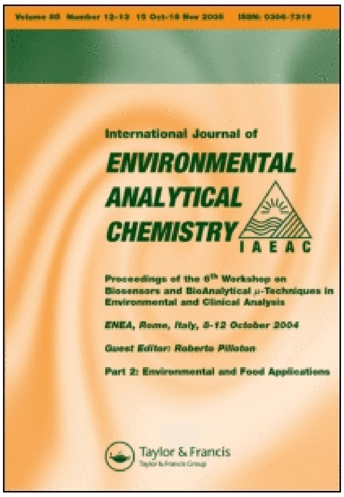

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Surface Studies by ESCA: Importance to Environmental Research

Shirley H. Hercules[a]; David M. Hercules[a]
[a] Department of Chemistry, University of Georgia, Athens, Georgia, U.S.A.

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Surface Studies by ESCA: Importance to Environmental Research†

SHIRLEY H. HERCULES and DAVID M. HERCULES

Department of Chemistry, University of Georgia, Athens, Georgia 30602, U.S.A.

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X-ray photoelectron spectroscopy (ESCA) is a technique which samples the first ca. 20 A of a surface. This important characteristic has direct relevance for environmental studies. The present paper reports some recent studies in our laboratory which indicate the potential of ESCA for examining surfaces of interest to environmental research. When an adhesive is stripped from a clean aluminum surface a very thin (ca. 20 A) layer of adhesive remains after stripping. Reactions on surfaces can be monitored such as organic functional groups attached to glass, leaching of metals from glass surfaces or the oxidation of lead sulfide. Quantitative analysis of species on surfaces is possible. By use of fiberglass mats containing chelating groups on their surfaces it is possible to scavenge trace metals from solution and to measure them quantitatively. Currently this technique permits detection of 20 ppb lead in solution.

INTRODUCTION

X-ray photoelectron spectroscopy (ESCA) is rapidly making a major impact as a new instrumental technique in chemistry. It is being applied to a wide variety of fields because it offers a combination of advantages which most other spectroscopic techniques lack. We have reviewed the fundamentals and instrumentation of ESCA along with potential applications for environmental studies in this Journal.[1] We have also reviewed the potential of ESCA as a technique for structural organic chemistry[2] as well as fundamentals and instrumentation.[3]

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ESCA measures core binding energies in atoms and molecules. Although measurement of absolute binding energies by ESCA is difficult, the important parameter for chemical studies is the chemical shift. ESCA chemical shifts occur in the core electron binding energies as the atomic electron density varies. For most elements chemical shifts correspond roughly to changes in oxidation state, approximately 1–2 eV per unit change in formal oxidation state number. Chemical shifts in organic compounds correlate with the charge on the atom calculated either by simple electronegativity or by molecular orbital techniques. Thus as the chemical nature of an atom varies, its ESCA peak shifts, thus distinguishing between different types of the same atom either in the same molecule or in the same system. By careful analysis of chemical shifts relative to those of known compounds, it is possible to detect rather subtle changes in the chemical environment using ESCA.

ESCA is primarily a surface technique because photoelectrons ejected deep in the sample are inelastically scattered. Although exciting X-rays penetrate the sample to approximately 10,000 A, the effective sampling depth in ESCA is considerably smaller. Various estimates of sampling depth have been given ranging from 4–100 A. For a given material the sampling depth depends upon the specific kinetic energy of the photoejected electron. Recently several authors have dealt with this problem in detail.[4–7] As a "ballpark" figure the average escape depth for most samples will be on the order of 20 to 30 A. The fact that ESCA primarily views the surface of a sample is an asset for certain environmental studies. It is a particularly powerful tool for the examination of surfaces and surface reactions. For example it has been used in preliminary studies[8] for the detection of atmospheric pollutants adsorbed on surfaces.

