

## Methods for Speciation of Metals in Soils: A Review

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### ABSTRACT

The inability to determine metal species in soils hampers efforts to understand the mobility, bioavailability, and fate of contaminant metals in environmental systems, to assess health risks posed by them, and to develop methods to remediate metal contaminated sites. Fortunately, great strides have been made in the development of methods of species characterization and in their application to the analysis of particulates and mixtures of solid phases in physics, analytical chemistry, and materials science. This manuscript highlights a selection of the analytical methods available today offering the greatest promise, briefly describes the fundamental processes involved, examines their limitations, points to how they have been used in the environmental and geochemical literature, and offers some suggested research directions in the hope of stimulating further investigation into the application of these powerful tools to the problems outlined above.

THE USE OF METALS in human history has yielded great benefits as well as unexpected harmful consequences. The generic term *metal* refers here to roughly 70 electropositive elements in the periodic table. As a group, they share some common physical, chemical, and electrical properties. Although metals constitute the majority of elements by type, in general they represent a small atomic and mass fractional abundance of the elements comprising the earth's surface and atmosphere, relative to the nonmetals. Further, while sharing common properties, metals exhibit wide ranges with respect to one another, in both chemical behavior and the measured values of those common properties. Historically, it has been the exploitation of these properties of metals which has led to successive waves of progress in the development of our modern technological society and its dependence on, and increasing appetite for metals. It is their chemical and radioactive behavior in biological systems (toxicity, mutagenicity, and carcinogenicity), realized within the past century, which pose the most serious risks. The elements of greatest concern include Pb (Group IV), Cd and Hg (Group II), and As (Group V). Other different types of metals, like Cs (an alkali

metal), Be, Sr, and Ba (alkaline earth metals), and U and Th (rare earth metals) also pose problems.

Man's perturbation of nature's slowly occurring life cycle of metals includes (i) the extraction, smelting, and processing of metal bearing ores into products, (ii) the distribution and use of these products by industry and consumers, and (iii) the return of these metals in a concentrated form to the natural environment through disposal of processing wastes and the discard of spent products. The metal or metals then become contaminants in the receiving environments. Part of the reason they become contaminants is seen within the description of the man-made life cycles above. They include (i) the rapidity of the man-made cycles relative to natural ones, (ii) the transfer of the metals from mines to random environmental locations where higher potentials of direct exposure occur, (iii) the relatively high concentrations of the metals in discarded products compared to those in the receiving environment, and (iv) the chemical form, or species, in which a metal is found in the receiving environmental system. The latter issue is the central concern of this paper.

The complexity of metal contaminated sites has and continues to be simplified to a measure of the total metal content. While total metal content is a critical measure in assessing risk of a contaminated site, total metal content alone does not provide predictive insights on the bioavailability, mobility, and fate of the metal contaminant. From the perspective of risk assessment the following example illustrates the importance of speciation. Using total metal concentration as the index of risk it follows that a site with a concentration of 5000 mg Pb kg<sup>-1</sup> is significantly more toxic than one which is 500 mg Pb kg<sup>-1</sup>. However, suppose that the only species of Pb in the 5000 mg Pb kg<sup>-1</sup> soil was galena (lead sulfide, PbS;  $K_{sp} = 10^{-28.1}$ ), while the only species of Pb in the 500 mg Pb kg<sup>-1</sup> soil was cerussite (lead carbonate, PbCO<sub>3</sub>;  $K_{sp} = 10^{-13.13}$ ). In absolute terms, from simple thermodynamic calculations alone, a greater amount of Pb is likely to be both mobile under water transport and bioavailable in soluble form to organisms in the soil with the *lower* Pb concentration, because cerussite is vastly more soluble than galena. Mobility is clearly dependent on chemical form. And although bioavailability and toxicity are complex processes and are biological species dependent as well as even genetically dependent within species, this example indicates that the chemical form of a metal contaminant is an important factor in assessing human health or ecological risks.

Why should speciation analyses be performed? The simple answer is that it is part of an overall approach to understand the complex chemistry and behavior of contaminants in environmental and biological systems. However, there are other more practical reasons. One is that improved knowledge and understanding of the

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Published in J. Environ. Qual. 34:1707–1745 (2005).  
Reviews and Analyses  
doi:10.2134/jeq2004.0014  
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chemistry of metals and their interaction with environmental system chemistries would enable fundamental progress in a variety of areas, for instance environmental, geological, agricultural, and economic. In the environmental field, an ultimate goal might be to use speciation analyses to accurately determine the human health or ecological risks posed by the metal species discovered and quantitated at a site and redirect this understanding into the design, selection, optimization, and monitoring of remediation strategies applied to clean up the site, if necessary. Today, with the advent of in situ, submolecular research tools to probe the local environment of metals, that ultimate goal may be within our grasp.

The primary objective of this manuscript is to offer to the geoscience research community a detailed outline of a number of possible techniques (old, new, and improved) that could be used for speciation analyses of metals in the natural environment, especially soils. It describes the physical processes exploited by the techniques and the types of information that can be obtained from them. It would be impossible to describe every analytical method (see Table 2 for a list of 283 techniques); therefore, we review the most promising ones from several diverse fields that could be employed in a research program. It is hoped that this manuscript will encourage those who have not yet attempted speciation analyses in their research to do so, while also enticing those already utilizing such techniques to employ a different method that complements or enhances their current capabilities. The scope of this review is broad, ranging from the simplistic (perhaps controversial) chemical extraction methods to sophisticated microfocussed X-ray absorption spectroscopic techniques available only at synchrotron radiation facilities. The authors realize the abundance and significance of recent literature; however, it is academic folly to believe that the most relevant research has been accomplished in only the past five years. Therefore, well-established, less-glamorous methods developed decades ago, have been included as they still have a valuable place as primary and secondary tools in the determination of metal species.

## CHEMICAL EXTRACTION METHODS

### Overview of Chemical Extraction Methods

Partial or sequential extraction methods are among the oldest and most commonly used methods of chemical partitioning of environmental solid samples. These techniques are easy to apply, inexpensive, and require little data analysis. However, it is vitally important to realize that the original work on sequential extraction was performed on sediment materials with trace metal concentrations (Tessier et al., 1979). Since then, many researchers have adapted these methods to study anthropogenic metal contamination and to predict or estimate bioavailability of various metal forms.

The idea behind these extraction methods is based on the assumption that a particular extractant is phase or retention mode specific in its chemical attack on a mixture of forms. For instance, it assumes that water

will remove only easily soluble forms, that buffered acetic acid will attack and dissolve only carbonates, and that  $\text{NH}_4\text{OAc}$  (or  $\text{MgCl}_2$ ) at pH 7 will liberate only adsorbates. Sequential application of a series of specific reagents coupled with elemental determination for each yields a fractionation pattern or a relative partitioning of metal forms into operationally defined "species." In sequential extraction schemes, reagents should be of an increasingly drastic chemical action, or of a totally different specificity, thus providing clear distinctions among sources of the extracts obtained. In practice, selectivity for a single phase or mode in a thermodynamic sense does not occur. Nor is there consistency of fractionation results between the various extractants of a given class (e.g., electrolytes or chelating agents) and different application methods used. This has prompted Kersten and Forstner (1986) to suggest that the operational species extracted be defined in terms of the reagent used rather than the phase or retention mode assumed attacked in the extraction.

In addition to the "fundamental" limitations cited above, there are two major factors which play a role in determining the success of a given extraction procedure. These are: (i) the chemical properties of the extractant and (ii) experimental parameter effects (e.g., length of time the extractant and sample are in contact, temperature, concentration, and solid to solution ratio). Further considerations apply if the extraction procedure is a sequential scheme for determining a fractionation pattern for a given soil or sediment sample. These include: (i) the sequence of steps, (ii) matrix effects (cross contamination and re-adsorption), and (iii) heterogeneity and physical associations of the solid components. Lastly, sample procurement, handling, storage, and preparation all affect the results in a crucial way. Contamination at any step, length of time, and temperature of storage, whether the sample is dried or stored moist, and whether oxygen is allowed to enter the system, can induce large methodological errors in the results of such extractions. For a more vigorous discussion of these see Batley (1989). In addition, there is a wealth of literature on specific research topics, as well as two detailed reviews specifically directed to the field of soils (Pickering, 1986) and sewage sludge-amended soils (Lake et al., 1984). The pitfalls and criticisms of these methods are recounted in the literature and are repeated here to illustrate the need to have independent methods available to perform speciation of metals in solid matrices.

### Shortcomings of Chemical Extraction Methods

There are several reviews that report on the most significant criticisms of the extraction methods of speciation (Pilkington and Warren, 1979; Nirel et al., 1985; Nirel and Morel, 1990; Scheckel et al., 2003). Those criticisms will be covered below. However, one criticism that seems important but not recognized is the origin of these methods. Since they were meant for trace metals in sediment materials, their application to heavily contaminated soils may be suspect when concentrations of the "trace" metals are no longer trace but major constit-

uents. In this situation, the metal chemistry is no longer dominated by the other major components of the system, but is itself controlling the chemistry of other elements.

The criticism above points out that the basic chemical assumptions behind the method may be suspect. In soil deposition, the concentration of the metal may be much higher. In addition, many source metal forms are artificial minerals, often unlike any natural species that are normally found. For example, relatively insoluble lead chromate salts have been used as pigments in yellow traffic paints. However, if this compound becomes distributed in soil and is stable under the soil conditions, what would a sequential extraction say about the form, which by assumption of this method, should not exist naturally? In addition, there are many sites contaminated with many different metals as well as man-made organic petrochemical wastes. How are such "unnatural" or unexpected species (and there may be many such examples in polluted soils) accounted for in schemes that have broad classes but a sediment chemistry model to guide interpretation?

In their critique, Nirel and Morel (1990) state that the operational definitions classifying extracts is a tautology and prevents the possibility of critically examining the logic of the schemes. Most critics claim validation of extraction schemes and the classes of "species" extracted have not been done. That is, comparisons of sequential extractions with thermodynamic models and direct instrumental analyses are lacking. The reagents used are also not as selective as many advocates assert. Salomons and Forstner (1984) point out extraction efficiencies vary according to the solid to reagent ratio and the length of contact time between the two. Drying, the particle size, and whether a sample has been ground or left intact also influence the results. In addition, the effect of equilibrium shifts as the extracts are removed or introduced from contact with the solid matrices is unknown. Re-adsorption of the trace element into other compartments can take place before solid-extract separation, while precipitation can occur during extraction or storage of the extract before elemental analysis. Recent research has demonstrated the pitfalls of sequential extraction procedures on examination of non-equilibrated systems. Scheckel et al. (2003) confirmed via X-ray diffraction (XRD) and X-ray absorption (XAS) spectroscopies that application of sequential extraction methods to Pb-contaminated, P-amended samples results in the formation of pyromorphite  $[\text{Pb}_4(\text{PO}_4)_3\text{Cl}]$  during the extraction steps. The over- and underestimation of metal concentrations or "speciation" in particular steps of an extraction method could pose serious consequences in addressing risk assessment based solely on extraction results.

These major criticisms leave much to be desired about extraction methods. However, in spite of these limitations, simple extractions do exhibit connection with empirical models of bioavailability and absorption (Ruby et al., 1996). Thus, they are being used and can mislead an investigator into unfounded confidence in interpretation of the results. So, with an appreciation for the

pitfalls and limitations of these techniques and the operational character of the species found, extraction schemes can be a useful tool in metal partitioning but should always be confirmed by other methods. As the discussion above implies, independent and more precise methods for species determination are badly needed. Such methods, of the spectroscopic nature, are now coming of age and are the focus of this manuscript.

## SOLID PHASE SPECIATION: INSTRUMENTAL TECHNIQUES

### Overview of Solid Phase Speciation

There are many ways in which the chemistry of a metal in soils or sediments can be explored. Attempts can be made to determine the species directly in the solid form in situ through physical instrumental methods (see below). These techniques generally exploit the interaction of energy probes (electromagnetic fields, i.e., photons, charged particles, atoms, and neutrons), sometimes as beams, with the sample to be analyzed. Another approach is through wet chemical extraction methods as described above. A third approach is to use mathematical environmental fate models to predict the species based on measurable soil parameters (pH, redox, etc.) and current theoretical understanding. The last two methods will not be discussed in this section as there are ample discussions elsewhere (Bodek, 1985; Bernhard et al., 1986; Batley, 1989; Broekaert and Güçer, 1989).

When energy probes interact with matter, they give rise to signals telling a story about their interaction. In some cases, little or no energy is exchanged, in others a variable amount is exchanged between probe and sample. Diffraction is an example of the first case, while inelastic scattering is an example of a continuously varying amount of energy exchanged. A histogram or plot of the intensities of the energy produced, within a sequence of narrow energy bands, by a sample under excitation by the chosen probe, is called a spectrum. In the instances in which discrete amounts of energy are exchanged between probe and sample, spectral lines are produced. The probes are giving up or, more rarely, absorbing fixed amounts of energy from energy levels of nuclei, atoms, molecules, and macroscopic lattice structures in solids and liquids. There are a great variety of spectroscopies available to obtain information about the structure of matter at the atomic scale to determine speciation. Figure 1 shows the electromagnetic (em) spectrum, the wavelength and frequency of various types of em radiation, their names, what types of transitions in matter give rise to them, and the type of spectroscopy that is involved in analysis with particular em radiations.

The situation involving trace metal contaminant speciation in soils is a much more complicated problem than quantitative assessment. There are several reasons for this: (i) the number of possible compounds is much greater than the number of elements, (ii) these forms, both inorganic and organic, are found in complex mixtures, not in the pure state, (iii) the mixtures are com-



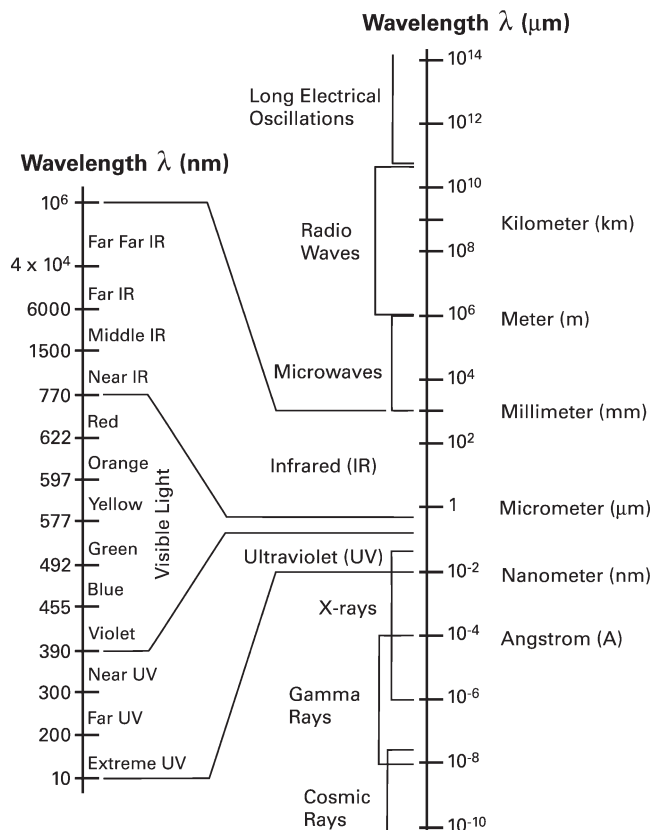


Fig. 1. The electromagnetic (em) spectrum.

posed of both known and unknown forms, (iv) they may be present in only trace amounts in very complex matrices, and (v) depending on how the contaminants were introduced, they may reside on the surfaces of soil fines or are themselves fine colloidal or separate particulate forms. These conditions place severe constraints on any technique(s) used to determine the forms. They imply the need for an in situ quantitative technique with high sensitivity, adequate resolution of the different components of complex mixtures, and perhaps some surface specificity or microanalytical capability. Various types of spectroscopy have been used with some success on the major molecular components of simple mixtures. Indeed, it is even suggested that, at present, some form of spectroscopy offers the best hope of being able to truly distinguish between competing sorption mechanisms at mineral surfaces (Sposito, 1986; Bertsch and Hunter, 1996; Scheidegger and Sparks, 1996a). While some advances in spectroscopic techniques for trace molecular determination have been made (Christian and Callis, 1986; Bertsch and Hunter, 1996; Scheidegger and Sparks, 1996a), a single such technique is unknown at present although synchrotron-based techniques have shown incredible promise during the past couple of decades.

For the time being, it seems clear that a battery of analytical techniques is necessary to achieve true species determination. It is also apparent that some amount of information desired will be subjected to tradeoff. The limitations of a technique might preclude simultaneous

acquisition of two pieces of information. For example, mass spectrometry has high sensitivity and ability to handle complex mixtures, and can yield structural information about discrete compounds and forms desorbed from surfaces. However, quantification is next to impossible and details of surface structure are lost in the destructive nature of the technique. Molecular fluorescence spectroscopy, IR, and XRD can unambiguously identify known compounds in simple mixtures and are nondestructive. However, the first two methods are limited to those compounds that fluoresce or have IR active bonds, while the XRD is limited to crystalline forms. Both IR and XRD have low sensitivity and difficulty with very complex mixtures and unknown forms. Physicochemical separation techniques could make samples accessible to the less sensitive methods via preconcentration. Nevertheless, all forms might not be separated, nor would they necessarily remain in the same proportions as in the original sample. The scope of a speciation approach will be defined by what type and by how much information is desired. The ultimate goal is to be able to do the former projects quickly and efficiently, and to acquire enough information to enable new theoretical techniques and predictive models to be developed. That is the challenge awaiting our discipline.

Sources for many of the details about the types of techniques which have been in general use for a number of years in analytical chemistry for qualitative and quantitative determination of elements and molecules as well as molecular structure elucidation can be obtained from general books on instrumental methods in analytical chemistry (Winefordner, 1976; Natusch and Hopke, 1983; Onori and Tabet, 1985; Skoog, 1985; Christian and Callis, 1986; Willard, 1988), methods for metal speciation (Bernhard et al., 1986; Patterson and Passino, 1987, 1990; Kramer and Allen, 1988; Batley, 1989; Broekaert and Güçer, 1989), and methods for surface analysis (Hochella and White, 1990; Bertsch and Hunter, 1996; Scheidegger and Sparks, 1996a). In addition, reviews and reports from symposia on specific methods, as well as their applications to soils, minerals, geologic materials, and environmental samples are common in the literature, for example: vibrational spectroscopies (IR, Raman spectroscopy) (Jackson, 1973; Giesekeing, 1975; Nicol, 1975; Beutelspacher and Van Der Marel, 1976; Zussman, 1977; Bell and Hair, 1980; Klute, 1986; Hawthorne, 1988; Perry, 1990), mass spectrometry (MS) and secondary ion MS (SIMS) (Jackson, 1973; Nicol, 1975; Natusch and Hopke, 1983; Karasek et al., 1985; Bernhard et al., 1986; Perry, 1990), nuclear magnetic resonance (NMR) (Jackson, 1973; Klute, 1986; Wershaw and Mikita, 1987; Hawthorne, 1988; Perry, 1990), proton induced X-ray emission (PIXE) (Johansson and Campbell, 1988), X-ray methods (Walsh, 1971; Jackson, 1973; Nicol, 1975; Zussman, 1977; Stucki and Banwart, 1980; Page et al., 1982; Natusch and Hopke, 1983; Bernhard et al., 1986; Klute, 1986; Hawthorne, 1988; Bish and Post, 1989; Brown and Parks, 1989; Valkovic, 1989; Hochella and White, 1990; Perry, 1990; Brown, 1990; Bertsch and Hunter, 1996; Fendorf and Sparks, 1996; Scheidegger and Sparks, 1996a; Brown et al., 1998), and chromatographic techniques (Vickery, 1983). Table 1 shows various in-

Table 1. Instrumental methods of chemical analysis.

