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SURFACE ANALYSIS TECHNIQUES AND THEIR USE IN POLLUTION DETECTION AND MEASUREMENT

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ABSTRACT

Surface analysis techniques such as Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), secondary ion mass spectrometry (SIMS) and ion scattering spectrometry (ISS) are reviewed. The advantages and limitations of these methods are compared with bulk analysis techniques such as x-ray fluorescence spectroscopy, atomic absorption and emission spectroscopy, gas chromatography, and neutron activation analysis. Results obtained using ESCA, AES, SIMS, ISS and x-ray fluorescence analysis from auto exhaust, laboratory prepared, clean air and biological samples are discussed. Possible future areas of research using surface techniques are discussed.

Introduction

In recent years the energy crisis has focused attention on using coal in vast quantities for liquification and gasification. Also, alternate energy sources such as solar, fusion, fission and other exotic fuels are being proposed. All these forms of energy generation will require characterization and detection of environmental pollution for regulatory purposes as well as for understanding the sources, environmental pathways, reservoirs, distribution and biological effects of these pollutants.

The usual bulk analysis techniques employed for detection and measurement of environmental pollutants are atomic emission spectroscopy, x-ray fluorescence spectroscopy, chemical analysis, gas chromatography and neutron activation analysis. Properties of these techniques are compared in Table 1 with those of recently developed techniques employed in areas of "surface" science, namely Auger spectroscopy, ESCA, ISS and SIMS. The minimum quantity detectable is generally less for the surface techniques since only a single layer of atoms is needed for analysis. On the other hand, when the contaminant is dispersed

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throughout a thicker sample, bulk techniques are more sensitive since a larger sample volume can be examined. The surface techniques can detect a broader range of elements; however, molecular species can be detected using gas chromatography.

A principal advantage of the surface techniques is the capability they provide for studies of spatial distributions of pollutants. For example, concentrations can be studied as a function of nanometer depths in environmental or biological samples.

In the present study, surface techniques were examined to demonstrate the feasibility and usefulness of using these techniques in the area of pollution detection, measurement and characterization.

We have analyzed samples from auto exhaust, a laboratory prepared sample and a clean air sample by surface techniques. An auto exhaust sample was also analyzed by x-ray fluorescence spectroscopy. The differences observed by these two techniques are discussed. The biological samples, (i) fish scale and (ii) fish otolith from commercial fish, were also analyzed to demonstrate the possibility of using surface techniques to study biological samples. Since our group did not have the analytical instrumentation, samples were analyzed by 3M Company, Varian Associates and Physical Electronics, Inc. X-ray fluorescence analysis was provided by the Instrumentation Division of Brookhaven National Laboratory. Principles and details of bulk analysis are not discussed here and can be found in (1,2,3). Basic principles of surface techniques are included and references are provided for detailed description of instrumentation.

Basic Principles in Surface Analysis

A. Auger Electron Spectroscopy (AES): Auger Spectroscopy is an analytical technique used to identify the elemental composition of a sample surface. The electron beam incident on the surface of the material has a fixed energy, eg. 1.5 keV. These electrons have sufficient energy to knock out an electron from an inner shell of an atom, and resultant vacancy is immediately filled by an electron from an outer shell. The difference in energy can be released in the form of a photon or by knocking out another electron from an outer shell called the Auger electron. These electrons are then analyzed using a standard Auger spectrometer (4). Auger electron energies are characteristic of the element from which they originate. Thus, the Auger spectrum gives a qualitative analysis of elements present on the surface. The number of Auger electrons emitted is proportional to the number of atoms of the element present on the surface, thus, the intensity of Auger peaks provides quantitative measurements (5). The energy of Auger electrons are low so that only those electrons produced in the first few layers (5 - 20 Å) of sample can leave the surface. Thus, the method is sensitive only for the elements present on the surface. More recently, Varma, et al. (6) have modified the standard Auger spectrometer to improve the sensitivity of this technique. Figure 1 (a) shows schematically the process of Auger electron production. The Standard Auger spectrometer can detect elements in concentration of the order of 0.1 atomic percent, and can detect all elements above helium. No Auger transitions exist for hydrogen or helium.

B. Electron Spectroscopy for Chemical Analysis (ESCA): In this method, a monoenergetic beam of x-rays is used to bombard the sample surface. Absorption of these x-ray photons by the atoms of the sample results in the emission of electrons which originate from the inner or core shells. The energy of the incident x-ray photon is shared between the energy of the emitted electron and the binding energy of this electron in its orbital. The energy spectrum of emitted electrons is measured by a spectrometer (7). Since the atomic structure of each element is unique, the measurement of energy of the emitted electrons from one or two orbitals of each element is sufficient to identify the elemental composition of the sample. All the elements have electrons that can be detected in this manner except for hydrogen. Chemical bond information can also be obtained from analysis of peak shapes, multiline structure and shifts in energy of the ejected electrons in an ESCA spectrum.

Free electrons produced in a solid are scattered by bound electrons in the solid and thus lose part of their energy before leaving the solid. These electrons, although they reach the spectrometer, are counted as background. Only those photoelectrons generated in the first few monolayers of sample have sufficient probability to escape the sample with negligible loss of energy. Thus, this is also a surface technique which samples depths of the order of 5-20Å of the specimen. Exact sampling depth depends on the sample being analyzed. Detection sensitivity of this method is about the same as that for AES. A schematic of the ESCA process is given in Figure 1(b).

C. Secondary Ion Mass Spectrometry (SIMS): In this technique, a sample surface is bombarded by a monoenergetic ion beam. The ion beam has sufficient energy and intensity to sputter ions from the sample surface. These sputtered ions are also called secondary ions. These secondary ions are mass analyzed using a standard mass spectrometer. By choice of appropriate electronics, both positive and negative secondary ions can be mass analyzed. The sampling depth in this technique is of the order of a monolayer, however, the sampling depth depends on other parameters such as sputtering rate, etc. (8). A schematic representation of SIMS is shown in Figure 1(c). All elements and isotopes in the periodic table can be analyzed using this technique. The sensitivity of SIMS depends on the scan rate and sputtering rate and can vary by about three orders of magnitude showing a general decrease in sensitivity for heavy elements. For some elements, sensitivity of parts per billion or less have been achieved.

D. Ion Scattering Spectrometry (ISS): In this method, the sample surface is bombarded by monenergetic noble gas ions as was the case for SIMS. (As a matter of convenience, the same ion beam can be used for simultaneous analysis of SIMS and ISS). Some of the incident ions undergo binary elastic collision with atoms in the first monolayer of the sample and will be scattered from the surface. For a scattering angle of 90° classical collision theory gives a relationship between the mass M_1 of the atom on the surface, and energy E_1 of the scattered ion in terms of the incident ion mass M_o and its initial energy E_o,

$$E_1 = \frac{M_1 - M_o}{M_1 + M_o} E_o.$$

In normal ISS spectroscopy the ions scattered at 90° are energy analyzed and thus a spectrum of intensity versus energy of scattered ion is obtained. The spectrum can then be analyzed for various elements present on the surface. The sampling depth for ISS is a single monolayer, because incident ions that penetrate the monolayer have a high probability of being neutralized by the matrix. Thus, even though these ions may be scattered at 90°, they will not be detected by ISS since they are neutral ions. A schematic representation of the ISS process is given in Figure 1(d). Details about the method can be found in (9).

Experimental

Sample Preparation: Nickel substrates 6mm x 12mm and 0.8 mm thick were prepared from ultrapure nickel sheet. These substrates were cleaned first using Alconox and then rinsed in ordinary tap water. Final rinse was done using deionized distilled water. The nickel substrate was then attached near the tailpipe of a 1971 automobile. The exhaust was collected by direct impact of exhaust gases onto the substrate. The automobile was driven for approximately 20 miles. Regular leaded gasoline was used in the automobile. After exposure to exhaust fumes, the substrate was carefully removed from the tailpipe and the sample analyzed. This sample will be referred to as auto exhaust in further discussions. For x-ray fluorescence analysis a 35 second sample of exhaust gasses from a 1969 Volkswagen was collected by impingment on filter paper to avoid interference which would be contributed by the thick Ni substrate employed in the surface analysis techniques.

To check the effect of the presence of several elements in the sample on analysis, known quantities of various salts were deposited onto a clean nickel substrate. This sample is referred to as Laboratory prepared sample. Reagent grade LiCl (1.5 g), $Li_2 SO_4 \cdot H_2O$ (1.66 g) and $Pb (No_3)_2$ (3.22 g) were first dissolved in 100 ml of distilled water. From this assay, 5 microliters of solution was evaporated on the nickel substrate using an infrared lamp. The amounts of various materials present on the substrate were calculated to be Cl (.063 mg), SO_4 (.062 mg), NO_3 (.060 mg), Li (.021 mg) and Pb (.101 mg). Other impurities in this sample were Ca (100 ppm), Fe (15 ppm), Cu (2 ppm) and Na (10 ppm).

Clean nickel substrates were also exposed to outdoor environmental air at Brookhaven National Laboratory. This sample is referred to as clean air in further discussion. This sample was exposed at location P-9 (approximately 2.5 km from the central complex of research buildings in the northeasterly direction) where routine environmental monitoring samples are obtained. The exposure was for approximately 5½ hours from 9:00 a.m. to 2:30 p.m. on March 26, 1976.

Biological Samples: Two biological samples (i) fish scales from a dead fish (presumed to have died from copper contamination), and (ii) fish otolith from a commercial fish, were prepared by the Biology Department of Brookhaven National

Laboratory. No cleaning, except for rinsing with tap water, was done on these samples.

Auto exhaust, laboratory prepared and clean air samples were analyzed by SIMS (both positive and negative), ISS, AES and x-ray fluorescence spectroscopy. SIMS and ISS were done by 3M Company, AES by Varian Associates using commercially available equipment. X-ray fluorescence spectroscopy was done by the Instrumentation Division of Brookhaven National Laboratory using a low power, high sensitivity laboratory-developed system. The biological samples were analyzed by AES, ESCA and x-ray fluorescence. AES and ESCA were performed by Physical Electronics Industries, Inc., and Varian Associates using commercially available systems. No SIMS or ISS was performed on these samples.

