



Rapid detection of tri-*n*-butyl phosphate on environmental surfaces using static SIMS

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Abstract

Static secondary ion mass spectrometry (SIMS) is an analytical method that can be used to detect the presence of tri-*n*-butyl phosphate (TBP) on environmental surfaces including minerals (e.g., basalts, quartz) and vegetation. Static SIMS instrumentation equipped with pulsed secondary ion extraction and a ReO_4^- primary ion gun permits the rapid acquisition of cation and anion mass spectra of sample surfaces with virtually no sample preparation: samples are merely attached to a sample holder using double-stick tape. SIM spectra were demonstrated to be sensitive to the mode of TBP adsorption to mineral surfaces: TBP adsorbed to Fe(II)-bearing phases, Fe(III)-bearing phases, silicate, and vegetation surfaces could be distinguished from one another. These results indicate that SIMS has broad applicability for the rapid characterization of environmental surfaces, and in some cases, is capable of identifying the mode of contaminant-surface interactions. The technique is also attractive because it can analyze milligram-size samples, and no waste is generated during analysis.

1. Introduction

The interaction of contaminants with surfaces is important because these interactions often have a profound influence on the transport, degradation, and remediation of contaminants in the environment [1]. Despite the importance of these interactions, actual environmental surfaces have been little studied because of difficulty in obtaining spectral information on the first monolayer. In this paper, it will be shown that static secondary ion mass spectrometry (SIMS) is a technique which is capable of rapidly generating a significant amount of chemical information from the first monolayer of mineral and vegetative surfaces, with little or no sample preparation.

Other surface analysis techniques have not experienced wide application for environmental samples because of the amount of rigor required for analysis. For example,

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reflectance infrared spectroscopy can provide very detailed spectral information, but it requires the surface of interest to be coated onto a reflectance element, and that the analyte be IR absorbing. Raman spectroscopy can also be extremely valuable for selected systems, but it suffers from low sensitivity to most contaminants, particularly at submonolayer coverages. Ultra-high vacuum techniques including X-ray photoelectron spectroscopy (XPS), Auger spectroscopy, and energy dispersive X-ray spectroscopy (EDS) require complex instrumentation, and generally work best only with highly controlled surfaces and aggressive vacuum conditions ($< 10^{-9}$ torr) [2].

In contrast, static SIMS is conceptually a simple technique: a sample is bombarded with energetic primary ions, which 'sputter' secondary ions into the gas phase, whereupon they are mass analyzed. 'Static' in this context refers to the condition where no spot on the surface is hit more than once, and hence the damage to the top monolayer is minimal. Static SIMS is thus differentiated from 'dynamic' SIMS, in which higher primary ion beam currents are used, and the surface of the sample is actually eroded during the analysis [3].

Despite the conceptual simplicity, static SIMS has not been widely applied to environmental samples. Several factors have contributed to this: (1) static SIMS has historically required complex instrumentation and high vacuum conditions; (2) the analysis of electrically insulating samples (like refractory minerals) has been impeded by surface charging; (3) the surface bombardment event is energetic, and for many systems, few molecular species are observed.

These limitations have been overcome by the development of a ReO_4^- primary ion gun [4], and a pulsed secondary ion extraction system [5]. Both of these advances have simplified the operation of the static SIMS instrumentation. The ReO_4^- primary ion is molecular (as opposed to atomic), massive (250 amu), and anionic; together, these attributes result in a high selectivity for the first monolayer of the sample, and generate substantially more molecular secondary ions than guns using atomic primary ions.

Pulsed secondary ion extraction is a technique that prevents surface charging of insulating samples. As an insulating sample is bombarded, its surface will usually acquire a positive charge, as a result of many electrons being sputtered. In pulsed extraction, the polarity of the secondary ion extraction lens is rapidly switched from positive to negative, which results in the surface of the sample being discharged as anions and cations are alternately extracted from the surface. Since both anions and cations are mass analyzed, pulsed extraction has the added benefit of acquiring the anion and cation SIM spectra at virtually the same time.

