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SIMS Analysis: Development and Evaluation 1995 Summary Report

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ABSTRACT

Secondary ion mass spectrometry (SIMS) was evaluated for applicability to the characterization of mercury (Hg) salts. It was found that sulfate and chloride species could be identified directly without sample preparation. Mercuric oxide could be identified by means of an apparently specific complexation reaction with formic acid. Mercury nitrate species could be identified by means of a complexation reaction with cyclohexylamine (CHA). Laser desorption ion trap mass spectrometry was evaluated for the ability to characterize ethylenediaminetetraacetic acid (EDTA) on environmental samples. No intact EDTA ions were observed, but a series of EDTA fragment ions were visible, and these could be readily detected on basalt and soil samples. Development of an ion trap SIMS instrument was completed: a perrhenate ion gun was interfaced to a Teledyne ion trap spectrometer, and the entire device was mounted on a cart. The technology was demonstrated using a prototype ion trap SIMS instrument for the detection of the Hg•CHA complexes formed from nitrate salts. The intensity of the perrhenate primary ion gun was improved, and the surface damage of the particle was shown to be small: these advances have led to serious consideration of ion gun technology transfer to Phi-Evans, Inc. Technology end users were identified at two sites at the Idaho National Engineering Laboratory: the Central Facilities Area 674 pond, and the acid pit of the Radioactive Waste Management Complex. The target problem at both sites is the need for Hg speciation on soil samples.

SUMMARY

New secondary ion mass spectrometry (SIMS) technology was evaluated for the identification and speciation of mercury, which is present at waste sites at the Idaho National Engineering Laboratory (INEL) and other DOE sites. Mercury (Hg) speciation was identified as a significant issue at the Central Facilities Area 674 pond, and at the acid pit of the Radioactive Waste Management Complex (both sites located at the INEL). The need for Hg speciation information is relevant in the context of environmental mobility. Mobile species have the potential to contaminate large areas of underground aquifers, and hence require remediative action. On the other hand, immobile species may pose no threat. In the present case, Hg speciation is significant because if the Hg is present in mobile forms such as chloride or nitrate species, then costly exhumation will be required. However, if Hg is present as immobile forms such as the oxide, then it is possible that no action need be taken.

These considerations motivated the investigation of Hg speciation using new SIMS instrumentation under development at the INEL. The technology has the advantages of being rapid (10 minutes or less), requiring no sample preparation, generating no laboratory waste, having capability for analysis of low- or non-volatile organic contaminants on surfaces, and is potentially transportable. In addition, SIMS has the capability for analyzing a variety of sample surfaces, including salts, rocks, soil and waste samples encountered at the INEL, Hanford, and other sites.

A variety of Hg salts were analyzed to establish fingerprints for the most significant Hg species anticipated. Generally, it was found that observation of Hg was difficult using static SIMS: no evidence for Hg could be found in the analyses of HgI_2, $HgNO_3$, $Hg(NO_3)_2$, $Hg(SCN)_2$, HgO, or HgS. However, in the case of Hg_2Cl_2, $HgCl_2$, and $HgSO_4$, Hg-bearing ions could be observed. In the case of the chloride compounds, $HgCl_3^-$ could be readily observed. In the case of the sulfate, $^-OHgSO_4$ and $^-OHgSO_4H$ could be observed.

Surface complexation reactions were developed for HgO and the Hg nitrate salts. When HgO was exposed to gaseous HCO_2H, a complex corresponding to $HgHCO_2^-$ was observed. It was noted that if the Hg(II) oxidation state is preserved, then Hg(II) must be inserting into either the C-H, or the C-O bond of the formate.

Hg•cyclohexylamine complexes could be observed starting from the Hg nitrate salts, and exposing them to cyclohexylamine. The identity of the complexes corresponded to $(C_6H_{11}NH)\text{-}Hg\text{-}(H_2N^+\text{-}C_6H_{11})$. Together with the nitrate observed in the anion SIMS spectrum, this complex provides evidence for the presence of Hg nitrate species.

The next step in the Hg speciation research is to apply the methods to the identification of Hg species on soil samples. This will be the focus of further effort in FY96, using INEL internal research funding.

Ethylenediaminetetraacetic acid (EDTA) is another analyte that is of significance to DOE, and is difficult to analyze for. The compound is a chelating agent which found widespread use in the DOE complex. In the environment, EDTA will chelate with uranium and other radioactive elements; the chelated elements will not sorb to mineral surfaces, and thus have a great mobility in the environment. EDTA is difficult to analyze for because it is extremely hydrophilic, and can exist in seven different forms *independent of complexation with a metal.*

When a metal is present, EDTA had previously been the subject of investigation, for the purpose of assessing applicability of SIMS for detection. While a fragment ion signature could be recorded using SIMS, the detection limits were high, and hence it was concluded that SIMS was not an optimal technique for this analysis.