Name	Technique				
	AEM	AES-SAM	AS	BEI	ED
<b>Related techniques</b>	analytical electron microscopy	Auger electron spectroscopy-scanning Auger microprobe	atomic spectroscopy	backscattered electron imaging	electron diffraction
<b>Incident (exciting) radiation</b>	TEM, STEM, HVEM, HREM	electron 0.1-100 keV	AAS, GRAAS, AFS, AES, AC, DC	electron 5-50 keV	SAED, LEED, RHEED
<b>Particle emitted</b>	electron 100-300 keV	Auger electron	visible photons	backscattered primary electrons	4-300 keV electrons
<b>Depth information</b>	transmitted electrons	Auger electron	transmitted or emitted photons	diffraction electrons	diffraction electrons
<b>Spatial resolution</b>	characteristic X-rays	1-20 Å	none	1 mm	yes, LEED, 1-20 Å
<b>Detection limit</b>	0.01-0.1 µm	150 Å-1 µm	50-110 µm (laser)	1000 Å	5-50 Å
<b>Detectable elements</b>	NA <sup>+</sup>	Li-U	0.1 ppb-100 ppm	0.50% difference only	NA
<b>Depth profiling</b>	C-U	yes	all	no	Li-U
<b>Chemical information</b>	no	some bonding	no	no	no
<b>Quantitative analysis</b>	no	yes, to 10% relative error	no	no	yes, species identity and structure
<b>Imaging</b>	yes	yes	no	yes	no
<b>Mapping</b>	yes	yes	no	yes	no
<b>Line traces</b>	yes	yes	no	yes	no
<b>Molecules detected</b>	no	no	no	no	yes
<b>Crystallographic information</b>	yes	no	no	no	yes
<b>Materials</b>	any solid	any solid	solids, liquids, and gases	any solid	microcrystalline samples
<b>Used on geological or environmental samples?</b>	yes	yes	yes	no	no
<b>Applications and information obtained</b>	thin film elemental analysis, structure of materials	absorbate analysis, elemental analysis of surface	elemental determinations in digested samples or vaporized solids (plasma, arc, and spark sources)	detection and mapping of elements	identifying microcrystalline phases
<b>Advantages</b>	exceptional resolution, good quantitation with X-ray analyses	high resolution, many elements, some valence and species info	accurate and precise, very low detection limits	mapping and imaging capability, inexpensive, fast	species by structure, exceptional resolution
<b>Disadvantages</b>	difficult sample prep, ultrathin sectioning needed, vacuum required	UHV/ac needed, charging, adsorbed gases	only elemental info, only one element at a time, interferences	elements not identified, only moderate resolution	only crystals, no quantitation
<b>Availability</b>	moderately common	rare	very common	relatively uncommon	moderately common
<b>Name</b>	<u>EDX</u>	<u>EELS</u>	<u>Electrochemistry</u>	<u>EPR or ESR</u>	<u>ESCA</u>
<b>Related techniques</b>	energy dispersive X-ray analysis	electron energy loss spectroscopy	electrochemistry	electron paramagnetic (or spin) resonance spectroscopy	electron spectroscopy for chemical analysis
<b>Incident (exciting) radiation</b>	electron 2-50 keV	HREELS, EXEELFS, ELNES, SEELS	ISE, CV, ASV, CD, potentiometry, voltammetry, coulometry	RF photons	XPS, UPS
<b>Particle emitted</b>	characteristic X-ray photons	inelastically scattered electrons	none	RF photons	X-ray or UV photons
<b>Depth information</b>	0.5-5 µm, depends on matrix	0.01-0.1 µm	none	RF photons	photoelectron
<b>Spatial resolution</b>	0.5-5 µm, depends on matrix	<0.04 µm	none	none	5-20 Å
<b>Detection limit</b>	0.10%	<0.1%	10 <sup>-11</sup> molar solutions possible	none found	2-800 µm, better with synchrotron X-rays
<b>Detectable elements</b>	Na-U (C-U)*	Li-U	ionic elements in solution and their ionic complexes	paramagnetic species	0.10% Li-U
<b>Depth profiling</b>	in cross sections	no	no	no	yes
<b>Chemical information</b>	no	much from several energy-loss regimes	yes, electrochemical	yes, electronic structure	yes, oxidation state and species
<b>Quantitative analysis</b>	yes, relative error	yes	yes	semiquantitative	yes, to 2% relative error
<b>Mapping</b>	no	no	no	no	no
<b>Mapping</b>	yes	yes	no	no	some

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Table 1. Continued.

	Technique				
	EDX	EELS	Electrochemistry	EPR or ESR	ESCA
Line traces	yes	yes	no	no	no
Molecules detected	no	no	yes, some complexes in solution	yes, chemical shifts	yes
Crystallography information	no	no	no	no	no
Materials	any solid	any solid	solutions of ionic species	liquids and solids	any solid, frozen liquids
Used on geological or environmental samples?	yes	no	yes	yes	yes
Applications and information obtained	elemental analysis of bulk or near surface regions	ultrathin film elemental analysis, core states, species like IR, bonding, structure	activities of ionic species in solutions, LC detection	trace analysis of paramagnetic species	species, surface elemental composition, valency states, chemical bonding
Advantages	good energy resolution, fast, multiple elements concurrently	immense amount of chemical information at the microscale	no standards needed, high sensitivity, inexpensive	NA	least destructive surface technique, best chemical information
Disadvantages	high detection limits, element interferences	few libraries of spectra, sample prep, little quantitation, difficult analyses, needs special beam	only for solutions species, destructive, not for solids	NA	UHVac needed, poor spatial resolution, long analysis time
Availability	moderately common	uncommon	common	very uncommon	relatively common, microprobe rare
Name	Fluorescence	FTIR	ISS	LAMMA	LRMS
Related techniques	optical fluorometry	Fourier transform infrared spectroscopy	ion scattering spectroscopy	laser microprobe mass analyzer	laser Raman microprobe spectroscopy
Incident (exciting) radiation	L RMS monochromatic laser light	infrared photons, wavelength 1-10 $\mu\text{m}$	ions at 0.2-2 keV	high power monochromatic laser photons	monochromatic light from laser
Particle emitted	visible photons	transmitted or reflected IR photons	ions	elemental and molecular ions	scattered light
Depth information	1500 $\text{\AA}$	0.5-2.5 $\mu\text{m}$	outermost atom layer	none	0.1 $\mu\text{m}$
Spatial resolution	0.5 $\mu\text{m}$	1-10 $\mu\text{m}$	1-100 $\mu\text{m}$	0.5 $\mu\text{m}$	0.5 $\mu\text{m}$
Detection limit	0.001-1000 ppm	0.1-0.5%	100 ppm-0.1% (bulk)	0.5% inorganic	1%
Detectable elements	REE and some metals	functional groups	Li-U	Na-U	functional groups
Depth profiling	no	no	semi-quantitative	no	no
Chemical information	yes	yes	no	some, molecular fragments	yes
Quantitative analysis	yes	semi-quantitative in bulk	semi-quantitative	semi-quantitative	yes
Imaging	yes	no	no	no	yes
Mapping	no	no	no	some	yes
Line traces	no	no	no	no	yes
Molecules detected	yes, some organics	yes, IR active molecules	no	organics yes, inorganics difficult	Raman active molecules
Crystallography information	no	some distinction between phases	no	no	some distinction between phases
Materials	a few solids and liquids	solids and organic liquids	any solid	solid sections and liquids	solid, liquid, gas or inclusions
Used on geological or environmental samples?	yes	yes	no	yes	yes
Applications and information obtained	organic analysis, rare-earth (REE) complexes, special non-REE complexes, as probes in other analyses, GC and LC detector	compound identification on surfaces, of powders, liquids etc., functional group ID, bonding GC detector	elemental composition, location of adsorbed species	microelement and molecular analysis	compound identification on surfaces, of powders, liquids, etc., functional group ID, bonding
Advantages	very sensitive, resolution okay, good quantitation, in situ, nondestructive	universal, good quantitation, moderate resolution, in situ, nondestructive	surface sensitive, okay detection limits	moderately good resolution, in situ, no charging	almost universal good libraries, resolution okay, in situ, water okay, nondestructive
Disadvantages	not universal, few applications, little structural info	low sensitivity, only okay for solids, avoid aqueous solutions	moderate resolution, no quantitation, no chemical info	destructive, no imaging or mapping	fluorescence interference, low sensitivity
Availability	uncommon, microscope is rare	common, microscope much less so	relatively uncommon	very rare	common, microscope much less so

Continued next page.

Table 1. Continued.

Name	Technique				OM
	Mössbauer spectroscopy	MS (general)	NAA	NMR	
Related techniques		mass spectrometry	neutron activation analysis	nuclear magnetic resonance spectroscopy	optical microscopy
Incident (exciting) radiation	gamma rays	TI, TD, EI, CI, FL, FD, ICP, MIP, DEP, GD, TOF, HRMS, MS-MS	thermal neutrons	RF photons	visible or UV photons
Particle emitted	gamma rays	ions	alpha ( <sup>4</sup> He <sup>++</sup> ), electrons, neutrons and -ray photons	RF photons	reflected or transmitted photons
Depth information	none	none	none	none	none
Spatial resolution	1-1000 ppm	0.00001-10 ppm	0.001-0.1 ppm	10-100 000 ppm, major constituents	0.2 μm in UV
Detection limit					NA
Detectable elements	isotopes with Mössbauer transitions, approximately 44 elements	H-U	H-U	nonferromagnetic elements with spin 1/2 nuclear isotopes (approximately 80)	NA
Depth profiling	no	no	no	no	NA
Chemical information	yes, structure, bonding	little	no	yes, structure and bonding	NA
Quantitative analysis	semiquantitative	yes, high precision with isotope dilution	yes, 2-10%	yes, 1-10%	no
Imaging	no	no	no	no	yes
Mapping	no	no	no	no	no
Line traces	no	no	no	no	no
Molecules detected	yes, chemical shifts	fragments, some whole	no	yes, chemical shifts	no
Crystallography information	no	no	no	yes, crude	morphology, crystal habit, and cleavage planes
Materials	solids	some solids and many liquids	solids and liquids	liquids and solids	any solid or liquid
Used on geological or environmental samples?	yes	yes	yes	yes	yes
Applications and information obtained	site locations, bonding, structure	elemental, isotopic, and molecular composition, one of the most often used GC and LC detectors	bulk element analysis	bulk organic ID, bonding and valency, structure	color, shape, texture, refractive index, luster, birefringence, and polarizing properties, mineralogy, cells, surface and internal morphology
Advantages	nondestructive, in situ	very low detection limits, wide applicability, some molecular info and structure, high precision possible, isotopic analysis	most sensitive, little sample prep needed, nondestructive	no standards needed, water okay, nondestructive	low cost, much info, in situ, little sample prep needed, nondestructive
Disadvantages	limited number of elements, need radioisotopes necessary, poor data analysis	destructive, vacuum needed, no microanalysis, not all materials can be analyzed	only elements, variable sensitivity, multicomponent analyses problematical	low sensitivity, not great for solids, limited number of elements	limited resolution, poor chemical info, no quantitation
Availability	very uncommon	common (EI) to very rare (for multi-ionization HRMS)	very rare	uncommon	very common
Name	PIXE	RBS	SEM	SIMS	UV-vis
Related techniques	proton induced X-ray emission	Rutherford backscattering spectroscopy	scanning electron microscopy	secondary ion mass spectrometry	ultraviolet-visible spectrophotometry and microscopy
Incident (exciting) radiation	0.3-4 MeV protons	He <sup>+</sup> 2 MeV	ESEM electron 1-50 keV	IMMA, IMP, IMA, FABMS ions, atoms for FABMS	UV or visible photons
Particle emitted	characteristic X-ray photons	<sup>4</sup> He <sup>++</sup>	secondary electrons	secondary ions	transmitted or reflected UV-vis photons
Depth information	none	200 Å-1 μm	none	30-100 Å	0.1 μm

Continued next page.

Table 1. Continued.

	PIXE	RBS	SEM	SIMS	UV-vis
Spatial resolution	2 $\mu\text{m}$ -20 mm	1 mm	50 $\text{\AA}$	0.02 $\mu\text{m}$ best, 1-5 $\mu\text{m}$ typical	0.5 $\mu\text{m}$
Detection limit	0.1-10 ppm	0.01-1%	NA	0.1-10 ppm	0.001-1000 ppm
Detectable elements	Na-U	Li-U	none	H-U	All
Depth profiling	no	yes, nondestructive	no	yes to 2 $\mu\text{m}$	no
Chemical information	no	no	no	some bonding	yes
Quantitative analysis	yes, 5%	yes	no	yes, to 25% relative error	yes
Imaging	yes	no	yes	yes	yes
Mapping	yes	no	no	yes	no
Line traces	yes	no	yes	yes	no
Molecules detected	no	no	no	fragments	yes, many
Crystallography information	no	yes	yes	no	no
Materials	any solid	any solid	any solid	any solid, some liquids	many solids and liquids
Used on geological or environmental samples?	yes	yes, rocks and minerals	yes	yes	yes
Applications and information obtained	elemental composition, location of adsorbed species	elemental composition, location of adsorbed species	surface and internal morphology	elemental, isotopic and molecular composition	most used method for elemental and molecular analysis, GC and LC detector
Advantages	lower background and detection limits over SEM-EDX	crystal information, nondestructive okay detection limits	ESEM in situ, good resolution, good quantitation with X-ray analysis	very sensitive, microbeams, imaging, mapping, isotopes	sensitive, resolution okay, good quantitation, in situ, nondestructive high precision
Disadvantages	special proton accelerator, only elemental information	poor resolution, special accelerator needed	charging, samples need coating, vacuum required	destructive, vacuum needed, poor precision	little structural information, not specific
Availability	rare	rare	common, ESEM no	relatively uncommon	very common, micro very rare
Name	WDX	XAS	XRD	XRF(MP)	
Related technique	wavelength dispersive X-ray analysis	X-ray absorption spectroscopy	X-ray diffraction	X-ray fluorescence microprobe	
Incident (exciting) radiation	electron 0.5-50 keV	XANES, EXAFS, SEXAFS	XPD	XRF X-ray tube, XRFMP	
Particle emitted	characteristic X-ray photons	anode X-ray sources transmitted or characteristic X-rays	X-ray tube or synchrotron X-rays	synchrotron X-rays only characteristic X-rays	
Depth information	0.5-5 $\mu\text{m}$ , depends on matrix	yes, SEXAFS	none	none	
Spatial resolution	0.5-5 $\mu\text{m}$ , depends on matrix	500 $\text{\AA}$ potential with synchrotron X-rays	500 $\text{\AA}$ -10 $\mu\text{m}$ synchrotron X-rays, none X-ray tube	500 $\text{\AA}$ -10 $\mu\text{m}$ synchrotron X-rays, none X-ray tube	
Detection limit	0.02%	approximately 500 ppm	1-5% mixtures (XPD)	1-10 ppm	
Detectable elements	Li-U	Li-U	Li-U	Li-U	
Depth profiling	in cross sections	no	no	no	
Chemical information	no	yes, oxidation state, species, coordination number, some structure	yes, species identity and structure	no	
Quantitative analysis	yes, relative error	no	yes, to 5-10%	yes, high precision	
Imaging	no	no	no	yes	
Mapping	yes	no	no	yes	
Line traces	yes	no	no	yes	
Molecules detected	no	yes	yes	no	
Crystallography information	no	some	yes	no	
Materials	any solid	solids and nonvolatile liquids	crystalline solids and polymers	solids and nonvolatile liquids	
Used on geological or environmental samples?	yes	yes	yes	yes	
Applications and information obtained	elemental analysis of bulk or near surface regions	coordination number, oxidation state, bonding of amorphous phases and ID	structure detection and ID of major species in mixtures	elemental composition	

Continued next page.



Table 1. Continued.

	Technique			
	WDX	XAS	XRD	XRF(MP)
Advantages	exceptional energy resolution, high signal to noise, low detection limits, excellent quantitation	in situ, nondestructive, low detection limits, species determination	in situ, large library of patterns, nondestructive	many elements, nondestructive, low detection limits, in situ, maps, imaging
Disadvantages	mechanical alignment and design problems, slow, one element at a time	rare, not many spectra available, poor with mixtures	insensitive, only crystalline materials	only elements, resolution 10 microns
Availability	relatively uncommon	rare, at synchrotron facilities	common	XRF common, XRFMP only at synchrotron facilities

† Not applicable.

strumental methods of chemical analysis, most for solid phases, some useful for solution species. Table 1 is extensive and covers most of what one would like to know about a given technique.

### Chemical Analysis of "Pure" Solids

The methods available to determine the specific molecular species of a "pure" solid material are numerous and well established. They include: (i) X-ray methods such as XRD, XPD, and XAS; (ii) magnetic spectroscopies like NMR, electron paramagnetic or spin resonance (EPR), and Mössbauer; (iii) electron techniques like SEM-EDX, TEM-STEM, and AES; (iv) vibrational spectroscopies (i.e., IR, Raman); and (v); MS. With these physical methods, the elemental composition and molecular structure of materials can be determined, establishing the differences even between isomers. Often with manufactured materials, prior knowledge of the elemental composition, structure of the ligands, and/or the formation or substitution reactions involved in the syntheses is exploited to aid determination of molecular structures formed. Unfortunately, with unknowns or natural samples, such information is lacking and must be intuited from general chemical principles about the behavior of the systems from which the samples were obtained.

The best scenarios are those of pure macroscopic single crystals. Such forms can be determined by X-ray crystallographic techniques. These analyses give bond angles and bond lengths to high precision (0.01 Å or better). Even so, mixtures of different phases and isomers, or oxygen, light, or X-ray sensitivity can make the structure determination difficult. These techniques depend on the symmetries of the molecular forms and their regular spatial arrangement to diffract the X-rays into a symmetric pattern of peaks (Bragg peaks) in two dimensions. The analysis of that symmetry pattern yields the desired information.