Sensitivity of ESCA must be viewed from three perspectives, namely, sensitivity to bulk constituents, sensitivity to surface layers, and relative ESCA sensitivities for various elements. First, the sensitivity of ESCA to different elements does not vary tremendously.[9] ESCA is least sensitive to light elements (such as boron) and most sensitive to heavy elements (such as lead or bismuth). The difference, however, is not greater than one order of magnitude. Therefore it is reasonably safe to say that ESCA has reasonable sensitivity for every element in the periodic table heavier than helium. Second, the bulk sensitivity of ESCA varies approximately as the atomic percentage. This means that ESCA will not be sensitive to trace materials distributed through the bulk of the sample. It has been demonstrated that for most types of measurements the lower limit of detection by ESCA is approximately 0.15% based on bulk percentage.[10] Third, the lack of bulk sensitivity occurs primarily because ESCA samples the surface. Therefore if the material is on the surface the actual number of atoms required to give an ESCA signal is very small. Signals have been detected from as little as 0.1% of a monolayer of heavy metals,[11] which amounts to about 10^{12} atoms. This places the absolute sensitivity of ESCA in the picogram range. High intrinsic sensitivity for material on a surface is important for several of the potential applications to environmental studies demonstrated here.

In summary, the utility which ESCA offers for environmental studies is four-fold: first, it is sensitive to almost all elements of the periodic table. Second, chemical shift gives some indication of the nature of the species present for a given element. Third, ESCA examines primarily the surface and surface reactions. Fourth, it is sensitive to a small number of atoms. We will now summarize some recent studies from our laboratory which bear implications for environmental research.

Detection of species on surfaces

Species adhering to a surface can be detected by ESCA even though the thickness of the surface layer is sufficiently small that it cannot be detected by conventional microscopy or even by electron microscopy. We have demonstrated this effect by stripping adhesives from a chemically cleaned aluminum surface.

Figure 1 shows three spectra obtained in an adhesive stripping experiment. The top spectrum (A) is that of a clean aluminum surface before the adhesive

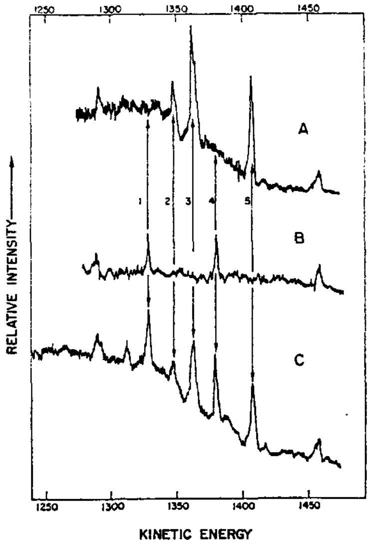


FIGURE 1 Adhesion of a polymer to an aluminum surface studied by ESCA. A. Spectrum from clean aluminum. B. Spectrum from polymer. C. Spectrum of aluminum surface after removal of polymer. Lines 1 and 4 are from silicon. Line 2 is from phosphorus. Lines 3 and 5 are from aluminum.

is applied. Note the presence of the two aluminum lines and the absence of any silicon lines. Of particular interest is the presence of the phosphorus 2p lines indicating that the aluminum had been cleaned with phosphate. The chemical shift of phosphorus indicates the species present on the aluminum surface is phosphide. The middle spectrum (B) is the ESCA spectrum of the thick adhesive applied to the aluminum surface. Note that the adhesive contains silicon as evidenced by the Si2s and Si2p lines. The exact formulation of the adhesive was unknown to us. The spectrum at the bottom of Figure 1 (C) shows the ESCA spectrum of the aluminum surface after the adhesive had been applied and removed by stripping. Note the presence of four major lines, two belonging to aluminum and two belonging to silicon.

One can draw several conclusions on the basis of the above experiment: first, that some of the adhesive remains attached to the aluminum surface when it has been stripped; second, that the layer of adhesive is ca. 20 A thick, because the aluminum lines can be seen through the adhesive layer. The obvious question arises as to whether the adhesive layer is on the aluminum surface in clumps or whether it is uniformly distributed. Our conclusion[12] is that it is uniformly distributed. First, the aluminum is quite shiny both before and after the adhesive has been stripped. Second, examination with an optical microscope showed no presence of small clumps of adhesive. Third, examination with a scanning electron microscope similarly indicated no small particles on the aluminum surface either before or after the adhesive was stripped.

The above is a powerful example of how ESCA can be used as a technique to detect the presence of a material on a surface. It also indicates how ESCA can be given a rough measure of the thickness of a surface layer whether the layer is deposited by physical means or simply by adsorption.

Studies of surface reactions

Another important aspect of many environmental studies is the nature of changes which occur when a surface is subjected to some chemical treatment. In this section we present examples indicating that ESCA is capable of giving information on this type of study.

