitable to investigations involving the solid/liquid interface (PAS is best suited to depth profiling of solid surfaces).

3. Internal reflection spectroscopy

Internal reflection spectroscopy is the technique of recording the optical spectrum of a sample material that is in contact with an optically denser but transparent medium and then measuring the wavelength dependence of the reflectivity of this interface by introducing light into the denser medium [13]. To quote Harrick: 'Total internal reflection (TIR) is a familiar phenomenon. It can be observed with a glass of water for example. If the side of the glass below the water level is viewed obliquely through the water surface, it appears to be completely silvered and one can no longer see objects behind it. The reason for this is that light striking the glass surface is totally reflected and therefore does not pass through the surface to illuminate these objects'. However; 'if one looks at ones' fingers touching the glass, the skin patterns are clearly evident which indicates that total reflection has been destroyed where contact is made, *viz.*, at the ridges of the skin but not at the valleys of the skin where no contact is made. This clarity is explained by the penetration of the electromagnetic field into the rarer medium a fraction of a wavelength beyond the reflecting surface and that when a suitable object is brought near enough to the surface to interact with this penetrating field, total reflection is destroyed'. This phenomenon is explained by the formation of a standing wave in the denser medium perpendicular to the reflecting surface, and an evanescent, non-propagating field in the rarer medium, the electric-field amplitude of which decays exponentially with distance from the surface.

So, in the case of internal reflection spectroscopy, reflectivity is a measure of the interaction of the evanescent wave with the sample material, with the resulting spectrum being characteristic of said sample material.

3.1. Principles of attenuated total reflection spectroscopy

ATR, developed simultaneously and independently by Harrick [14] and Fahrenfort [15], is a type of internal reflection spectroscopy in which the sample is placed in contact with an internal reflection element (IRE) of high refractive index. Infrared radiation is focussed onto the edge of the IRE, reflected through the IRE, and then directed to a suitable detector (see Fig. 1). Although complete internal reflection occurs at the sample/IRE interface, radiation (the evanescent wave) penetrates a short distance (d_p) into the sample (depending upon the wavelength, λ , of the incident light), where it can be absorbed. An absorption spectrum of the sample in contact with the IRE can thus be obtained, the spectrum being dependent upon a number of parameters including angle of incidence (θ) and the refractive indices of the IRE material (n_1) and the sample (n_2), respectively [Eq. (1)]. The penetration depth is defined as the distance required for the amplitude of the electric field to fall to e^{-1} of its value at the surface [13].

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - (n_2/n_1)^2}} \quad (1)$$

The incident infrared light passes through the optically denser IRE and reflects at the surface of the sample. The propagating light passing through the IRE (an optically thin, non-absorbing medium) then forms a standing wave perpendicular to the total reflecting surface. Thus, if the sample absorbs radiation, the propagating wave interacts with the sample and becomes *attenuated*. The reflectance of the attenuated wave can be expressed as:

$$R = 1 - \alpha d_e \quad (2)$$

where d_e is the effective layer thickness and α the absorption coefficient (or

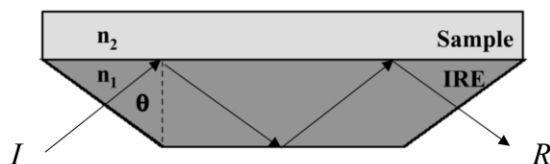


Fig. 1. Schematic diagram of a horizontal ATR (HATR) sampling accessory illustrating the parameters of significance to spectral acquisition (I = incident radiation; R = reflected radiation).

absorptivity) of the layer. The energy loss in the refractive wave is termed attenuated total reflectance. For multiple (N) reflections, the total reflectance or reflected power, R^N , is expressed as:

$$R^N = (1 - \alpha d_e)^N \quad (3)$$

with reflection losses increasing in proportion to the number of reflections. Where $\alpha d_e \ll 1$, the above equation can be expressed as follows:

$$R^N \approx 1 - N\alpha d_e \quad (4)$$

The effective layer thickness, d_e , is a measure of the strength of the coupling to the sample and is defined as the thickness required in transmission measurements to obtain the same absorbance as that from a single reflection at the phase boundary of a medium:

$$d_e = a/\alpha \quad (5)$$

where the absorption parameter, a , is defined as the reflection loss per reflection:

$$a = (100 - R)\% \quad (6)$$

3.2. Attenuated total reflection spectroscopy and surface analysis

As previously mentioned, FTIR spectroscopy has the ability to characterise the surfaces of solids. It has been used extensively in this manner, in areas as diverse as catalysis [16–19] and polymer characterisation [20–23]. Techniques such as transmission FTIR [24–26] and diffuse reflectance FTIR (DRIFT) [27–29] spectroscopy have been widely utilised in the study of solid surfaces. Importantly, FTIR spectroscopy also has potential for the examination of solid surfaces in solution. FTIR/ATR provides a means of producing infrared spectra from in situ investigations of the solid/aqueous interface [13]. The last 10–15 years has seen FTIR/ATR become increasingly popular as a research tool in this area.

Where other surface analytical techniques require the solid to be removed from solution, washed, and subjected to ultra-high vacuum prior to analysis (completely changing the surface characteristics of the solid under examination), *ATR provides a viable means of investigating the solid / liquid interface without altering the surface characteristics of the sample.* In addition, the short, highly reproducible pathlength obtainable with ATR (0.4–4 μm for ZnSe/H₂O for example), permits the accurate subtraction of water, and facilitates the investigation of aqueous systems.