Static SIMS is substantially different from conventional analytical schemes for organic contaminants, which typically employ chemical extraction followed by chromatography with one of a variety of detectors. The extraction-based analyses produce information on contaminants which originate from the sample bulk and surface, and are capable of excellent sensitivity because extracts from large samples may be concentrated during sample preparation. In contrast, it is emphasized that no sample preparation is required for static SIMS, and it provides information on contaminants adsorbed only to the sample surface. It must also be stated that quantitation is problematic for static SIMS (like most other surface analysis

techniques), but that in many cases the minimum detectable quantity is comparable to that achievable using extraction methods. Static SIMS is capable of analyzing milligram-sized samples, and generates no chemical waste.

In the present study, environmental samples were exposed to tri-*n*-butyl phosphate (TBP), and then analyzed in order to assess the efficacy of static SIMS for TBP detection. TBP is important because it was used as an extractant for U and Pu as part of fuel reprocessing conducted at DOE sites, and hence it is anticipated that TBP will be encountered during site remediation activities [6].

2. Experimental

2.1. Secondary ion mass spectrometer: the ReO_4^- primary ion source and pulsed extraction

The studies described in this paper were performed using a static SIM spectrometer which has been described previously, but was initially equipped with a SF_6 primary ion gun [7]. The studies reported herein were all performed using a new solid state ceramic ion source producing a ReO_4^- beam [4]. This source consists of a sintered mixture of a rare earth oxide and $\text{Ba}(\text{ReO}_4)_2$ pressed into a small Re tube that, when heated to $\sim 800^\circ\text{C}$, emits the ReO_4^- molecular anion into the gas phase. The use of a molecular ion in SIMS provides increased sensitivity for molecular species compared to standard atomic ion guns such as Cs^+ [8]. In all of the examples presented, the primary beam current was approximately 100 pA, and the beam was focused to $\sim 2\text{ mm}$ diameter: thus the primary ion flux was about $3\text{ nA}/\text{cm}^2$. The energy of the primary ReO_4^- ions was 10 keV.

A schematic diagram of the pulsed extraction [5] SIMS instrument is shown in Fig. 1. The mass spectrometer is a quadrupole [EXTREL Corp., Pittsburgh, PA,

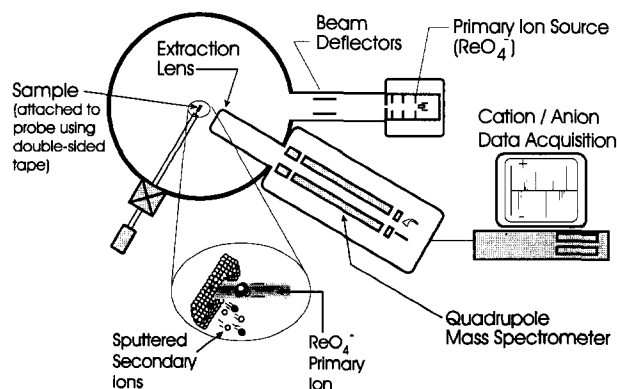


Fig. 1. Schematic diagram of static SIMS instrument. A quadrupole mass spectrometer is used for mass measurement of secondary ions.

USA] fitted with our own secondary ion extraction lens, a set of RF only prefilter rods, and a positive/negative ion detection system. The mass spectrometer, ion optics, and detector voltages are computer controlled, and can be alternated from positive ion to negative ion collection status at 50 Hz using a control and data acquisition system developed for this instrument. The ratio (time analyzing positive ions)/(time analyzing negative ions) can be adjusted; for most of the sample analyses reported in this work, a ratio of 3–1 worked well.

2.2. Scanning electron microscopy (SEM) and energy dispersive X ray (EDS) analyses

The mineral compositions of the mineral samples were investigated using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). No attempt was made to cut or polish the basalt chips prior to SEM and EDS (or SIMS) analyses so that the samples would be typical of those which would be encountered in the field. SEM images were obtained using an Amray Model 1830 instrument, which was operated with a 20 keV electron beam. EDS analyses were performed using a Fisons-Kevex Delta 5 instrument. As in the case of the SEM analyses, 20 keV incident electrons were used. The spatial resolution for this analysis is 1–2 μm , which corresponds to the diameter of the volume excited by the incident electron. The EDS analyses were standardless, and the data reduction employed ZAF (Z #, absorption, fluorescence, Magic V package) correction. Alternatively, data was reduced using the extended phi rho Z (XPP) method, which is more accurate for lighter elements. For elements which are > 5 atom %, the accuracy of this method is on the order of 4–8% when operating in the standardless mode.

