

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

### Air Pollution Analysis from Exposed Surfaces by Simultaneous ISS/SIMSt

F. W. Karasek<sup>a</sup>; A. Maican<sup>a</sup>; H. H. Hill Jr.<sup>b</sup>

<sup>a</sup> Guelph-Waterloo Centre of Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada <sup>b</sup> Department of Chemistry, Washington State University, Pullman, Washington, U.S.A.

**To cite this Article** Karasek, F. W. , Maican, A. and Hill Jr., H. H.(1978) 'Air Pollution Analysis from Exposed Surfaces by Simultaneous ISS/SIMSt', *International Journal of Environmental Analytical Chemistry*, 5: 4, 273 – 292

**To link to this Article:** DOI: 10.1080/03067317808071152

**URL:** <http://dx.doi.org/10.1080/03067317808071152>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Air Pollution Analysis from Exposed Surfaces by Simultaneous ISS/SIMS†

F. W. KARASEK and A. MAICAN

*Guelph-Waterloo Centre of Graduate Work in Chemistry,  
Department of Chemistry, University of Waterloo,  
Waterloo, Ontario N2L 3G1, Canada*

and

H. H. HILL, Jr.

*Department of Chemistry, Washington State University,  
Pullman, Washington 99164, U.S.A.*

(Received March 7, 1978)

Unique analytical data from simultaneous analysis by ion scattering spectrometry and secondary ion mass spectrometry demonstrate a potential for air pollution monitoring from surfaces. A piece of aluminum siding with discolored paint, a section of filter paper containing airborne particulate matter, and a heavily corroded bicycle spoke were chosen as characteristic samples of non-ideal surfaces. Mn and  $Mg_2SiO_4$  were identified as atmospheric pollutants. ISS demonstrated a detection limit of  $1 \text{ ng/mm}^2$  for Cu with a resolution of 0.18 for  $^{65}\text{Cu}$  and  $^{63}\text{Cu}$  while the SIMS valves were  $100 \text{ pg/mm}^2$  and 1.4, respectively. Specific problem areas for trace analysis of non-ideal surfaces include ISS sensitivity and SIMS contamination. Techniques for reducing residual contamination are discussed and demonstrated.

KEY WORDS: Atmosphere, particulates, surface analysis, ISS, SIMS

## INTRODUCTION

The recent development of a multiplicity of analytical techniques enabling spatial, depth, point and bulk analysis of surface elements can be credited

---

†Paper presented at the 8th Annual Symposium on the Analytical Chemistry of Pollutants, April 1978, Geneva, Switzerland.

to the semiconductor industry. Semiconductors are ideal samples upon which to develop new surface analysis techniques because they are synthetically grown under carefully controlled conditions producing smooth and reproducible surfaces. Surface analyses are also routinely used in areas such as catalysis and materials research but until recently have been limited to surfaces in which interferences from structural perturbations were minimized.

The extension of surface analysis to air pollution monitoring has received recent attention.<sup>1,2</sup> Linton *et al.*<sup>1</sup> point out that the concentration of toxic elements at the surface of airborne particulate matter would enhance the dangers of environment contamination and human toxicity. Their studies using a combination of secondary ion mass spectrometry and Auger electron spectrometry indicated surface enhancement of Pb, Tl, Mn and Cr on fly ash collected from the combustion of midwestern United States bituminous coal. Of greater environmental concern than fly ash collected in stacks is particulate matter in suspension in the atmosphere. These particles are sufficiently small to be inhaled deeply into the lungs. X-ray photoelectron spectroscopy (ESCA) was used to compare particulate matter collected from city, suburban and country air<sup>2</sup> and significant quantities of Pb, S, N and Si were found in urban and suburban air.

Another potential application of surface techniques to air pollution measurement is the analysis of materials exposed to polluted air. These surfaces may contain a toxin history such that their analysis would produce a more reliable picture of general atmospheric conditions than the conventional atmospheric sample. Yet, the analysis of such surfaces is challenging. Proper blanks, reliable calibration curves and adequate sensitivity present particular problems with a weathered non-homogeneous surface.

This paper evaluates the simultaneous operation of two surface techniques, ion scattering spectrometry (ISS) and secondary ion mass spectrometry (SIMS), for identification and measurement of air pollutants. ISS distinguishes surface elements by measuring the energy ratio of ions before and after they collide with the surface. Helium, neon, and argon ions are commonly used as probe ions and their proper selection allows optimum resolution of elements of interest. Probe ions also sputter and ionize elements from the surface. These secondary ions can then be separated and identified by mass spectrometry. Simultaneous detection of ions scattered and sputtered from surfaces produce data that corroborate or complement one another.<sup>3,4</sup>

A series of investigations characterize the ISS/SIMS techniques for air pollution analysis. Airborne particulate matter collected on filter paper, a

section of discolored painted aluminum siding, and a heavily corroded bicycle spoke were chosen as typical samples. Sensitivity and contamination studies were conducted to illustrate the advantages and difficulties of applying these techniques to air pollution analyses.

## EXPERIMENTAL

### Instrumentation

The instrument used was the model 520BISS/SIMS (3M Company, St. Paul, Minnesota). During standard operation, a stainless steel sample holder with six sample positions is keyed into the analyzing chamber; the chamber is sealed and evacuated to  $10^{-8}$  torr with a zeolite absorption pump, an ion pump, and a system of titanium sublimators;  $^3\text{He}$ ,  $^4\text{He}$ ,  $^{20}\text{Ne}$  or  $^{40}\text{Ar}$  is backfilled into the chamber to  $5 \times 10^{-5}$  torr; and a 2 mm diameter beam of  $^3\text{He}$ ,  $^4\text{He}$ ,  $^{20}\text{Ne}$  or  $^{40}\text{Ar}$  ions with a charge density of 27 to  $30 \mu\text{A}$  is focused on the target. Scattered ion energies are evaluated with a  $127^\circ$  sector electrostatic energy analyzer at a  $90^\circ$  angle from the incident beam while sputtered ions (positive or negative) are separated and measured with a modified UTI 100C quadrupole mass spectrometer (Uthe Technology International, Sunnyvale, California).