3.3. Cell geometry

A number of different ATR cell designs are available to the interfacial spectroscopist. The geometry of the ATR cell is an important consideration when planning

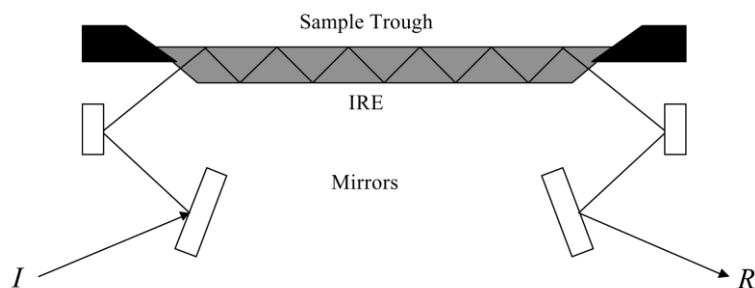


Fig. 2. Schematic diagram of a typical, commercially available horizontal ATR cell equipped with trough plate suited to studies of the solid/liquid interface (I = incident radiation; R = reflected radiation).

interfacial studies and is, to a certain extent, largely determined by the type(s) of studies envisaged. If contemplating experiments involving adsorption to particulate matter for example, a horizontal trough configuration would most likely be appropriate. However, if adsorption to the IRE (or a thin film coated to the IRE) is the target of the investigation, horizontal (chamber), vertical (tunnel), or immersion (DipperTM) type designs may prove more suitable. Additional sampling features such as variable angle, flow-through, and heating capabilities should also be considered. By varying the angle of incidence, it is possible to vary the depth of penetration of the infrared radiation into the sample, making it possible to investigate changes in interfacial and surface phenomena with distance from the bulk solid surface.

3.3.1. Horizontal (flat and trough plate) sampling accessories

One of the most commonly used ATR sampling geometries in the investigation of interfacial phenomena is the horizontal trough plate design. The trough plate design is essentially identical to the flat plate design often used for polymer film and solid surface analysis, the only difference being the incorporation of a small trough directly above the IRE so that the sample can be adequately contained (see Fig. 2). Such cell designs are readily available through a large number of infrared accessory manufacturers.

The horizontal ATR cell geometry has a number of advantages over chamber/tunnel and immersion type designs. Their main advantage lies in the fact that the IRE surface is (as the name suggests) horizontal. As a result, any particulate or suspended material (adsorbent) present will (dependent on a number of factors) settle onto and cover the IRE surface, facilitating investigation of the solid/liquid interface. It is for this reason that the majority of work reported involving adsorption to particulate matter in solution has involved the use of such cell geometry. It is of course quite possible to measure adsorption from solution directly onto the IRE or onto a thin film adsorbed to the IRE with a horizontal

ATR cell, and a number of such studies have been reported. In such instances, however, chamber or immersion type cells may also be utilised. Another factor that may have contributed to the widespread use of horizontal ATR cells is price and availability. Horizontal ATR cells are relatively simple in design, use relatively cheap and readily available trapezoidal IREs, and are available through a relatively large number of manufacturers. They are also relatively simple to use and maintain, with cleaning relatively straightforward. In addition, such cells are generally quite robust. It should also be pointed out that most horizontal ATR cells can be purchased with (or converted for) flow-through capability. A variable angle of incidence option is also often available.

3.3.2. Chamber (horizontal and vertical) sampling accessories

Another common ATR cell geometry for the investigation of adsorption processes is the chamber design, in either the vertical (see Fig. 3) or horizontal mode (see Fig. 4). Such designs involve the use of a sample chamber surrounding a centrally positioned IRE. One of the more commonly used chamber designs is the Circle™ cell (Spectra-Tech, Shelton, USA), which utilises a horizontal cylindrical IRE of the type depicted in Fig. 4. Similar products incorporating horizontal IREs are made by Axiom Analytical (Tunnel Cell, Irvine, USA) and Harrick (TubeCell™, Ossining, USA). Harrick also produce a chamber type configuration in the vertical mode (Prism Cell). The major advantage of such cells is that they are ideally suited to applications requiring a flow-through capability. Such designs are, however, generally not suited for the investigation of adsorption to particulate or suspended material, as good, reproducible contact with the IRE is almost impossible to obtain. Cleaning can also be a problem, as the IREs themselves are often not readily accessible.

3.3.3. Immersion sampling accessories

Less common, but nonetheless worthy of mention, are the immersion type ATR accessories of the Dipper™ (Axiom Analytical; Irvine, USA) variety (see Fig. 5).

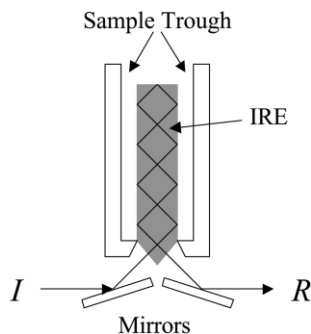


Fig. 3. Schematic diagram of a typical 'chamber' ATR cell. The liquid sample surrounds the upright IRE (I = incident radiation; R = reflected radiation).

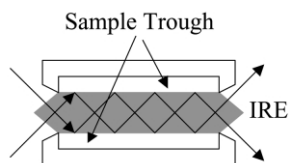


Fig. 4. Schematic diagram of a typical 'cylindrical' or 'tunnel' ATR cell, incorporating cylindrical IRE. The sample fills the chamber (or tunnel) surrounding the IRE.