If one cannot obtain large single crystals, a collection of the crystallites (essentially a powder), is examined by XPD. As this is the X-ray diffraction pattern of a large number of tiny crystals immersed in the beam, it appears as the sum of many single crystal patterns oriented in numerous random directions. The result (on a photographic plate) is a series of concentric diffraction rings, symmetric in the azimuthal angle. The intensity distribution for fixed azimuth yields a one-dimensional pattern of peaks. A probable structure can be obtained from information acquired from the distribution and number of peaks, while refinement consists of a comparison of this peak pattern with those of compounds with similar chemistry and known structure. There are also techniques in which neutrons (ND) (Stucki and Banwart, 1980; Hawthorne, 1988) or electrons (ED) are used instead of X-rays as probes to produce the diffraction pattern (see ED below).

For noncrystalline materials the Bragg peak patterns of diffraction disappear. Thus other techniques must be employed to determine molecular structure. NMR can be used to yield structural information about compounds, although less refined than X-ray diffraction,

for both crystalline and amorphous substances. NMR originates from the precession of the spin magnetic moment of a nucleus, if not exactly zero, in an externally generated macroscopic magnetic field. The frequency of this precession is proportional to the external field strength and has values in the radio frequency (RF) range (i.e., megahertz, MHz). Nuclei with a spin quantum number of 1/2 are the most advantageous to exploit, as they exhibit only two spin energy states or levels, whose energy difference is also proportional to the external field strength. Other nuclei of greater spin values also process, but have a larger number of energy levels. Under absorption of energy, these nuclei can flip their magnetic moment direction, thus changing energy levels. This causes the absorption spectra of spin 1/2 nuclei to be simpler than others.

It is through these RF absorption spectra that the chemical information is obtained. This is accomplished through an analysis of the chemical shifts and coupling constants observed in the NMR spectrum for a given element. Large sets of data on chemical shifts and coupling constants collected for the element of interest within a number of different structures provide the basis for empirical tables that correlate the parameters with structural features. The chemical shifts are changes in the energy of the nuclear magnetic transitions involved, due to the effect of the electronic configuration of the molecule (which shields the nucleus from the externally applied fixed field) near the absorbing nuclei. Nuclear spin-spin coupling provides the origin of the splittings observed (the source of the derived coupling constants) and these too are dependent on molecular geometry and the types and spins of the nuclei of neighboring atoms. Coordination and analysis of each of the pieces of information above allows deduction of structural features. Large uncertainties in the structures obtained are a consequence of the complexity of analysis and deviations from the expected correlations. In terms of quantitative analysis, the areas under the absorption bands are proportional to the number of nuclei absorbing. Integration over the absorption region produces a "step" whose height is proportional to the number of nuclei. Comparison of a given peak of the unknown with that of a standard yields the concentration of the unknown.

The excitation of vibrational or rotational transitions in molecules yields infrared absorption bands (wavelength approximately 1–1000  $\mu\text{m}$ ) characteristic of the types of atoms and their bonds. However, only those bonds that have an overall dipole moment and vibrational modes yielding a change in that moment give rise to infrared absorption and emission. A complementary effect that yields information about changes in polarizability from vibrational excitation, rather than dipole moment as in IR, is the Raman effect. It is seen in the non-elastic scattering of photons, usually from a laser source, by molecules in the sample. A fraction of the energy of a certain number of photons in the incident beam is taken up by molecular vibrational excitations. The spectrum is obtained by observing the relative frequency shift of peaks, created by the detection of non-elastically scattered photons, from the elastically scat-

tered peak. Both IR and Raman spectroscopies can be performed using optically focused beams, thus permitting analysis of microsamples. However, greater beam intensities and finer resolution are achievable using visible light lasers, thus giving Raman a distinct advantage in that area although synchrotron IR is many orders of magnitude brighter in intensity than traditional laboratory IR equipment.

Both IR and Raman spectra, coming from molecular transitions, yield information about molecular structure, as certain spectral features are characteristic of pairs (or groups) of atoms and bond types. The presence or absence of particular bands will help narrow the identification of a species, given its molecular weight. It will, at the very least, yield partial structural features associated with given "functional groups," such as commonly found ring or chain structures and anionic groups. While NMR and IR-Raman spectra give structural information that can help narrow possibilities, the method of obtaining structure is a deductive art relying on experience, intuition, and large computer accessible databases or handbooks of known spectral features.

Mass spectrometry can also be a valuable tool to elucidate the structure of unknown molecular forms. With proper volatilization and ionization, ions representing both the parent molecule and a fragmentation pattern (unique, given the ionization energy) are recorded. Certain mass analyzers are often paired with specific ionization methods due to mass range anticipated, resolution desired, and duty cycle (pulse or continuous) of the ion beam. Some general ionization methods are field ionization (FI), chemical ionization (CI), and electron impact (EI) in increasing order of hardness (degree of ionization).

Softer ionization yields more parent molecular ions for identification by accurate molecular weight determination, while harder ionization gives a richer spectrum of fragments for structural studies. Other techniques, particularly for solids, are the thermal desorption (TD), field desorption (FD), Cf-252 plasma desorption (PD), laser desorption (LD), secondary ion MS (SIMS), and fast atom bombardment (FAB) techniques. The last three techniques present the possibility of focused microprobe beams (1  $\mu\text{m}$  for LD, 0.02  $\mu\text{m}$  for SIMS). These methods attempt to dislodge atoms or molecules from the surfaces of samples. Provided the mass analyzer has sufficient resolution, assessment of the mass of the parent molecule can sometimes yield at least the proper chemical formula. Mass fragmentation patterns give information about functional groups present in the molecule. As with other spectral analyses, experience and database accessibility are extremely important.

Although the sharp diffraction peaks of crystals do not exist for amorphous materials, some X-ray techniques still have a role in their structure determination. Assuming that amorphous phases of solids have little long range order but still possess molecular structures with fixed atomic arrangement, X-ray absorption spectroscopy (XAS) and X-ray scattering (XRS) provide structural information about the local environment of the element whose absorption edge is being exploited.

XAS research is typically limited to synchrotron radiation sources scattered throughout the world. The various XAS techniques include extended X-ray absorption fine structure (EXAFS) spectroscopy, a surface variant (SEXAFS), X-ray absorption near edge structure spectroscopy (XANES, also called NEXAFS), and small and wide (or large) angle X-ray scattering (SAXS and WAXS or LAXS), the last two being coupled with anomalous scattering analysis techniques.

EXAFS originates in the modulation of the X-ray absorption spectrum as a function of energy (the defined fine structure). This is due to the local chemical environment around the absorbing atom affecting the outgoing photoelectron wave produced under X-ray excitation. The strength of that wave backscattered from near neighbors modulates the absorber atom's electronic wave function and thus its ability to absorb further X-ray photons. XANES provides information about the oxidation state of the atom whose absorption edge is probed. WAXS exploits the modulation of the amorphous scattered X-ray intensity as a function of angle. It too is dependent on the local chemical environment around a scattering atom through the interference due to neighboring atoms. In EXAFS and WAXS-ASA, intensity patterns are collected, processed, and Fourier transformed to produce radial distribution functions (RDFs), giving one-dimensional information about the distances to atomic shells. The identity of the atoms and their number in a shell are also available from the data, but with less certainty, relying on other information and chemical intuition to aid determination.

Generally speaking, each of the techniques discussed can require several grams of the material (with MS being the notable exception) to successfully determine the molecular form or structure. As mentioned before, a priori information and chemical intuition are extremely important in the process. The techniques above have relatively high detection limits, except for mass spectrometry. This implies that impurities, which are always present, usually do not contribute to the spectra and can be ignored.

### Chemical Analysis of Mixtures

The discussion above focused on deriving the structure of pure compounds (which is the identification of the species). In the case of mixtures, "speciation" could take on a different meaning. It could merely imply identifying the presence of known forms within the mixture and their relative abundance. Or, it could imply isolation of unknown forms for a full or partial chemical characterization. In general, binary mixtures are simpler to handle than ternary mixtures and so on. Absolute amounts of the forms and their abundance ratios are additional important aspects of mixture determination. For instance, if you have a few picograms of material with five different components, the problem is very different than if you have a few grams with two or three components. Similarly, if you have a mixture of three components with two of them being of the "trace" variety, it is very different again from an ABC mixture composed

of 20% A, 30% B, and 50% C. A definition of concentration ranges adapted from Davies (1980) is shown below:

major constituent: 1.0 to 100%

minor constituent: 0.01 to 1.0%

trace constituent:  $10^{-6}$  to  $10^{-2}\%$

ultra-trace constituent:  $<10^{-6}\%$

When looking for trace or ultra-trace constituents, "uninteresting" major and minor components are generally referred to as the matrix in which the former are found. In addition, when looking at very small samples ( $<10^{-2}$  g), and/or small spatial dimensions (say  $<0.5$  mm), one performs a microanalysis.

There are roughly three ways to proceed with mixture analyses. The first is to attempt to separate the components of the mixture in a straightforward fashion. This depends on what is known beforehand about the mixture. General methods of obtaining particular fractions of a mixture by physicochemical separations are well documented (see below). Separations could be by mineral type, particle size, density, magnetic properties, solubility, or volatility, and accomplished through sieving, filtration, density gradients, flotation, or the application of electric or magnetic fields, solvents, or heat.

The second general procedure for determination of mixtures is to subject it to some spectroscopic method that yields molecular identification as in the pure compound speciation section above. The result is a superposition of the spectra of the different components of the mixture. Depending on the complexity of the spectra of the individual components and the number of these components, this superposition can be relatively simple or exceedingly complex. The method is to attempt to iteratively determine the weights necessary to achieve the best fit of a superposition of pure component spectra (previously determined) to the complex spectrum of the mixture. This can be used both qualitatively and in quantitative analysis. Alternatively, techniques involving subtraction of the major component spectra may allow the appearance of the minor or trace component spectra.

The last procedure is the microanalysis and/or microprobe methods. The use of focused beams implies that small areas or volumes, and thus smaller amounts of the materials investigated can be sampled or viewed, either destructively or nondestructively. The ability to produce finer focused beams of electrons has steadily improved over the last few decades (now down around approximately 1 nm), while the focusing of beams of ions or atoms is now approaching the practical limits (approximately  $0.02 \mu\text{m}$  on the University of Chicago's SIM-SIMS device). With the improvements in materials and the advent of synchrotron sources, focused X-ray beams are becoming a plausible reality (range  $10 \mu\text{m}$  to  $50 \text{ nm}$ ). Lastly, optical microscopes can produce UV, visible (often lasers), and IR beams in the range of  $0.2$  to  $10 \mu\text{m}$  in diameter. This latter range of diameters is at the diffraction limit for these radiations but near-field optics utilizing very fine pointed optical fibers



might enable this limit to be sidestepped, at least with monochromatic sources. In this arena, the host of spectroscopies developed and exploited with these beams allows speciation of mixtures at the microscale.

Physicochemical separation and spectroscopic methods are applicable to gases and liquids, while solids, particles, powders, colloids, and the like can be treated by them as well as microanalysis and/or microprobe methods. However, if desorption processes for solids in mass spectrometry could be understood well enough or perhaps designed to allow the emission of whole parent molecules or complexes it would be most advantageous. This method coupled with a high-resolution tandem mass spectrometer might provide the separation and sensitivity for detection and identification of species from a mixture of solid phase forms. This last possibility might well lie in the distant future, so for now the methods discussed above must suffice. Table 1 displays the various types of analyses one could perform, in terms of information and physical distribution, and the various spectroscopic and nonspectroscopic methods available to permit access to that information. Table 1 was compiled, augmented, and updated from a number of sources (Nicol, 1975; Winefordner, 1976; Natusch and Hopke, 1983; Christian and Callis, 1986; Kelley, 1987; Adams et al., 1988; Kiss, 1988; Willard, 1988; Eighmy et al., 1994; Bertsch and Hunter, 1996; Scheidegger and Sparks, 1996a).

### Physicochemical Separation Methods

Individual particles in a typical environmental or industrial sample may range from submicrometer to millimeter dimensions, from clays and silts at the lower end (<50  $\mu\text{m}$ ) to sands and gravels. Total metal concentrations tend to vary with particle size; higher concentrations ( $\mu\text{g g}^{-1}$ ) being found in the smaller particles (Forstner and Wittmann, 1981; Salomons and Forstner, 1984) due to available surface area ( $\text{m}^2 \text{g}^{-1}$ ).

The usual procedure employed for the physical separation of different size fractions involves sieving (for particles >20  $\mu\text{m}$  in effective diameter), gravity sedimentation, and differential centrifugation (Rose et al., 1979). The size fractions thus obtained can then be analyzed directly, or subjected to sequential chemical extractions (Gibbs, 1977; Tessier et al., 1979; Forstner and Patchineelam, 1980). If chemical extractions are planned, the initial sieving should be performed on the fresh sample, that is, without any preliminary drying (see below).

An alternative procedure, as pioneered by prospectors panning for gold (Theobald, 1957), involves separation of the particles according to their density. Such methods, often involving the use of heavy organic liquids having specific gravities in the range 1.5 to 3.3, are used in the mineral processing industry and for characterizing clays, but environmental applications have been slow to appear. Warren and coworkers (Pilkington and Warren, 1979; Dossis and Warren, 1980) subjected several near-shore marine sediment samples to density gradient centrifugation, using mixtures of acetone and tetra-

rabromoethane to give a series of liquids of specific gravities 2.2 to 2.75. The sediment components were separated into organic debris, conglomerates, quartz + calcite shells, magnesium calcite shells, aragonite shells, and heavy minerals. Cadmium, lead, and zinc were preferentially concentrated in the organic subfraction, but the Cd to Pb to Zn ratios were similar in each subfraction regardless of mineralogy. Galena ( $\text{PbS}$ ), sphalerite ( $\text{ZnS}$ ), hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) were identified in various density subfractions by X-ray diffraction techniques.

A final approach, of more limited application, involves the separation of particles according to their magnetic properties. It is often combined with other separation methods, such as density and/or size fractionation, in a compound scheme. There have been many published reports of the application of this method to separate Fe oxides and chloritic clays from other constituents in soils (Schulze, 1981), before trace metal analysis of airborne particulates (Hopke et al., 1980; Hulett et al., 1980; Cabaniss and Linton, 1984), of roadside soils (Olson and Skogerboe, 1975) and urban dusts (Linton et al., 1980), and of sewage sludge and sludge amended soil (Essington and Mattigod, 1991), and in at least one report (Hulett et al., 1980) the magnetic particles were found to be enriched in the trace metals Cd, Co, Cr, Cu, Mn, Ni, and Zn.

### Chemical Analysis of Surfaces, Sorbates, and Microsamples

A surface interface can be defined as a boundary physically separating two substances. These could be different solid phases of the same material, immiscible liquids (liquid–liquid interface), or interfaces between vacuum–solid, vacuum–liquid, liquid–solid, and gas–solid or gas–liquid mixtures. Although from a physical and macroscopic point of view, a surface is a boundary, at the atomic scale, a clear-cut surface is not easily discerned. There are many chemical processes going on at surfaces: sorption, desorption, evaporation, condensation, ionic exchange processes, dissolution and precipitation, inner and outer sphere complexation, diffusive migration, catalysis, etc. (Sparks, 1995; Trivedi and Axe, 2001). This section will refer to gas–solid or liquid–solid interfaces and the chemistry of sorbed species interacting at those interfaces. In particular we will be concentrating on the solid surfaces of soil particulates in contact with gases and liquids. Figure 2 shows the regimes of bulk, thin film, and surface analysis, in a rough conceptual schematic (Briggs and Seah, 1990).

Why does one need to look at the surfaces of environmental sorbents? To understand macroscopic observations, one must examine the microscopic environment to fully comprehend the overall reaction. Understanding the molecular level will lead to better models and predictability of fate, mobility, bioavailability, reactivity, and speciation of a contaminant (Sparks et al., 1999; Bertsch and Hunter, 1996; Scheidegger and Sparks, 1996a). It is a basic fact that most of the chemistry of soil– and sediment–water interfaces depends on the



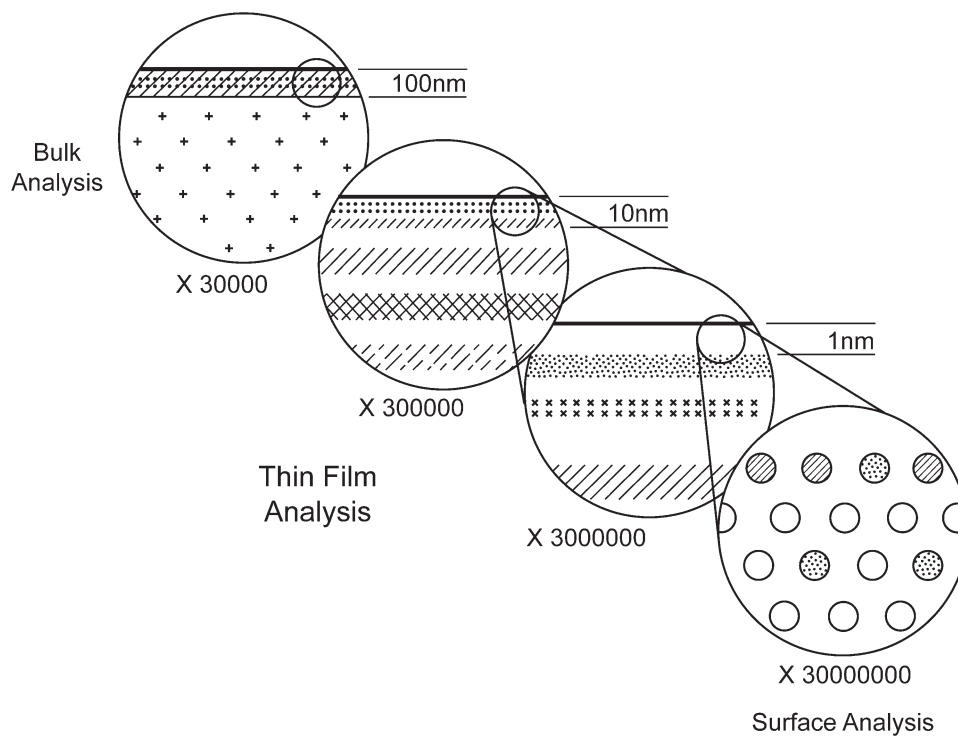


Fig. 2. A depiction of the regimes of bulk, thin film, and surface analysis (from Briggs and Seah, 1990, with permission).

chemistry and structure of surface complexes. Further, the control of and the nature of soil solution species are determined by the surface solid phases present in the environment. Lastly, knowledge of the physical distribution, as outlined in earlier discussions, is crucial for a clear understanding of contaminated systems such as soils. This knowledge permits a rational approach to the design, selection, optimization, and evaluation of remediation techniques. Determination of mobility, fate, solubility, and bioavailability with this knowledge also makes risk assessment and monitoring more effective (Ryan et al., 2004).

With the complexity of heterogeneous environmental systems and materials, the inability of any single technique to obtain all of the desired information or for it to be acquired simultaneously is an impossible fact that must be faced. Because of this, it is clear that a combination of techniques, each providing a piece to the puzzle, will be necessary for a clear picture. Direct answers to questions must give way to inference and intuition. Much use must be made of a priori information about what species are possible, through what is known about the chemistry of the element considered and the natural system into which it is introduced (Porter et al., 2004). Knowledge of the form in which the metal contaminant originally appeared (or into which it evolves before reaching its destination) is obviously an important piece of information. In addition, although some techniques lack sensitivity or do not provide direct molecular information, this does not preclude employment of them in speciation analysis.