2.3. Sample origin and preparation

Basalt samples were collected from the Blackfoot River area of southeast Idaho, the Central Facilities Area of the Idaho National Engineering Laboratory (INEL), and the Elephant Mountain Area of the Department of Energy Hanford site, in southeast Washington state. Quartz and soil samples were collected from the Raritan, NJ area. Leaf samples were collected from a local lawn.

Rock samples were prepared by hitting a large rock with a hammer, to form small chips 2–4 mm across. The exposed rock chips were attached to a sample holder using double sided tape. Soil samples were prepared for analysis by attaching double sided tape to a sample holder, and rubbing it in the sample until it was coated. Leaf samples were prepared by cutting a 3.8 mm disc, and attaching it to a sample holder using double sided tape. Typical time for sample insertion was on the order of 5–10 min, including time for evacuation in the insertion lock. Samples were exposed to TBP solutions in water and CH_2Cl_2 , and were also exposed to TBP vapor, and then admitted to the static SIM spectrometer through an insertion lock. The sample chamber was typically operated at $\sim 2 \times 10^{-6}$ torr for samples such as minerals and plant leaves that can have high outgassing.

3. Results and discussion

3.1. Analysis of TBP on quartzic samples

Rock samples from the Raritan, NJ area were collected and characterized using scanning electron microscopy (SEM) and energy dispersive X-ray (EDS); these analyses revealed that the samples were predominantly silicate (SiO_2). When the samples were exposed to TBP and subsequently analyzed using SIMS, a number of abundant cations were observed (Fig. 2). The most prominent cation which was attributable to TBP was m/z 99⁺, and this ion arises when TBP is protonated on the quartz surface, and subsequently undergoes the loss of three C_4H_8 molecules (Reaction 1) [9]. A lower abundance ion at m/z 155⁺ observed in the spectrum arises from the elimination of two C_4H_8 molecules. The presence of these ions is an indicator that TBP must be adsorbed at or near a site which is capable of supplying a proton. m/z 99⁺ is observed on most mineral samples, but is dominant on quartz. Several other ions are observed at lower abundance which are also attributable to TBP: m/z 137⁺, 125⁺, and 119⁺. These are attributable to other processes and will be discussed later.

A variety of lower mass ions are also observed in the cation spectrum which are attributable to surface contaminants other than TBP (Fig. 3). It is emphasized that most of the surfaces studied exhibit these ions, irrespective of whether they have been exposed to TBP. Ions at odd masses are generally assigned to hydrocarbons, or

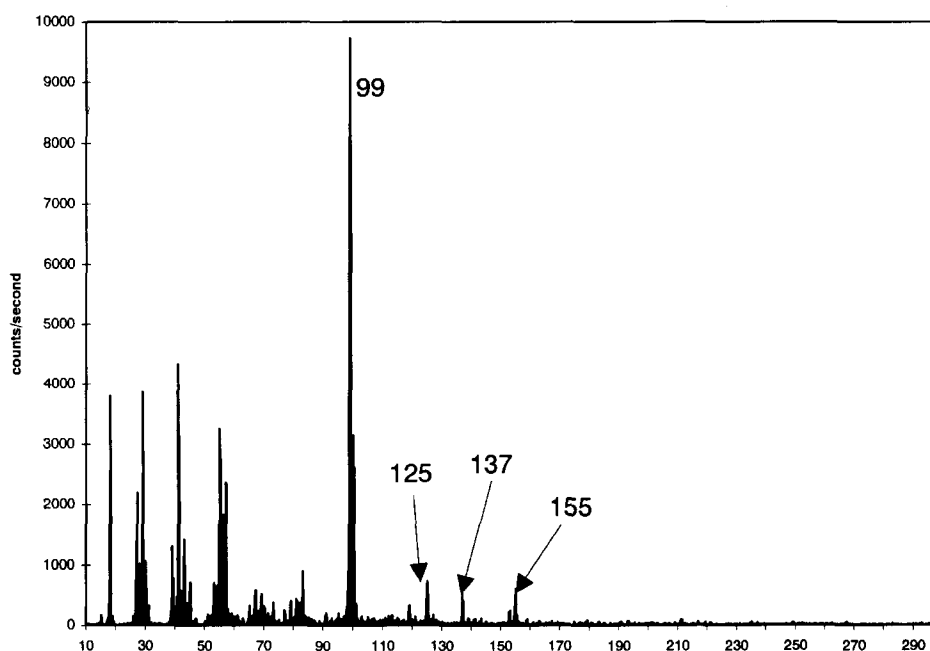
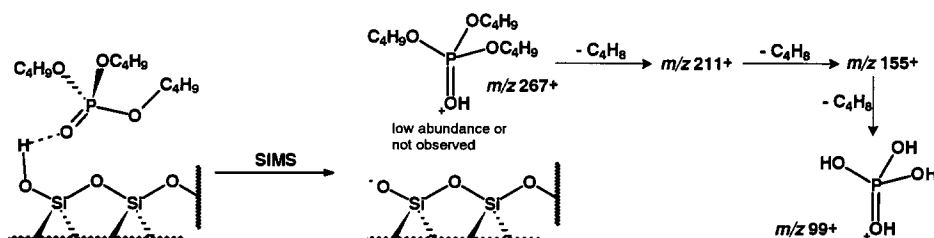