The authors are unaware of any reported interfacial investigation using immersion ATR cells, however, there seems no reason why such cells could not be used for such purposes. Such designs provide a certain amount of sampling flexibility, however, they are limited in that they generally only involve one or two reflections, and hence suffer from reduced sensitivity (compared to designs offering substantially more internal reflections). Where sub-sampling presents a problem, immersion type designs permit (to a certain extent) the IRE to be brought to the sample (rather than vice versa). Cleaning is also straightforward. Immersion ATR designs may prove particularly useful in industrial and/or process type environments where the ability to quickly present samples to the IRE may be advantageous, or when on-line or at-line sampling is required.

3.4. IRE material

A wide variety of materials are commercially available for use as IREs. The more common among those available include silicon, zinc sulfide (Cleartran or Irtran), zinc selenide, germanium, KRS-5 (TlBr/TlI), and AMTIR (Amorphous Material Transmitting Infrared Radiation; GeAsSe glass). Other materials such as

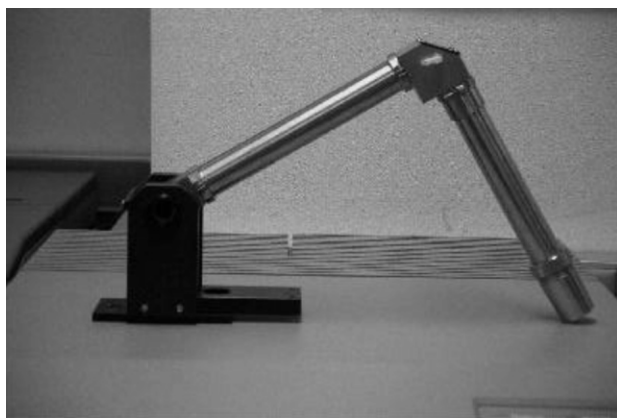


Fig. 5. The Dipper™ (Axiom Analytical, Irvine, USA) ATR cell.

diamond, cadmium telluride, silica and alumina (sapphire) have also been used in the manufacture of ATR crystals. Choice of IRE material is obviously dependent upon a number of factors. These include (in no particular order) the spectral range of interest, the adsorbent/adsorbate system under investigation, the nature of the solvent being used, the pH of the system, the physical and chemical properties of the different crystal materials available, and lastly, their respective cost. A summary of the properties of various types of commercially available IREs can be seen in Table 1. Careful consideration must be given to the choice of a suitable IRE if interfacial investigations are to be successful.

4. Interfacial spectroscopy

The last 10–15 years has seen FTIR/ATR widely used in the in situ investigation of adsorption from solution. The main focus of this research has been adsorption from solution directly onto the IRE, onto a thin film coated onto the IRE, or onto a finely dispersed solid making good contact with the IRE. Silicon, germanium, zinc selenide and KRS-5 IREs have been regularly used as adsorbents themselves (other materials have also been utilised) and IRE coatings have included elemental silicon, alumina and eicosane (to name but a few). Of particular interest has been the growing volume of literature concerning adsorption from aqueous media onto finely dispersed solids. Various metal oxide, silicon based, and other mineral systems have been investigated, with ligands such as oxalate, sulfate, salicylate, benzoate, phthalate and oleate studied, along with a number of surfactants including xanthates, sulfates and sulfonates, and quaternary ammonium compounds. These studies have generally relied upon the use of (relatively) high surface area (10–300 m²/g), insoluble solids while also being performed under relatively mild conditions (pH 4–10), however, some exceptions do exist.

4.1. Methodology

Interfacial spectra are readily obtained using FTIR/ATR by combining carefully planned experiments with careful spectral manipulation. The methodology involved is best illustrated by way of example, with none more suitable than our recent studies concerning the adsorption of quaternary ammonium (QA) surfactants to the surface of sodium oxalate in an aqueous environment [2,3]. A study complicated by the solubility of the adsorbent (sodium oxalate) in the solvent of interest (water).

Spectra in this instance were, not surprisingly, dominated by the strong infrared absorbance of water. Thus, in order to acquire useful spectra of the compound(s) of interest, a water reference spectrum was always subtracted from the sample spectrum. In the case of the aqueous QA samples, a water spectrum (recorded immediately after acquisition of the QA spectrum) was subtracted from the QA/water spectrum (subtraction factor = 1) yielding a spectrum of the aqueous

Table 1
Physical and chemical properties of IRE materials

IRE material	n	Hardness (Knoop) ^a	ρ (g/cm ³)	Solubility (g/100 g H ₂ O)	Melting point (°C)	Cleaning agents	Transmission range (cm ⁻¹) ^b	General comments
AMTIR	2.5	170	4.40	i	300 ^c	Alcohol, acetone, toluene, water	11 000–1000	Relatively hard, brittle. Resistant to acids. Attacked by strong alkalis.
CdTe	2.7	56	6.20	i	1040	Alcohol, acetone, water	10 000–500	Very brittle, easily cracked/scratched. Attacked by oxidisers and acids. Slightly soluble in acids.
Diamond	2.4	7000	3.5	i	3500	Alcohol, acetone, water	4500–2500 1667–33	Very hard. Good for high pressure and corrosive work. Attacked by K ₂ Cr ₂ O ₇ and concentrated H ₂ SO ₄ .
Ge	4.0	550	5.32	i	936	Alcohol, acetone, toluene, water	5000–900	Hard, brittle. Subject to thermal shock. High reflection losses. Attacked by hot H ₂ SO ₄ and aqua regia.
Quartz	1.4	174	2.6	i	1610	Alcohol, acetone, water	25 000–2200 250–FIR	Mostly used in UV-Vis and NIR regions. Attacked by HF. Water insoluble.
Sapphire	1.7	1370	4.00	i	2030	Alcohol, acetone, toluene, water	33 000–2800	Very hard and inert. Attacked by concentrated acids and alkalis.
Si	3.4	1150	2.33	i	1420	Alcohol, acetone, water	9500–1500 350–FIR	Hard, brittle. Resistant to thermal and mechanical shock. Attacked by HF and HNO ₃ .
KRS-5	2.4	40	7.45	0.05	415	Methyl ethyl ketone	14 000–400	Deforms under pressure. Toxic. Soluble in alkalis, not in acids. Attacked by complexing agents (NH ₄ ⁺) salts.