It was felt that laser desorption might succeed in desorbing EDTA where SIMS had been unsuccessful. For this reason, a research project was undertaken by Dr. Luke Hanley of the University of Illinois-Chicago, to determine if laser desorption ion trap mass spectrometry could be used to desorb and detect EDTA. It was found that while no intact molecular ions could be observed, a rich fragment ion signature was easily recorded. While this result was similar to that obtained using SIMS, the detection limits using the laser desorption ion trap mass spectrometer were substantially lower (200 picomoles) than in previous experiments conducted using the quadrupole SIMS instrument.

Another objective of the SIMS development project was to develop an ion trap SIMS instrument, because it was felt that this type of instrument would be inherently small, robust, and have enhanced analytical power derived from selected ion storage and mass spectrometry/mass spectrometry (MS/MS) capabilities of the ion trap. In late FY94, procurement was initiated for a Teledyne ion trap, and this unit was received toward the end of November, 1994. Work immediately began to modify the ion trap so that it would accommodate a direct insertion probe and a primary ion gun. These modifications were completed in FY95. Testing of the instrument was also initiated. Demonstration of the capability of the ion trap SIMS instrument was accomplished using a prototype instrument, using the Hg nitrate - cyclohexylamine system. Specifically, formation and selected ion storage of the $(C_6H_{11}NH)\text{-}Hg\text{-}(H_2N^+\text{-}C_6H_{11})$ complexes, followed by MS/MS to form product ions, was demonstrated.

In order for SIMS to effectively impact chemical characterization, commercial vendors will be required to supply and service SIMS technology. For this reason, transfer of SIMS technology has been an important aspect of the SIMS Demonstration Program. Licensing of data acquisition and instrument control software to Extrel (Pittsburgh, PA), was accomplished in FY94. Technology transfer work in FY95 concentrated on readying primary ion gun technology for transfer to Phi-Evans. This involved successful modification of the perrhenate ion gun, so that primary ion currents in excess of one nanoamp could be maintained. In addition, the benign nature of the perrhenate primary ion was demonstrated by bombarding poly(ethyleneterphthalate) for a prolonged period of time. The damage cross sections from this experiment were less than those recorded in comparable experiments using Ar^+, Xe^o, or Xe^+ as primary bombarding particles. At the present time, Phi-Evans is considering licensing the perrhenate primary ion gun. Finally, Teledyne remains interested in transferring INEL detector technologies. These technology transfer efforts will be continued in FY96.

FY96 will be the last year for DOE-OTD funding of the SIMS Demonstration project. The tasks associated with the funding for FY96 involve technology transfer only. Over the life of the project, two significant spin-offs have resulted: Hg speciation research has led to significant applications related to actual contamination sites at the INEL, and the tri-*n*-butylphosphate research has led to new possibilities for probing contaminant-surface interactions with basalt. Both areas hold potential for significant cost savings in characterization and remediation efforts. It is anticipated that the ion trap SIMS instrumentation developed under the program will have a significant impact on these and other applications.

Contents

Figures

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ACRONYMS and SYMBOLS

Acronym or Symbol	Definition
AFG	arbitary waveform generator
amu	atomic mass unit
Ba	barium
C	carbon
Ca	calcium
CA	California
CHA	cyclohexyl amine
Cl^-	chlorine
cm	centimeters
EDTA	ethylene diamine tetraacetic acid
Fe	iron
FY	fiscal year
Ga	gallium
H	hydrogen
HCO_2^-	formate
HCO_2H	formic acid
Hg	mercury
$HgCl_2$	mercury(II) chloride
Hg_2Cl_2	mercury(I) chloride
HgO	mercury(II) oxide
HgS	mercury(II) sulfide
$HgSO_4$	mercury(II) sulfate
HNO_3	nitric acid
INEL	Idaho National Engineering Laboratory
K	potassium
keV	kiloelectron volt
m/z	mass to charge ratio
MS	mass spectrometry
MS/MS	mass spectrometry/mass spectrometry
Na	sodium

ACRONYMS and SYMBOLS, continued

Acronym or Symbol	Definition
NaOH	sodium hydroxide
$NaNO_2$	sodium nitrite
$NaNO_3$	sodium nitrate
NCS^-	thiocyanate
Ni	nickel
NO_2^-	nitrite
NO_3^-	nitrate
O	oxygen
PA	Pennsylvania
pH	- log of hydrogen ion concentration, a measure of acidity
PNL	Pacific Northwest Laboratory
ReO_4^-	perrhenate
RF	radio frequency
RWMC	Radioactive Waste Management Complex
SIMS	secondary ion mass spectrometry
SWIFT	stored waveform inverse Fourier Transform
TBP	tributyl phosphate
US	United States