Fig. 2. Cation SIMS spectrum of Raritan rock (quartzic) that had been exposed to 1 $\mu\text{g}/\mu\text{l}$ TBP/ H_2O .



Reaction 1. Formation of $m/z\ 99^+$ during the SIMS analysis of TBP adsorbed to protonating surfaces, e.g., quartzic rocks.

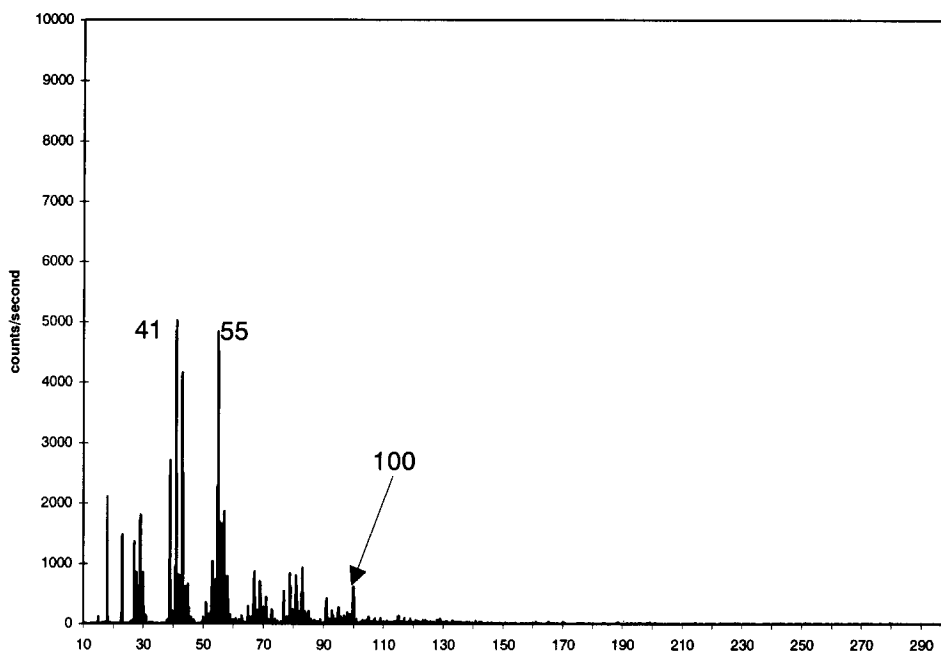


Fig. 3. Cation SIM spectrum of Raritan rock that had not been exposed to TBP.

oxygen-bearing hydrocarbons present on the sample surface, and have compositions of $\text{C}_n\text{H}_{2n+1}^+$, $\text{C}_n\text{H}_{2n-1}^+$, $\text{C}_n\text{H}_{2n-3}^+$, etc., and or $\text{C}_n\text{H}_{2n+1}\text{O}^+$, $\text{C}_n\text{H}_{2n-1}\text{O}^+$, $\text{C}_n\text{H}_{2n-3}\text{O}^+$, etc. Na^+ is observed at $m/z\ 23^+$, K^+ contributes to the ion abundance at $m/z\ 39^+$, and Fe^+ contributes to the ion abundance at $m/z\ 56^+$ when the element is present. Cyclohexyl amine, which is a contaminant of our laboratory air, accounts for the remainder of the abundant ions observed in the spectrum: $m/z\ 100^+$, 83^+ , and 18^+ .