Table 1 (Continued)

IRE material	n	Hardness (Knoop) ^a	ρ (g/cm ³)	Solubility (g/100 g H ₂ O)	Melting point (°C)	Cleaning agents	Transmission range (cm ⁻¹) ^b	General comments
ZnSe	2.4	137	5.27	i	1520	Alcohol, acetone, water	20 000–700	Hard, easily cracked. Low reflection losses. Attacked by acids and strong alkalis. Toxic.
ZnS	2.2	178	4.08	i	1830	Alcohol, acetone, water	14 000–1000	Good resistance to thermal and mechanical shock. Attacked by acids and strong oxidising agents.

^a kg/mm².^b Transmission range as an IRE.^c Maximum useful temperature in air.

Table 2

Illustration of the spectral manipulation process leading to the acquisition of interfacial spectra

Test	Spectrum 1	Spectrum 2	Spectrum 3	Manipulation	Spectrum 4
Dosed	Slurry	– Supernatant	= Solid1	Solid1 – Solid2	= Interface
Blank	Slurry	– Supernatant	= Solid2		

form of the QA. A similar procedure was used to obtain interfacial spectra of adsorbed QAs, with spectral subtraction of a supernatant from a suspension, yielding a spectrum of the solid phase and the interfacial region. Further subtraction of a spectrum of a control solid phase (without adsorbate) *resulted in a spectrum of the interfacial region only*. In this instance, interfacial spectra of the adsorbed QAs were acquired as follows:

The adsorbent/adsorbate slurry was quickly sampled (from the same depth on each occasion) using a digital micropipette, and the sample carefully placed in the horizontal ATR trough plate making sure that the IRE was completely covered. The surface of the ATR plate and IRE were kept level to ensure an even and reproducible covering of solid oxalate.

The solid oxalate was then allowed to settle onto the ZnSe IRE for a period of 10 min, after which spectral acquisition was commenced (1024 scans co-added, taking approximately 15 min). During this time the remaining sample was centrifuged.

Upon acquisition of the *slurry* spectrum, the ATR plate was carefully removed from the sample compartment of the FTIR, and the slurry removed by means of pipette. The surface of the IRE was then thoroughly cleaned with a jet of water, the process being repeated a number of times, and dried under a stream of air before being carefully returned to its original position in the sample compartment (using guide pins attached to the ATR accessory). A *supernatant* spectrum was subsequently acquired by pipetting the supernatant onto the clean IRE surface, using the same number of scans as previously outlined.

After ATR correction (for varying depth of penetration with wavelength),¹ subtraction of the *supernatant* spectrum from the *slurry* spectrum yielded a *surface* spectrum. Further subtraction of an *untreated surface* from a *treated surface* resulted in a spectrum of the *interfacial* region, showing adsorbed QAs (see Table 2; all subtraction factors used were in the range 1.00 ± 0.05). Factors outside this range suggested poor or unreproducible IRE contact or inadequate ATR plate re-alignment, and were rejected. In such cases, the spectral acquisition was repeated (however, this was rarely the case).

¹In ATR, the depth of penetration of the infrared beam into the sample varies with the wavelength of the radiation – the longer the wavelength, the greater the depth of penetration. The effective pathlength of the spectrum collected thus varies with the wavelength of the radiation. ATR correction accounts for this variation in effective pathlength by scaling the ATR spectrum accordingly. Most FTIR software packages incorporate an ATR correction algorithm.

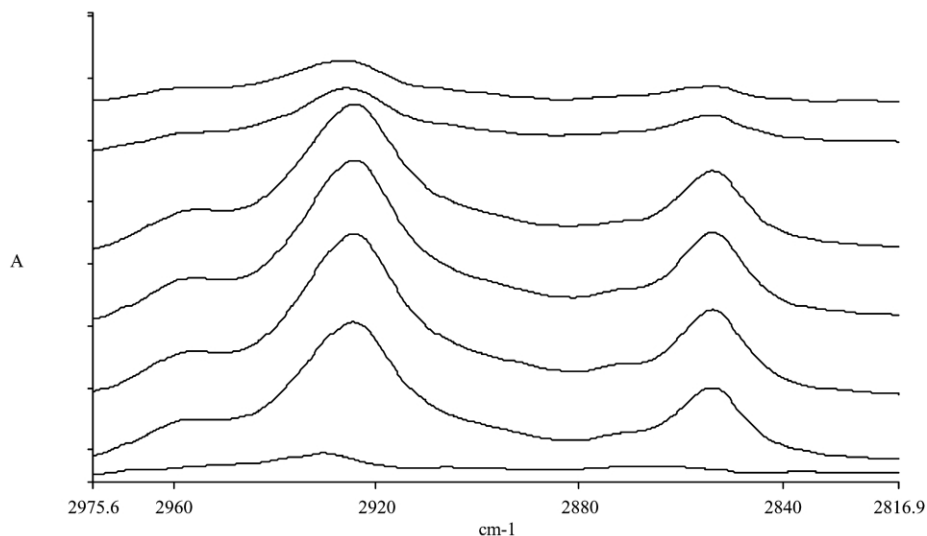


Fig. 6. Interfacial spectra of adsorbed tetradecyltrimethylammonium bromide (at 0, 3, 5, 7, 10, 20 and 50 ppm initial solution concentration, bottom to top) adsorbed to the surface of sodium oxalate in an aqueous, high ionic strength, high pH environment [3].