A review by Brown (1990) and a book by Ferguson (1989) each present a lexicon of different methods that have been used in the physicochemical analysis of partic-

ulates, surfaces, and species sorbed on them. Table 2 is a lexicon that was compiled and augmented from these two sources (Ferguson, 1989; Hochella and White, 1990). Some of the methods are the same spectroscopies mentioned before or are enhanced versions of them. Others are recently developed techniques exploiting the interactions of photons, electrons, ions, atoms, and static fields with the surfaces and detecting particles emitted, scattered, and reflected from those surfaces or, alternatively to measure the loss in beam intensity due to absorption by the sample. Figure 3 shows schematically how many of the surface analysis techniques are designed around beams of the aforementioned probes.

Most chemical analysis techniques are divided between destructive and nondestructive methods. Mass spectrometric techniques are clearly destructive because they must dislodge the surface material to analyze it. Most of the other techniques are considered to be nondestructive. NMR and IR clearly are nondestructive as they utilize non-ionizing radiation. In the others, some form of beam damage can and often does occur. Indeed, lasers, 30-keV electron beams, ion scattering probes, and X-rays all cause damage. Lasers do so with high intensity and conversion of the energy into heat, while charged particle beams and X-rays are ionizing radiation, which break bonds and at high intensities also sputter material off of the surfaces. Thus care must be taken with all such techniques to prevent surface alteration due to sample heating and direct beam damage.

Since there are so many techniques, what will follow will not be an exhaustive representation of the possible techniques. For more details than is given below, an excellent introductory review of surface analysis is given by Kelley (1987), while exhaustive coverage can be

Table 2. Terms for methods.

Initialism	Technique	Probe
AAS	atomic absorption spectroscopy	
ADES	angle-dispersed electron spectroscopy	photon
ADPD	angle-dependent photon-electron diffraction	photon
AEM	analytical electron microscopy	electron
AEPS	Auger-electron appearance potential spectroscopy	electron
AFM	atomic force microscope	field
AES	atomic emission spectroscopy	
AES	Auger electron spectroscopy	electron
AFS	atomic fluorescence spectroscopy	
AMPA	Auger microprobe analysis (also AMP)	electron
APS	appearance potential spectroscopy	electron
ARAES	angle-resolved Auger electron spectroscopy	electron
ARPES	angle-resolved photo-emission spectroscopy	photon
ARUPS	angle resolved ultraviolet photo-electron spectroscopy	photon
ARXPS	angle resolved X-ray photo-electron spectroscopy	photon
ASV	anodic stripping voltammetry	
ASW	acoustic surface-wave measurements	photon
ATR	attenuated total reflectance (IR)	photon
BIS	bremsstrahlung isochromate spectroscopy	electron
BLE	bombardment-induced light emission	atom
BSE	back-scattered electrons	electron
CAT	computer-aided tomography	photon
CBD	convergent-beam diffraction	electron
CEMS	conversion electron Mössbauer spectroscopy	photon
CFS	constant final-state spectroscopy	photon
CI-MS	chemical ionization mass spectroscopy	
CIS	constant initial-state	photon
CIS	characteristic isochromat spectroscopy	electron
CL	cathodoluminescence	electron
CMR	contact microradiography	photon
COL	colorimetry (IR, visible, UV, X-ray, and -ray absorption spectroscopy)	photon
CPAA	charged-particle activation analysis	atom
CPD	contact potential difference (work function measurements)	field
CTEM	conventional transmission electron microscopy	electron
CV	cyclic voltammetry	
DAPS	disappearance-potential spectroscopy	electron
DCEMS	depth-selective conversion electron Mössbauer spectroscopy	photon
DCP	direct current plasma	
DEPMS	direct exposure probe mass spectrometry	
DLTS	deep-level transient spectroscopy	electron
DNMR	double nuclear magnetic resonance	photon
DPP	differential pulse polarography	
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy (IR)	photon
DRS	difference reflectance spectroscopy	photon
DRS	diffuse reflectance spectroscopy (IR, UV-vis)	photon
E-2E	electron coincidence spectroscopy	electron
EAPFS	extended appearance potential fine structure	electron
EBIC	electron-beam-induced conductivity	electron
ECP	electron channeling pattern	electron
EDC	energy distribution curve	
EDS	energy-dispersive (X-ray) spectrometry (also EDAX or EDX)	electron
EDPD	energy-dependent photo-electron diffraction	photon
EDX	energy-dispersive X-ray analysis (also EDS or EDAX)	electron
EDXD	energy-dispersive X-ray diffraction	photon
EELS	electron energy loss spectroscopy	electron
EEM	emission electron microscopy	heat
EI-MS	electron impact ionization mass spectrometry	
EL	electroluminescence	
ELDOR	electron double resonance	photon
ELL	ellipsometry	photon
ENDOR	electron nuclear double resonance	photon
EMA	electron microprobe analysis	electron
EMOSS	emission Mössbauer spectroscopy	photon
EMPA	electron microprobe analysis (see EPMA)	electron
EMS	electron momentum spectroscopy	electron
ENDOR	electron-nuclear double resonance	photon
EPMA	electron probe microanalysis (see EMPA)	electron
ES	emission spectroscopy	photon
ESCA	electron spectroscopy for chemical analysis	photon
ESD	electron-stimulated desorption	electron
EDDI	electron-stimulated desorption of ions	electron
ESDIAD	electron-stimulated desorption ion angular distribution	electron
ESDN	electron-stimulated desorption of neutrals	electron
ESEM	electron spin-echo envelope modulation	
ESEM	environmental scanning electron microscope	electron
ESR	electron spin resonance	photon
EXAFS	extended X-ray absorption fine structure	photon
EXEELFS	extended electron energy loss fine structure	electron

Continued next page.

Table 2. Continued.

Initialism	Technique	Probe
FAAS	flameless atomic absorption spectroscopy	
FAB-MS	fast-atom-bombardment mass spectroscopy	atom
FD	flash desorption	phonon
FDM	field-desorption microscopy	field
FD-MS	field-desorption mass spectrometry	field
FDS	field desorption spectroscopy	field
FEED	field emission energy distribution	field
FEES	field electron energy spectroscopy	field
FEM	field electron microscopy	electron
FEM	field emission microscopy	field
FES	field emission spectroscopy	electron
FI	field ionization mass spectrometry	
FIM	field ion microscopy	atom
FIM-APS	field ion microscope-atom probe spectroscopy	field
FIR	far infrared spectroscopy	photon
FMR	ferromagnetic resonance	photon
FQHE	fractional quantum hall effect	electron
FTIR	Fourier transform infrared spectroscopy	photon
FYEXAFS	fluorescence-yield extended X-ray absorption fine structure	photon
GC	gas chromatography	
GD-MS	glow discharge mass spectrometry	ion
GDOS	glow discharge optical spectroscopy	atom
GFAAS	graphite furnace atomic absorption spectroscopy	
GLAEXAFS	glancing angle extended X-ray absorption fine structure	photon
HEAD	helium atom diffraction	atom
HEED	high-energy electron diffraction	electron
HEIS	high-energy ion (back-) scattering	atom
HOLZ	high-order Laue zone	photon
HREELS	high-resolution electron energy loss spectroscopy	electron
HREM	high-resolution electron microscopy	electron
HRMS	high resolution mass spectrometry	
HVEM	high-voltage electron microscopy	electron
IAES	ion-induced Auger electron spectroscopy	atom
IAS	inelastic atom scattering	atom
ICAP	inductively coupled argon plasma (also ICP)	
ICISS	impact collision ion scattering spectroscopy	atom
ICP-MS	inductively coupled plasma-mass spectrometry	
ICP-OES	inductively coupled plasma-optical emission spectroscopy	
IELS	ion energy loss spectroscopy	ion
IETS	inelastic electron tunneling spectroscopy	field
IIEE	ion-induced electron emission	ion
IIRS	ion-impact radiation spectroscopy	ion
IIXS	ion-induced X-ray spectroscopy	ion
ILEED	inelastic low-energy electron diffraction	electron
ILS	ionization loss spectroscopy	
IMMA	ion microprobe mass analysis	ion
IMPA	ion microprobe analysis	ion
IMPACT	implantation-perturbed angular correlation technique	atom
IMXA	ion microprobe X-ray analysis	ion
INS	ion neutralization spectroscopy	atom
IPES	inverse photo-emission spectroscopy	electron
IQHE	integral quantum hall effect	electron
IR	infrared spectroscopy	photon
IRAS	infrared absorption spectroscopy	photon
IRS	internal reflectance spectroscopy	photon
IS	ionization spectroscopy	electron
ISD	ion-stimulated desorption	ion
ISN	inelastic scattering of neutrons	neutron
ISE	ion selective electrode	
ISS	ion scattering spectroscopy	ion
ITS	inelastic tunneling spectroscopy	field
LAMMA	laser microprobe mass analysis (see LIMA)	photon
LC	liquid chromatography	
LEED	low-energy electron diffraction	electron
LEELS	low-energy electron loss spectroscopy	electron
LEERM	low-energy electron reflection microscopy	electron
LEISS	low-energy ion scattering spectroscopy	atom
LEPD	low-energy positron diffraction	positron
LIMA	laser ionization mass analysis (sometimes known as LAMMA)	photon
LMP	laser microprobe	photon
LOES	laser optical emission spectroscopy	photon
LRMS	laser Raman microprobe spectroscopy	photon
LS	light scattering	photon
MBRS	molecular beam reactive scattering	molecule
MBSS	molecular beam surface scattering	molecule
MEIS	medium-energy ion scattering	atom
MEM	mirror electron microscopy	electron
MIP-MS	microwave induced (helium) plasma mass spectrometry	

Continued next page.

Table 2. Continued.

Initialism	Technique	Probe
MODOR	microwave optical double-resonance spectroscopy	photon
MOLE	molecular optical (Raman) laser examination	photon
MOSS	Mössbauer spectroscopy	photon
MS	mass spectroscopy	heat
MS	magnetic saturation	field
MS-MS	mass spectrometry-mass spectrometry (also tandem MS)	
SR	muon spin rotation	muon
NAA	neutron activation analysis	neutron
ND	neutron diffraction	neutron
NDT	nondestructive testing	
NEXAFS	near-edge X-ray absorption fine structure	photon
NIRS	neutral impact radiation spectroscopy	neutral
NIS	neutron inelastic scattering	neutron
NMR	nuclear magnetic resonance	photon
NQR	nuclear quadrupole resonance	photon
NS	neutron scattering	neutron
ODMR	optical double magnetic resonance	photon
OES	optical emission spectroscopy	
OM	optical microscopy	photon
PA	positron annihilation	positron
PAC	perturbed angular correlation	photon
PAM	photo-acoustic microscopy	photon
PAS	photoacoustic spectroscopy	photon
PD	photodesorption	photon
PEEM	photo-emission electron microscopy	photon
PELS	proton energy loss spectroscopy	proton
PEM	photoelectron microscopy	photon
PES	photo-electron spectroscopy	photon
PESEM	photo-electron scanning electron microscopy	photon
PESM	photo-electron spectromicroscopy	photon
PEYS	photo-electron yield spectroscopy	photon
PIXE	proton-induced X-ray emission	proton
PMDR	phosphorescence microwave double-resonance spectroscopy	photon
PRA	prompt radiation analysis	neutron
PSD	photo-stimulated desorption	photon
PSID	photo-stimulated ion desorption	photon
PYS	partial yield spectroscopy	photon
QENS	quasi-elastic neutron scattering	neutron
QMS	quadrupole mass spectroscopy	
RAIRS	reflection-absorption infrared spectroscopy	photon
RBS	Rutherford back-scattering	atom
RED	reflection electron diffraction	electron
ReFEXAFS	reflection extended X-ray absorption fine structure	photon
REM	reflection electron microscopy	electron
RHEED	reflection high-energy electron diffraction	electron
RSMR	Rayleigh scattering Mössbauer radiation	photon
SACP	selected-area channeling pattern	electron
SAD	selected-area diffraction	electron
SAD	small-angle diffraction	electron
SAED	selected-area electron diffraction	electron
SALI	surface analysis by laser ionization	photon
SAM	scanning Auger (electron) microscopy	electron
SAM	scanning acoustic microscopy	photon
SANS	small-angle neutron scattering	neutron
SAXS	small-angle X-ray scattering	photon
SC	surface capacitance	field
SDMM	scanning desorption molecule microscope	electron
SE	secondary electron	electron
SEAM	scanning electro-acoustic microscopy	electron
SEE	secondary electron emission	electron
SEELFS	surface extended electron energy-loss fine structure	photon
SEM	scanning electron microscopy	electron
SERS	surface-enhanced Raman scattering	photon
SESCA	scanning electron spectroscopy for chemical analysis	electron
SEXAFS	surface extended X-ray absorption fine structure	photon
SHEED	scanning high-energy electron diffraction	electron
SHMS	secondary-ion imaging mass spectroscopy	ion
SI	surface ionization	photon
SIMS	secondary-ion mass spectroscopy	ion
SIPS	sputter-induced photon spectroscopy	photon
SIS	surface infrared spectroscopy	photon
SLAM	scanning laser acoustic microscopy	photon
SLEELM	scanning low-energy electron loss microscopy	electron
SLEEP	scanning low-energy electron probe	electron
SNMS	secondary neutral mass spectroscopy	atom
SNS	spallation neutron source	neutron
SOM	scanning optical microscopy	photon

Continued next page.



Table 2. Continued.

Initialism	Technique	Probe
SOMSEM	scanning optical microscopy	electron
SPAES	spin-polarized Auger electron spectroscopy	electron
SPAM	scanning photo-acoustic microscopy	photon
SPLEED	spin polarization low-energy electron diffraction	electron
SR	synchrotron radiation	photon
SRS	surface reflectance spectroscopy	photon
SSIMS	static secondary-ion mass spectroscopy with slow sputtering rate	atom
SSM	scanning secondary-ion microscopy	atom
STEM	scanning transmission electron microscopy	electron
STM	scanning tunneling microscopy	electron
STS	scanning tunneling spectroscopy	field
STXM	scanning transmission X-ray microscopy	photon
SXAPS	soft-X-ray appearance potential spectroscopy	electron
SXE	soft-X-ray emission	electron
SXM	scanning X-ray microscopy	photon
SXS	soft-X-ray emission spectroscopy	electron
TCP	transmission channeling pattern	electron
TDPAC	time differential perturbed angular correlation	photon
TD-MS	thermal desorption mass spectrometry	heat
TDS	thermal desorption spectroscopy	photon
TE	thermionic emission	phonon
TELS	transmission energy loss spectroscopy	electron
TEM	transmission electron microscopy	electron
THDS	thermal helium desorption spectrometry	heat
THEED	transmission high-energy electron diffraction	electron
TI-MS	thermal ionization mass spectrometry	heat
TL	thermoluminescence	heat
TM	tunneling microscopy	field
TMS	tandem mass spectrometry	
TOFAP	time-of-flight atom probe	atom
TOF-MS	time-of-flight mass spectrometry	
UPS	ultraviolet photo-electron spectroscopy	photon
UT	ultrasonic testing	phonon
WAXS	wide-angle X-ray scattering	photon
WDX	wavelength dispersive X-ray analysis	
XANES	X-ray absorption near-edge structure	photon
XAS	X-ray absorption spectroscopy	photon
XEM	exoelectron microscopy	photon
XES	exoelectron spectroscopy	photon
XES	X-ray emission spectroscopy	electron
XFS	X-ray fluorescence spectroscopy	photon
XPD	X-ray powder diffraction (also XRPD)	photon
XPS	X-ray photo-electron spectroscopy	photon
XRD	X-ray diffraction	photon
XRF	X-ray fluorescence	photon
XRM	X-ray microscopy	photon
XRPD	X-ray powder diffraction	photon
XRSW	X-ray standing wave	photon
YS	yield spectroscopy	photon
ZAP	zone axis pattern	photon

found in Briggs and Seah (1990) and Kiss (1988). Both, however, are geared toward manufactured materials research, rather than geochemical or environmental applications; for the latter consult Hawthorne (1988), Brown (1990), Perry (1990), Bertsch and Hunter (1996), and Scheidegger and Sparks (1996a).

### Special Method: Chromatography Coupled with Plasma Spectroscopic Techniques (e.g., ICP-MS, ICP-AAS or OES, MIP-MS, and Direct Solids Analysis MS)

Each of the techniques listed above uses plasma to vaporize and/or ionize a sample exposed to it or injected into it. This is not a surface technique, but is a useful speciation tool, especially for isotopic studies. An ICP-MS uses a quadrupole mass analyzer for detection, while ICP-AAS and OES utilize atomic absorption or emission spectrophotometers as the detectors. Instead of an ICP, using Ar gas plasma, one can have a He microwave induced plasma (MIP) source. Due to the high tempera-

tures of the plasma, all molecular information is destroyed, and thus only elemental and/or isotopic species can be determined. Excellent reviews of the application of ICP to examine metals from soil environments can be found in the literature (Bacon et al., 1997; Barefoot, 1998; de la Guardia and Garrigues, 1998; Yamasaki, 2000).

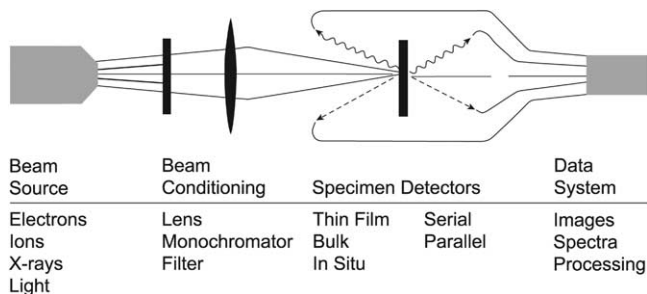


Fig. 3. Schematic of the basic layout of instrumental development for chemical analysis of surfaces and interfaces (from Kelley, 1987, with permission).

Each of these methods suffers from “spectral interferences” due to matrix effects (AAS–AES), or from the formation of molecular ions with oxygen or carrier gases (in MS). All require prior separation of complex mixtures, either via wet chemistry or a GC or LC system, on which they rely heavily for true speciation. Therefore, generally speaking, only volatile or solution complexes or species can be studied. In the case of solids, either laser ablation (LA) or a glow discharge (GD) plasma yield ions for direct mass analysis or for passage into a plasma torch. This avoids errors due to sample preparation (i.e., incomplete digestions, transfer losses, and improper dilutions). Both LA and GD suffer, however, from difficulties in quantification and reproducibility because of lack of standards and of course, permit only elemental and isotopic determination. Alternatively, using the isotope dilution technique, high precision elemental determinations to very low detection limits are possible (Denoyer et al., 1982; Lee and Kittrick, 1984; Nirel and Morel, 1990).