Recently we have studied the use of ESCA to monitor changes in chemically treated fiberglass surfaces.[13] We have used calibration curves of binary mixtures of components of glass calibrants for measuring the concentration of elements at the surface of a glass. A typical calibration curve for calcium is shown in Figure 2. This curve was prepared using binary mixtures of calcium carbonate and silica and was applied to the measurement of the calcium concentration on the glass surfaces. A similar approach was used to measure the aluminum concentration in fiberglass surfaces using aluminum oxide-silica mixtures.

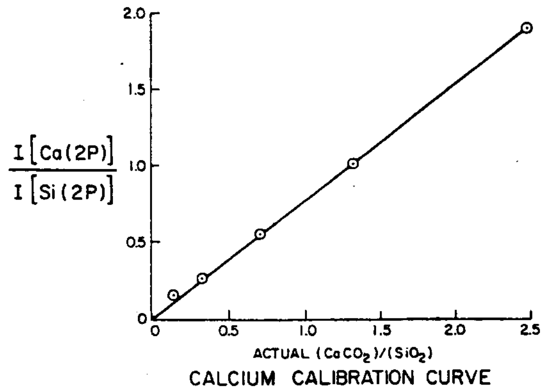


FIGURE 2 Calcium calibration curve.[13] Slope = 0.771. Standard deviation = ±0.011.

Using this type of calibration curve it was possible to monitor the changes in calcium and aluminum content of both E glass and S glass when these surfaces were given one of four treatments, namely, rinsed with an organic solvent, heat treated, treated with hot concentrated sulfuric acid, and treated with aqua regia. The results of these treatments are shown in Table I. It is apparent that the organic solvent does not change the surface calcium or aluminum concentration of glass. Treatment with either aqua regia or sulfuric acid leaches the aluminum and calcium completely. Heat treatment does not change the aluminum content of the glass surface, but increases the calcium content.

Upon seeing an increase in calcium content we undertook a study to determine if there was any relationship between the calcium content and the temperature of heat treatment. Figure 3 plots the negative log of the diffusion

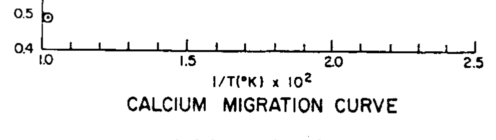


FIGURE 3 Calcium migration curve.

constant in the glass as a function of reciprocal temperature, indicating there is a relationship between the two despite the large scatter in the data. This indicates that as the temperature is increased calcium diffuses from the bulk of the glass to the surface, which is initially calcium poor.

We also were able to study the effect of pH on the leaching of aluminum from a glass surface by sulfuric acid. Figure 4 shows the results of this study.

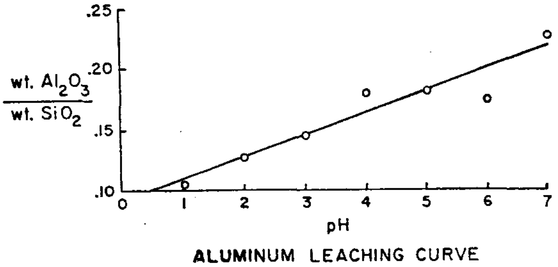


FIGURE 4 Aluminum leaching curve.

It gives the weight ratio of aluminum to silicon as a function of pH for a glass surface that has been immersed in a solution for 5 minutes. It is apparent that as the pH decreases the rate of leaching increases significantly. It is also apparent from Figure 4 and the data in Table I that virtually no leaching occurs at pH 7.

TABLE I
Results of qualitative surface treatments
Calcium intensities[a]

Glass	Initial Measurement	Benzene Rinse	Heat	Hot Conc. H_2SO_4	Aqua Regia
E	0.375	0.376	0.563	0	0
S[b]	0	0	0	0	0

[a] Peak Area Ratio Ca(2p)/Si(2p).
[b] S glass contains no calcium.

Aluminum intensities[a]

Glass	Initial Measurement	Benzene Rinse	Heat	Hot Conc. H_2SO_4	Aqua Regia
E	0.222	0.222	0.216	0	0
S	0.425	0.418	0.438	0	0

[a] Peak Area Ratio Al(2p)/Si(2p).