Using this process of spectral subtraction, interfacial spectra of adsorbed alkyl-trimethylammonium bromides were obtained (see Fig. 6). Regardless of the adsorbent/adsorbate system in question, the basic principles of this methodology can be readily applied to other systems where the nature of the solid/liquid interface is of interest.

4.2. Adsorption to the IRE

One of the easiest ways to obtain information concerning the nature of the solid/liquid interface is to observe, spectroscopically, adsorption directly to the surface of the IRE itself. Assuming an appropriate IRE material is available, such studies are relatively straightforward, and not reliant upon some of the factors intrinsic to studies involving deposited or particulate adsorbents. One of the most commonly used IRE materials for such investigations is silicon (or the native oxide thereof). Parry and Harris [30] used FTIR/ATR to measure the rates of chemical modification reactions at silica surfaces. By oxidising a silicon ATR crystal under dry oxygen, they were able to produce a model silicon dioxide (SiO_2) layer which was used to investigate the binding kinetics of diphenylchlorosilane from carbon tetrachloride solution. Using this technique, they were able to obtain both in situ kinetic and structural information, as well as an understanding of the effect of the silica layer on the sensitivity of the ATR measurements. Similarly, in related studies, Azzopardi and Arribart [31] and Berquier [32] describe (at the native oxide

layer of a silicon IRE) the formation of an organosilane layer and adsorption of acetone and polymethylmethacrylate (once again using carbon tetrachloride), respectively. Both studies involved the use of ATR cells equipped with flow-through capability, and report 'high sensitivity' through the use of the FTIR/ATR technique. Other studies of adsorption to silicon IREs from organic solvents include those of Nunn et al. [33] and Ozanam et al. [34] who have investigated surfactant adsorption processes and the hydrogenated silicon surface, respectively. Nunn and co-workers probed the adsorption of amine and sorbitan based surfactants from deuterated toluene onto the native silicon oxide layer, and were able to calculate the Gibbs surface excess concentration and hence construct adsorption isotherms for each surfactant. By rinsing the IRE with hydrofluoric acid, Ozanam et al. obtained a surface covered with covalently bonded hydrogen, which they were then able to use to investigate the semiconductor/electrolyte interface for a series of organic electrolytes.

A number of aqueous systems have also been investigated where the silicon IRE acts as the adsorbent. Sukhisvilli and Granick have recently reported the results of work focussed on polyelectrolyte exchange [35] and amphiphile adsorption [36] processes. The polyelectrolyte study focussed upon a family of poly(1,4-vinyl)pyridines and the kinetics of their exchange at the silica surface, while the second body of work investigated the orientation and order of 1,4-dimethylpyridinium (the segmental analogue of the aforementioned polymer) adsorption to a silanol IRE surface layer. In two papers dealing with adsorption to the native silica layer, Neivandt et al. used infrared [37] and infrared/ultraviolet (UV) [38] ATR to probe surfactant and surfactant/electrolyte adsorption, respectively. Using polarised infrared light, the orientation of cetyltrimethylammonium bromide (CTAB) adsorbed at the solid/solution interface was determined over a range of pH values (2–10) [37]. A similar study investigated the coadsorption of polystyrenesulfonate and CTAB on silica, with FTIR/ATR combined with UV/ATR to determine the surface excess of both polymer and surfactant, again over a range of pH values similar to that reported above [38]. Killmann and Reiner [39] used negatively charged hydrophilic and neutral hydrophobic silica surfaces of flat silicon crystals to obtain isotherms for the adsorption of poly-L-lysine and poly-L-glutamic acid. Fan and Ng [40] investigated the photoelectrochemical characteristics of the *p*-silicon/potassium ferri-ferrocyanide electrolyte interface, and found adsorption to be affected by both the applied voltage and the intensity of illumination.

Materials other than silicon, have also been used for FTIR/ATR based interfacial investigations. While not as prevalent as silicon, germanium has been used as the substrate for a number of interfacial studies. Yang and co-workers have reported the use of germanium in the investigation of the adsorption of stearic acid from carbon tetrachloride [41], as did Couzis and Gulari who looked at the adsorption kinetics of polystyrene onto germanium from the same solvent [42]. The observation of octadecyltrichlorosilane monolayer self-assembly (from bicyclohexane) on a germanium IRE surface was the aim of work reported by Cheng et al. [43], while Matsui and co-workers combined electrophoresis and ATR in order to measure the adsorption of sodium decanoate onto germanium from aqueous

solution. In doing so, they were effectively using the germanium IRE to concentrate the analyte at the solid/liquid interface [44].

Alumina (Al_2O_3) was used as an IRE material by Yang et al. in their study of stearic acid adsorption [41]. Fan and Ng used cadmium telluride in probing the photoelectrochemical characteristics of the n-CdTe/acetic acid solution interface [45]. Free and Miller [46] used a fluorite (CaF_2) IRE in their investigation of the adsorption kinetics of oleate and linoleate, and were able to demonstrate that the adsorption process was not controlled by convective diffusion. Fluorite was again used as an adsorbent in an ongoing study that also involved alumina and sylvite (KCl). The results of the aforementioned investigations, focussing on the surface phase transitions of adsorbed collector molecules including oleate, xanthate, dodecylsulfate, and octylamine, were summarised in a paper by Kellar and co-workers [47].