Results and Discussion

A. Auto Exhaust: Figures 2 and 3 show spectrum obtained by positive SIMS and negative SIMS, respectively. Mass-range scanned was from 1-100 atomic mass units. Figure 4 and 5 show ISS spectra. For figure 4, the incident beam was 2 keV neon ions and for figure 5 it was 1 keV $^3He^+$. Figure 6 shows an Auger spectrum for this sample. X-ray fluorescence analyses results for the Volkswagon auto exhaust sample and a blank filter paper are shown in figures 7 and 8 respectively. From figure 2, which shows positive SIMS results, one can clearly see the variety of elements present in auto exhaust fumes (e.g., Li, B, Na, Ag, Al, Si, Cl, K, Ca, Ti, Fe, Ni, Cu, Zn, etc.). From the negative SIMS analysis shown on figure 3, other elements such as O,F,S and Br can be identified. Note that in this spectrum (fig. 3) two isotopes of chlorine and bromine were clearly identified. Some of the elements, such as Ti, may have been present due to impurities present in the nickel substrate.

ISS results are shown on figures 4 and 5. Here heavy elements such as Br and Pb are apparent. Figure 4 shows variation in concentration of bromine and lead in this sample as a function of depth. One can clearly see that concentration of bromine and lead reach a constant level after the first few angstroms of the surface has been removed by sputtering. In the ISS analysis with low mass $^3He^+$ions, as shown in figure 5, other elements such as Cl, S, O, C, etc., can be identified. The AES spectrum from the sample (figure 6) shows the presence of elements like S, Cl, C, O, etc., but surprisingly does not show any lead or bromine. This could have been due to mishandling of the sample during shipment or sample preparation. The x-ray fluorescence spectrum of the Volkswagon exhaust sample (Figure 7) reveals the presence of Pb, Br, Cu, Zn, Fe and probably Se. Of these, Fe, Cu and Zn are also present on the blank filter paper (Figure 8) though probably in smaller quantities, especially for Fe. Thus, this technique readily detected Br, Pb and Fe, but not some of the lighter elements (Li, B, Na, Al, K, Cl, C, O and S) detected by surface techniques. (Some of these latter elements may be contributed by the Ni substrate used for the surface technique samples).

B. Laboratory Prepared Sample: Figure 9 shows a positive SIMS spectrum of the laboratory prepared sample at low and high sensitivity. In this spectrum, Li, B, Li_2, Ne, Na, Mg, Al, Li_2O, Li_2OH, K, Ca, Fe, Ni, Cu were detected. The mass scan was from 1-100 atomic mass units, thus heavy elements like lead, etc., are not seen in the spectrum. Figure 10 shows negative SIMS for the same sample, in this case elements C, CH, O, OH, F, C_2 H_2. S and Cl were observed. Figure 11 is a depth profile of this sample over approximately 1000Å and shows concentration variation of three elements O, Cl and C. Figure 12 shows an ISS spectrum with the incident ion being $^3He^+$. In this spectrum elements C, O, S, Cl, Ni, and Pb were observed. Figure 13 shows an AES spectrum of this sample and shows the presence of Ni, Pb, S, Cl, and O. A comparison of SIMS, ISS, and AES suggests that SIMS identified all the elements that were present on the sample including the impurities, ISS and AES detected some of the elements. Thus, SIMS appears to be a more sensitive technique than ISS or AES.

C. Clean Air Sample: Figure 14 and 15 show ISS spectra from the clean air sample when Ne and $^3He^+$ incident ions were used, respectively. One surprising finding was the presence of bromine in this sample. Figure 16 shows the AES spectrum for this sample. No bromine was detected in this spectrum.

D. Biological Samples: The fish scale and otolith samples were analyzed by AES, ESCA, and x-ray fluorescence. AES was difficult to perform due to charging of the sample surface by the incident electron beam, especially for fish scales. The qualitative results obtained using AES and ESCA showed the presence of calcium and oxygen in otolith and mostly silicon in fish scales. An in-depth analysis of the otolith sample showed a calcium to oxygen ratio, which generally increased with depth. No other heavy elements were detected. X-ray fluorescence detected only Ca in otolith and Si in fish scales.

Conclusions

It thus appears from these analyses that, for the environmental samples, SIMS has higher sensitivity than AES or ISS. But SIMS does not identify chemical composition, thus AES or ESCA in tandem with SIMS might be an excellent analytical technique. However, with AES, charging of the sample surface can be a problem since electrons are used as the excitation source. Also, the electron beam is somewhat damaging to biological surfaces. Thus, for biological samples, we feel ESCA which uses low energy x-rays as the excitation source is preferable to AES.

Applications of Surface Analysis Techniques

The basic difference between surface and bulk techniques is the ability to analyze, with the surface techniques, elemental composition present on the surface, i.e., the first few monolayers of the sample. By suitable sputtering techniques, known amounts of sample surface can be removed, thus depth profiling is possible. This depth profiling has an advantage in that pollution deposited as a function of time can be studied. If the pollutants have a tendency to segregate to the surface, or surface concentration is higher than bulk, then surface analysis is apt to give results more closely related to biological hazard for low solubility particles. It has been shown by Linton, et al. (10) that, for small particles (such as fly ash from coal burning), the surface concentration of toxic trace elements can be much greater than the concentration determined by bulk analysis.

Sensitivities as high as one part per trillion can be achieved by surface techniques if the impurities can be concentrated on the surface. For example, there are about 10^{15} atoms per square centimeter on a surface. Analyzing one square centimeter of the surface at sensitivity of 100 parts per million, one can detect 10^{12} atoms. If we can scavenge these 10^{12} atoms from 100 ml of solution, we can achieve a bulk sensitivity of about one part per trillion for most metals. The problem of scavenging and depositing 10^{12} atoms on the surface is not an easy one, however, Hercules' (11) recent technique employing chelating agents shows great potential in this regard. This procedure is not required for those samples in which impurities are already present on the surface.

Identification of chemical forms of these elements in pollution samples can shed some light on the concentration of those compounds which are more biologically reactive. This, for example, will include identification of various oxides, nitrides or carbides. The chemical composition information is lost when wet chemical analysis or bulk analysis is performed on these samples.

Surface chemical reaction rates can also be studied with these techniques, to determine production or decrease in various chemical compounds as a function of concentration of environmental insults.

These techniques are also capable of providing valuable information on marine samples. For example, transfer of pollutants from fly ash or other objects to the marine waters and sediments.

The measurement of trace element concentrations in biological samples (like hair, nails, teeth, etc.) as a function of distance along the growth direction can provide a measure of the body's uptake of heavy metals or other chemical constituents as a function of time. Historical and baseline data can be obtained from museum pieces, stones and other antiques and can be correlated to environmental insults, epidemiological data and medical data, for application in health effects studies.

Acknowledgment

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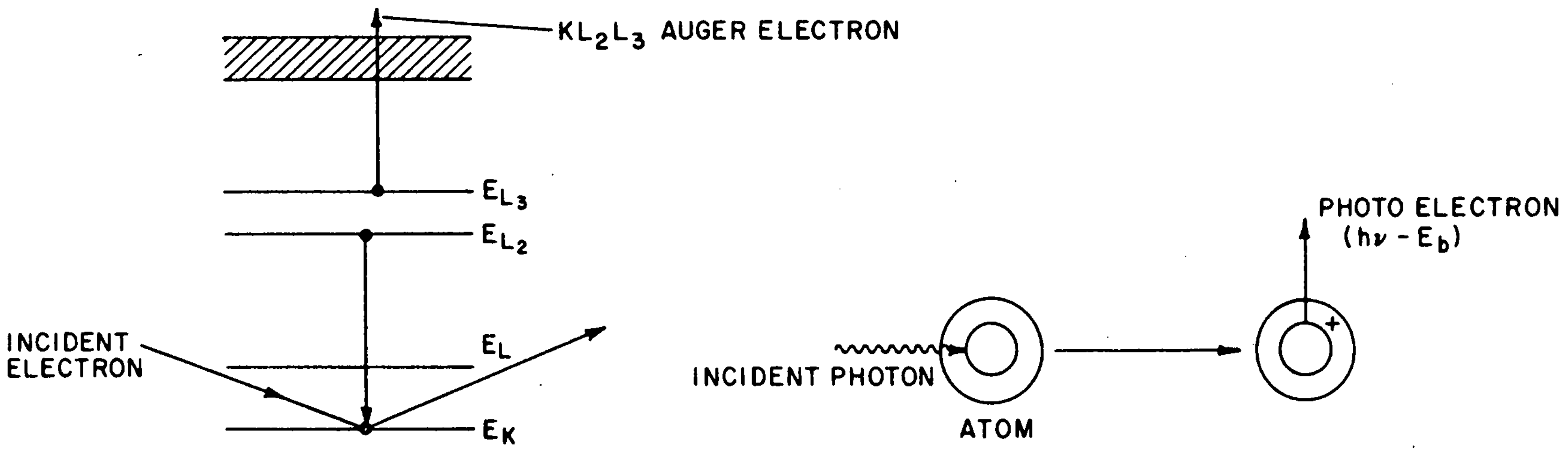
TABLE - 1

Comparison of Various Properties of Surface and Bulk Analysis Techniques

Techniques	Minimum Detection (gm)	Chemical Information	Depth Analysis	Elements Detected	Destructive (D) Nondestructive (ND)	Surface (S) Bulk (B)	Temperature Dependence
Atomic Absorbtion	$10^{-8} - 10^{-10}$	None	No	All, except rare gases, C,H,O,N,S,P and Halogens	D	B	Small
Atomic Emission	$10^{-8} - 10^{-10}$	None	No	Same as above	D	B	Extreme
X-ray Fluorescence	$10^{-7} - 10^{-12}$	None	No	$Z > 12$	ND	B	None
Auger Spectroscopy	$10^{-12} - 10^{-13}$	Some	Yes	$Z > 2$	ND-maybe	S	None
ESCA	$10^{-12} - 10^{-13}$	Moderate	Yes	$Z > 1$	ND	S	None
ISS	$10^{-12} - 10^{-13}$	Some	Yes	Except H, He	ND	S	None
SIMS	$10^{-9} - 10^{-14}$	None	Yes	All	D	S	None
Chemical	10^{-9}	None	No	All	D	B	None
Gas Chromatography	$10^{-9} - 10^{-12}$	None	No	Organic Compounds	D	B	Extreme
Neutron Activation	$10^{-6} - 10^{-13}$	None	No	Many	ND	B	None