The anion spectra of the quartzic samples were more simple: ions at $m/z\ 79^-$ (PO_3^-) and 63^- (PO_2^-) are attributable to TBP (i.e., not observed in the spectra of unspiked samples). Ions at $m/z\ 16^-$ (O^-), 17^- (OH^-), 60^- (SiO_2^-), 76^- (SiO_3^-), and 77^- (HOSiO_2^-) are observed in the spectra of spiked and unspiked samples, and are consistent with the quartzic nature of the sample.

Raritan soil samples were also exposed to TBP and analyzed. EDS revealed that these samples were also predominantly SiO_2 , but also contained some Fe, which is consistent with the brown color of the samples. SIMS analysis produced cation spectra which were very similar to those obtained for the quartzic rock, with the exception that m/z 137^+ and 119^+ abundances were enhanced. The origin of these ions will be discussed in the following section.

3.2. Analysis of TBP on reducing basalt samples

TPB was next analyzed on a series of basalt samples which were collected from the Blackfoot River area of southeast Idaho, and from the Elephant Mountain formation, which is located on the Hanford reservation in south-central Washington state. The cation SIM spectra of TBP on both samples contained prominent m/z 137^+ and 119^+ secondary ions, in addition to an abundant m/z 99^+ (Fig. 4). The former ions are formed as a result of TBP being adsorbed to a Fe(II) site on the mineral surface. SEM and XPS were used to confirm the presence of abundant ilmenite (FeTiO_3), ulvospinel (Fe_2TiO_4), and olivine (e.g., FeMgSiO_4) phases, all of which contain Fe(II). When the TBP-exposed samples are bombarded, the compound undergoes H^- abstraction and reduction, which normally results in a low abundance m/z 249^+ ion [9]. m/z 249^+ subsequently undergoes the elimination of two C_4H_8 to form m/z 137^+ , which then eliminates H_2O to form m/z 119^+ (Reaction 2). The requirement for Fe(II) for production of m/z 137^+ and 119^+ is supported by the observation of these ions in the

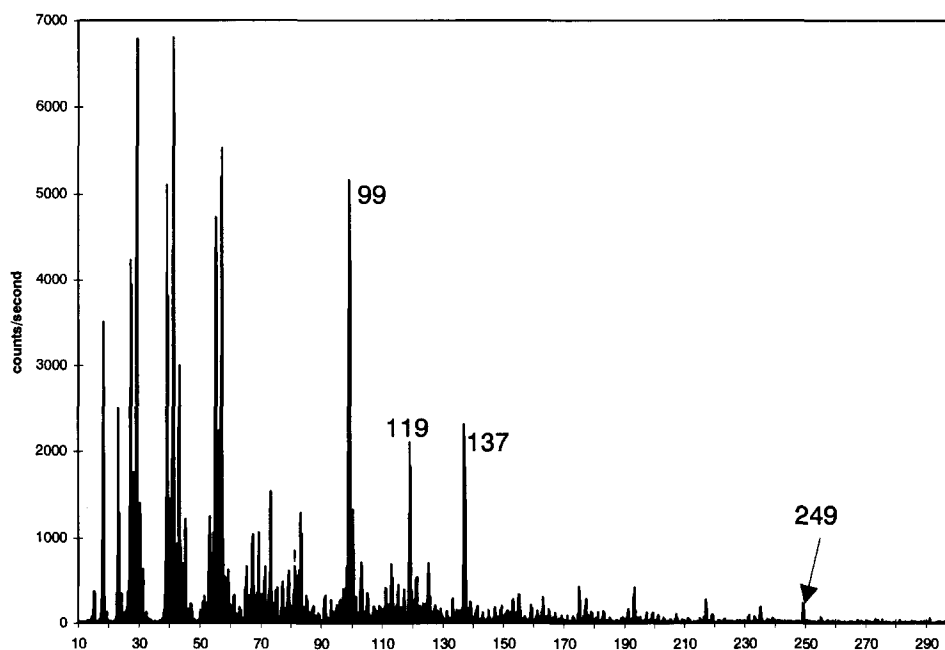
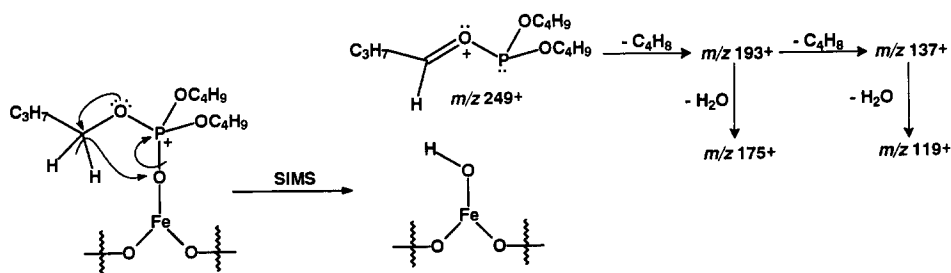