FTIR/ATR studies involving adsorption directly to the IRE have (as previously mentioned) been used to investigate biological systems (lipid bilayers and Langmuir–Blodgett deposited films for example). The use of FTIR/ATR in such systems has been reviewed elsewhere (see Overview), and is considered beyond the scope of this review, however, a brief discussion was considered warranted. In one of the first reported applications of FTIR/ATR to the investigation of interfacial phenomena, Haller and Rice qualitatively determined the molecular orientation of Langmuir–Blodgett (LB) deposited calcium stearate monolayers on an alumina IRE [48]. Similarly Ahn and Franses used polarised infrared light to determine molecular orientation in a variety of LB films on germanium and silicon IREs [49]. The types of lipid bilayers investigated using FTIR/ATR include the phospholipids 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine [50] and dimyristoylphosphatidic acid [51]. Interested readers are directed to the works cited previously (Section 1) for a more detailed discussion.

4.3. Adsorption to coated IREs

An extremely effective (and popular) means of performing interfacial research using FTIR/ATR is the coating of the IRE itself with the substrate or adsorbent of interest. A large number of IRE materials have been used for such studies (including ZnSe, Si, KRS-5, Ge, and Al_2O_3), with an even greater number of IRE coatings reported (as discussed below). Such interfacial studies are really only limited by the ability to deposit a thin, uniform, self-supporting layer of the adsorbent of interest upon the IRE. Any coating techniques must, however, be reproducible and result in good, uniform contact with the IRE. In addition, the coating must be thin enough to permit investigation of the interfacial layer, this in turn being dependent upon the IRE/coating/solvent system being used (and resultant depth of penetration of the evanescent wave). Some typical values reported for IRE coatings include 50, 60, 100, 210, 210–420 and 150–400 nm for polystyrene/Si [52], Al_2O_3 /ZnSe [53], Al_2O_3 / SiO_2 [54], Al_2O_3 /ZnSe [55], haematite/ZnSe and Al_2O_3 /ZnSe [56] coating/IRE combinations, respectively.

In a series of papers investigating adsorption phenomena at the alumina/water

interface [56–60], Sperline et al. were able to produce an alumina coated ZnSe IRE using controlled rf sputtering. Using these alumina coated IREs (having a thickness of 150–400 nm), they were able to perform linear dichroism studies of sodium dodecyl sulfate (SDS) [56], sodium dodecylbenzenesulfonate [57], and 4-octyl-, 4-decyl-, and 4-dodecylbenzenesulfonate adsorption at the alumina/water interface [60]. In addition to this, the temperature dependent interfacial structure of adsorbed SDS was investigated [59], as was the co-adsorption of benzophenone with SDS [58]. The investigators were able to quantitatively determine surface excess values for the adsorbed species on alumina, as well as information relating to the orientation of the adsorbed compounds. The effects of factors such as pH, ionic strength, and temperature were also investigated.

Following on from the work described above, have been studies examining the adsorption of other species to alumina coated ZnSe IREs. Sperline himself has been involved in attempts to understand the mechanism of humus coatings on mineral (alumina) surfaces [61,62] and the interaction of alkyl phosphates with the alumina surface [55]. Linear dichroism studies of adsorbed humic material suggested that the carboxylate groups present were not free to rotate [61], with different adsorption isotherms observed for the hydrophilic and hydrophobic humic fractions (suggesting different mechanisms of adsorption) [62]. The in situ alkyl phosphate analysis [55] centred on the extent of adsorption and spatial chain orientation of the adsorbed species at the alumina/water interface. Using a similar sputtering technique to that described by Sperline et al., Couzis and Gulari [53] probed the interaction dynamics and structure of adsorbed (sodium) laurate at the alumina/water interface. Their findings suggested that the laurate was irreversibly adsorbed at pH values below that of the isosteric point of alumina. By evaporating ultrapure aluminium onto pre-cleaned silicon wafers, Chen and Frank [54] observed that the adsorption of stearic acid from hexadecane onto the oxidised aluminium (Al_2O_3) surface led to monolayer formation.

A number of studies focussing upon the orientation, mobility and distribution of surface active species in latex have been undertaken using FTIR/ATR. Whilst not strictly adsorption experiments as such, said studies still demonstrate the ability of FTIR/ATR to investigate or monitor interfacial processes. By depositing thin latex films on KRS-5 IREs, Urban and co-workers used ATR to study the orientation and mobility of surfactants at the polystyrene/poly(*n*-butylacrylate) latex interface [63], and acid functionalities at the EA/MAA latex–substrate interface [64]. They were also able to monitor surfactant behaviour and particle size effects in styrene/*n*-butylacrylate films [65]. Amalvy and Soria also coated KRS-5 with latex films in order to study the distribution of SDS therein [66], noting that both the film–air and film–substrate interfaces showed significant surfactant enrichment.

A number of studies report the use of polymer coated IREs for the investigation of interfacial processes. Scheuing used an eicosane coated ZnSe IRE to monitor the interfacial interactions of hydrophilic and hydrophobic ethoxylated alcohols [67]. By using a flow-cell, he was able to monitor the removal of the hydrocarbon layer by the flowing action of the surfactant in question. Polystyrene [52], polypropylene [68], and cellulose [69] coatings have also been employed to study the

adsorption of SDS, various polyelectrolytes, and surfactant dispersions, respectively.