## TECHNIQUES USED IN SURFACE CHEMISTRY

### Mass Spectrometric Techniques

Mass spectrometric techniques study surfaces by the removal or sputtering of molecular ions and ion fragments from those surfaces to identify them. The following techniques are essentially ionization methods usually coupled with an appropriate mass analyzer. All share the sensitivity of mass spectrometric techniques. The relative detection limits as measured in  $\mu\text{g g}^{-1}$  are in rough range of  $10^{-3}$  to  $10^1$  while the absolute detection limits range from  $10^{-19}$  g to  $10^{-7}$  g (Winefordner, 1976). Mass range and mass resolution depend on the type of mass analyzer; however, the best mass resolution sometimes allows deduction of the molecular formula. Of the methods below, the softest ionization is the FD method, and it produces the largest number of whole parent ions. Very little ionization into fragments is desired if the analysis is of a mixture of compounds with a limited list of possible components. However, fragmentation is desirable for possible structural studies of an unknown.

There are several drawbacks to MS techniques (Winefordner, 1976). The most obvious is that during removal of surface material, the technique destroys the sample surface. Systematic errors can at times be very serious. Learning to optimize instrumental conditions, to obtain good mass spectra, and to achieve quantitative analysis for a particular experiment may require some months to years of experience with an instrument. A complex mix of metal species on soil particles may prevent acquisition of an analyzable spectrum even for experienced personnel. Solids, in general, pose great difficulties for mass spectrometric analysis. Most of the MS techniques below require the samples to be under vacuum. Since gases, moisture, and other volatiles are part of a soil matrix, outgassing will be a limitation. Lastly, since the method is a destructive one, it does not yield informa-

tion about how sorbed species are bound to the surfaces of interest.

Many groups develop new methods themselves by customizing commercial instruments or constructing them from scratch (Olson et al., 1992; Budde, 2001). Certainly, such options always exist and perhaps a combination of some of the methods below might provide the maximum amount of information needed for speciation in soil or other environmental matrices. Listed below are some of the MS methodologies used to analyze organic materials, solids, and their surfaces. A number have been applied to soils or their components.

### Ionization Techniques

**Secondary Ion Mass Spectroscopy (SIMS).** This technique utilizes ion beams created from gas (Ar) or liquid metal sources, such as gallium. It is, of course, destructive of the sample as it causes sputtering of ions from the surface examined (Becker and Dietze, 1998). Mass spectra reveal the presence of the elements liberated by the beam and are similar in appearance to the LAMMA spectrum (Fig. 4), discussed below. It has been used for polymers, large biomolecules, surfaces, and particulates. It has also been utilized in the study of surface predominance of elements in airborne particles and for observation of phosphate precipitation onto goethite surfaces (Keyser et al., 1978; Farmer and Linton, 1984; Grasserbauer, 1986; Martin et al., 1988; Willard, 1988). It has also been used to generate depth profile maps of leached vitrification glasses for nuclear waste disposal (Lodding et al., 1992). Additionally, SIMS has been employed to observe Pb and Zn adsorption on Al- and Fe-coated sand (Coston et al., 1995) and to examine heavy metal distribution in maize roots grown in highly contaminated greenhouse soils (Kaldorf et al., 1999).

**Fast Atom Bombardment (FAB).** This is a variant of SIMS using an uncharged atom beam that gives molecular ions and structurally significant fragment ions, much the same as SIMS. A neutral atom beam is created and directed onto samples, and the sputtered ions are drawn into a mass analyzer. Alternatively, the sample is dissolved in a liquid matrix, which acts to neutralize the charge of the ion beam. This has been utilized for both biomolecule and metal species studies. It might be very useful for the study of spiked humic fractions and their extracts. It could also be useful in the study of solids and particulates (Bernhard et al., 1986; Willard, 1988; Caprioli, 1990).

**Ion Microprobe Mass Analyzer (IMMA).** This is the microprobe version of SIMS (0.2- $\mu\text{m}$  beam diameter) with a sophisticated high-resolution two stage mass analyzer (Ferrer and Thurman, 2003). Can be used for study of surfaces, particulates, and thin sections (Willard, 1988).

**Laser Microprobe Mass Analyzer (LAMMA).** This technique gives molecular ions at low laser intensity and fragments at higher intensity. The sputtered ions are drawn into a time of flight (TOF) or Fourier transform (FT) mass analyzer. It has been applied to organics, organometallics, soil particles and thin soil sections. Fig-

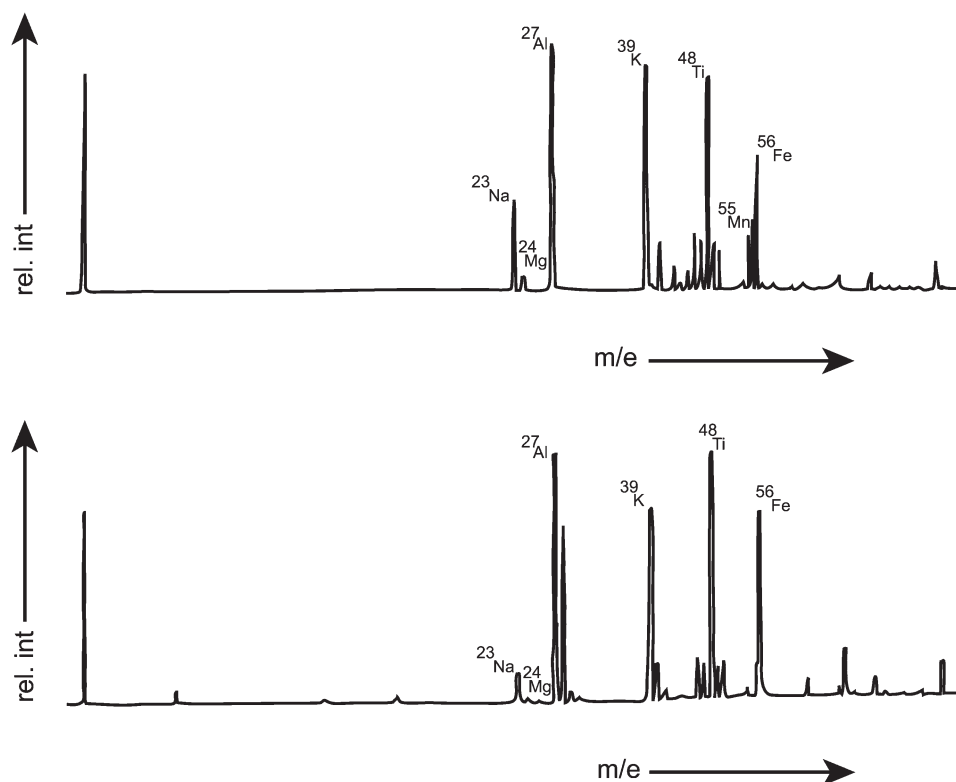


Fig. 4. Laser microprobe mass analyzer (LAMMA)-500 positive ion spectra taken at two points on the same thin film section. Note the difference in elemental composition (from Henstra et al., 1981, with permission).

ure 4 depicts LAMMA mass spectra of two different points in a thin soil section (Henstra et al., 1981), showing a different elemental composition at the two points. It is also referred to as surface analysis by laser ionization (SALI) (Nitsche et al., 1978; Henstra et al., 1981; Muller et al., 1981; Denoyer et al., 1982; Hercules et al., 1982).

**Californium-252 Plasma Desorption (PD).** In this technique, a sample coated onto a thin foil is exposed to a Cf nucleus fission fragment which forms microplasma, sputtering molecular ions from the surface. Its utility for soil particles would be very limited, if at all. It could be useful for organic and organometallics that could be isolated from soils (Willard, 1988).

**Field Desorption (FD).** This is a method in which a sample is placed on an electrode, heated, and negatively charged, from which the molecular ions are desorbed. Samples are usually solutions applied to a carbon whisker electrode from which the solvent has been evaporated. It can be applied to solids if they can be fashioned into fine point ("whiskered") (Lehmann and Schulten, 1977; Schulten, 1979, 1982; Grasserbauer, 1986; Willard, 1988).

**Thermal Desorption (TD).** In TD, samples are heated on a tungsten filament or in a sample cup to 2300 K. Species boiled off of the surface have a probability to be ionized; other techniques utilize an electron impact ionizer. This could be useful for soil sample surface studies or isotope ratio studies (Willard, 1988; Bacon et al., 1992). It has been used to determine organic matter and metal carbonate contents of soils (Gaal et al., 1994)

and to distinguish between organomercurials and metallic Hg in contaminated sites (Hempel et al., 1995).

### Specialized Mass Analyzer and Separation Techniques

**Mass Spectrometer–Mass Spectrometer (MS–MS).** This is also referred to as a tandem mass spectrometer (TMS). This utilizes two mass spectrometers (say MS1 and MS2) with different mass range, mass resolution, and ionization technique. MS1 might have a low ionization, high mass resolution, and large mass range capability. This gives large numbers of whole molecular ions viewed over a very broad mass range. Then, in one particular mode of study, a single ion spectral line from MS1 will be passed to MS2. MS2 will have a high ionization, low mass resolution, smaller mass range capability. This will be utilized to elucidate the structure of the (fixed mass) molecular ion line generated by MS1 using an ion fragmentation pattern. This technique coupled with prior chromatographic separations and/or proper ionization of solids could be an extremely powerful tool for a speciation project. It offers the separating ability needed for very complex mixtures. It has been used in the study of large biomolecules (Bernhard et al., 1986; Willard, 1988), explosives (Casetta and Garofolo, 1994), and chemical warfare components (Black et al., 1994).

### Electron Techniques: Imaging, Spectroscopy and Diffraction

Electrons behave as both particles and waves. These aspects of electron behavior have allowed the develop-

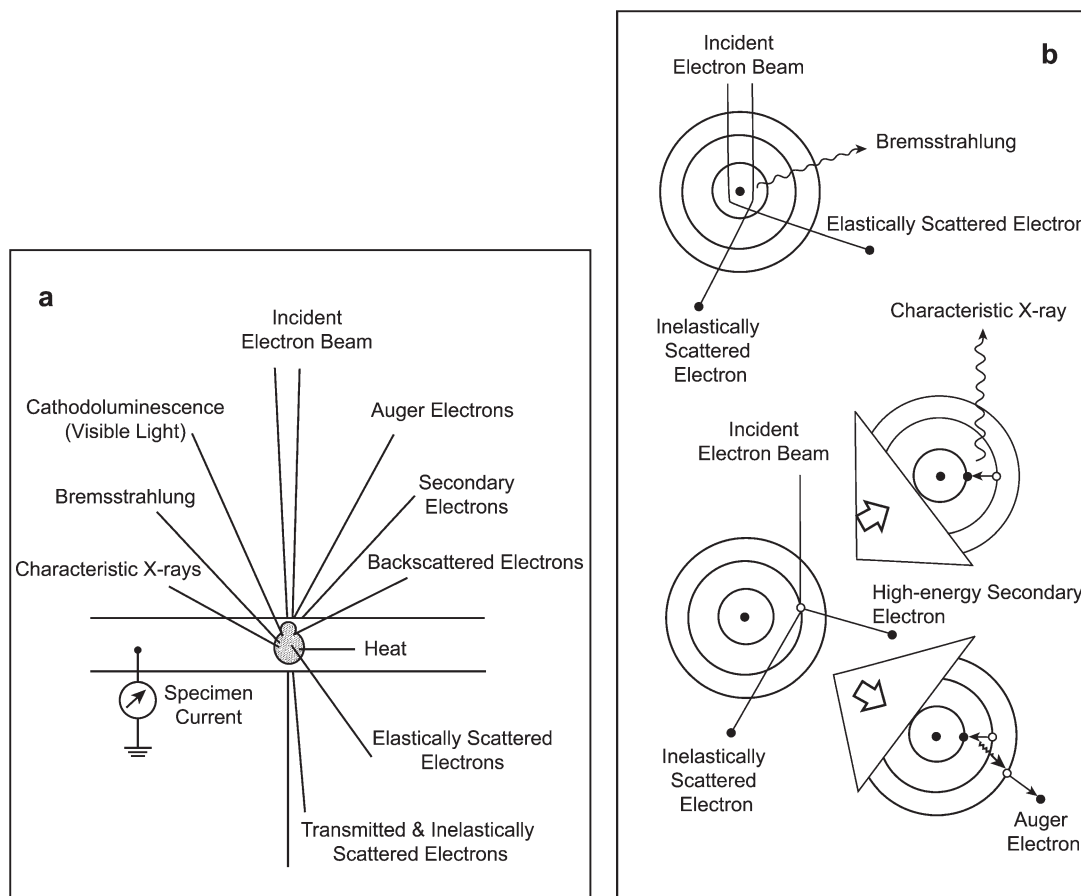


Fig. 5. Interaction of an electron beam with matter regarding (a) macroscopic depiction of the numerous information signals available for analysis and (b) microscopic interpretation of atomic processes that produce some of the information signals.

ment of methods for obtaining a great deal of information from solids, surfaces, and particulates. This is accomplished by looking at the scattering or diffraction of the electron beams (SEM, TEM, EELS, ED) and X-rays or electrons produced by excitation of atoms (SEM-EDX or WDX, EPXMA, AES, XPS) for both imaging and spectroscopy. Figure 5 depicts the many forms of radiation and other effects that occur when an electron beam impinges on a solid material. It also shows the atomic processes involved in the production of these information signals. The ability to focus electron beams to very small spot size (approximately 20 Å) and to raster them, as well as their inherently short wavelength (approximately 0.1 Å) yields excellent spatial resolution for elemental mapping and for topographical imaging of surface variation and structure. Electron spectroscopies give us much more information about matter on surfaces or at the submicron scale. EELS yields molecular information from primary electron energy losses to atoms and molecules, while AES and XPS do so via shifts in energies of electrons ejected from atoms bound in molecular associations, relative to the energies expected from those same atoms in a free state. Note that although XPS is an electron spectroscopy, it can only be explored through X-ray excitation and is discussed in a subsequent section. Electron diffraction is yet one more

way to identify and to characterize microchemical species through their crystal structure, if crystalline.

### Scanning Electron Microscopy–Energy Dispersive X-Ray Analysis (SEM-EDX)

SEM is analogous to optical microscopy with illumination from above. It probes the surface morphology and topography at the nanometer scale. The EDX technique is one in which the electron microscope beam scans a surface and the X-ray fluorescence, emitted by surface atoms interacting with the beam, is detected. The X-rays are characteristic of the atoms emitting them and give a semi-quantitative profile of the elemental composition. Figures 6 and 7 are of two soils, the former has approximately 170 000 mg kg<sup>-1</sup> and the latter about 100 mg kg<sup>-1</sup> Pb. Lead is clearly visible in Fig. 6 (top), and it seems to be in Fig. 6 (bottom) also. However, this is most likely sulfur, as the Pb peak shape is very different from that in Fig. 6 (top) and is shifted to lower energy; note that all of the other common elements (Al, Si, Ca, and Fe) do not change their position or appearance. This is an example of a misleading spectral overlap. Here the S K<sub>α</sub> (2.307 keV) and the Pb M<sub>α</sub> lines (2.393 keV) are within the energy resolution of the EDX detectors (approximately 0.15 keV), thus they are often difficult to separate or identify. This method has been



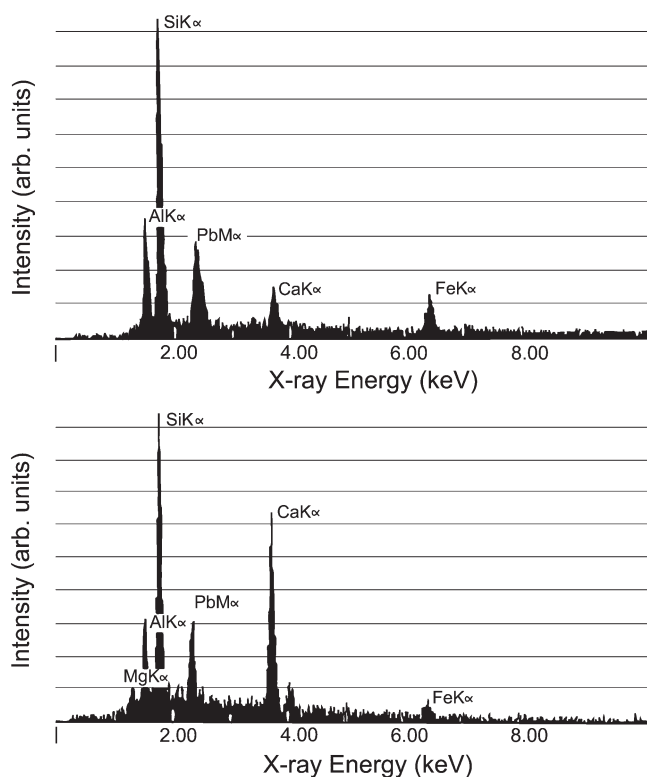


Fig. 6. Energy-dispersive X-ray (EDX) spectra of soil samples illustrating a spectral overlap of Pb and S.

used in petrology (Welton, 1984) and to study sediment and suspended trace metal contaminants in rivers, bays, and marine sites (Ramamoorthy and Massalski, 1978; Jedwab, 1979; Luther et al., 1980; Norrish et al., 1986), aquatic colloids (Leppard, 1992), sewage sludge and sludge-amended soil, solid metal phases (Essington and Mattigod, 1985, 1991), airborne particulates and fly ash (Linton et al., 1976; Keyser et al., 1978; Farmer and Linton, 1984; Hansen et al., 1984), clay minerals (Beutelspacher and Van Der Marel, 1968; Jaynes and Bigham, 1986), Fe and Al sesquioxide coatings on mineral-soil particle surfaces (Hendershot and Lavkulich, 1983), humic matter (Tan, 1985), Pb (and other metals) in house and urban dusts (Linton et al., 1980; Hunt et al., 1992) and in soils (Smart and Tovey, 1982; Whalley, 1985; Bain et al., 1986; Mattigod et al., 1986; Rybicka et al., 1994; Yarlagadda et al., 1995; Adamo et al., 1996; Garcia-Rizo et al., 1999; Welter et al., 1999), metals in solidified matrices (Neuwirth et al., 1989; McWhinney et al., 1990; Cocke et al., 1992; Roy et al., 1992; Cotter-Howells and Caporn, 1996), ferric oxides (Landa and Gast, 1973), and as a tool to determine trace metals by electrodeposition (Chong et al., 1990). The technique is limited by low sensitivity with EDX, but can be improved by using wavelength dispersive X-ray analysis (WDX). Although WDX increases sensitivity, it can add greatly to the time required for the X-ray analysis (Kiss, 1988). Another limitation is spatial resolution of the elemental mapping for this and EPXMA. This is due to the scattering of primary and secondary electrons deep within the material yielding X-rays from a large fixed volume about 3  $\mu\text{m}$  across, irrespective of the beam spot size (Fig. 7).

Most samples must be dried and coated with a conductive material and placed in a high vacuum, which is a limitation for most charged beam techniques. However, resolution continues to improve, and recent designs have given genesis to environmental SEM. ESEM is able to tolerate the presence of up to 10 torr of gases in the sample chamber. They use large differential pumping, place samples very close to the beam and secondary electron detector, and lastly, take advantage of the gas to both eliminate sample charging (thus coating) and to act as a preamplifier. These considerations permit 50  $\text{\AA}$  resolution at 10 torr and virtual in situ analyses of moist or unprepared samples (no drying or coating).