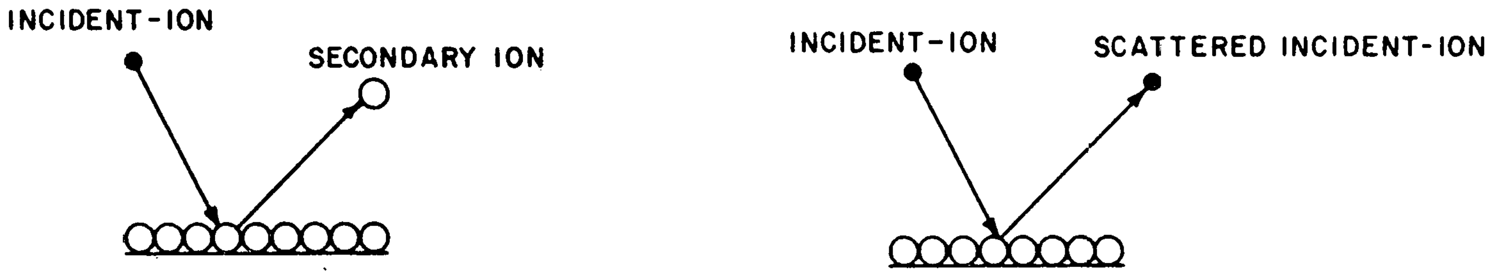


(a)

Schematic representation of Auger process.

(b)

Schematic representation of ESEA process.



(c)

Schematic representation of SIMS process.

(d)

Schematic representation of ISS process.

Figure 1

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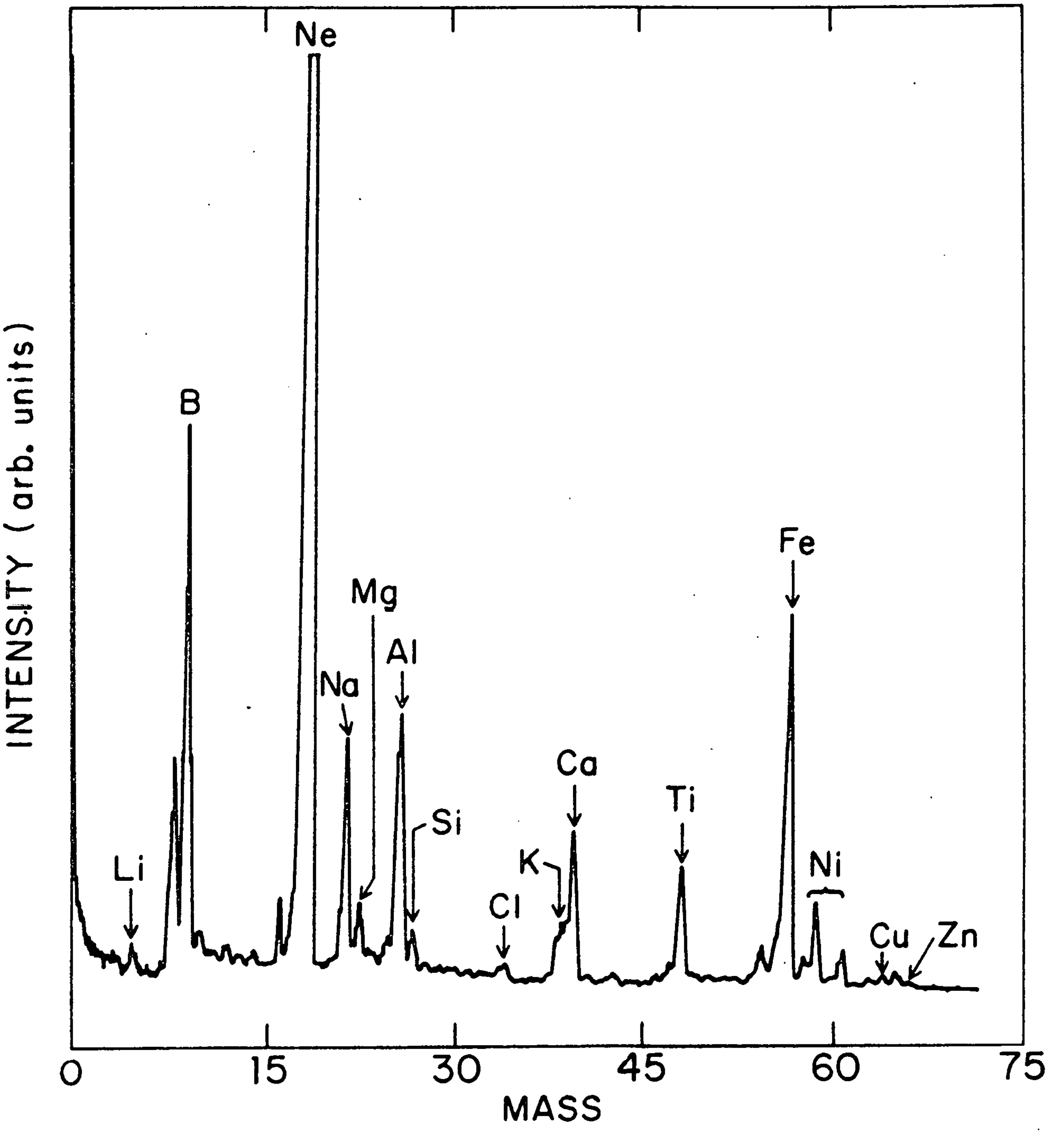

Figure 2. Positive SIMS spectrum of auto exhaust sample.

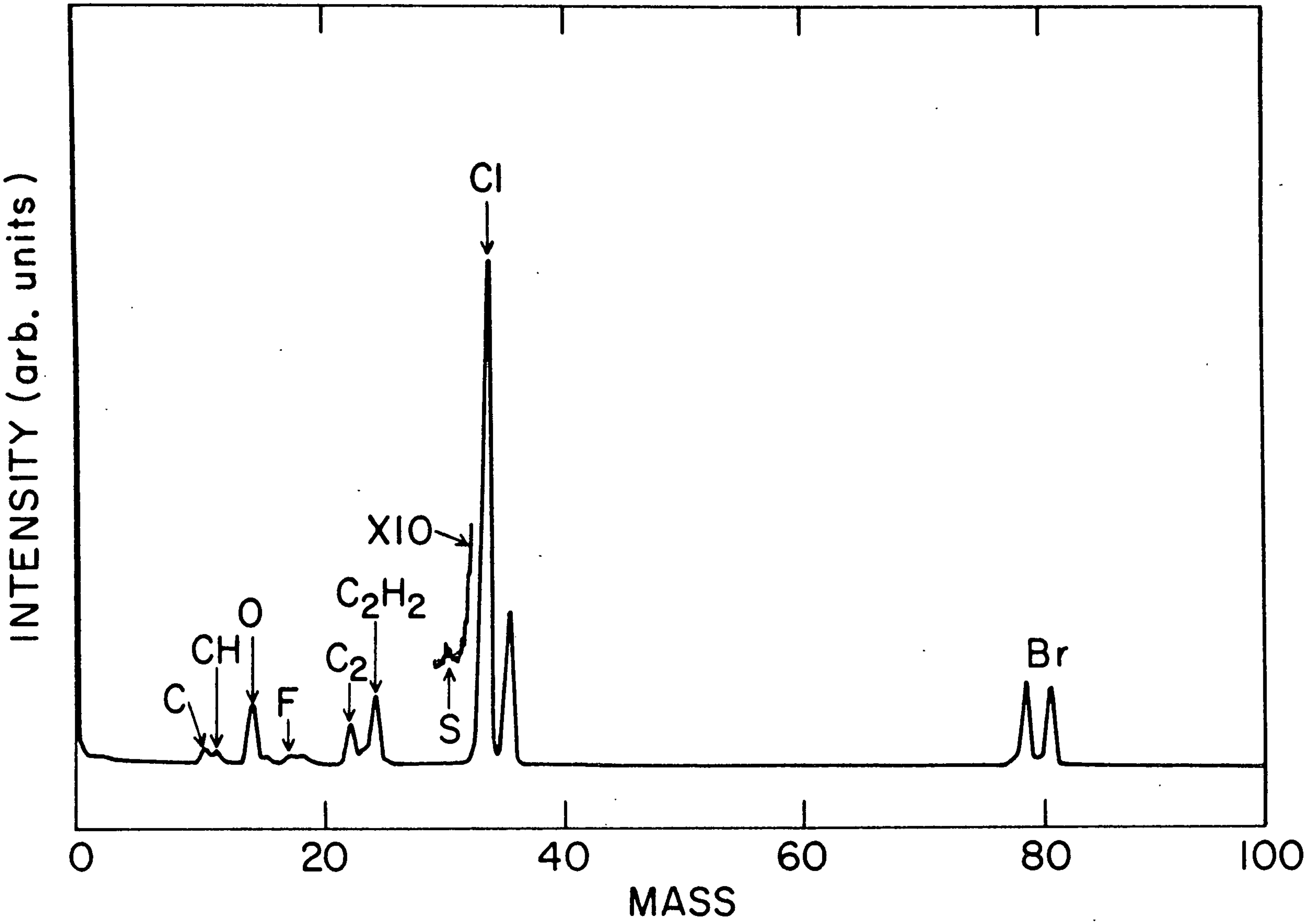

Figure 3. Negative SIMS spectrum of auto exhaust sample.