### Sensitivity studies

Standards were prepared from a number of aqueous solutions containing various concentrations of a metal salt (0.1, 0.3, 1, 3, 5 and  $10 \mu\text{g/ml}$ ). Standard solutions were prepared from each of the following salts:  $\text{CuCl}_2$  anhydrous,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . One ml of each solution was delivered from a buret and evaporated a drop at a time on a Pt foil resting on a glass microscope slide that was warmed over a hot plate. Each drop was completely evaporated before the next was applied so that the entire 1 ml sample was deposited in an area of about one  $\text{cm}^2$ . Distilled water was used for a procedural blank. Each sample was bombarded with Ne ions at 1.5 keV. Electron spectroscopy for chemical analysis (ESCA) data were also obtained for a set of  $\text{Cr}^{3+}$  standards (0.1, 1 and  $10 \mu\text{g/mm}^2$ ) from Hewlett-Packard.

### Contamination studies

Ultrapure foils of copper, silver and aluminum were used as samples to demonstrate contamination within the instrument and to develop methods that reduce these interferences. The copper foil was analyzed first, the silver foil second and the aluminum foil third. To eliminate contamination

by sputtered atoms from other samples, only one sample was introduced into the vacuum chamber at a time. Next, an ashless filter paper was sputtered for 3 hours after which the analysis of the aluminum foil was repeated. Throughout these experiments both ISS and positive SIMS were obtained simultaneously with 2.5 keV  $^{20}\text{Ne}$  ions.

### **Aluminum siding analysis**

Two samples of painted aluminum siding were analyzed. One had been discolored by exposure to the atmosphere, and the other had not been exposed to the atmosphere and was used as a control. Both samples plus a strip of ashless filter paper were analyzed with  $^3\text{He}$  ions in the following order: the ashless filter paper, the control piece of aluminum siding, and the discolored sample.

### **Atmospheric particulate analysis**

Airborne particulate matter, collected by passing air through a Hi-Vol filter for 24 hours was supplied by the Air Resources Branch of the Ontario Ministry of the Environment, Toronto, Ontario, Canada. Two samples, representative in appearance, were chosen for analysis. Each was carefully cut into a number of 1-cm<sup>2</sup> pieces, placed in a glass soxhlet extraction thimble, and extracted for 16 hours with cyclohexane. The extract was collected, concentrated, and chromatographed for analysis of the organic material adsorbed onto the particulate matter.<sup>5</sup> The filter paper cuttings containing the nonextractable material were retrieved, dried in an oven at 200°C for 2 hours and loaded into the spectrometer for surface analysis. Control samples of ashless filter paper and unused Hi-Vol filter paper taken from the same package as that which was used were dried and handled in the same manner as the samples.

### **Bicycle spoke analysis**

A heavily corroded bicycle spoke that had been near a home in Fort Francis, Ontario, Canada, was supplied for analysis by the Air Resources Branch of the Ontario Ministry of the Environment. Metal surfaces in this area corroded at an especially rapid rate when exposed to the atmosphere. A true blank was not available so an operational blank was produced by filing the corroded surface and then polishing the spoke to a shiny finish. This pseudo blank was then cleaned with water and methanol. Both it and the sample were dried in an oven at 200°C for 2 hours before being mounted in the instrument. First helium was used as the probe gas and then argon. Both positive and negative SIMS data were obtained.

## RESULTS AND DISCUSSION

Few literature references have been made to the absolute sensitivity and detection limit of the ISS/SIMS instrument. One reason for this is the difficulty that exists in evaluating the effects that differing elemental or chemical surface compositions have on the quantitative yield of neighboring ions. Influences of surface structure appear to be most important for ISS while the influences of surface matrix are of paramount concern in SIMS. Sensitivities have been reported in the part per million atomic range for SIMS<sup>6</sup> although these values may vary as much as three orders of magnitude as a result of the sample's chemical composition.<sup>7</sup> Furthermore, available quantitative information is difficult to extrapolate to air pollution because they have been obtained from ideal, smooth surfaces. In the surface analysis of air pollutants, elements of interest are not embedded in a metal matrix but are added to a support matrix by adsorption or chemical interaction or, in the case of the particulate matter, simple mechanical implantation on a filter.

Surface standards for these studies were produced by evaporating known amounts of salts onto platinum supports. This method was employed to estimate the quantitative response of materials that are not an integral part of the surface structure. Unfortunately, accurate calibration techniques are virtually non-existent and one can envision numerous uncontrollable parameters such as heterogeneous depositions of the salt on the platinum surface. However, this method was checked by an independent laboratory with ESCA. In Figure 1, the direct correlation of data between SIMS and ESCA for separate sets of chromium standards justify the use of these standards in evaluating relative sensitivities of surface techniques.

The ISS calibration curve shown in Figure 2 indicates that the minimum detectable amount of Cu is approximately  $1 \text{ ng/mm}^2$  with similar limits (varying less than a factor of four) for the Ba, Cr, Ni and Mn. Saturation of the platinum surface occurs with metal concentrations on the order of  $100 \text{ ng/mm}^2$ .

Positive SIMS results shown in Figure 3 are similar in shape to the ISS curves but the sensitivity and resolution for each of the test compounds were at least an order of magnitude better in the SIMS mode. For example, the signal-to-noise ratio of the  $4 \text{ ng/mm}^2$  copper standard was 60 for SIMS and 4 for the ISS. Resolution of the  $^{65}\text{Cu}$  and  $^{63}\text{Cu}$  peaks (the separation between the two peaks divided by the average peak width) was 1.4 for the SIMS and 0.18 for the ISS. As in the ISS calibration curves, the SIMS data was nonlinear and reached saturation with concentrations approximately  $100 \text{ ng/mm}^2$ . These curves exemplify those expected as surface substances increase in concentration.