Fig. 4. Cation SIM spectrum of Blackfoot River basalt that had been exposed to $1 \mu\text{g}/\mu\text{l}$ TBP/ H_2O .



Reaction 2. Formation of m/z 137⁺ and 119⁺ during SIMS analysis of TBP adsorbed to reducing surfaces, e.g., Fe(II)-bearing minerals.

spectrum of TBP adsorbed to ferrous oxide (FeO). Thus the observation of these two ions in the SIM spectrum is indicative of TBP adsorption to Fe(II) on the basalt surface.

The anion spectrum of TBP on the Fe(II) bearing basalt samples was similar to that observed for the quartzic samples: only m/z 79⁻ and 63⁻ could be ascribed to TBP.

3.3. Analysis of TBP on Fe(III)-bearing samples

Analysis of TBP on magnetite (Fe₃O₄, which has both Fe(II) and Fe(III)) revealed the presence of an abundant m/z 153⁺ (Fig. 5), in addition to the previously described m/z 137⁺, 119⁺, and 99⁺. The m/z 153⁺ ion arises via hydride abstraction of TBP, followed by the elimination of two C₄H₈ molecules (Reaction 3) [9]. The hydride abstraction appears to require the presence of Fe(III) on the surface. This hypothesis is supported by the analysis of TBP on ferric oxide (Fe₂O₃): in this spectrum a prominent m/z 153⁺ is observed, but m/z 137⁺ and 119⁺ are absent.

The anion spectrum of TBP on the Fe(II) bearing basalt samples was similar to that observed for the quartzic samples: only m/z 79⁻ and 63⁻ could be ascribed to TBP.

3.4. Analysis of TBP on leaf surfaces [10]

The cation SIM spectrum of TBP adsorbed to leaf surfaces (grass, dandelion, clover) contained no ions which could be ascribed to TBP. Abundant ions were observed in this spectrum, but they were generally at lower mass, and were attributable to surface contaminants other than TBP (as in the case of the surface contamination described earlier). In contrast, anions attributable to TBP were observed at m/z 209⁻, 153⁻, 79⁻, and 63⁻ (Fig. 6). At the present time, we do not have a clear hypothesis for the mechanism of formation of these ions. A likely scenario is that m/z 209⁻ is formed by the loss of H⁺, followed by a rapid loss of C₄H₈ (Reaction 4). m/z 153⁻ would then arise by the elimination of a second C₄H₈. Presumably, this hypothesis would require the presence of surface sites capable of accepting a proton, but we have no evidence for such sites on leaf surfaces at this time. The mechanism for the formation of m/z 79⁻ and 63⁻ is unknown at this time.