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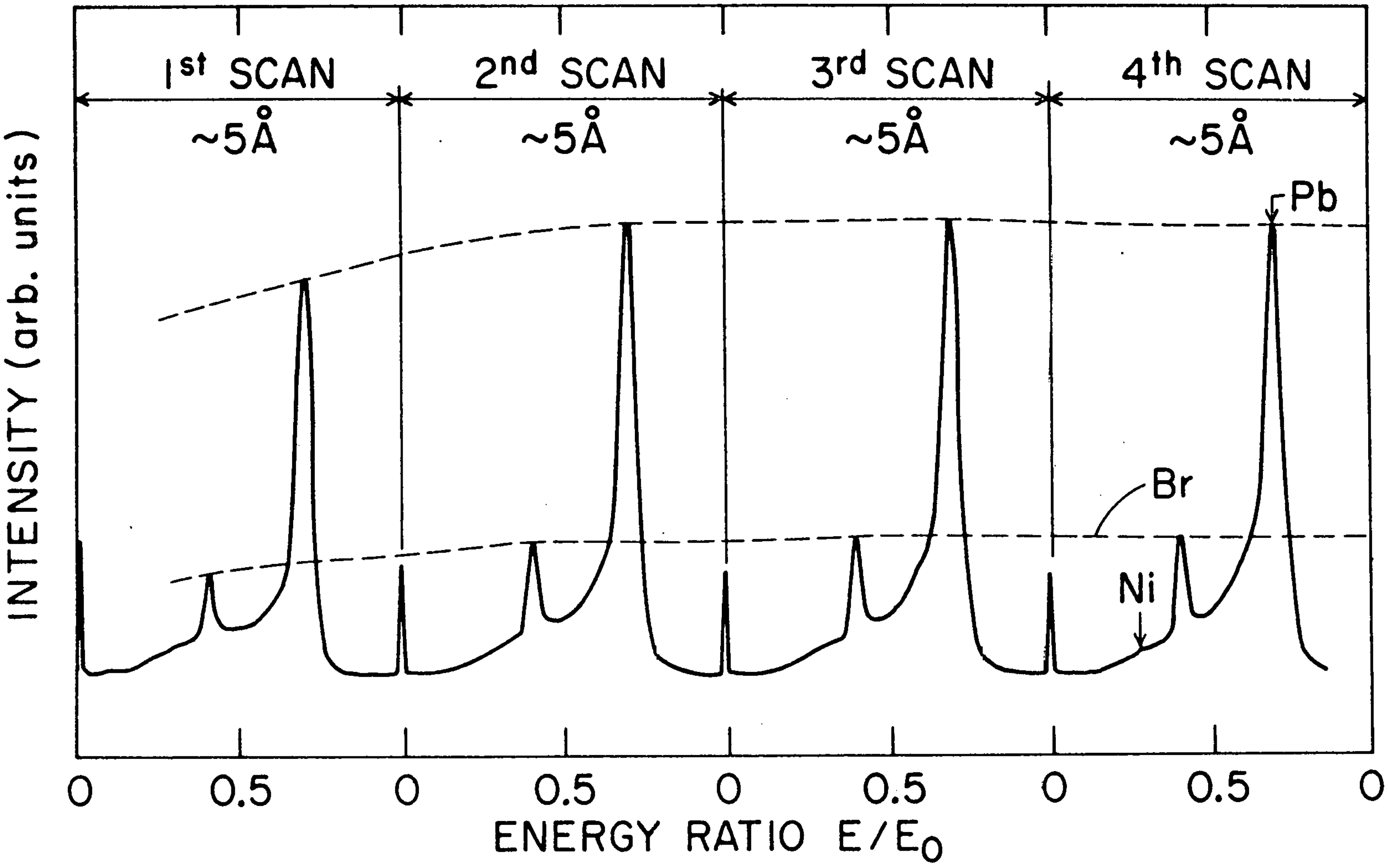

Figure 4. ISS spectra of auto exhaust sample for incident beam of 2 keV neon ions.

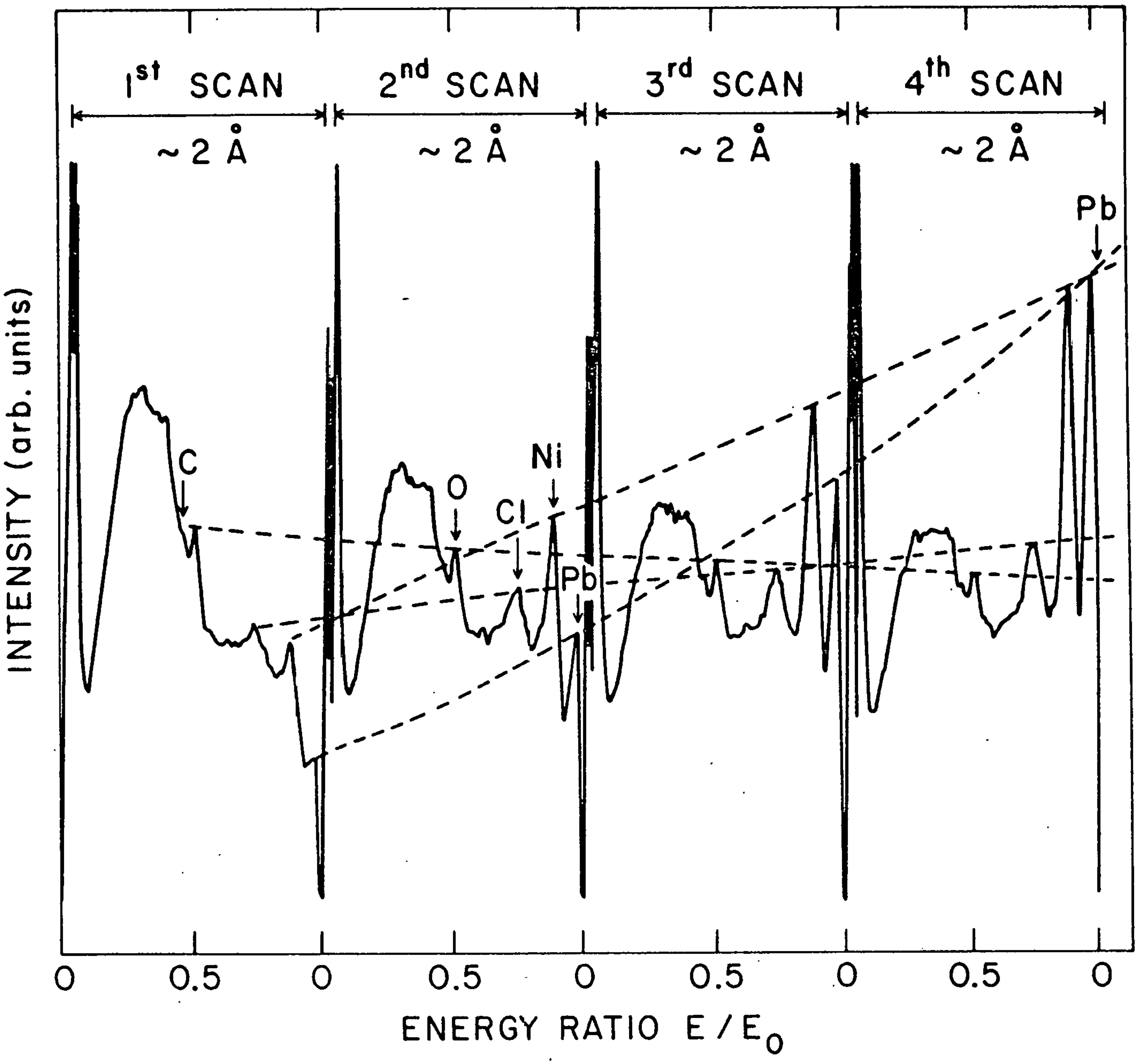

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Figure 5. ISS spectra of auto exhaust sample for incident beam of 1 keV $^3He^+$ ions.

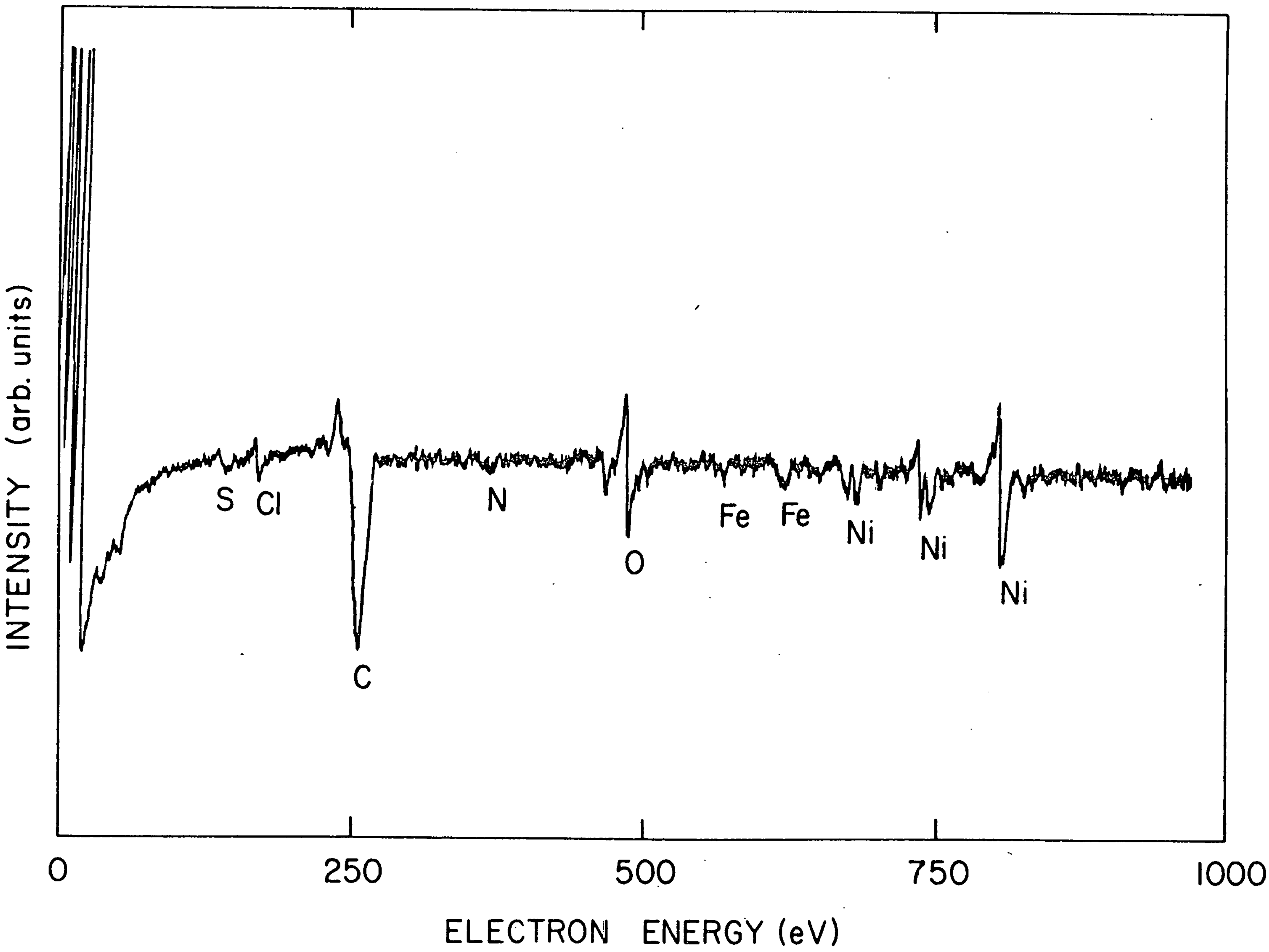

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Figure 6. Auger spectrum of auto exhaust sample.