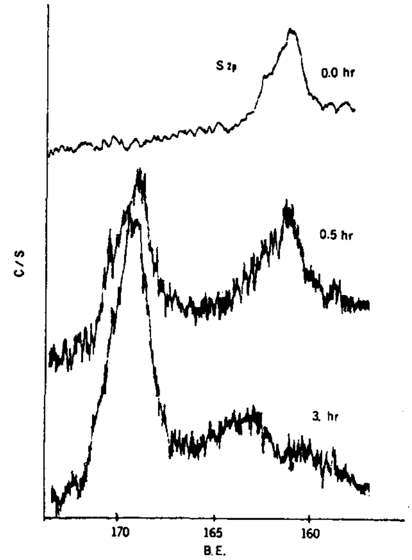
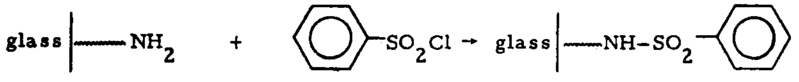


FIGURE 5 ESCA study of the oxidation of lead sulfide. Top—S2p spectrum before oxidation. Middle—S2p spectrum after 0.5 hrs oxidation. Bottom—S2p spectrum after 3.0 hrs oxidation.

It is also possible to study the oxidation of surfaces using ESCA. Figure 5 shows three spectra of the sulfur 2p lines of PbS taken when a vacuum deposited sample of PbS was subjected to oxidation in a stream of oxygen. At the top of the figure the peak labeled 0.0 hours shows that the only sulfur species present on the PbS surface is sulfide. The middle figure indicates that after a half hour oxidation some of the sulfur has been converted to sulfate while some remains as the sulfide. The spectrum at the bottom of Figure 5 indicates that after 3 hours of oxidation all of the sulfur on the surface has been converted to sulfate, and that no sulfide remains. The small peak at 164 eV binding energy is a satellite peak in the spectrum. This figure demonstrates quite clearly that ESCA is capable of observing chemical changes as a surface is subjected to different treatments or conditions.

It is also possible to observe changes which occur in organic molecules on a surface. We have studied the surface reactivity of organic functional groups attached to fiberglass via silylating reagents.[13]

Figure 6 shows spectra obtained in the sulfonation of a glass surface with an amino group attached:



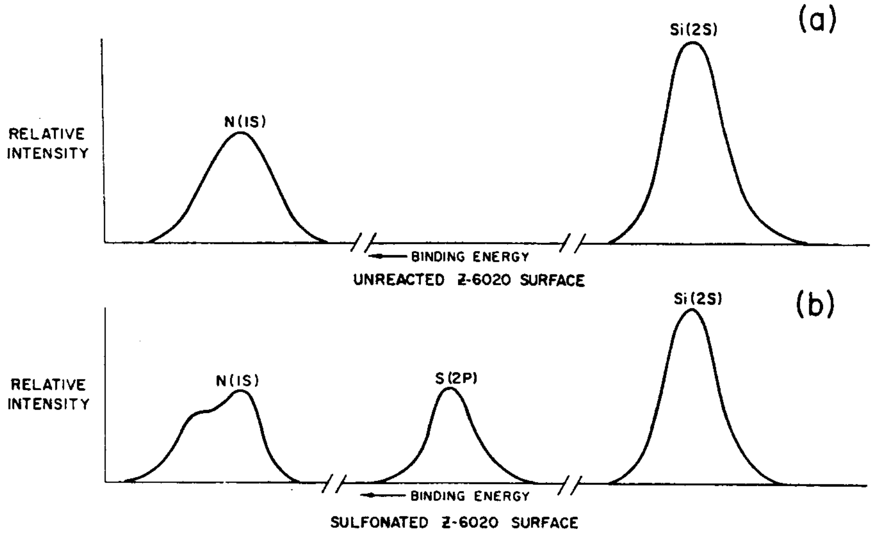


FIGURE 6 ESCA spectra for sulfonated Z-6020 surfaces.[13] (a) Z-6020 surface before reacting with benzenesulfonyl chloride. (b) Same surface after reaction.

The top spectrum (a) shows the silicon and nitrogen lines from a glass surface containing the amine function, attached to the glass surface by Dow-Corning Z-6020 silylating reagent. The glass containing the amino function was subjected to sulfonation by benzene sulfonyl chloride. After sulfonation spectrum B was obtained. Note that both the silicon and nitrogen peaks remain but a sulfur peak, characteristic of sulfonamide, has appeared. It is also interesting to note that the nitrogen spectrum now shows two peaks, indicating that sulfonation of the nitrogen was not complete.