### Electron Probe with X-Ray Microanalysis (EPXMA)

This is an electron microprobe that has the same capability as SEM in elemental mapping and associations between elements but without the imaging optics. The instrument often is coupled with wavelength dispersive X-ray analysis (WDX). This coupling, along with high beam current and long dwell times, make the detection limits for the electron microprobe much lower than SEM-EDX. Samples are often polished sections, as EPXMA has been much used in the analysis of rocks and minerals (Cadwell and Weiblen, 1965; Smith, 1965). Two-dimensional images of the elemental distributions on the polished surfaces are mapped point by point. Embedding and polishing has been applied in many cases of smaller particles in addition to the techniques of pressing into metal foil (White, 1964) and ultramicrotomy (Ogura, 1981). Reviews of EPXMA in soils (Cescas et al., 1968; Walsh, 1971; Klute, 1986; Hochella and White, 1990), use in sediment trace element analysis (Lee and Kittrick, 1984; Norrish et al., 1986), suspended estuarine particulates (Bernard et al., 1986), element and complex sorption on Fe and Al minerals (Goh et al., 1986; Kuo, 1986), and As and Pb minerals in mine waste contaminated soils (Davis et al., 1992) can be found in the literature.

### Transmission Electron Microscopy and Scanning TEM (TEM-STEM)

This is an electron microscopy that is analogous to optical microscopy in which illumination is from below (transmission). That is, the imaging optics (magnetic coils) is on the opposite side of the sample from the beam source. The sample, in general, is milled or sectioned to provide electron transparent foils for TEM analysis. If the sample is particulate or a powder, a number of methods have been put forth in the literature to prepare them for TEM. The particles could be embedded in an epoxy before ultramicrotomy, or ground and polished on diamond lap polishers. Other methods call for a suspension of them to be deposited onto a thin film (graphite or colloidal), or centrifuged and fixed onto a grid with a water-soluble melamine resin. Several references (Spurr, 1969; Barber, 1971; Ogura, 1981; Bachhuber and Frosch, 1983; Kushida et al., 1983; Nomizu and Mizuike, 1986; Nomizu et al., 1987, 1988; Frosch and Westphal, 1989; Perret et al., 1991) describe

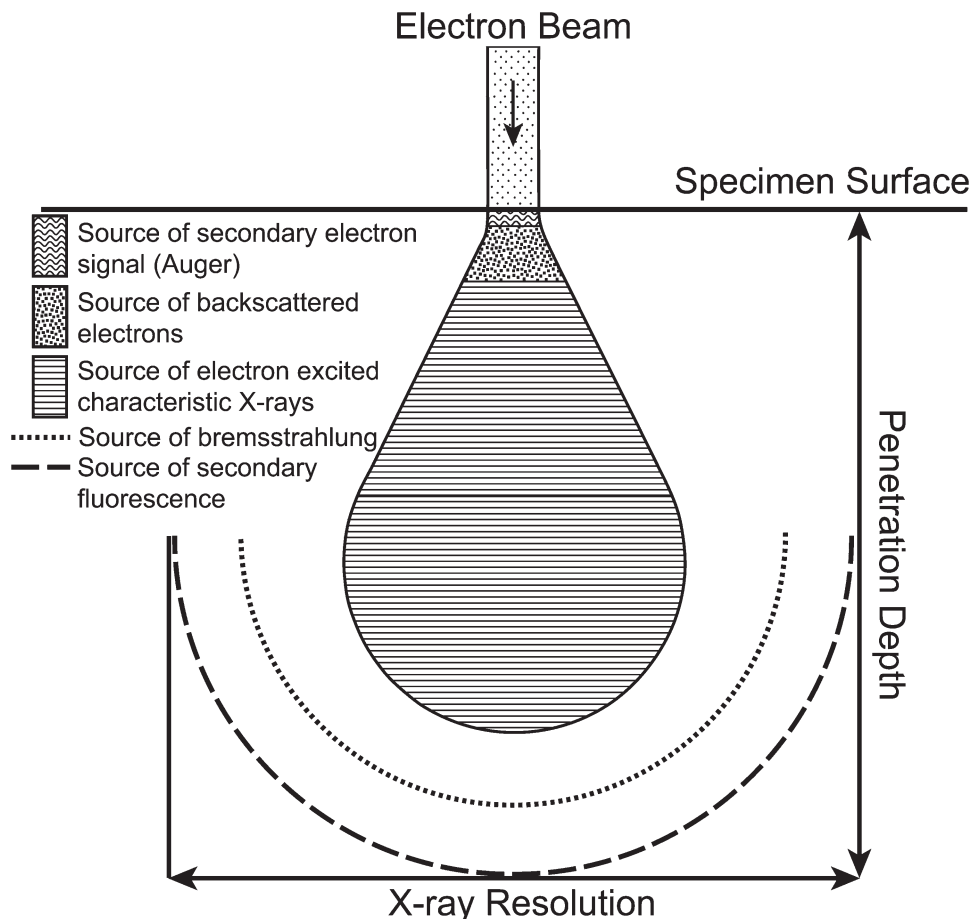


Fig. 7. Scattering and sources of electrons due to penetration of an electron beam into a specimen bulk surface.

the details. The lower the accelerating voltage of the primary beam, the thinner the samples must be to achieve transparency. Selected area electron diffraction (SAED) is usually available on TEM–STEM units, EDX is easy to add, and EELS is another important tool to use with TEM for gathering microchemical information. TEM–EDX has both advantages and drawbacks with respect to SEM–EDX analyses. One advantage is that the resolution for X-ray mapping is significantly better for TEM than SEM due to the simple fact that the volume excited is much smaller (from the thinness of sections viewed in TEM, Fig. 8). TEM also has much greater spatial resolution for imaging, with 2 to 5 Å features often visible. A drawback is that with the smaller volume fewer X-rays are produced and detected. Therefore, the very small volume examined is a drawback (statistically) relative to the enhancement of resolution. The question that arises is, What can be inferred about macroscopic samples in bulk, much less the site from which they were gathered, from the tiny amount of each sample that is probed? Some of the drawbacks with respect to SEM can be lessened with the use of a STEM. STEMs combine the best of both SEM and TEM, in that each mode of operation is possible with these instruments. This technique has been used in conjunction with the microchemical tools mentioned above to study characterization of ultra-small particles (Iijima,

1985) and iron-rich clay minerals (Ghabru et al., 1990), crystallinity of ferric oxides (Landa and Gast, 1973), precipitation of phosphate on goethite (Martin et al., 1988), effects of tannic acid on Cu and Zn retention on Al oxides (Goh et al., 1986), nanometer size Au inclusions in pyrite grains (Bakken et al., 1989), characterization of submicron aquatic colloids (Nomizu and Mizuike, 1986; Nomizu et al., 1987, 1988; Perret et al., 1991; Leppard, 1992), study of bacteria as nucleation sites for inorganic minerals in lake sediments (Ferris et al., 1987), organic matter and their structures in surface and fresh waters (Leppard et al., 1990; Filella et al., 1993), and the distribution and encapsulation of metal species in solidified matrices from solidification and stabilization remediation technologies (Neuwirth et al., 1989; Roy et al., 1992; Coston et al., 1995; Barnett et al., 1997; Klich et al., 1999).

#### Electron Energy Loss Spectroscopy (EELS)

This encompasses many modes of energy loss and thus spectroscopies. The one most often exploited is the plasmon EELS, where primary electrons lose energy to plasmons (a quasi-particle). Extended electron energy loss fine structure (EXEELFS), energy loss near edge structure (ELNES), and surface EELFS (SEELFS) are examples of energy loss spectroscopies that yield infor-

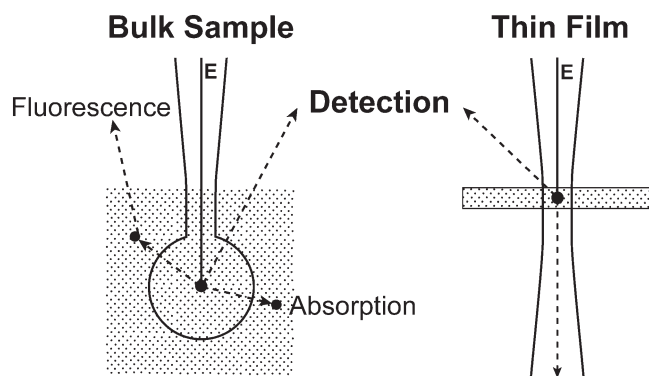


Fig. 8. Resolution enhancement of transmission electron microscopy (TEM; thin film) over scanning electron microscopy (SEM; bulk sample) due to smaller material volume excitement by the electron beam (adapted from Wenk, 1976).

mation very similar to EXAFS and XANES. The losses are roughly in the 10- to 500-eV range. In the submilli- to milli-eV energy loss range is high resolution EELS. HREELS measures energy losses experienced by a very monoenergetic electron beam due to its interaction with molecular vibrational states of molecules adsorbed onto surfaces of interest. It provides structure information similar to that of IR and Raman spectroscopy (Bell and Hair, 1980; Hochella and White, 1990). Although there are rare references to EELS use in soil studies, it has been more commonly used on small particles and supported metal catalyst studies (Iijima, 1985) and to examine metal toxicity on soil microfauna (Kohler et al., 1995; Pawert et al., 1996; Neumann et al., 1997; Bringezu et al., 1999).

### Auger Electron Spectroscopy (AES)

Auger electron (AE) emission is an alternate atomic relaxation phenomenon to the emission of fluorescent X-rays. The process is dominant for low energies and low atomic number atoms, while X-ray fluorescence dominates at the opposite ends, making Auger somewhat complementary to X-ray fluorescence. The energies of AE are characteristic of the emitting atoms and are analyzed in much the same way as photoelectron energies (see below). The spectra can yield chemical information, although it is rare. That is because the AE energies depend on two energy levels, not just one as with XPS. The chemical environment thus influences both levels in different ways and is hard to predict. AES can be considered both an electron technique and an X-ray technique as both probes can liberate AE; refer to Fig. 5b and place an X-ray photon for the incoming primary electron. The lower the energy of the Auger electrons, the more surface sensitive is the analysis utilizing them. This is because such electrons can only escape from within a material near its surface, approximately 1 nm (Fig. 7). This phenomenon also makes the microprobe versions, scanning Auger microprobe or microscopy (SAM), better than X-ray analysis via electron excitation. Since the Auger electrons only emanate from the illuminated surface, the excitation that occurs beneath the surface, as for SEM-EDX and EPXMA, does

not play a role in the mapping spatial resolution. Thus at low energies, at least, the elemental mapping resolution approaches the beam spot size. This technique has been widely applied to the study of surfaces in a number of different fields (Turner, 1988). In the field of geochemical studies of solid surfaces, soils, and sediments, AES has been applied to determine trace element concentrations on the surfaces of oil fly ash particulates and sediments (Trimble et al., 1999) and sorption of metals (Coston et al., 1995; Astrom, 1998; Nooney et al., 1998). The drawbacks are that it is primarily an elemental determination technique and requires a high vacuum for low energy electron detection, while charging and adsorbed gases or material distort and damp the Auger spectra (Linton et al., 1976, 1983; Keyser et al., 1978; Martin et al., 1988).

### Electron Diffraction (ED)

In ED the wavelike nature of electrons is exploited in much the same manner as X-rays to elucidate the crystalline structure of matter. TEM-STEMs can do this at the nanometer scale in transmission on thin sections or edges of particulates via selected (or spot) area ED or SAED. With SEM and other electron probes one can perform surface crystallographic analysis with low energy electron diffraction (LEED) or reflected high energy electron diffraction (RHEED). These diffraction methods have been utilized in mineral studies (Wenk, 1976; Fryer, 1979; Drits, 1987; Barnett et al., 1997; Cotter-Howells et al., 1999), soils (Jackson, 1973; Smart and Tovey, 1982), sorption of phosphate on goethite (Martin et al., 1988), small particles with supported catalysts (Iijima, 1985), and 50 to 200 Å gold inclusions in pyrite ores (Bakken et al., 1989).

### Ion Probes

Ion probe methods exploit the interaction of ions with matter. They interact with samples differently than electron beams and are related to the microbeam and ion probes of mass spectrometry. In general, however, the aim is not to sputter or damage the specimen, but to look at other interactions between the ions and the sample atoms. Some of the interactions include ion induced X-ray emission, ion-nuclear scattering, and energy loss of the scattering ions. The two techniques below are examples of this type of technique.

### Proton Induced X-Ray Emission (PIXE)

As mentioned before in the section on SEM-EDX, the emission of X-ray fluorescence by bombardment with an electron beam from an SEM is a method by which an elemental analysis can be performed. The surfaces of particles can also be bombarded with protons or ions of heavier atoms. These too will induce production of X-ray fluorescence that can be studied. Protons are more massive than electrons and give rise to a lower bremsstrahlung background (the continuous X-ray background due to deceleration of the charged particle), hence enhanced detectability limits over SEM-EDX for



certain elements. There is, with proper focusing and collimation of the beam, a microprobe version of PIXE to enable the direct study of particulate surfaces, with corresponding lower absolute detection limits. In the best-case scenarios, PIXE can approach  $10^{-18}$  grams of analyte on very small matrix particles (Cahill, 1980). In SEM-EDX, the SEM allows the lateral mapping of the location of the elements on the surface. Lateral surface mapping with PIXE is most likely not as achievable as with SEM, due to the rastering capability of the latter. Again, as with SEM-EDX this is a quantitative elemental surface determination technique and, as such, it does not provide species or molecular information. However, determination of the concentrations on the surfaces of particles and elemental associations are important pieces of information. In environmental studies, PIXE has been applied to examine trace metal contaminants in sediments and to mineral surfaces (Folkmann, 1975; Johansson and Johansson, 1976; Cahill, 1980; Burnett and Woolum, 1983; Grossmann et al., 1985; Martin et al., 1988; Protz et al., 1993; Matsuda et al., 1996; Kramer et al., 1997; Rajander et al., 1999).

#### Rutherford Backscattering Spectrometry (RBS)

This is a technique in which alpha particles (i.e., ionized He nuclei) are accelerated to approximately 1 MeV, collimated much like protons in PIXE, and directed onto the sample surfaces of interest. The alpha particles then scatter from nuclei of the atoms of the sample being probed. Those scattered at angles greater than 90 degrees are detected and their energies are measured. Alpha particles are more readily backscattered by elements of higher atomic mass than by those of lower atomic mass. This gives rise to some crude discrimination between elements, while sensitivity for specific elements depends on the element and the matrix in which it is found. However, its main use is in its ability to distinguish the depth in the material from which the scattered alphas originate. This is due to the rate of energy lost by the scattered alpha particles to atomic electron shells of the matrix material, which is well understood from nuclear and particle physics studies. Its utility lies in its function as a spatial distribution tool. Depth probing can be done over a range from approximately 100 Å to 1 μm and can have a depth resolution of approximately 20 Å (Hawthorne, 1988). The lateral spatial resolution is very poor (approximately 1 mm); however, better ion optics could conceivably reduce this by several orders of magnitude. SIMS instruments can produce ion beams of roughly 20 nm in diameter, and alpha beams might be focusable to such dimensions. Due to the poor elemental discrimination, the technique would be most applicable to samples of low relative atomic mass with heavy impurities (Hawthorne, 1988; Kramer et al., 1997). This might make it a useful tool in the study of heavy metal (Hg, Pb, Th, and U) sorption and precipitation in light element soil matrices. It has been applied to the studies of rocks and minerals (Davies, 1980), one being the analysis of the surface chemis-

try of dissolving feldspar (Casey et al., 1989) and depth profiling of H, Si, Al, and Ca in the mineral.

#### X-Ray Methods

The use of X-rays in the study of surfaces is experiencing a surge in interest due to the availability of intense synchrotron X-ray sources. The ejection of core shell electrons by the absorption of an X-ray photon (XPS), AES, and SEXAFS from Auger emission after core emission and emission of fluorescent X-rays (XAS), as well, can serve as analytical tools for obtaining chemical information. See Fig. 5b and substitute an X-ray photon for the primary electron. This occurs by observing the shifts in core shell energy levels due to valence electrons. It is clear that with few synchrotron facilities, X-ray methods that could benefit will only be conducted for very specialized and important work and as beam time is available. This will not enable routine analyses to be performed using them. However, the development of microprobes (500 Å to 10 μm beam diameters) at these facilities will make some microchemical characterization methods extremely powerful and useful in geochemical studies.

#### X-Ray Photoelectron Spectroscopy (XPS, or ESCA)

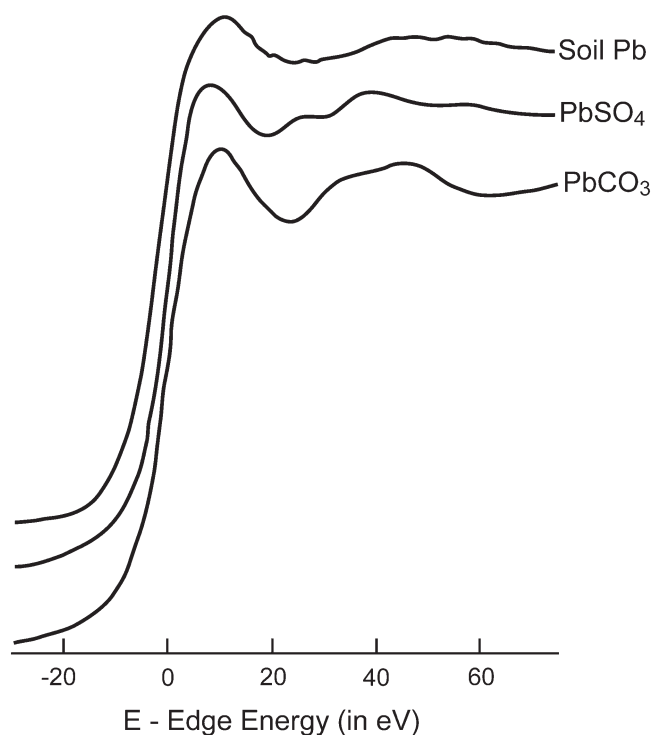
Photoelectrically emitted electron kinetic energies are measured with an electrostatic deflector and an electron detector. Two different energies are measured to distinguish photoelectric effect electrons from Auger electrons. Shifts of the binding energies of a given atomic species are measured relative to that of some known compounds (chemical shifts) taken under the same instrumental conditions. These can reveal the oxidation state of the trace metal in molecules on the surfaces of particles. Also known as electron spectroscopy for chemical analysis (ESCA), the technique has been used in the trace analysis of metal species on fly ash particles, ferromanganese nodules, Pb adsorption on montmorillonite, Co(II) on MnO<sub>2</sub>, Cr(x)<sup>3+</sup> species adsorbed on clays, silicate adsorption on gibbsite, cation exchange by layered silicates, metal precipitation, and phosphate absorption onto goethite (Counts et al., 1973; Czuha and Riggs, 1975; Koppelman and Dillard, 1975, 1978, 1980; Alvarez et al., 1976; Linton et al., 1976, 1983; Adams et al., 1977; Keyser et al., 1978; Adams and Evans, 1979; Bancroft et al., 1979; Murray and Dillard, 1979; Dillard et al., 1981, 1982, 1984; Cabaniss and Linton, 1984; Farmer and Linton, 1984; Martin and Smart, 1987; Martin et al., 1988; Turner, 1988; Soma et al., 1989; Vempati et al., 1990; Johansson et al., 1992; Junta and Hochella, 1994; White and Peterson, 1996; Olazabal et al., 1997; Chang and Liu, 1998; Gier and Johns, 2000). Further progress will be made as X-ray focused microprobes are utilized in conjunction with XPS.