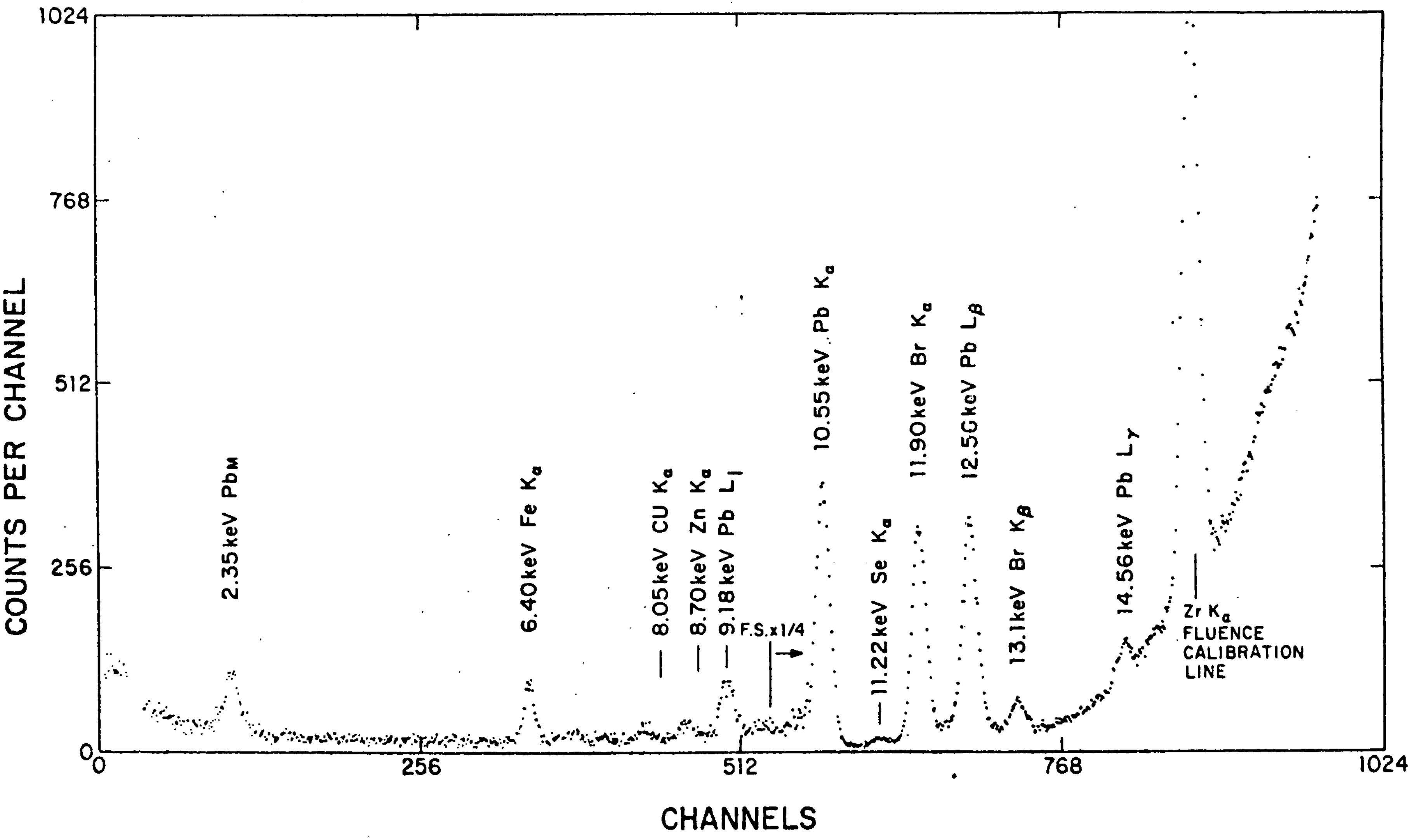

Figure 7. X-ray fluorescence spectrum of auto exhaust sample.

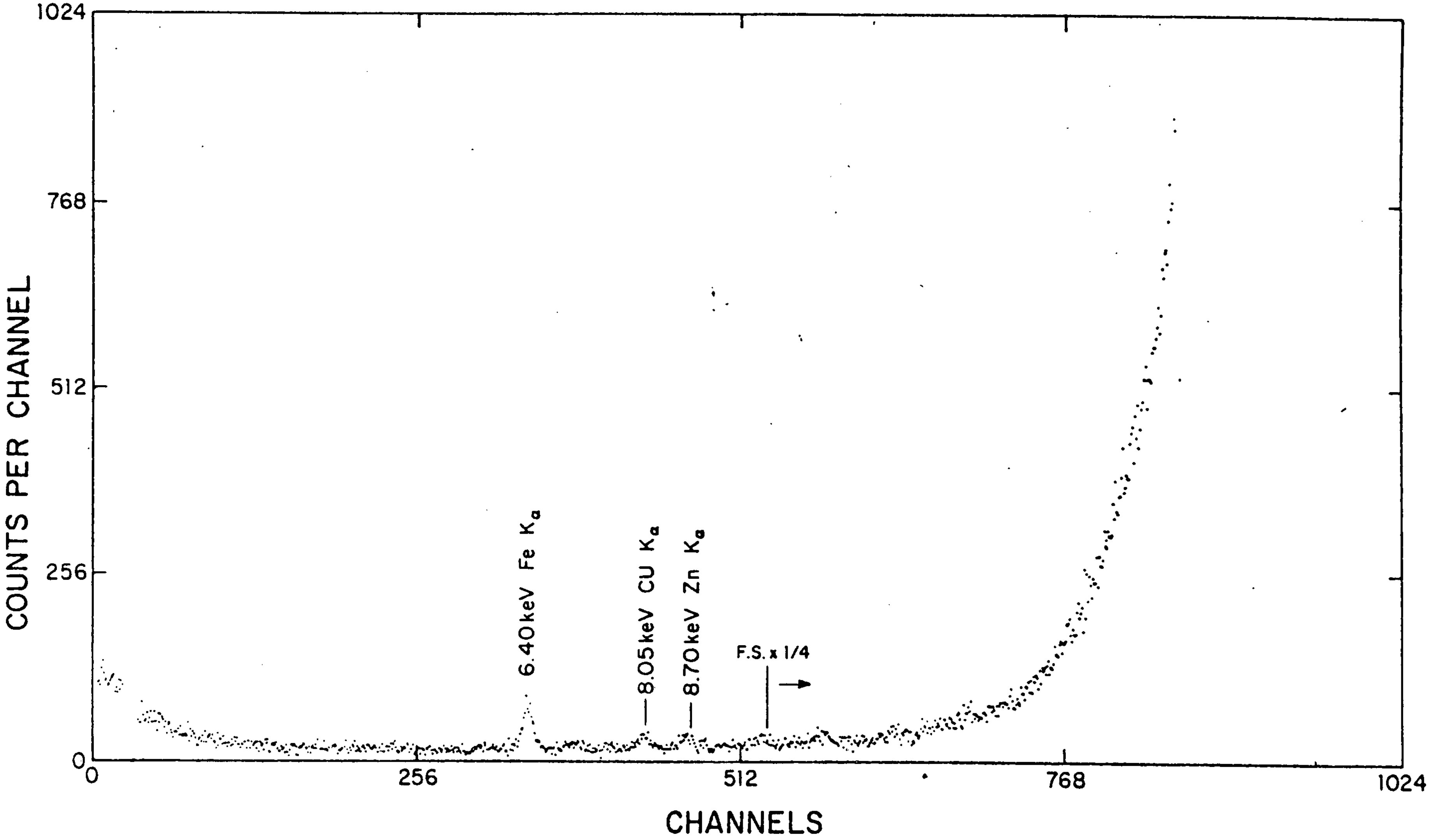

Figure 8. X-ray fluoresence spectrum of blank filter paper.