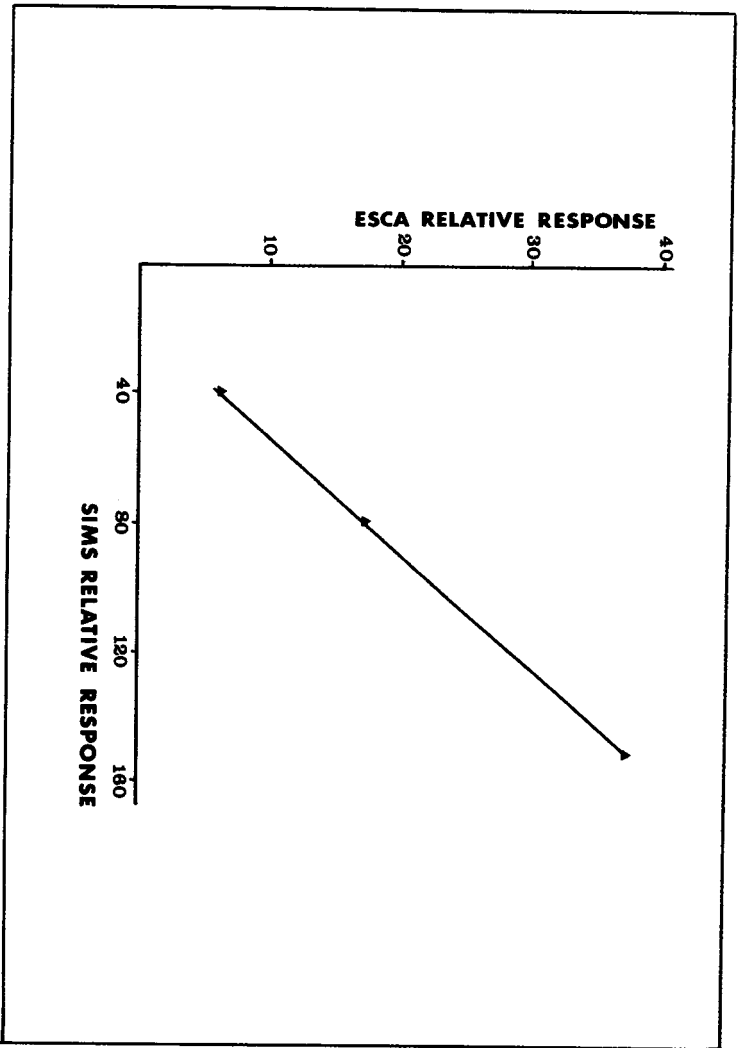


FIGURE 1 Relative responses of ESCA versus positive SIMS for three Cr standards deposited on a Pt foil. Cr concentrations were  $1.0 \text{ ng/mm}^2$ ,  $10 \text{ ng/mm}^2$ ,  $100 \text{ ng/mm}^2$ .

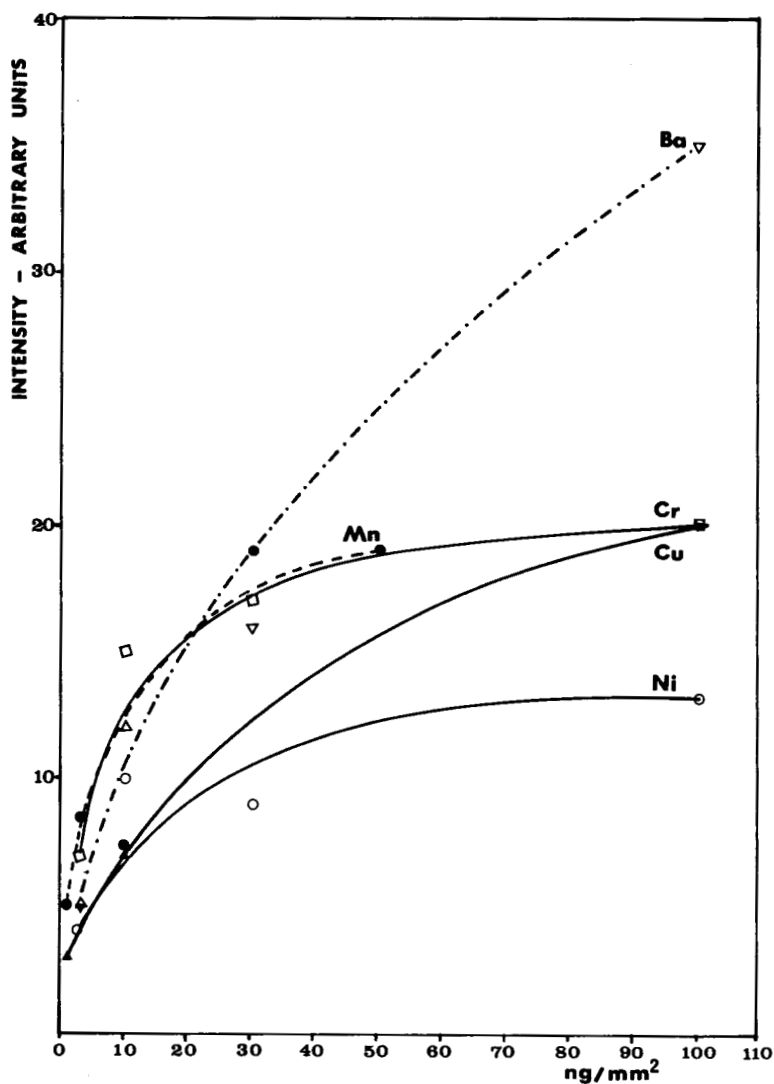


FIGURE 2 ISS calibration curves for Ba, Mn, Cr, Cu and Ni with  $^{20}\text{Ne}$  as the probe gas. Simultaneously obtained with the SIMS data of Figure 3.