As previously stated, these types of studies are limited only by the ability to produce a suitable coating of the adsorbent of interest. It is not surprising then that a large and varied collection of materials (other than those already described) have been studied using FTIR/ATR. By sputtering a germanium IRE with a very thin layer of gold (5 nm) and then coating it with lithium, Zhuang et al. studied the reactivity of lithium toward propylene carbonate and poly(ethylene oxide) [70] at various temperatures. The lithium metal/electrolytic solution interface was also investigated in situ by electrodepositing lithium onto a germanium IRE [71]. By evaporating thin silver films onto the IRE and using it as the working electrode, Osawa et al. undertook the real-time monitoring of electrochemical dynamics using surface-enhanced ATR [72]. A number of workers have succeeded in coating clays and clay minerals to ZnSe IREs for the purpose of studying adsorption mechanisms and surface acidity [73]. Adsorbates have included polyamine, polyacrylic acid, polyethylene glycol [74] and various nitroaromatic compounds [75].

The first in situ infrared spectroscopic measurements of surface excess solvated ion concentrations in the electrical double layer resulting from metal oxide surface charge were reported by Dobson, Connor and McQuillan. The basis of the technique (surface titration by internal reflection spectroscopy; STIRS) was the deposition of a titanium dioxide (TiO_2) gel film onto a ZnSe IRE [76]. Using STIRS, they were able to monitor hydrous metal oxide charge and adsorption. Using a similar technique, they were also able to study the adsorption of lactic acid on TiO_2 and cadmium sulfide (CdS) semiconductor photocatalyst surfaces [77]. Connor et al. [78] again used sol-gel techniques to investigate the chelation of aluminium, titanium, and zirconium oxides by catechol, 8-quinolinol, and acetylacetone, concluding that the adsorbates bound to the surface metal ions in a bidentate manner. Other mineral/adsorbent systems investigated include haematite/sulfate [79], silica/ethyl acetate [80], and silica/octylphenol polyethylene oxide and dodecyltrimethylammonium bromide [81]. Haematite coatings [79] were deposited from solution, and silica coatings were prepared by spluttering [81] and withdrawal of the IRE from a suspension of fumed silica [80].

4.4. Adsorption to particulate matter in contact with the IRE

In addition to interfacial research involving adsorption to the IRE, or to a thin coating or layer attached to the IRE, FTIR/ATR has proved to be an ideal tool for investigating adsorptive process occurring in particulate systems. Providing a number of important criteria are met, such studies can provide extremely useful information concerning the nature of the adsorbed layer on particulate matter. This makes FTIR/ATR ideal for studying colloidal surfaces, many hydrometallurgical processes, and other significant industrial areas such as flotation and flocculation.

To acquire good interfacial spectra in particulate systems, a number of criteria must be met, the most important of these being good, uniform contact between the

particulate matter and the IRE. If this requirement cannot be met, successful interfacial studies are unlikely, and any sort of quantitative interfacial spectroscopy can be all but ruled out. One means of maximising adsorbent/IRE contact is through the use of *high surface area* (HSA) solids. As well as increasing the likelihood of obtaining good (and reproducible) IRE contact, the use of HSA solids also allows for a higher adsorbate surface density, thereby increasing the likelihood of acquiring quality interfacial spectra. Our results suggest that the use of a relatively high surface area solid is vital to the success of interfacial studies using FTIR/ATR [2,3]. The majority of the studies reported in the literature use solids with surface area greater than 10 m²/g. Our studies of adsorption to sodium oxalate were carried out using a finely ground solid with a surface area of 3.3 ± 0.4 m²/g [2], and Mielczarski et al. have reported studies involving solids having surface areas of the order of 0.5–1.0 m²/g [82]. The majority of studies, however, have involved the use of much higher surface area solids (> 50 m²/g). Finally, it is vital that sufficient time be allowed for the particulate matter in solution to settle onto the IRE surface.

A large number of interfacial studies have been performed on metal oxide, metal hydroxide, and metal oxyhydroxide systems, with the work often industrially driven and/or applied in nature. Kung and Hayes [83] investigated the adsorption of two surfactants, CTAB and cetylpyridinium chloride (CPC), to the surface of HSA silica (255 m²/g), stating that the high surface area, small particle size silica was found to be optimal for conducting CIR (cylindrical internal reflectance) studies. Spectroscopic results showed the formation of micelle-like, surfactant-aggregate clusters on the silica surface even at low surfactant surface coverage. Although not investigating interfacial processes, one group of workers have used FTIR/ATR to quantitatively analyse silica samples in aqueous media [84]. Using this technique, they report detection limits of approximately 0.001%. A second group have recently applied ATR to the measurement of silica-gel particle size [85], finding band intensity increasing with decreasing particle size (as expected, based on the nature of the evanescent wave).

Goethite (α -FeOOH) has been the subject of a number of studies. Tejedor-Tejedor et al. characterised benzoic and phenolic complexes at the goethite/aqueous solution interface using CIR [86], obtaining information on the structure of the complexes between oxo anions and the surface of colloidal goethite. In a study similar to that outlined above, Tejedor-Tejedor and co-workers then used ATR to quantitatively analyse colloidal goethite particles in aqueous suspensions [87], developing a methodology for determining the quantity of suspended material 'seen' by the technique. Sun and Doner prepared HSA goethite (80.2 ± 3.8 m²/g) from ferric chloride and sodium hydroxide, and used it to investigate arsenate and arsenite bonding structures [88].