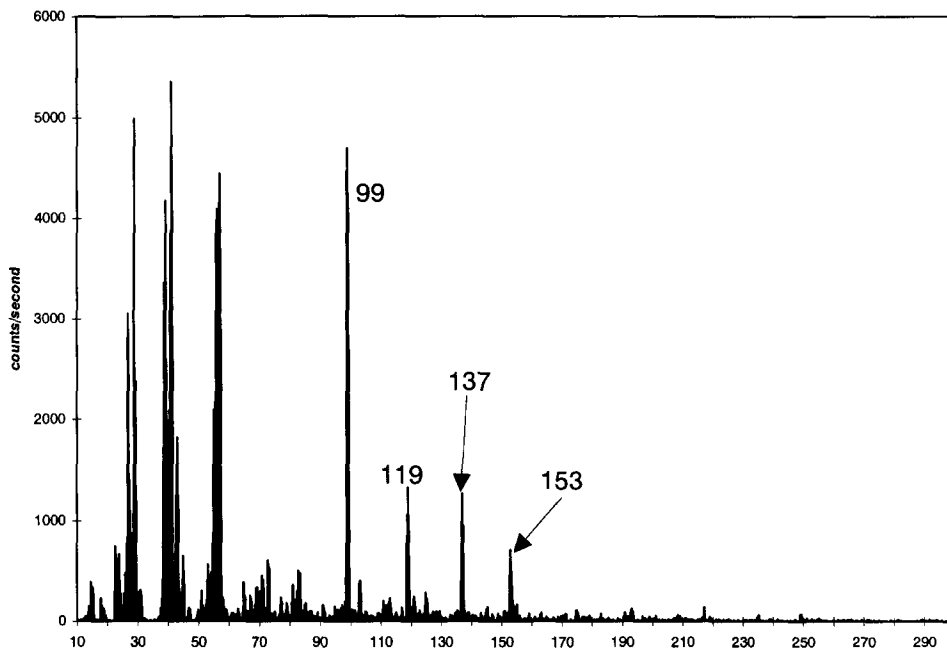
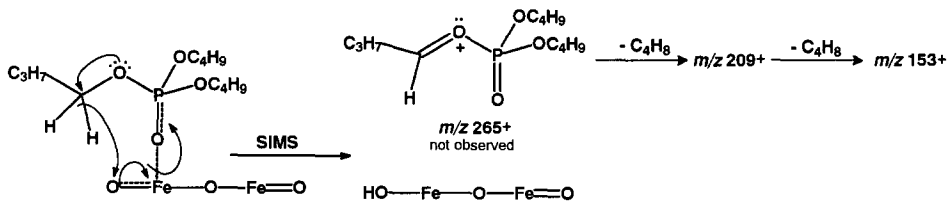


Fig. 5. Cation SIMS spectrum of magnetite that had been exposed to 1 $\mu\text{g}/\mu\text{l}$ TBP/ H_2O .



Reaction 3. Formation of m/z 153⁺ during SIMS analysis of TBP adsorbed to Fe(III)-bearing minerals.

3.5. Sensitivity of SIMS analysis, and observation of TBP adsorbed from the gas phase

Quantitation for static SIMS has historically been difficult, because the surface chemistry and morphology of environmental samples are complex, and have a great impact on the sputtering of contaminant ions. These difficulties notwithstanding, experiments were conducted to determine the minimum detectable quantity of TBP observable on mineral surfaces. Under conditions where the sample surface is smooth, a fraction of a monolayer can be observed: for comparison purposes, it is noted that 0.5 monolayer, converts to approximately 1 ng/mm^2 (assuming 2.5 $\text{nm}^2/\text{molecule}$ on the surface).