It is likely that with this crude surface deposition technique, a homogeneous monatomic layer of the standard is not achieved. Many of the atoms of the standard are undoubtedly shielded from the ion beam (especially when low molecular weight probe gases are used) within the



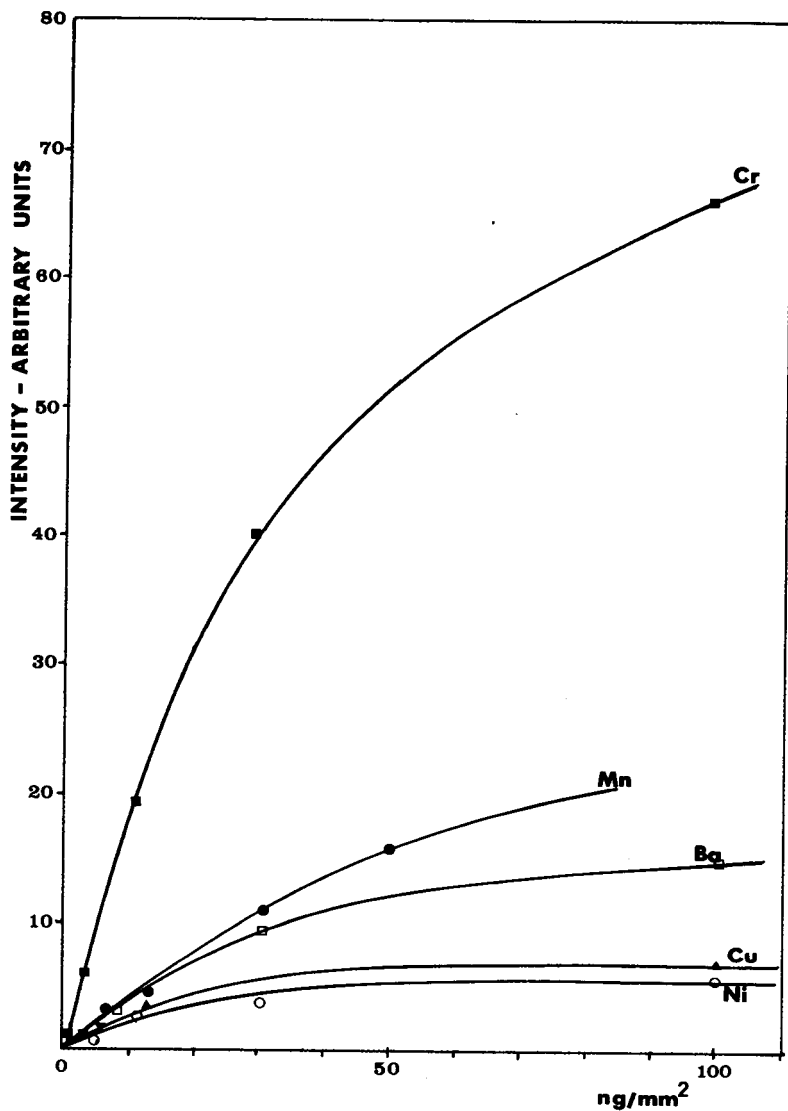


FIGURE 3 SIMS calibration curves for Ba, Mn, Cr, Cu and Ni with  $^{20}\text{Ne}$  as the probe gas. Simultaneously obtained with the ISS data of Figure 2.

crystal lattice of nucleation centers. Nevertheless, these measurements represent an approximation of the sensitivities that can be expected from surface conditions that exist in the non-ideal samples we have chosen to study.

Each calibration curve was obtained by ordering the samples from the lowest concentration to the highest. This practice insures against extraneously high responses at the lower concentration levels by contamination from concentrated standards. When a blank was repeated at the end of the study, the ISS spectrum was clean while the SIMS spectra contained peaks for all the elements that had been analyzed.

Memory effects in SIMS arise because atoms from previous samples are sputtered from the target and remain as residual gas or are deposited on instrument walls, the sample holder, and even other samples held in the same sample holder. A set of experiments were devised to determine the principal source of contamination and procedures to lessen its interference. Figure 4(a) illustrates contamination in a spectrum of 99.995% aluminum. The Cr, Ni and Fe peaks arise from previous sputtering of the sample holder. The Cu peaks are memory effects from a previously sputtered copper foil that had been held in the same sample holder but the copper had been removed from the instrument and the vacuum pumped down and backfilled with fresh probe gas several times before this Al spectrum was obtained. The Ag peaks occur from a previous analysis of a silver foil contained in a different sample holder. Contamination was always more significant when sample holders were not changed between analysis but was still present even when different sample holders were used. The failure of interchanging sample holders to eliminate contamination indicates that a source of the contamination is atoms or ions sputtered from previous samples onto walls and other permanent fixtures of the vacuum chamber. One reason that previous workers have not considered this a major problem may be that data from material composition analysis can often be obtained at higher attenuations where small contamination peaks are of little consequence. In analysis of surfaces for adsorbed pollutants the interest is not in major elements but in minor and trace substances since pollutants are contaminants themselves and can generally only be expected in low concentrations. The difficulty in distinguishing a pollutant peak of low intensity from that of an instrumental contaminant was of major concern in these analyses. Investigations of methods for reducing this problem produced the following recommended procedures.

Cleaning the instrument by bombarding ashless filter paper was the most effective method of eliminating extraneous peaks. Figure 4(b) shows the absence of silver and copper peaks in a spectrum of the same aluminum foil analyzed in Figure 4(a). Between the analysis of Figure 4(a) and that of Figure 4(b) a piece of standard ashless filter paper had been sputtered with argon ions for 3 hours. The high energy backscattered ions apparently cleaned surfaces that were the source of contamination. Sputtering a metal of low secondary ion yield (e.g., Pt or Au) also proved