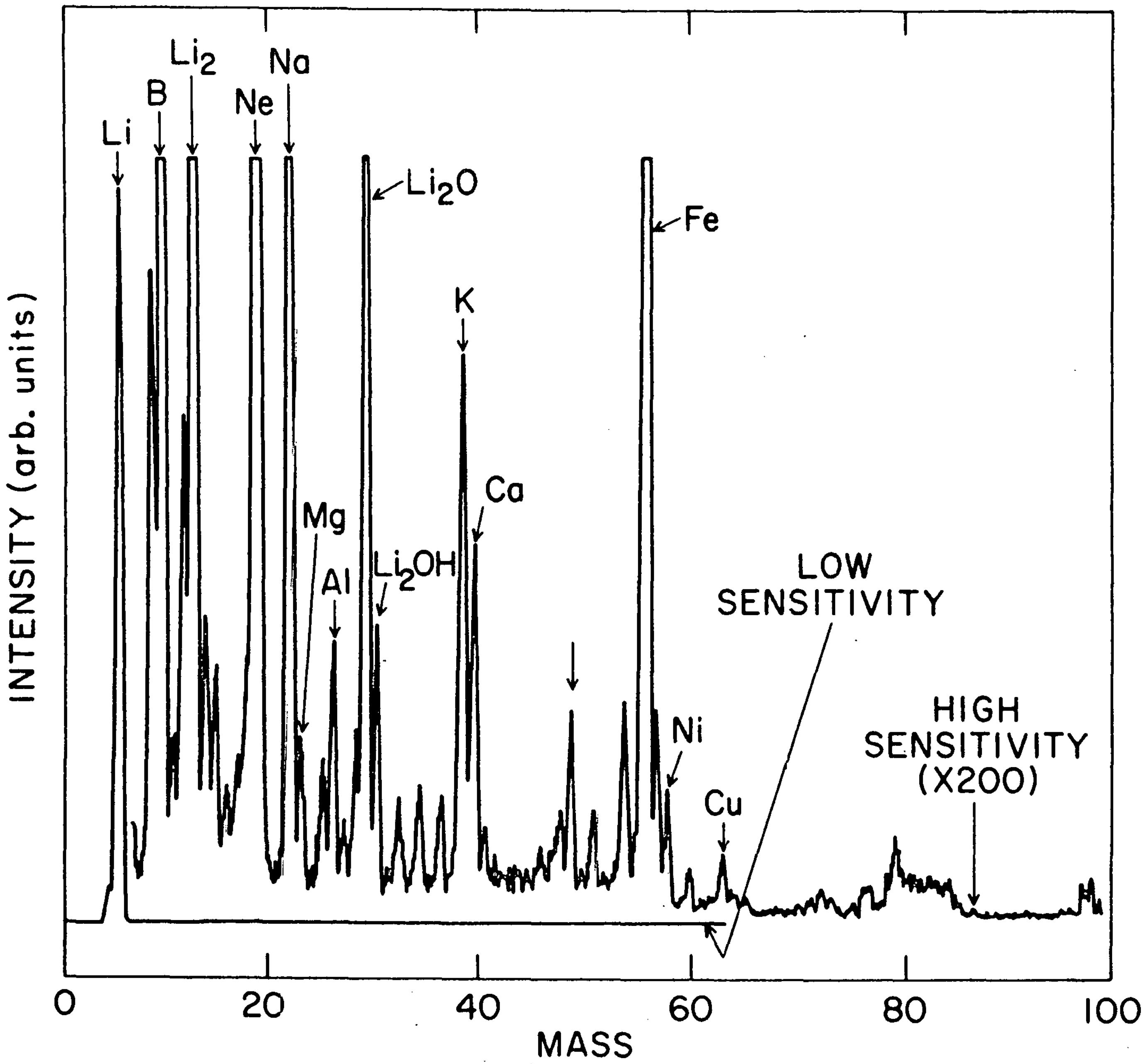

Figure 9. Positive SIMS spectrum of laboratory prepared sample (both at high and low sensitivity).

3-1088-77

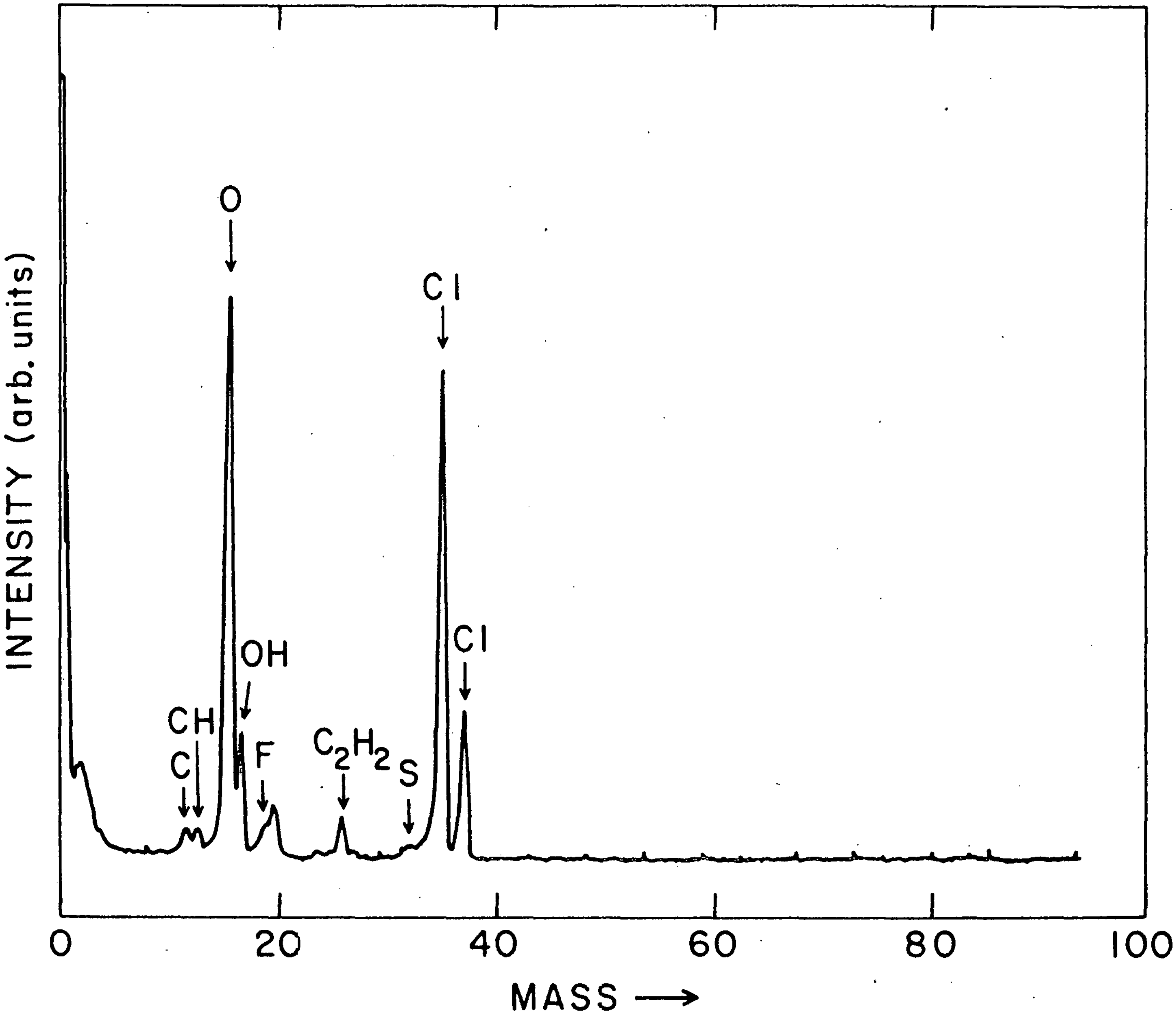

Figure 10. Negative SIMS spectrum of laboratory prepared sample.

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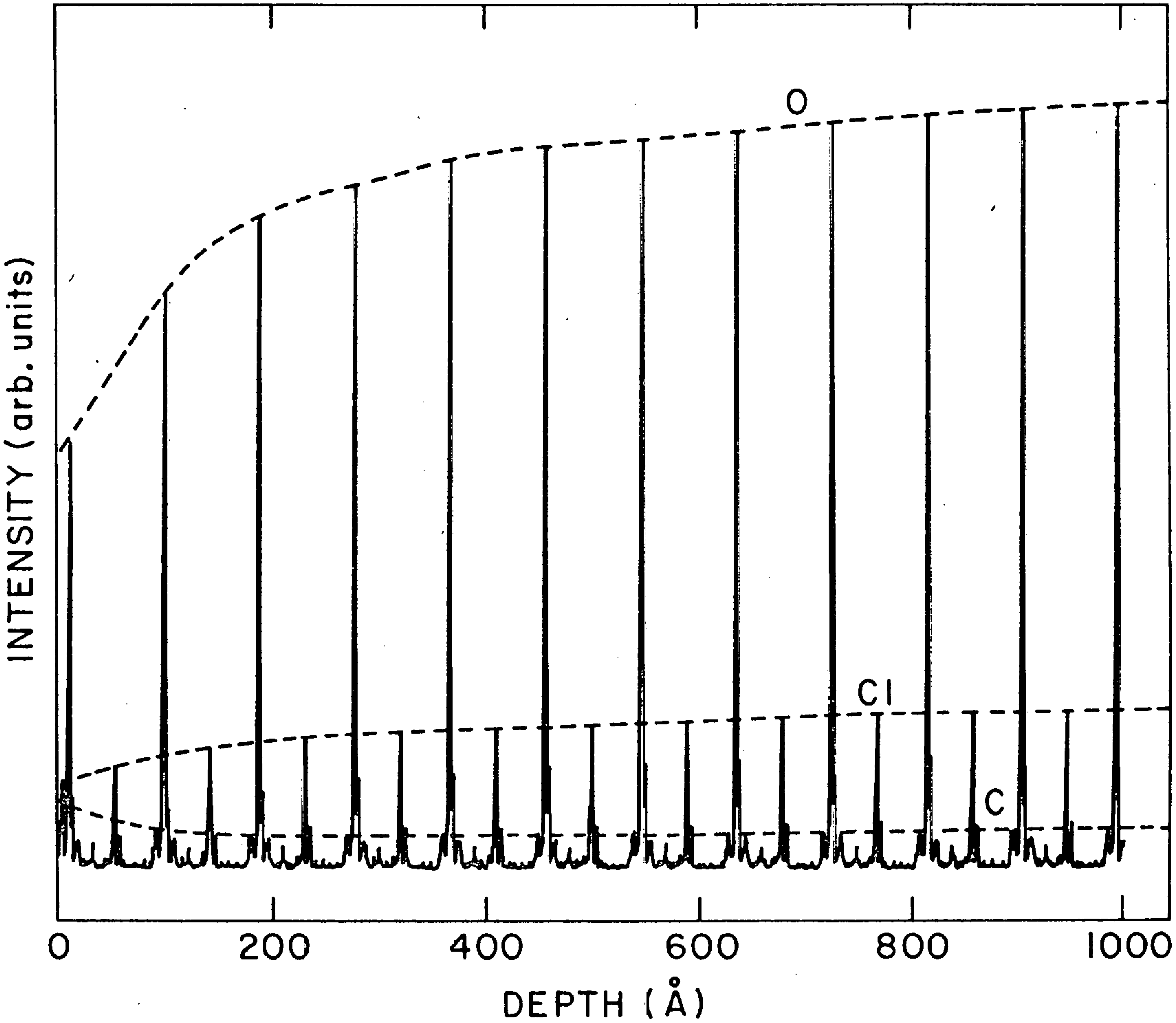

Figure 11. SIMS spectrum of laboratory prepared sample showing a depth analysis from 0 - 1000Å.