#### X-Ray Absorption Spectroscopy (XAS)

This spectroscopy includes EXAFS, XANES, and its surface variant, SEXAFS. The ability of a sample (element) to fluoresce strongly influences its ability to ab-



sorb photons of a given energy and modulations of that absorption spectrum (near a metal absorption edge) are due to the local chemical environment of the absorbing metal. Such modulations are called the fine structure and from them the chemical information is obtained, namely oxidation state, interatomic bond distances, coordination number, and coordinating atom identity. The methods are also in situ, a distinct advantage, not requiring vacuum for sample analysis except for SEXAFS. Even with the intensity of synchrotron X-ray sources, detection limits in the solid phase are currently about  $100 \text{ mg kg}^{-1}$  for bulk analysis and  $10 \text{ mg kg}^{-1}$  for micro-focused investigations. Additionally, XAS by itself has difficulty with multicomponent mixtures (of the same element) and little quantification; however, innovative application of linear combination fitting or principle component analysis have accomplished much in this area for complex environmental samples (Beauchemin et al., 2002; Isaure et al., 2002; Scheinost et al., 2002; Roberts et al., 2002; Scheckel and Ryan, 2004). Nevertheless, as an indicator of species and structure, XAS has at least an order of magnitude advantage over any other technique identifying true fundamental species (e.g., XRD, NMR, IR, Raman, XPS, etc.). X-ray microprobe techniques that utilize a microfocused beam ( $<10 \mu\text{m}$ ) for XAS speciation and XRF mapping permit researchers to examine localized hotspots (via XRF mapping) to determine spatial heterogeneity (Lu et al., 1989; Isaure et al., 2002; Roberts et al., 2002). SEXAFS, which looks at the intensity variation of Auger emission, rather than X-ray emission, as a function of beam energy, is surface sensitive for the same reason as AES. With microprobe versions, this technique could be very useful for surface studies. Applications of XAS directly to soils and soil components have been pursued actively for the past decade and results are readily found in the literature. A preliminary study looked at the comparison of a soil lead sample ( $2000 \text{ mg kg}^{-1}$  Pb by weight) with lead sulfate and carbonate. The XANES region spectra are shown in Fig. 9. The spectra bear little resemblance to one another resulting in the ability to compare known references to unknown samples. In the field of earth sciences, sorption of metals (Co, Se, Pb, and Np) to mineral surfaces, such as Al and Fe hydrous oxides, has been explored (Hayes et al., 1987; Chisholm-Brause et al., 1989a, 1989b, 1990a, 1990b; Roe et al., 1991; Combes et al., 1992). Other studies of the formation of Fe oxides (Combes et al., 1986, 1989, 1990) and of humic matter characterization (Bloom and Leenheer, 1989) have been undertaken. In recent years, EXAFS has played an important role in the geochemical community as a tool to decipher between sorption mechanisms (i.e., adsorption vs. precipitation [bulk vs. surface]) (Scheidegger et al., 1996a, 1996b, 1997, 1998, Scheckel et al., 2000). EXAFS has been employed to definitely show that sorption of metals such as Co, Ni, and Zn on clay minerals and soils results in the formation of hydroxide-like or mixed metal-Al precipitates of the hydrotalcite-type under ambient reaction conditions (near-neutral pH, low metal concentrations, and short time scales) (O'Day et al., 1994, 1996; Scheidegger et al., 1996a,



**Fig. 9.** Comparison of X-ray absorption near-edge structure (XANES) spectra for a Pb-contaminated soil (SoPb),  $\text{PbCO}_3$ , and  $\text{PbSO}_4$ .

1996b, 1997, 1998; Scheidegger and Sparks, 1996b; Towle et al., 1997; Thompson, 1998; Roberts et al., 1999; Scheinost and Sparks, 2000; Ford and Sparks, 2000; Manceau et al., 2000; Scheckel and Sparks, 2000). A number of excellent reviews of the application of XAS to geologic materials are available (Bernhard et al., 1986; Hawthorne, 1988; Brown and Parks, 1989; Hochella and White, 1990; Fendorf and Sparks, 1996; Scheidegger and Sparks, 1996a; Brown et al., 1998).

#### **X-Ray Diffraction or X-Ray Powder Diffraction (XRD or XPD)**

This has been utilized in the metals characterization of aerosol particulates, sludges, urban street dusts, Fe- and Al-oxides, and clays in soils and in lead spiked Portland cement. Physical methods of separation (particle size, density, and/or magnetic properties) have been utilized in soils, sediments, sludges, etc., to preconcentrate the analyte of interest. The detection limits of this technique are approximately 1 to 5%, but can be significantly enhanced using synchrotron sources. Protocols vary from a wide angular survey (useful for major components of a mixture), to a search for specific unique peaks, using a very narrow angular search range, expected for a compound suspected to be a minor component. Again this technique is useful in soil systems only for crystalline forms (minerals or metals) above a certain size limit (Sawhney, 1969; Francis and Tamura, 1972; Olson and Skogerboe, 1975; Johansson and Johansson, 1976; Cahill, 1980; Henry and Knapp, 1980; O'Connor and Jaklevic, 1981; Schulze, 1981; Wolfel, 1981; Burnett and Woolum, 1983; Fukasawa et al., 1983; Boyle and Lindsay, 1985; Goh et al., 1986; Jaynes and Bigham,

1986; Ghabru et al., 1990; Essington and Mattigod, 1991; Tan and Henninger, 1993; Rybicka et al., 1994; Cotter-Howells and Caporn, 1996; Chang and Liu, 1998; Ma and Uren, 1998; Morin et al., 1999; Manceau et al., 2000).

### **X-Ray Fluorescence Microprobe (XRFMP)**

This technique is a microprobe version of the standard XRF element determination technique mentioned earlier. However, it is only available at synchrotron radiation X-ray facilities. The intense X-ray beams from these sources can be focused to less than 10  $\mu\text{m}$  to furnish a fairly intense spot of X-rays. Under the probe, atoms in the sample produce characteristic X-rays, which are then detected using an EDX spectrometer. Recent workshops have been held to demonstrate the use of the microprobe and a form of X-ray microtomography in the earth and soil sciences. Growing application of XRFMP exist in the literature (Anderson et al., 1993; Sutton et al., 1994; Tokunaga et al., 1994; Perry et al., 1997; Hansel et al., 2001, 2002; Roberts et al., 2002), and this will definitely increase over the next several years. The advantages are easy sample prep, simple analysis, line mapping, low detection limits, moderate resolution, and in situ analysis. Most importantly it can be utilized in tandem with XAS so that mapped hotspots can be analyzed with the microfocused beam. The disadvantages are the resolution and the nonroutine nature of synchrotron experiments and beam time availability.

### **Auger Electron Spectroscopy (AES)**

This was discussed in the electron spectroscopies section; however, it may also be produced under X-ray excitation. The utilization of X-ray microprobes will undoubtedly revolutionize this form of Auger microscopy.

## **Vibrational Spectroscopies (Infrared and Raman)**

### **Fourier Transform Infrared Spectroscopy (FTIR)**

As mentioned before, this vibrational-rotational spectroscopy yields information about functional groups and molecular structure. The FT analysis improves signal to noise over dispersive IR (approximately 30 $\times$ ), thus allowing increased sensitivity and time-resolved studies. FTIR has been applied to the sorption of molecules at metal oxide surfaces (mainly gas sorption). It has also been used to study metal sorption on clay minerals, solid phase metal precipitates, interlayer compositions, metal-doped vs. undoped Portland cement, humics and metal-humic interactions, and fossil fuel fly ash inorganic species (Nakamoto et al., 1961; MacCarthy et al., 1975; Vinkler et al., 1976; Tan, 1977; Henry and Knapp, 1980; Piccolo and Stevenson, 1982; Gerasimowicz and Byler, 1985; Christian and Callis, 1986; Goh et al., 1986; Amarasiriwardena et al., 1988; Sposito et al., 1988; Bowen et al., 1989; Ortego et al., 1989, 1991; Ortego, 1990; Siantar et al., 1994; Depège et al., 1996a, 1996b; Gan et al., 1996). Applications to soils can be found in a number of references (Jackson, 1973; Gieseking, 1975; Nicol, 1975; Zussman, 1977; Klute, 1986; Haw-

thorne, 1988; Perry, 1990), while large collections of spectra exist for clay minerals (Beutelspacher and Van Der Marel, 1976) and minerals used in the coatings industry (Afremow et al., 1969). It might be limited to heavily spiked mineral and soil samples, due to its rather high detection limits (1–20%). Figure 10 shows how one identifies an unknown compound using IR spectra as an example (Bio-Rad, 1991). The spectra A, B, and C are three library IR spectra, while the bottom is an unidentified soil contaminant spectrum. Comparison clearly shows that known compound C is a spectral match and identifies the contaminant as compound C.

### **Surface Enhanced Raman Spectroscopy (SERS)**

This is a variant of basic Raman spectroscopy, where a sample, whose surface is to be explored, is placed on a silver surface and the enhanced signal comes from the interference set up between the two surfaces. This enhancement can be several orders of magnitude greater than conventional Raman spectroscopy (Hochella and White, 1990). It has been used to characterize humic and fulvic acid fractions in soils (Francioso et al., 1996, 1998).

### **Laser Raman Microanalysis (LRMA)**

Using a focused laser (approximately 1  $\mu\text{m}^2$  area or larger) one can do Raman spectroscopy on a microscale, exciting transitions which can give molecular information about the surfaces (to approximately 0.1  $\mu\text{m}$  depth) and particulates greater than 1  $\mu\text{m}$  across. Heating of the particle surface can be a problem. Originally developed for the analysis of radioactive dust particles, it has been used on geological and biological samples to identify inclusions and particulates (Delhaye and Amelincourt, 1975; Rosasco et al., 1975; Delhaye et al., 1977, 1980; Grasserbauer, 1986; Mernagh and Trudu, 1993; Dong and Pollard, 1997; Boughriet et al., 2000). Reviews can be found in Hawthorne (1988) and Perry (1990). Near field optical microscopy, utilizing very finely pointed optical fibers to produce a visible light spot at the hundreds of Å scale, might allow LRMA spectroscopy at the submicrometer scale.

### **High-Resolution Electron Energy Loss Spectroscopy (HREELS)**

This technique is listed under the electron spectroscopies but one particular mechanism of energy loss is through coupling to electronic and molecular energy states. See above.

### **UV-Visible and Luminescence Spectroscopies**

UV-visible spectroscopy is a sensitive technique that exploits the absorbance of ultraviolet and visible electromagnetic radiation by molecular and atomic electronic states. Many solids are opaque in both the visible and UV regions (i.e., the absorbance is infinite which does not permit useful information about molecules in such solids to be obtained). Reflection spectroscopy can be done as with IR spectroscopy (i.e., diffuse reflectance). Most inorganic ions are colorless in solution and

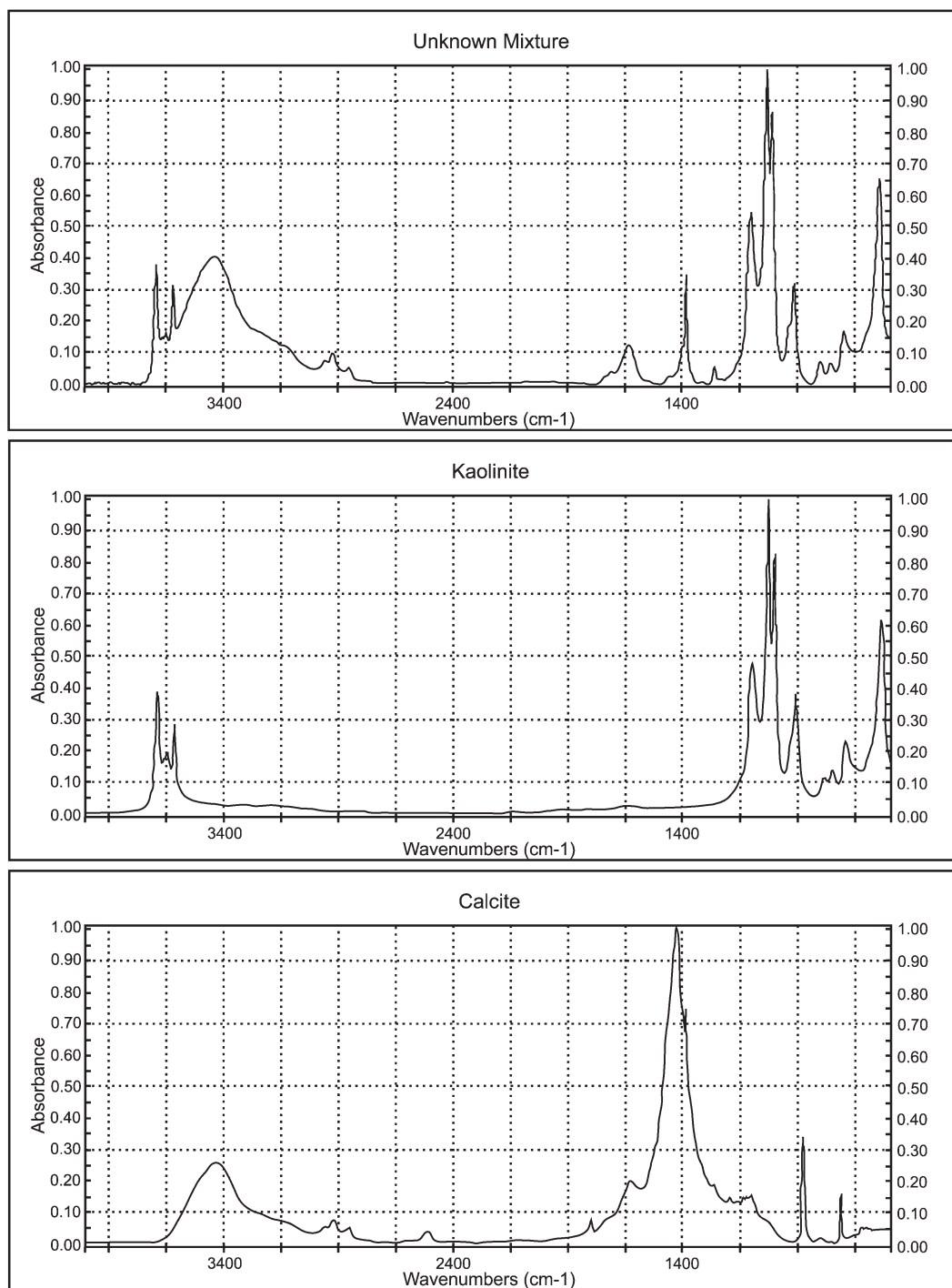


Fig. 10. Infrared (IR) spectra for an unknown mixture identified best by kaolinite and calcite (from Bio-Rad, 1991).

need some organic agent which forms a colored species with the inorganic to effect identification. It can be utilized as a detection system for high performance liquid chromatography (HPLC) and has some utility in colorimetric determination of inorganic ions and in photometric titrations. There are organic molecules with functional groups that are UV-vis active and are referred to as chromophores. This can be used to help determine molecular structure or identity, but the number of such groups is small. It also can give “negative” information

(i.e., specific groups cannot exist in the molecule if no absorbance is seen at the specified wavelength). However, the major problem with the technique is that it lacks specificity (i.e., many molecules will absorb in similar ways).

Luminescence is radiation that originates when atoms or molecules undergo a radiative transition from a longer-lived “meta-stable” excited state to a lower state. These meta-stable states exist for much longer times, on the atomic time scale, than most other atomic excited

states. This is demonstrated in that emission of such radiation continues long after the exciting radiation ceases. In photoluminescence, which includes fluorescence and phosphorescence, the excited atomic state arises from photon absorption. There are many other excitation mechanisms that produce luminescence. Some of these are chemical reactions (chemiluminescence), heat induction (thermoluminescence), biological activity (bioluminescence), vibrational excitation (sonoluminescence), and electrical excitation (electroluminescence) to name a few. There are both atomic and molecular luminescence spectroscopies. Atoms, which have the required metastable energy levels, are well known, while the majority of organic molecules which luminesce are aromatics (ring structures) or aliphatics (chain structures) with  $\pi$  orbital bonding structures.

These spectroscopies can be a very sensitive technique for the identification of molecules with active organic functional groups. With lasers used to excite the fluorescence lines, focused microprobe versions exist which can yield some idea of physical and/or surface distributions of certain sorbed organic constituents. Fluorescence has been used for peak detection in chromatography. Detection limits in the  $\mu\text{g kg}^{-1}$  and  $\text{ng kg}^{-1}$  ranges are possible with lasers. Metals with luminescence states have been used as probes of the binding sites of humic materials (Miano et al., 1988; Shoty and Sposito, 1988; Sposito et al., 1988; Susetyo et al., 1991), as chemical bonding influences the excited state lifetimes. The main drawback of the methods is that they are not universally applicable (i.e., only a few particular systems will luminesce) (Winefordner, 1976; Christian and Callis, 1986; Willard, 1988). Many of the methods here could be utilized as microprobes (Christian and Callis, 1986), created by optical microscopes (approximately 0.2- to 10- $\mu\text{m}$  probe size) or by scanning tunneling photon microscopy or near field microscopy with probes down to approximately 500 Å.

### Magnetic Spectroscopies (NMR, EPR, etc.)

Magnetic spectroscopies include NMR, which was previously mentioned, as well as electron paramagnetic resonance (EPR) spectroscopy and Mössbauer spectroscopy. NMR spectroscopy fundamentals were discussed previously. As pointed out there, the best NMR spectra are obtained from elements that have spin 1/2 nuclei (approximately 80 elements have such isotopes). EPR is a different technique that exploits electron spin-flip transitions in the atoms of paramagnetic substances. These are substances in which the electronic configuration of one of the atoms in a given oxidation or ionization state in the material has a net atomic magnetic moment due to the spins and angular momenta of unpaired electrons. Certain atoms, then, will exhibit paramagnetism in some oxidation or ionization states and not in others. This makes the determination of which elements can be examined with EPR less definable. In any event, the spin-flip transitions lead to absorption of RF energy, which occurs at specific frequency, thus the resonance phenomena.