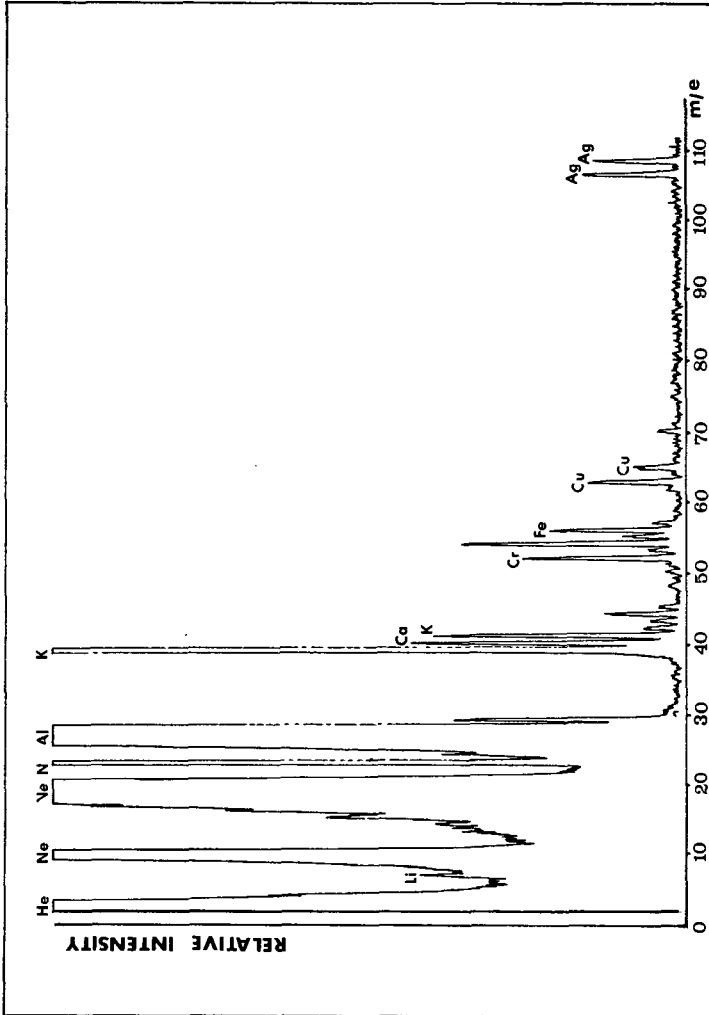


FIGURE 4(a) Positive SIMS spectrum ( $^{20}\text{Ne}$  at 2.4 keV) of an aluminum foil illustrating contamination from previously analyzed standards.

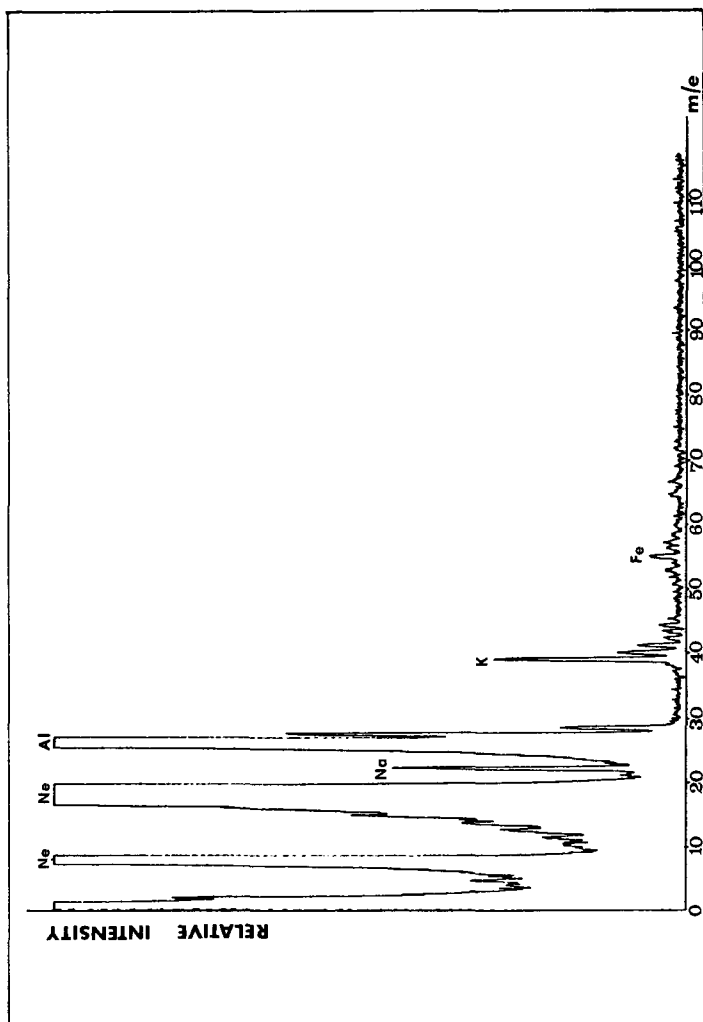


FIGURE 4(b) Positive SIMS spectrum under similar conditions after instrument has been cleaned by sputtering ashless filter paper with  $^{20}\text{Ne}$  at 2.5 keV for 1 hour.

to be an efficient means of cleaning the instrument. A principal advantage of these metals vs. filter paper is that a build-up of charged species does not occur in the vicinity of probe gas impact. Bombarding the non-conducting filter paper permits charge build-up in the target zone. This charge build-up can be neutralized by thermal emission of electrons in the target area but insufficient neutralization can lead to deflection of the ion beam to the conducting stainless steel sample holder inducing contamination from iron, nickel and chromium. In the following analyses either a platinum foil or an ashless filter paper with proper charge neutralization was used to reduce or eliminate cross contamination between samples.

The three environmental samples were studied in order of increasing surface roughness. The aluminum siding with the discolored paint was analyzed first. Figure 5 compares the ISS spectra of the exposed and unexposed painted aluminum siding samples. Figure 6 does the same for the positive SIMS spectra that were simultaneously obtained with the respective ISS spectra. ISS spectra are primarily helpful in determining the relative depth of the weathered layer of paint. Both the control and the sample were scanned repeatedly at 4-minute intervals. Thus each spectrum is taken at a different depth since the ion beam is continuously bombarding the surface and sputtering away exposed atoms. After 8 minutes of sputtering the control spectrum remains similar to the initial control spectrum, but for the exposed sample aluminum and oxygen peaks become dominant after only 4 minutes of sputtering, indicating that the ion beam has sputtered through the paint to the aluminum surface. Carbon from the surface paint can be clearly identified on the control sample while potassium, an omnipresent element, may have its origin as a contaminant from surface handling. Since different materials sputter at different rates, it is difficult to determine actual film thickness without suitable standards.

SIMS spectra were obtained simultaneously only with the first ISS spectrum because of memory contamination. The presence of aluminum, potassium, and carbon compounds in Figure 6(b) agrees with that found in the ISS. The peak for residual neon in Figure 6(a) indicates probe gas contamination from the previous cleaning process. Neon, however, was completely excluded when the system was pumped out and backfilled with helium after introduction of the sample. Sodium, like potassium, is another element that readily occurs on surfaces from handling. If contamination of the surface from handling had occurred, an ISS peak for sodium at  $E/E_0$  of 0.769 would have been expected to be larger than that of potassium. (Direct comparison of their peak intensities in SIMS is less reliable due to differences in ionization potential and matrix considerations.) From eva-





luation of the ISS and SIMS data it appears that potassium is a real component of both the control and the sample, while sodium is a residual contaminant within the vacuum system. Note from Figure 4(b) that both sodium and potassium are elements difficult to clean from the system.