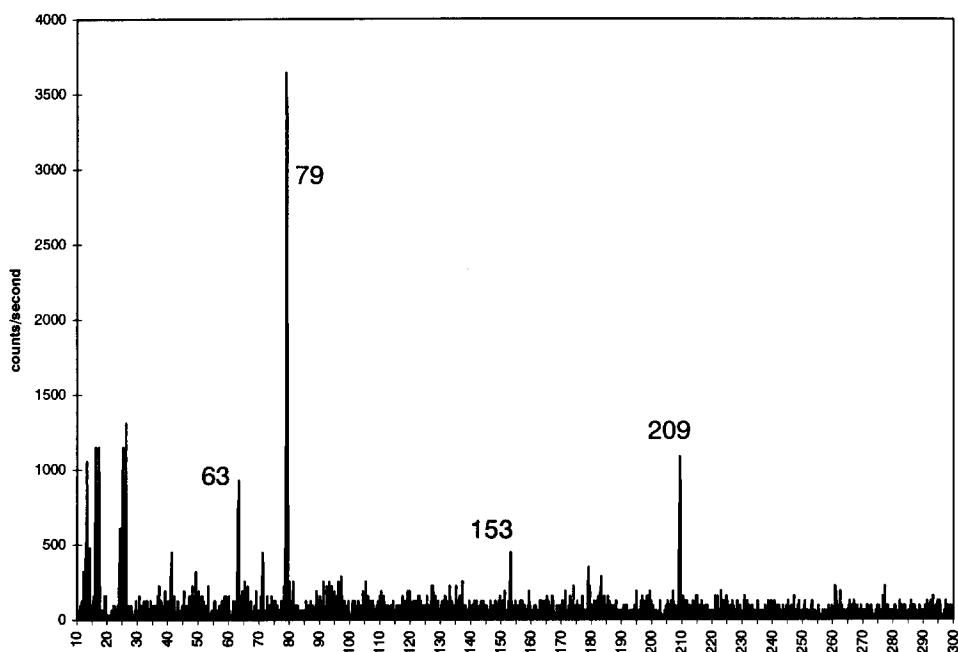
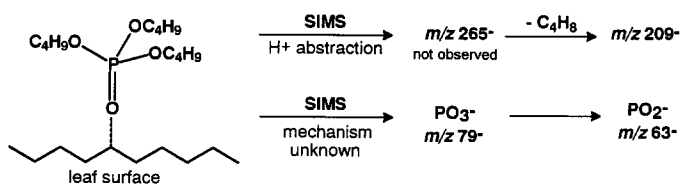


Fig. 6. Anion spectrum of a blade of grass that had been exposed to 1 $\mu\text{g}/\mu\text{l}$ TBP/ H_2O .



Reaction 4. Formation of $m/z\ 209^-$ during SIMS analysis of TBP on leaves.

A consequence of the sensitivity of static SIMS is that TBP can be detected on the surfaces of samples that have been exposed to gas phase TBP. Under ambient laboratory conditions, TBP will rapidly adsorb to mineral surfaces if neat TBP is opened in the vicinity of the samples. We have also determined that TBP will adsorb to the walls of the instrument insertion lock, where it can subsequently desorb and then re-adsorb on previously unexposed mineral samples. The quantity of TBP involved in these processes has not been determined, but is thought to be small.

4. Future directions

Continuing studies are likely to elucidate the role of mineral and leaf surface chemistry in contaminant adsorption: it is anticipated that factors like acidity,

basicity, oxidation, reduction, and surface chelation will be important for different analytes, and that these factors will alter the appearance of the SIM spectra. The range of compounds amenable to SIMS has yet to be defined.

The instrumentation used in the present study is a laboratory-based unit which requires a controlled environment. New generation mass analyzers, specifically ion traps, have been developed, and they feature a smaller size, lower cost, higher analytical selectivity and sensitivity, and more robust operating characteristics. These features make ion traps more portable than their predecessors, and in fact ion traps have found application in on-site field characterizations. Work is underway in our laboratory and others to interface SIMS with ion trap technology; it is expected that this work will result in instrumentation which will be capable of providing characterization at, or near the site where the samples originate.

5. Conclusions

Static SIMS instrumentation equipped with pulsed extraction and ReO_4^- primary ion gun technology can very easily provide identification of TBP on mineral and leaf surfaces. In addition, the SIM spectra are sensitive to the mode of contaminant-surface interactions on the first monolayer of mineral and leaf samples. This is significant because there are few techniques which are capable of addressing this interfacial region. The importance of acquiring both the anion and cation spectra is also emphasized by this study, because the surface chemistry dictates whether positive or negative contaminant ions will be formed. Static SIMS has other attributes which make it attractive for characterization of environmental samples. The technique is rapid (typical analysis is on the order of 5–10 min), primarily because no sample preparation is performed, other than attaching the sample to a sample holder using double-sided tape. Static SIMS only requires a milligram-sized sample, and the analysis generates no waste. It is anticipated that new advances in static SIMS instrumentation will result in much broader application of this technique to the investigation of contaminants on environmental surfaces.

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