This series of experiments indicates that ESCA is capable of monitoring chemical changes on surfaces (such as glasses or clays) as these are subjected to various treatments. ESCA can observe oxidation state changes which occur on the surfaces of minerals or clays and can monitor reactions of organic functional groups either chemically attached or adsorbed to a surface.

Trace metal determination

A recent development in ESCA is the use of fiberglass surfaces coated with chelating groups to determine trace metals in aqueous solutions.[15] The sensitivity of ESCA to trace materials is low because ESCA samples primarily the surface of the sample. However if a trace material can be concentrated on a surface, then the sensitivity of ESCA becomes high. We have developed[15] chelating glasses which show great promise for adapting ESCA as a technique for trace metal analysis in a wide variety of environmental samples.

Figure 7 shows the reactions used to prepare a glass surface containing a dithiocarbamate group and its ability to react with lead. In A the glass surface reacts with Dow–Corning Z-6020 to form B which is a silylated glass surface containing the diamino function discussed earlier. This glass surface is reacted with carbon disulfide and base to give C which is the sodium salt of the dithiocarbamate. It is interesting that only one of the amino groups react as indicated by the nitrogen:sulfur ratio in the product C as measured by ESCA. When a solution containing lead ions is reacted with C, they bind as indicated in D so that the lead is now held on the surface of the glass.

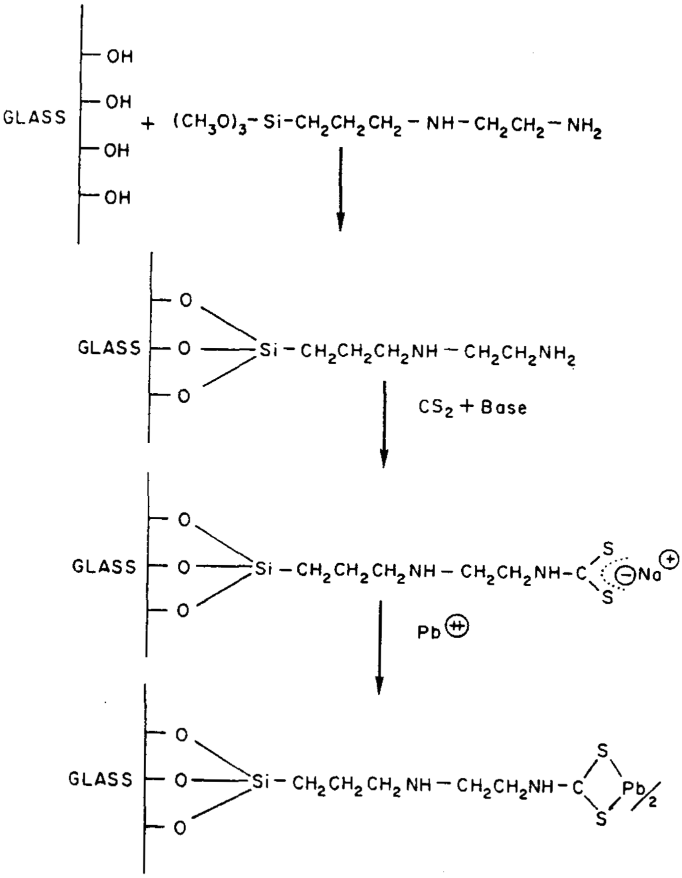


FIGURE 7 Reaction scheme used to prepare dithiocarbamate coated fiberglass surfaces.

Using chelating glass discs to remove trace metals from solution is accomplished with the apparatus shown in Figure 8. This consists of two pieces of Teflon indicated by the open and hatched areas. A fiberglass disc sits in the depression between the two. The disc used is about 0.5 cm in diameter. Solution is flowed down the channel indicated by the dashed lines and through the disc allowing reaction of the solution with the metal. Using this type of apparatus a volume of 100 ml can be reacted with a fiberglass disc in the matter of 10–15 minutes.