Su and Suarez acquired interfacial information on carbonate speciation between solid and aqueous phases for the aluminium and iron oxides gibbsite [Al(OH)₃] and goethite [89], in an attempt to further understanding of surface adsorption mechanisms of dissolved organic carbon species on soil minerals. Similarly, Biber and Stumm studied the surface coordination of salicylic acid on a number of aluminium

and iron oxides [90]. The solid phases examined included α -, δ -, and γ - Al_2O_3 , α - Fe_2O_3 , and α - and γ - FeOOH , although δ - Al_2O_3 was the main focus of the study. Results suggested that chemical composition of the metal oxide, and not morphology, determined the structure of the ligand surface complex. Gibbsite was also the subject of recent study investigating surfactant (alkyltrimethylammonium bromide) adsorption under high ionic strength, high pH conditions [91], in which micelle-like structures were detected at the gibbsite/aqueous interface. Boehmite (AlOOH) was the subject of a study by Nordin et al. [92] aimed at probing the adsorption of *o*-phthalate at the water boehmite interface, with the samples analysed as wet pastes after removal of the supernatant. A second paper from the same group investigated the complexation of a polycarboxylic acid at the same interface [93], with the samples again analysed as wet pastes. Walker and Weisenborn [94] studied the solid/aqueous interface between 8-hydroxyquinoline and tantalum pentoxide using a CIR based technique, finding the structure of the adsorbed species to be similar to that of the chelated tantalum oxinate formed in the bulk solution.

Kubicki et al. also used wet pastes to investigate the bonding mechanisms of salicylic acid adsorbed onto illite clay [95] in an attempt to further understanding of the chemical bonding between natural organic matter and clays. Binder and co-workers used the same wet paste technique to perform infrared dichroism measurements on the alkyl chain packing of an ionic detergent (DTAB) intercalated between silicate (illite) layers [96], and were able to shed light on the orientation of the polar head-group of the surfactant. Shewring et al. monitored suspensions of the gel-like clay bentonite whilst undergoing evaporation in order to investigate surface hydration processes [97]. Bentonite hydration was found to be accompanied by the formation of an extended electrical double layer between the platelets.

Various fluoride and sulfide mineral systems have been probed in situ using FTIR/ATR. The mechanism of SDS adsorption to fluorite (CaF_2) was the subject of a study by Gonzalez-Martin et al. [98], who also pressed the solids against the IRE surface after removing them from solution (analysis as a wet paste). The nature and structure of the adsorption layer on apatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] contacted with oleate solutions was investigated by Mielczarski and Cases [99], who combined in situ and ex situ infrared techniques to obtain complimentary information. Vucinic and co-workers, once again using the wet paste method, have reported a series of studies dealing with ethylxanthate adsorption on galena (PbS), sphalerite [$(\text{Zn}, \text{Fe})\text{S}$] [100,101], pyrite (FeS_2) [102] and cerussite (PbCO_3) [103]. Chernyshova and Tolstoy also investigated xanthate adsorption to galena and pyrite [104], with their work again involving the pressing of mineral pastes onto the IRE surface. Copper based sulfide ores were the target of another study by Mielczarski et al. [82] which characterised the surface products resulting from the interaction of an aqueous xanthate solution with chalcopyrite (CuFeS_2), tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$), and tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$). By pressing the adsorbent against a germanium IRE, Raszka and Strojek used FTIR/ATR to investigate the activation of the flotation of silicon carbide (SiC), with oleate being the adsorbate of interest [105].

Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) (a Bayer process solid) was the subject of an in situ FTIR/ATR study aimed at investigating adsorption process occurring under extreme (high ionic strength, high pH) conditions which mimicked as closely as possible those encountered in the Bayer process [2,3]. The adsorption of an homologous series of alkyltrimethylammonium bromides was studied, with hemimicellar surfactant aggregates found at the oxalate/aqueous interface even at low surfactant solution concentrations. Adsorption was found to be dependent upon the length of the surfactant alkyl chain, and the presence of a pre-adsorbed Bayer humic extract, this in turn being highly suggestive of some type of interaction between the two. Based upon the interfacial spectra obtained, dose–response curves for the four quaternary ammonium compounds studied were generated. Extent of adsorption was found to increase with alkyl chain length until the point was reached where alkyl chain of the adsorbed compound adopted a coil-like structure, thereby reducing the amount adsorbed compared to the shorter chain homologues.

5. Summary

There is little doubt that the FTIR/ATR technique offers surface chemists and scientists the chance to obtain novel in situ information concerning interfacial processes. As an investigative technique it is becoming increasingly popular, and may now be considered one of the tools of choice in the field of interfacial chemistry. Atomic force microscopy (AFM) can now provide similar information in situ, however, factors such as cost, availability and the degree of operator expertise required can make this technique inaccessible. FTIR/ATR on the other hand, provides a readily accessible, efficient and cost-effective means of performing interfacial studies, and does not require highly skilled and trained operators.

FTIR/ATR has become an invaluable part of our ongoing research program into the surface chemistry of Bayer process solids. The technique currently plays an integral role in all of our interfacial studies, and will continue to do so for the foreseeable future. Given the relative ease with which FTIR/ATR can be applied, and the large number and type of systems to which it is amenable, it is not surprising that the use of FTIR/ATR as an investigative, in situ interfacial tool is constantly increasing. With advances in spectrometer speed and sensitivity (combined with reduction in costs), this trend is more than likely to continue.

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