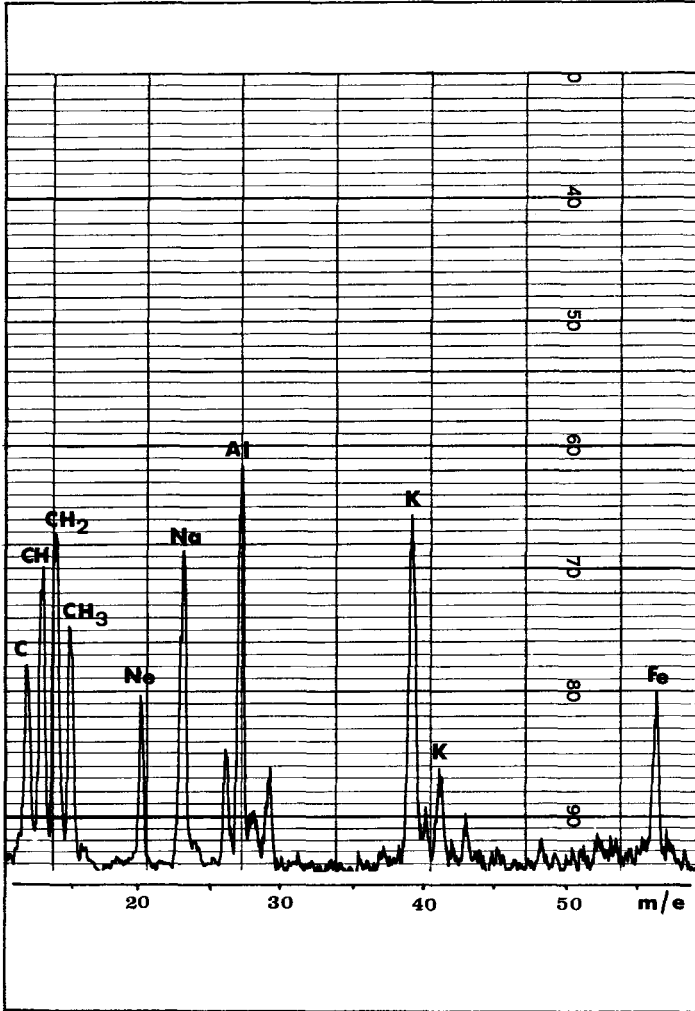


FIGURE 6(a) Positive spectrum with  $^3\text{He}$  at 2 keV of a clean unexposed section of painted aluminium siding. Spectrum was obtained simultaneously with the first spectrum shown in Figure 5a.



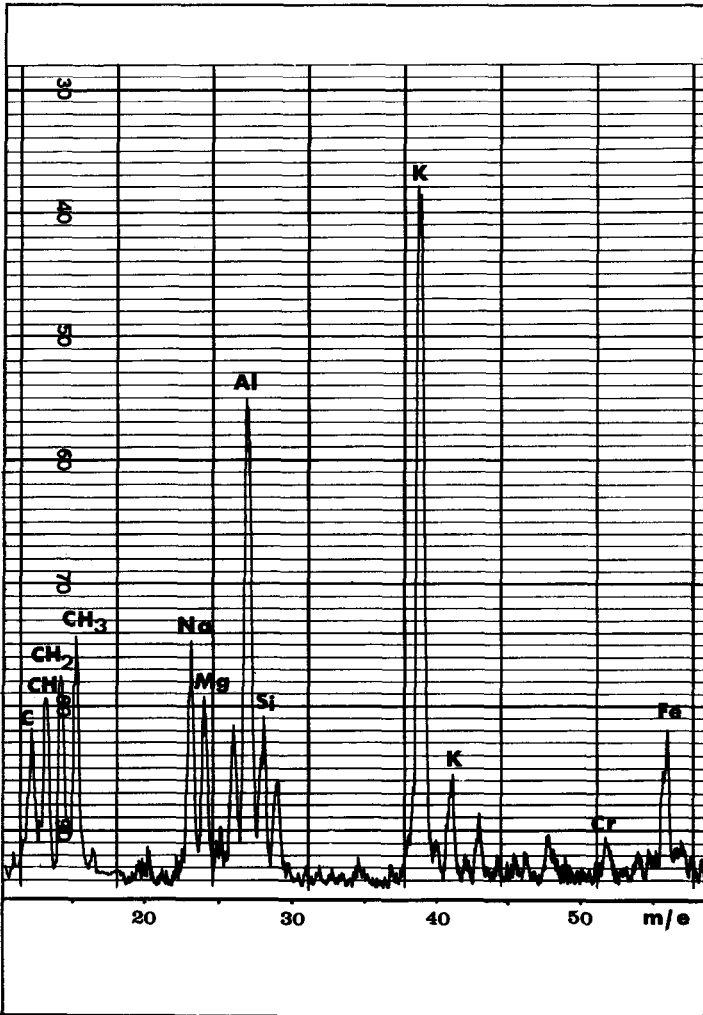


FIGURE 6(b) Positive SIMS spectrum with  $^3\text{He}$  at 2 keV of a discolored exposed section of painted aluminium siding. Spectrum was obtained simultaneously with the first ISS spectrum shown in Figure 5b.

Also, the presence of iron in both SIMS spectra of Figure 6 and its absence in the ISS spectra suggest instrumental contamination.

Significant differences between SIMS spectra are the peaks for magnesium and silicon. These peaks occurred in the discolored sample of Figure 6(b) but not in the control sample indicating that magnesium and silicon were adsorbed onto the surface from the atmosphere. The major contaminating species from the atmosphere was most probably  $\text{Mg}_2\text{SiO}_4$ .