Mössbauer spectroscopy is a technique that depends on the presence of certain nuclear gamma-ray transitions coupled with the lack of recoil of the nuclei emitting or absorbing the gamma rays. Very few elements (approximately 44 known) possess such characteristic nuclear isotopic species, Fe being the most well known and exploited (Hawthorne, 1988). Other environmentally important metals with Mössbauer transition nuclei include the alkali metal Cs, the heavy metal Ba, transition metals Ni, Zn, and Hg, other metals like Sn, Sb, Te, and the radioactive metals, Th, Pa, U, Np, and Pu. Few of these elements though have the Mössbauer isotopes in high enough natural abundance to be exploited. Shifts in the transition energies are due to the local site chemistry surrounding the Mössbauer atom. Thus, speciation is possible for Fe compounds and the influence of substitutional elements for Fe in Fe compounds. It should be noted that the magnetic properties of Fe are detrimental to the detection and quality of NMR signals. This means that Fe bearing compounds or materials are difficult to study with NMR, while they are ideal for Mössbauer study.

### Nuclear Magnetic Resonance (NMR)

NMR has seen recent improvements in sensitivity and structure determination and new developments like magic angle spinning (MAS-NMR) and solid state NMR. Larger magnetic fields yield greater sensitivity and large superconducting magnets are being utilized. These have allowed NMR to be applied to the earth, soil, and environmental sciences. Reviews on the application to earth sciences and clays (Stucki and Banwart, 1980; Stebbins and Farnan, 1989; Lens and Hemminga, 1998) have been written, while NMR has been applied to hydroxy-aluminum characterization and speciation (Bertsch et al., 1986a, 1986b; Woessner, 1989; Lobartini et al., 1998), metal contamination in soils (Bank et al., 1989; Krosshavn et al., 1993; Ashley, 1996; Kim et al., 1996; Calace et al., 1997; Grassi and Gatti, 1998; Denaix et al., 1999), and to the structure of humic substances (Stucki and Banwart, 1980; Gerasimowicz and Byler, 1985; Wershaw and Mikita, 1987; Preston, 1996; Schulten and Schnitzer, 1997). Figure 11 is from Stucki and Banwart (1980) and displays the NMR spectra of humic substances with varying percentages of carbon.

### Electron Paramagnetic Resonance (EPR)

EPR has been utilized in the study of humic and fulvic acids (Riffaldi and Schnitzer, 1972; Goodman and Cheshire, 1987; Paciolla et al., 1999; Jezierski et al., 2000) and their interaction with metals (Cheshire et al., 1977; Templeton and Chasteen, 1980; Senesi and Sposito, 1984; Senesi et al., 1985; Sposito et al., 1988; Davies et al., 1997; Jezierski et al., 1998). It has also been used to study sorption and precipitation of  $\text{Mn}^{2+}$  on  $\text{CaCO}_3$  surfaces (McBride, 1979), influence of phosphate on Cu(II) sorption on  $\text{Al}(\text{OH})_3$  (McBride, 1985), and the intracrystalline distribution of cations and chemistry of kaolinite and metal oxides (Muller et al., 1995).



## Mössbauer

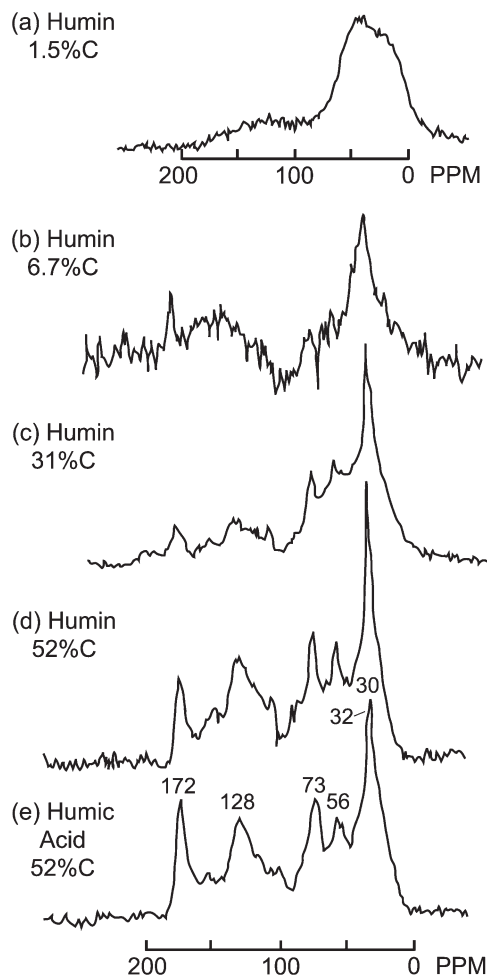
Mössbauer spectroscopy has found a niche in soil and environmental studies in the study of Fe speciation in a bay sediment (Capobianco et al., 1987), Al-substituted Fe-oxides (Wolska et al., 1994; Friedl and Schwertmann, 1996; Schwertmann et al., 2000), iron-rich clays in soils (Golden et al., 1979; Amarasiriwardena et al., 1988; Weed and Bowen, 1990; Scheinost et al., 1998; Scheinost and Schwertmann, 1999), green rust [Fe(II)-Fe(III) hydroxide-sulfate] formation (Hansen et al., 1994; Trolard et al., 1997; Genin et al., 1998; Refait et al., 1999), and Fe(III)-fulvic acid complexes (Kodama et al., 1988). Critical reviews can be found in two references (Stucki and Banwart, 1980; Hawthorne, 1988; Murad, 1998; Rancourt, 1998; Vandenberghe et al., 2000).

This concludes a review of the major physical methods of analysis for determining solid phase species and their physical distribution. There are, of course, many other methods that were not reviewed. This does not contain an in-depth discussion of the physical principles behind the method nor does it give a comprehensive report on the applicability to soils per se. However, it is hoped that it will give to the reader a flavor for the possibilities that do exist with currently available instrumentation and of some of the studies found in the literature, to which these methods have been applied.

## SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

This report has reviewed the various types of speciation techniques that are possible to answer relevant questions regarding the contamination of soils, sediments, natural waters, and biota by heavy metal forms. This includes both the dispersion of natural forms, such as galena in mine tailings, and the creation and dispersion of anthropogenic forms not likely to exist naturally, such as lead chromate for paints. Many of the issues germane to metal contamination were pointed out in the introduction. That section also mentioned the application of such experimental efforts to other areas of practical interest, such as chemistry, geology, mining, and agriculture. It is important to realize that many of the aforementioned techniques arose from those areas of study (as well as biology and medicine) and have been and are being adapted to the investigation of environmental problems. Conversely, any improvements in the methods to answer environmental questions will likewise benefit these other disciplines.

A major effort for the study of metals in environmental systems should have two overall goals. The first is the development of quick, accurate, and reproducible methods to determine major metal forms. This goal is meant as an aid to improve rapid assessment and monitoring of environmental systems and can yield short-term benefit. This would come in the form of increased knowledge from geological, mining, and agricultural surveys, environmental risk assessment and monitoring, as well as possible remediation technology selection and efficiency tests. A second goal would be to develop



**Fig. 11. Carbon-13 cross-polarization magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectra of humic material extracted from one soil, then subjected to further purification. Note the spectral features which appear with increasing carbon content (from Stucki and Banwart, 1980, with permission).**

comprehensive speciation approaches, including chemical extractions, instrumental methods, and predictive models, as well as kinetics and equilibrium experiments. This second goal will allow for the growth of understanding and of the knowledge base for true technological advancements. It is also a long-range goal with long-term benefit.

However, there are difficulties. The chemical extraction methods are relatively easy to apply, but they are plagued with a number of problems detailed in the literature. The instrumental methods offer the possibility of comprehensive speciation analysis, but are expensive, are not yet well developed methodologies in some cases, and often have limited access. The thermodynamic models are adequate for some aqueous situations but cannot yield ratios of solid phase partitioning given the solution species distribution. As no one approach is adequate a combining approach which attempts to form a consistent picture of the system provides a path forward. This "internal" consistency among independent approaches is the best that can be achieved before development of better methodologies. When the methods confirm one another, greater confidence in the results can be enjoyed.

It is clear that the different approaches are independent yet complementary to one another. Chemical extraction methodologies and thermodynamic models point in a direction to start looking with more sophisticated and comprehensive instrumental analyses. Instrumental analyses and thermodynamic models can help confirm extraction results and improve them by discovering where and why they may fail or are not specific enough. Instrumental analyses and extraction schemes can help improve thermodynamic models by checking their utility in certain situations and by elucidating the phases and chemical mechanisms needed to enhance predictive ability. Physical surface methods can be utilized with kinetics studies to explain sorption processes and their mechanisms. Additionally, equilibrium studies enable the acquisition of better thermodynamic stability parameters to improve the models.

Since the types of systems to be studied are so varied and many sites are contaminated by a number of different toxic metal, organic, and/or radioactive wastes, few techniques can be eliminated from consideration. It is also worth stressing a need to balance knowledge desired with a practical need to solve problems. A full speciation of all metal forms and their relative concentrations in a sample might be most desirable, but may not be needed in all cases. A speciation scheme is sufficient if it yields the information needed to answer the questions posed by the problem at hand.

There are a number of studies that can only be done with instrumental techniques. Refinement and confirmation of extraction schemes for metal species are important roles for instrumental methods. For the determination of unknowns, and in bulk and surface structural analyses, physical instrumental methods are the only choice. Extraction methods and geochemical models cannot determine unknowns or molecular structure. For the study of surface sorption processes and mechanisms, physical techniques are competitive with kinetics studies and can often complement them. Lastly, determination of whether a metal form is a separate particulate form or is a sorbed form is possible with some probe techniques. Thus, for these reasons alone physical instrumental methods should be developed and explored.

What types of instrumentation and methods should a facility interested in speciation of metal forms have access to? The following should be mentioned:

For surface studies and microchemical analyses with element identification, mapping, and physical correlation:

- environmental scanning electron microscopy with energy (and/or wavelength) dispersive X-ray analysis (in situ structure, morphology, mapping, and diffraction)

and some species identification:

- scanning transmission electron microscopy with selected area electron diffraction (embedded crystal species from microtomed or polished sections)
- low energy electron diffraction (surface crystal species)

- high resolution electron energy loss spectroscopy (molecular identity)
- extended electron energy loss fine structure (structure and valence of amorphous or crystalline microstructures)
- laser Raman microanalysis (molecular information of surfaces or inclusions at the micrometer scale, submicron if scanning tunneling photon or near field microscopy)
- mass spectrometric techniques (highest sensitivity with molecular information available)
- laser microprobe mass analyzer (surface desorption and sections of embedded soils)
- field desorption MS (surface desorption)
- thermal desorption MS (surface desorption)
- fast atom bombardment MS (surface desorption)
- secondary ion mass spectrometry SIMS or IMMA (surface desorption of particulates and study of thick sections)
- high resolution MS and tandem MS (mass analysis)

For analysis of separates isolated from contaminated samples or for spiked systems or separates, element identification:

- X-ray methods (at synchrotron facilities for sensitivity and focused beam capability)
- X-ray fluorescence microprobe (elemental mapping)
- X-ray microtomography (elemental mapping in three dimensions)

species identification:

- X-ray methods (better at synchrotron, but not necessary for XPS or XPD, microprobe versions possible in the future)
- X-ray photoelectron spectroscopy (oxidation state)
- X-ray absorption spectroscopy (structure, oxidation)
- X-ray powder diffraction (molecular structure)
- Fourier transform infrared spectroscopy and microscopy (molecular identification and structure)
- solid state nuclear magnetic resonance (molecular)
- chromatography (molecules, ions, oxidation states, and complexes)
- liquid chromatography (for solutions)
- gas chromatography (for volatiles)

For bulk analysis of elements, in solids:

- X-ray fluorescence
- neutron activation analysis
- spark source mass spectrometry
- glow discharge solids mass spectrometry

- laser ablation mass spectrometry (different from LAMMA, LIMA)

in solutions:

- inductively coupled plasma mass spectrometry (isotope dilution technique)
- atomic absorption spectroscopy
- electrochemical techniques

for sample preparation:

- pellet press
- grinders, mills, and sieves
- diamond cutting saws and microtomes
- ultracentrifuge
- petrographic analysis polishers (tripod and others)
- filtration papers and ultrafiltration membranes

For physical properties analysis:

- soil surface area equipment (BET, Hg)
- soil particle size equipment

The sample preparation and physical properties instrumentation are self-explanatory. Although a central location for most of the purchasable instruments mentioned would be a bonus, it may not be necessary to have them all in one place. A central location, however, does permit multiple spectroscopic analyses to be done on the same samples at roughly the same time, thus reducing possible inconsistencies or changes due to time, sample non-homogeneities, or contamination in storage or transport. Location near a synchrotron research facility would also be a plus, enabling better access to these high intensity X-ray sources.

The most promising techniques are those utilizing electron and X-ray microprobes. Both have the capability to image micrometer (X-ray microtomography) and submicron (SEM) structures and create high lateral resolution elemental maps of surfaces and structures down to detection limits of 10 mg kg<sup>-1</sup> (for EMPXA with WDX) and 1 mg kg<sup>-1</sup> (for XRFMP). Lateral physical association of elements from chemical mapping can suggest the identity of the forms present. In a transmission mode, the beams will yield diffraction patterns on interaction with microcrystals in the samples, thus providing structural information and identification. EELS in its various forms can yield a wealth of chemical information on the microscale with finely focused electron beams. Focusing mirrors to obtain small beam sizes have made XAS (EXAFS, XANES, and SEXAFS) possible for microsamples, permitting structural information for amorphous microsamples and particulate surfaces in samples, at the 0.1- to 10- $\mu$ m scale, realizable. The focused X-ray microprobe beams could also be utilized for high spatial resolution XPS (ESCA), and AES (X-ray induced Auger) of small surface areas and particles. Currently, the X-ray techniques mentioned can only be done at a synchrotron radiation facility. Environmental SEM is a recent development that eliminates the drawbacks associated with

ordinary SEMs. The samples can be analyzed in situ, moist, in air, and without preparation or coating, providing images of features down to 40 Å at 10 torr pressures. Improved X-ray detection has made possible mapping of elements as light as boron, using windowless or thin-window EDX detectors.

Some of the other promising instrumental methods for true speciation are the mass spectrometric techniques. The main reason is that they are far more sensitive than most of the other techniques. In general most methods have detection limits greater than 100 mg kg<sup>-1</sup>, while mass spectrometry can reach down to the  $\mu$ g kg<sup>-1</sup> level and sometimes even ng kg<sup>-1</sup>. High resolution MS can yield accurate molecular masses, while tandem mass spectroscopy can handle complex mixtures and matrices. It is also possible to study gas, liquid, or solid samples, the desorption methods discussed being the most capable of liberating molecules from solids. Improvements in the ability to perform quantitative analyses and increase precision with MS techniques should be pursued. However, an unavoidable characteristic of MS methods is that they are destructive of the sample, thus forfeiting surface structure and bonding information. Their obvious positives more than make up for this drawback and make MS methods important to explore and develop.

The development of new MS methods would first consist of finding the right combination of desorption methods, mass analyzers, resolution, and other characteristics. The question of detection limits, quantification, and development of standards would then follow as the final developmental effort. A tandem mass spectrometer system, coupled with an HPLC (for solution species and humics) and several ionization techniques, including lasers (LAMMA) or ion beams (SIMS) for solids might be able to handle the complexity of mixtures of metal forms in soils. It could be used to study both contaminated and pristine soils, separates, and extracts. This would be a large investment, requiring time and judicious study but would pay big dividends. The final product would most likely be a research instrument and not a workhorse service instrument for large-scale routine analyses.

The molecular spectroscopy of surfaces is a final area of promise. Vibrational spectroscopies are inherently insensitive due to the low transition probabilities for those energy states in molecules. Thus, only limited improvements can be expected from more intense sources and more sensitive detectors as found at synchrotron facilities. Infrared microprobes also suffer from diffraction limited resolution difficulties, namely that objects smaller than the wavelength of radiation used in imaging or probing cannot be seen. This can be observed in the limitations of optical microscopes vs. electron microscopes. For infrared radiation, it is even worse, since IR wavelengths range from 1 to 1000 microns. Thus objects smaller than 1  $\mu$ m cannot be probed in IR. However, a laser Raman microprobe can see finer detail and smaller structures since it is a visible laser being focused. High resolution electron energy loss spectroscopy can also be finely focused, in principle, as could



X-rays for micro X-ray photoelectron spectroscopy. Along with improvements in source intensities and detector technology, these spectroscopies may indeed allow very significant surface molecular studies to be performed in the future. These methods are nondestructive; however, to maintain that advantage they might require limits on source beam intensities that could heat or damage the sample surfaces of interest. These spectroscopies are needed to enable study of sorption processes and mechanisms and bonding of species to surfaces of environmental particulates. This complements the strength of the mass spectrometric techniques.

The other techniques listed above can serve in other ways. Using magnetic, particle size and/or density separations, or selective extractions one can overcome some of the limitations of standard XRD, FTIR, and solid state NMR. Analytes of interest can be physically pre-concentrated using the above methods, raising their relative concentration with respect to the matrix. Alternatively, a spectrum (or pattern) of the analyte plus matrix could be taken, a selective extraction performed to remove the analyte from the matrix, and a final spectrum (or pattern) obtained. The difference between the two spectra (patterns) would yield the spectrum (pattern) of the analyte. Lastly, they can be used on samples that have been spiked or on samples taken from very heavily contaminated real systems of interest, which are above the thresholds for these techniques.

A remaining possibility that might be entertained is the following. One might be able to obtain useful information available only to an insensitive technique, at concentrations below thresholds imposed by inherent limitations of that technique. This might be accomplished by building a matrix of consistent inference patterns between the results of the insensitive technique and those of a dissimilar but more sensitive analytical method. The matrix would be created for many paired sets of data from the two techniques above the concentration threshold for the less sensitive method and extrapolated to below that threshold, using data generated by the more sensitive one. This might be possible using neural computing, statistics, or pattern recognition algorithms.

Thus, there are a number of reasons for applying direct instrumental methods to the solid phase. As seen from the above discussion, there are a number of very promising prospects for obtaining direct speciation and surface information unobtainable in any other way. To confirm the efficacy of a given technique or techniques, three steps should be taken. There should be initial feasibility studies, in which a method is merely tried. If the trial indicates some promise, it should be followed by pilot studies in which the methods are applied in a well-planned manner and the results analyzed for content and relevance. These trials should be conducted on several samples that have had some previous characterization. The samples chosen should be representative of a meaningful range of concentration of the contaminant and of basic soil characteristics. Lastly, a competent technician, a data analyst for the technique, and someone familiar with the sample and its characterization

should perform each technique tested. It should be thoroughly tested, especially if the results of the tests are inconsistent with the stated abilities of the technique. A failure might merely indicate that optimum sample preparation, experimental protocol, or adequate analyses were not performed.

It is hoped that this report will stimulate further exploration into the possibilities and gives a flavor for what might be expected from such studies.

#### ACKNOWLEDGMENTS

The authors are indebted to Dr. William Slack, the University of Cincinnati Geochemical Group Supervisor on 68-C-0031, who managed the effort and reviewed the draft report which served as the foundation of this manuscript.

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