3-1084-77

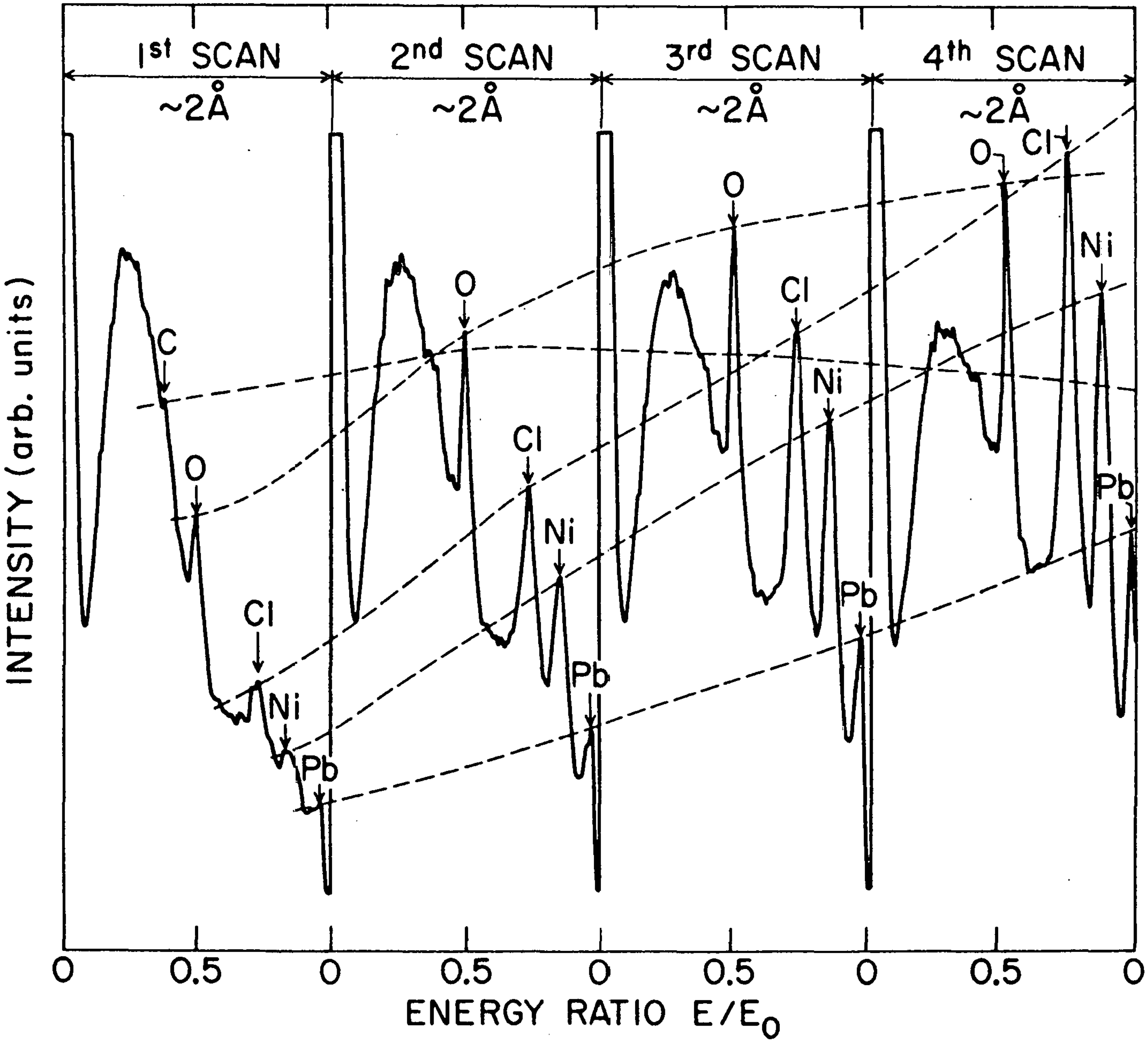

Figure 12. ISS spectrum of laboratory prepared sample for incident beam of $^3He^+$.

3-945-77

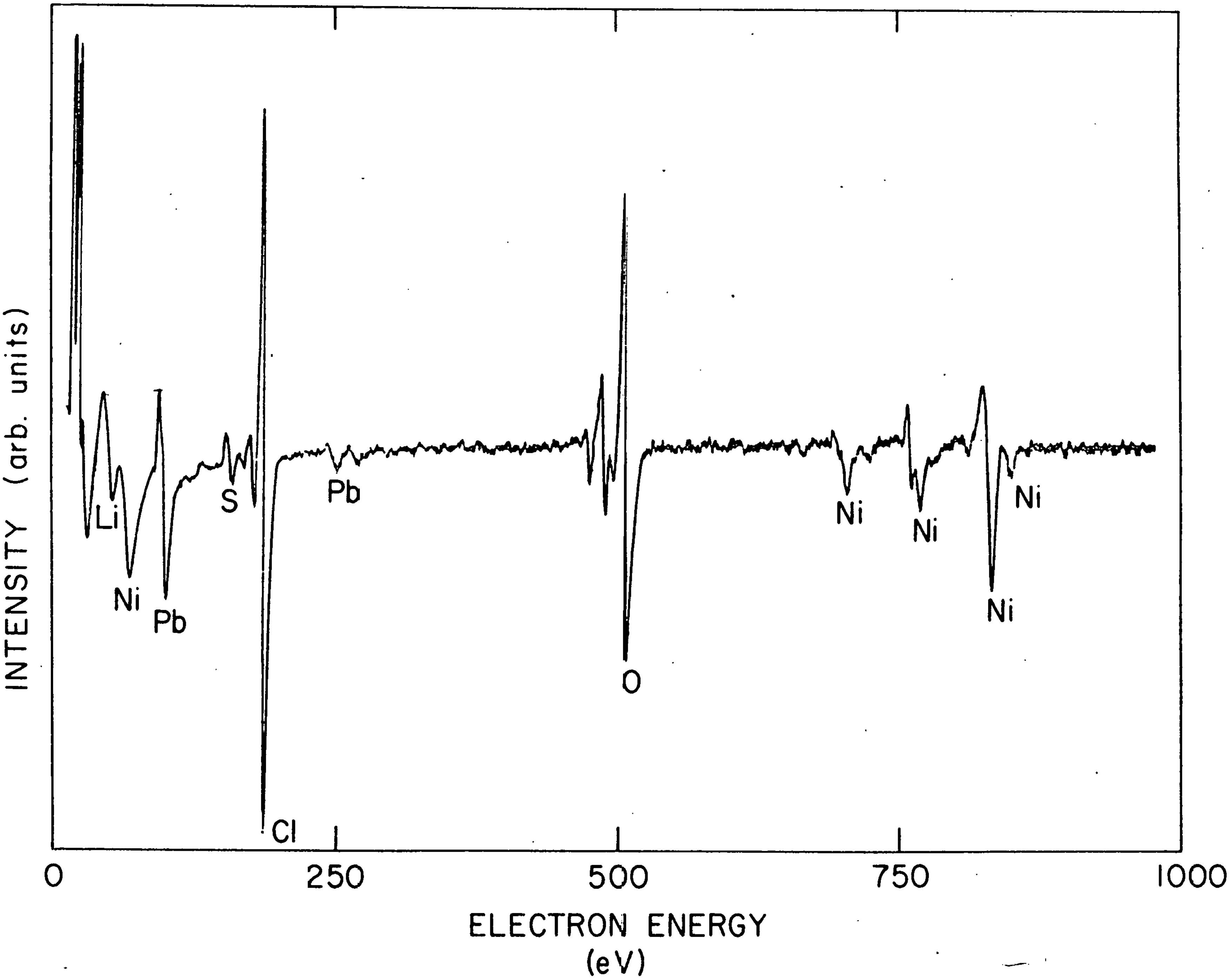

Figure 13. Auger spectrum of laboratory prepared sample.