Compounds such as  $\text{Mg}_3\text{SiO}_4$  are most commonly transported through the atmosphere as small particles in suspension. For analysis, these particles are collected and concentrated by passing large volumes, typically  $3,000 \text{ M}^3/24 \text{ hrs}$ , of air through a filter paper. Direct analysis by ISS/SIMS of the particulate matter on these filters after extraction of adsorbed organic material produced the spectra shown in Figures 7 and 8. The helium ISS spectrum showed a small peak for oxygen and an unidentified peak in the  $0.9E/E_0$  range. Resolutions for elements in this region can be increased by using a heavier probe gas. Neon produced a small peak having an ill-defined maximum at an  $E/E_0$  of about 0.47 (Figure 7). This peak corresponds to either iron or manganese. The SIMS spectra in Figure 8 is required to identify the peak as manganese. Manganese has also been identified as a particulate contaminant by AES/SIMS techniques.<sup>1</sup>

Peaks for manganese and lithium were the only ones observed in the SIMS spectra that were not also seen in the blank.  $\text{He}^+$ ,  $\text{Ne}^{++}$  and  $\text{Ne}^+$  are probe gas ions,  $\text{Al}^+$  and  $\text{Fe}^+$  are believed to be cross contaminants and  $\text{O}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  originate from the filter paper. Both ISS and SIMS were required for the interpretation of these spectra. Contamination free ISS spectra assured that peaks were real and high resolution SIMS spectra aided their identification.

The third surface analyzed was that of a bicycle spoke taken from an area in Ontario where metal exposed to the atmosphere corroded rapidly. The natural curvature and surface roughness of this sample increased the difficulty of analysis but the conductive nature of the sample eliminated the need for charge neutralization. The two sets of spectra that were obtained (one with helium and the other with argon) were corroborated by the 3M Contract/Demonstration Laboratory in St. Paul, Minnesota with a 3M Model 520B ISS/SIMS instrument.

Little qualitative differences between the blank and the sample could be established. Peak intensities indicated that the corroded surface may have been enriched in potassium, sodium, oxygen, chlorine, fluorine and sulphur. Since many of these conclusions were based on differences in peak intensities of 10% or less, effects that differing surface structures have on scattering and ion yields reduce their validity. Pretreatment of the blank with methanol resulted in a prominence of hydrocarbon ions such as  $\text{CH}_3^+$ ,  $\text{CH}_2^+$ ,  $\text{CH}^+$ . Chromium was the only element unquestionably on the surface of the exposed sample and essentially absent on the blank. This, however, is contributed to surface enrichment of chromium in the stainless steel process and not to atmospheric conditions. In general the ISS/SIMS technique showed little evidence of difference between the sample and the blank indicating that, if atmospheric pollutants were the cause of rapid

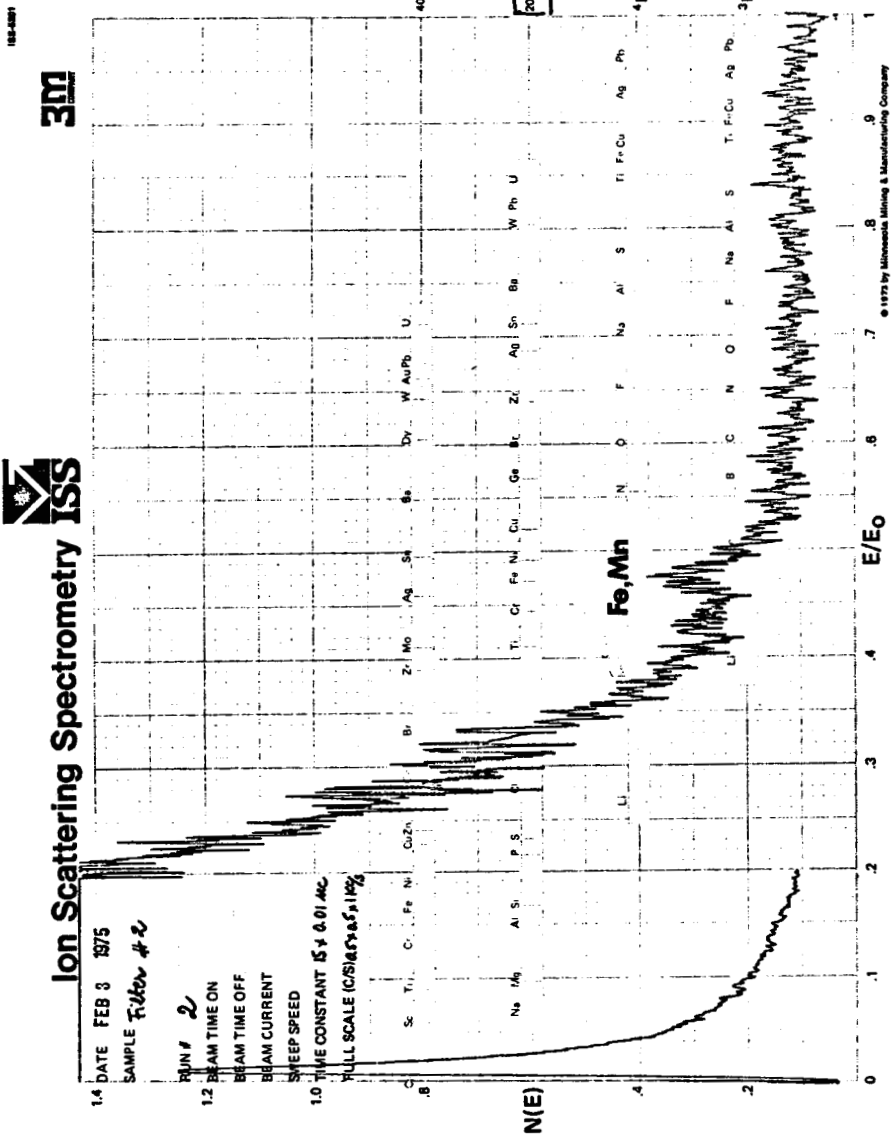


FIGURE 7 ISS spectrum using <sup>20</sup>Ne at 1.5 keV of atmospheric particulate matter on Hi-Vol filter paper.