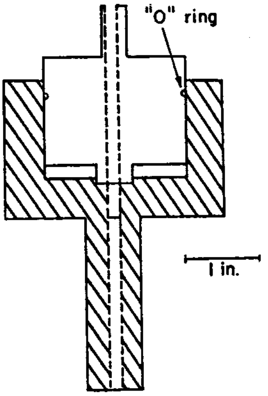


FIGURE 8 Diagram of holder used for reacting trace metals and fiberglass discs.[15]

Figure 9 shows the lead 4f spectrum obtained from a fiberglass disc which had been used to scavenge the lead from a 100 ml of a 200 ppb solution. The presence of the silicon 2s line serves as an excellent internal standard for quantitative analysis of the lead. We are presently developing a number of chelating glasses with a variety of functional groups attached which should permit analysis for a wide variety of trace metals using ESCA.

An interesting possibility presented by the chelating glass-ESCA technique is doing multi-element analyses using a single disc. For example, a dithiocarbamate glass should be able to scavenge several heavy metals from the solution. The spectrum observed in Figure 10 was obtained from 100 ml of a solution containing 1 ppm each of bismuth, lead, thallium, and mercury. It is clear that the peaks of each of these elements is evident, although the mercury unfortunately overlaps with the silicon 2p peak.

Although the results reported here for trace metal analysis are of a preliminary nature, it is apparent that the ESCA chelating glass technique offers considerable potential for trace metal analysis, not only for a single element but for multi-element analysis as well. Furthermore, because the chelating glasses contain organic functional groups having pH-dependent chelating

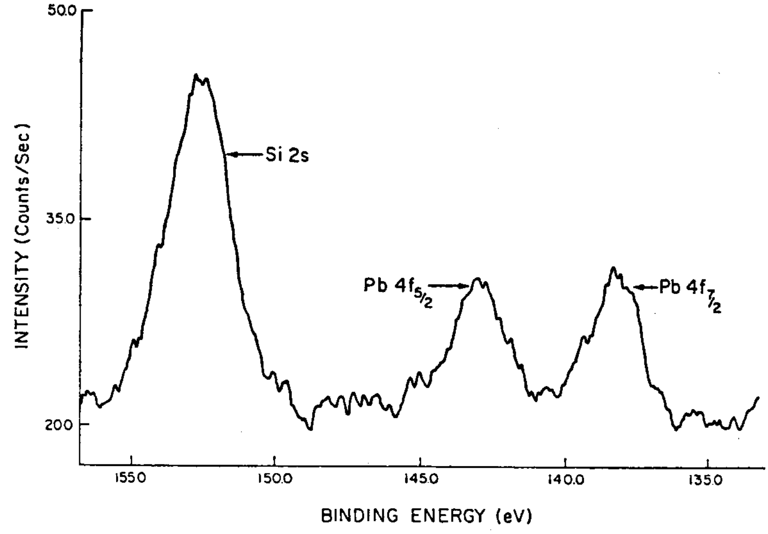


FIGURE 9 ESCA spectrum of lead obtained from a solution containing 20 ppb lead.[15]

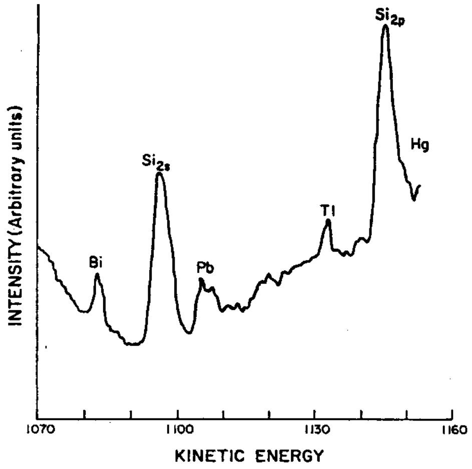


FIGURE 10 ESCA spectrum from a solution containing 1 ppm each: bismuth, lead, thallium and mercury.

characteristics, these glasses should also be useful in several other ways. First, they should be capable of defining the chelating power of a medium at a particular pH by competitive reaction for metals with the chelates in the medium. Second, this type of approach can be very useful in speciation studies, again based on competition of species in solution and the chelating agent on the surface of the glass for the metal.

Conclusions

On the basis of the studies presented here it is apparent that ESCA will assume importance as an instrumental technique in environmental studies. It will be particularly important where studies of surface reactions or surface species are necessary. It also offers great potential as a technique for trace metal analysis, both for multi-element analysis and for speciation studies.

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