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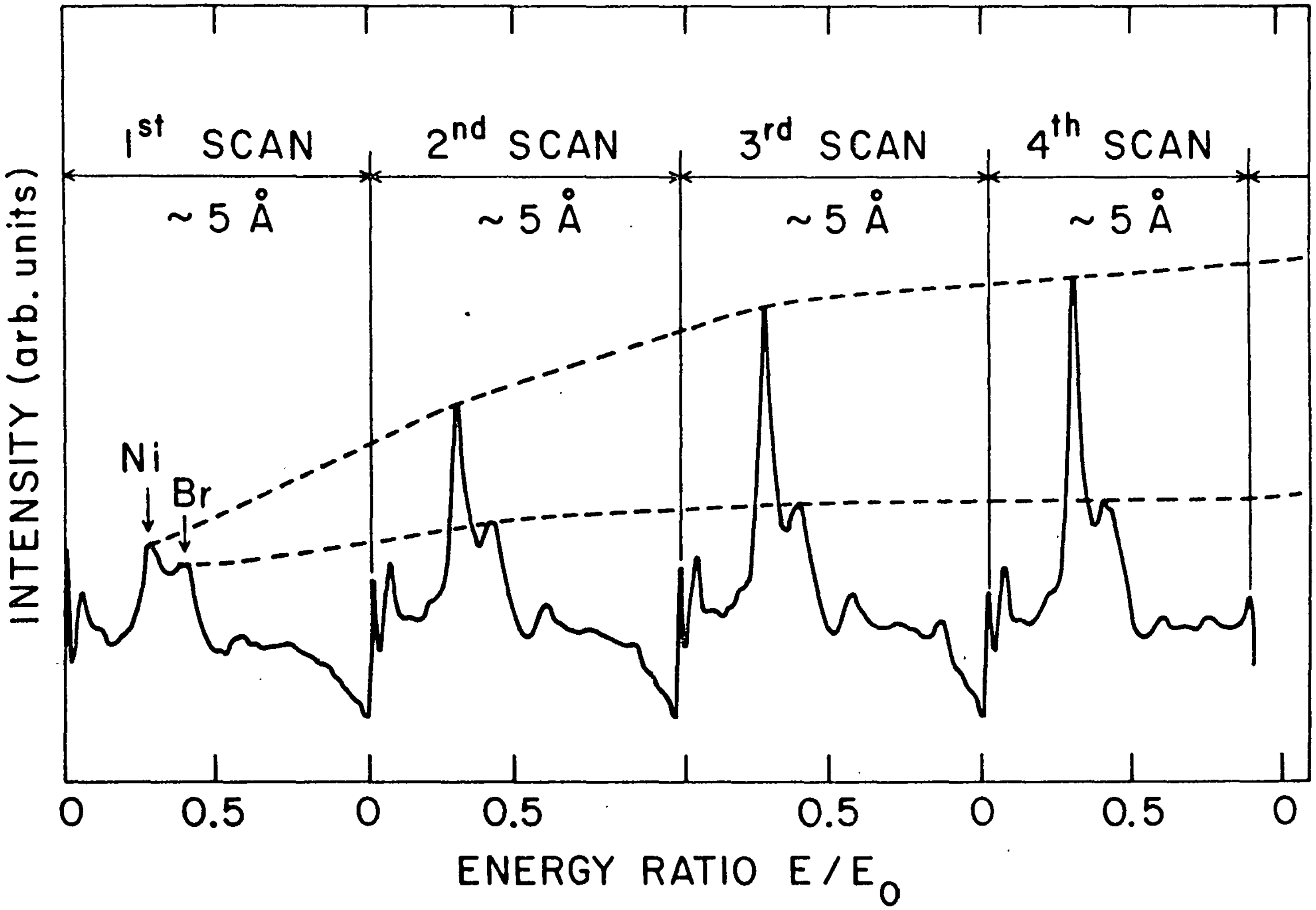

Figure 14. ISS spectra of the clean air sample for incident beam of neon ions.

3-1085-77

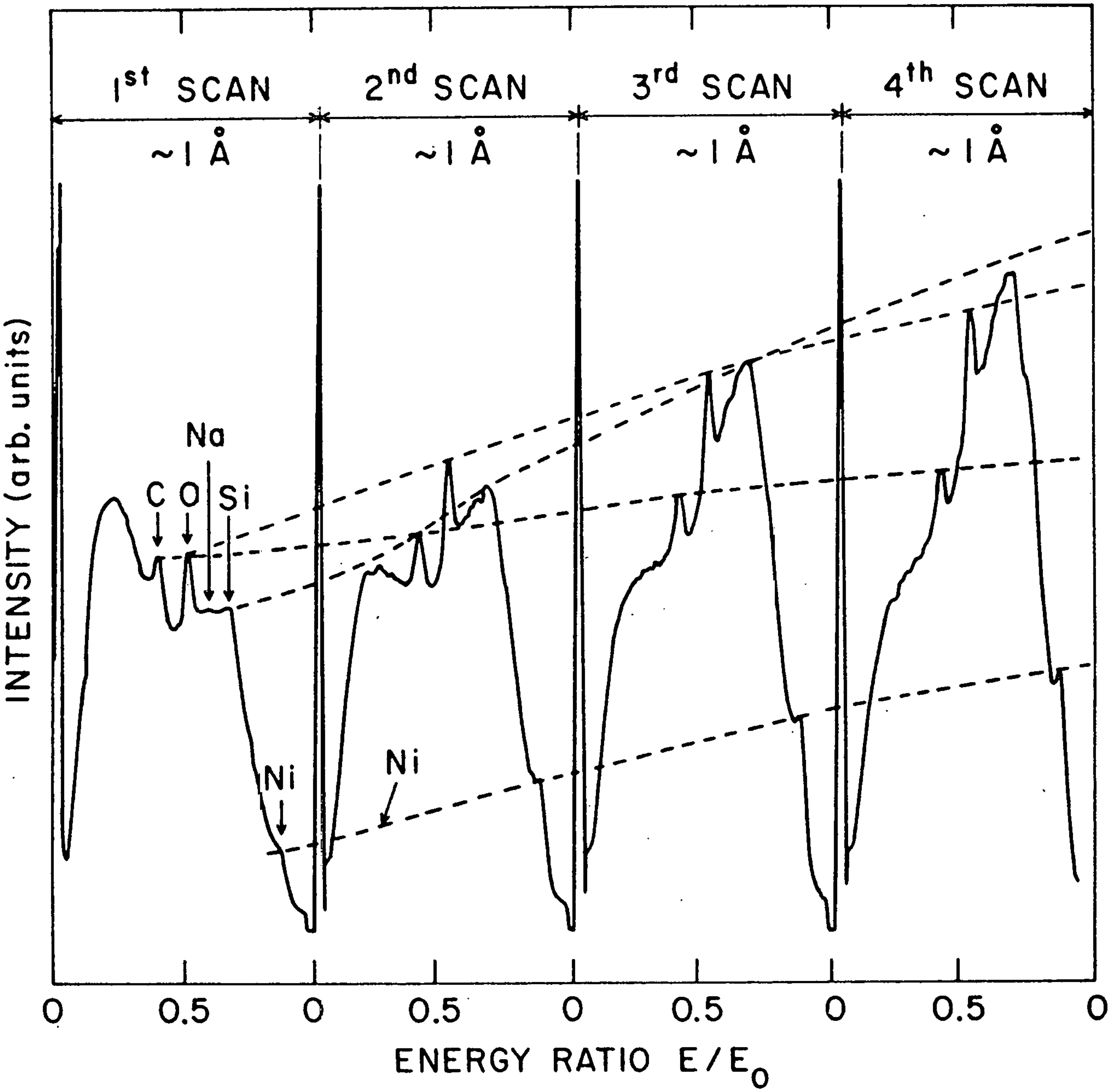

Figure 15. ISS spectra of the clean air sample for incident beam of $^{3}He^{+}$ ions.

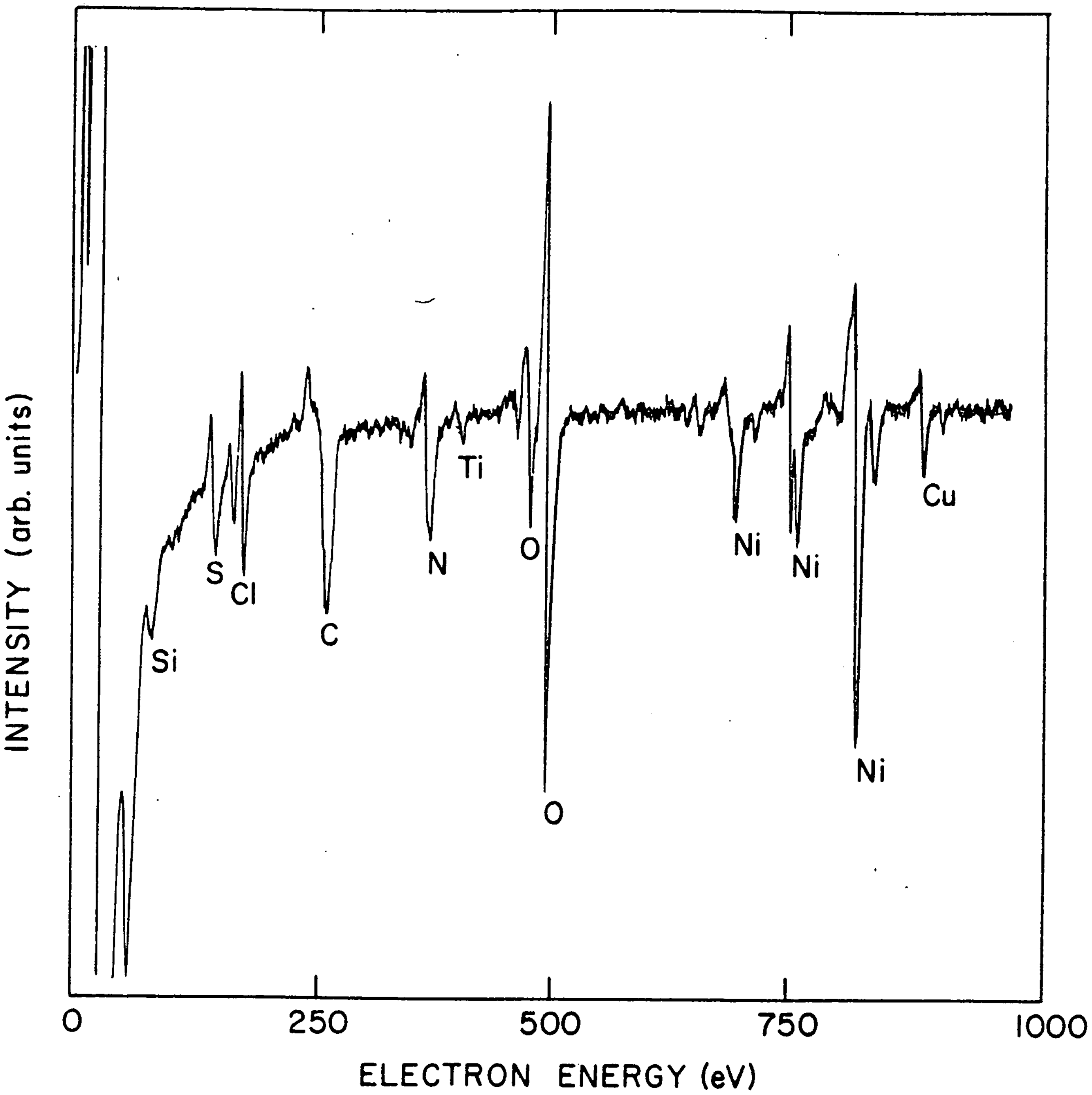

Figure 16. Auger spectrum of clean air sample.