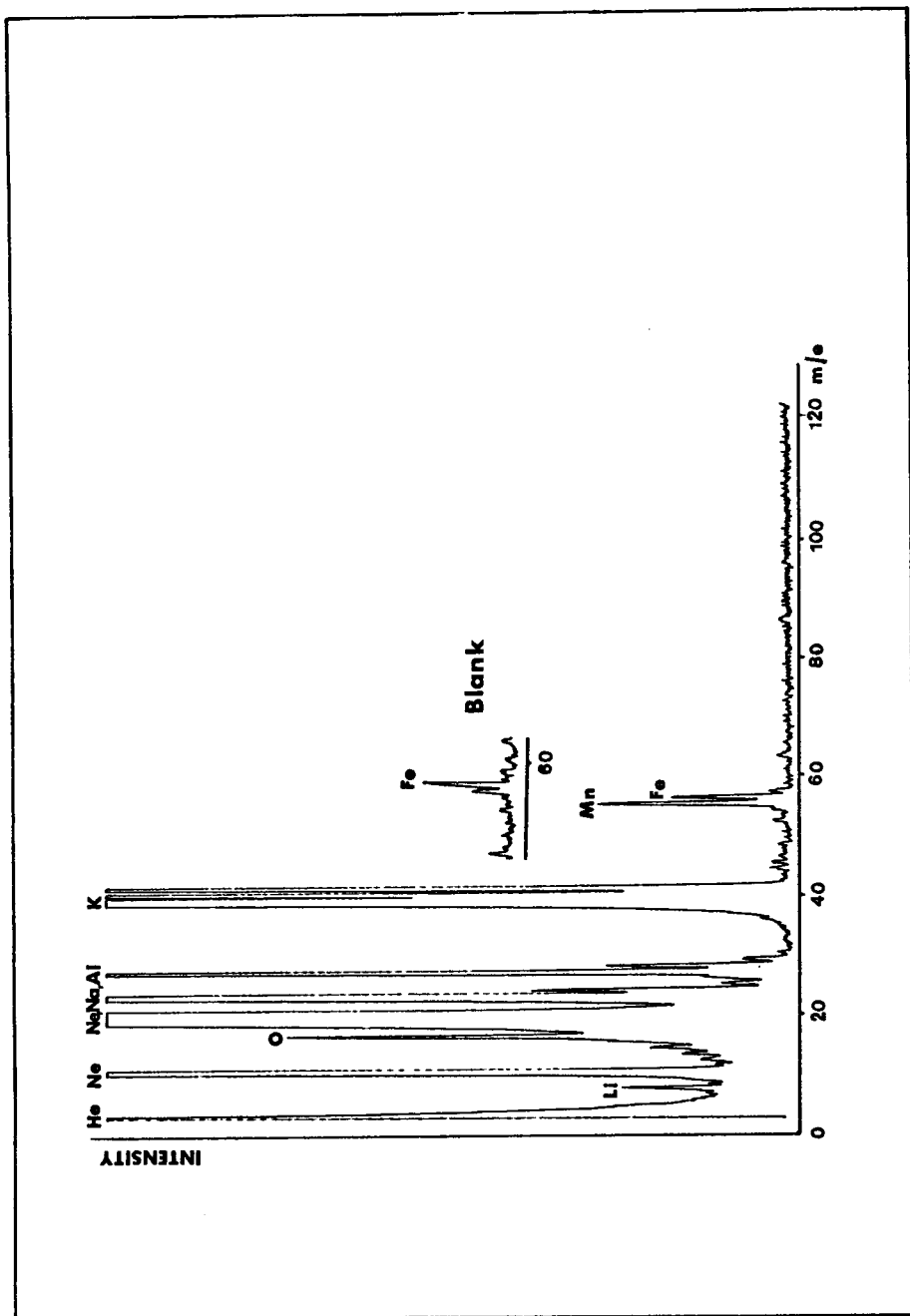


FIGURE 8 Positive SIMS spectrum of atmospheric particulate matter on Hi-Vol filter paper taken simultaneously with the ISS spectrum of Figure 7. Blank spectrum was of an unused Hi-Vol filter paper.

corrosion, they were not significantly different in composition from the bicycle spoke or that they did not accumulate on the spoke in sufficient quantities to be detected.

In summary ISS/SIMS analysis has the advantage of two sets of data obtained simultaneously. Major problems appear to be sensitivity of the ISS and contamination of the SIMS. Sensitivities are reduced for the analysis of non-ideal surfaces when compared to those reported in the literature for smooth polished surfaces. A major problem in establishing this technique quantitatively is the lack of dependable standards and, for trace analysis, the cross contamination of samples. Sputtering ashless filter paper or a low-ion yield metal are the most efficient methods of reducing contamination within the instrument but highly sensitive analyses require several hours of clean-up time between samples, reducing the number of analyses and increasing the frequency of opening, pumping down and backfilling the vacuum chamber. In this study the maximum rate of analyses was 1 blank or sample per day. Obviously more extensive studies and developments are warranted before routine use of this technique can be recommended. Nevertheless, several atmospheric pollutants were identified with this technique demonstrating a potential for air pollution analysis from exposed surfaces.

### Acknowledgement

This research was supported in part by the Ontario Ministry of the Environment, Air Resources Branch.

### References

1. R. W. Linton, P. Williams, C. A. Evans, Jr. and D. F. S. Natusch, *Anal. Chem.* **49**(11), 1514 (1977).
2. G. R. Grieger, *American Laboratory*, April, 77 (1976).
3. J. A. Leys and J. T. McKinney, presented at the Ninth Annual Conference of the Microbeam Analysis Society of America, Ottawa, Canada, July 22-26, 1974.
4. M. Grudner, W. Heiland and E. Taglauer, *Appl. Phys.* **4**, 243 (1974).
5. H. H. Hill, Jr., K. W. Chan and F. W. Karasek, *J. Chromatogr.* **131**, 245 (1977).
6. R. E. Honig, 6th International Mass Spectrometry Conference, Edinburgh, September, 1973.
7. H. W. Arner, *Surface Science* **47**, 301 (1975).
8. H. Niehus and E. Bauer, *Surface Science* **47**, 222 (1975).
9. W. L. Baun and J. S. Solomon, *Anal. Chem.* **48**, 931 (1976).