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1.0 INTRODUCTION

1.1 FY95 Program Overview

The purpose of the title program is to develop static secondary ion mass spectrometry (SIMS) instrumentation and methodology capable of detecting the presence of trace quantities of metals and other low volatile analytes, and also identifying the chemical species of these contaminants. There were three broad objectives to the FY95 program:

1. Demonstrate applicability of SIMS, and laser desorption ion trap mass spectrometry, to contaminant speciation issues, particularly mercury speciation and ethylenediaminetetraacetic acid (EDTA) detection.
2. Develop ion trap SIMS instrumentation to the point where it could be demonstrated.
3. Transfer SIMS components to private enterprise.

SIMS has undergone improvement at the Idaho National Engineering Laboratory (INEL), and as a result, SIMS possesses many of the attributes that are desirable for a characterization technology: it has good sensitivity and selectivity, requires no sample preparation, generates no waste, and has the potential for moderate cost and transportability. Since mercury (Hg) speciation is a significant characterization issue within DOE, Section 2 of this report will describe characterization of mercury species using the newly-developed SIMS technology.

While SIMS has been shown to be applicable to a broad spectrum of characterization problems, it (like all other analytical approaches) is not a panacea, and thus has limitations. For example, an analyte of interest to DOE and the U. S. Geological Survey is EDTA, but surfaces contaminated with EDTA respond poorly to particle bombardment (i.e., SIMS). In this case, it was felt that the difficulty in characterization arose from extremely strong contaminant-surface binding, or perhaps from unfavorable ionization chemistry. It was hypothesized that laser irradiation might be able to accomplish ionization/desorption in this case, and thus prove to be a valuable complement to the particle bombardment approach. Section 3 of this report describes characterization of EDTA salts and contaminated soils using laser desorption ion trap mass spectrometry. This work was performed by the Dr. Luke Hanley at the University of Illinois at Chicago.

SIMS does not require any sample manipulation prior to analysis; indeed, this is one of the very attractive features of the technique. However, there are limitations associated with sensitivity and selectivity that are a consequence of the lack of sample extraction and concentration. It was felt that an instrument capable of selective ion storage and mass spectrometry/mass spectrometry (MS/MS) would overcome some if not most of these limitations. Since an ion trap is a device which can store and excite ions, an objective of the program was to interface INEL SIMS technology with an ion trap. Section 4 of this report will describe this work.

The final objective of the SIMS Development program was to transfer SIMS components to private industry. Section 5 of this report will describe progress in this area.

1.2 Program Background

The SIMS Analysis Program was initiated in April of 1992, and was initially focused on the detection of low-volatile and non-volatile organic contaminants which have been used as chelating or complexing agents for radionuclides. The program began by looking at tributyl phosphate (TBP), EDTA and other chelating agents. This research was conducted using a laboratory-based quadrupole SIMS instrument, and demonstrated that TBP could be very sensitively detected on a variety of mineral surfaces.[1] Furthermore, the SIM spectrum of TBP was observed to change, depending on the chemical nature of the mineral surface.[2] This observation suggested that TBP could be used as a probe molecule for assessing surface chemistry. In addition, investigations showed that SIMS signatures of EDTA, and metals including lead could also be obtained. In the case of EDTA, however, the detection limits achievable were only on the order of 1 part-per-thousand, and hence it was concluded that SIMS was not the optimal technique for EDTA assessment. This motivated the laser desorption ion trap mass spectrometry research that was conducted in FY95.

In December of 1993, the SIMS Development Program was reoriented toward the characterization of "salt cake". There exists a need for analytical methods which can give inorganic species information with minimal sample handling and no waste generation, because salt cake originates (primarily) from extremely radioactive waste tanks on the Hanford reservation. A collaboration was initiated with the Laser Ablation Mass Spectrometry program at Pacific Northwest Laboratory (PNL), and simulated salt cake samples were generated and sent to INEL for SIMS analysis. All of the major chemical species that were added to the simulated salt cake were detected in the INEL SIMS analysis, with the exception of EDTA. These species included nitrates, nitrites, cyanides, carbonates, hydroxides, peroxides, and metal-anion complexes of Fe, Ni, Na, K, and Ca. The data compared favorably with a more sophisticated and expensive SIMS instrument at Charles Evans & Associates, Inc. The INEL instrument, which is equipped with a novel perrhenate (ReO_4^-) primary ion gun, gave abundant molecular secondary ions from the salt cake samples. The Evans instrument produced excellent mass and spatially resolved spectra using a Ga^+ primary ion gun, but was not as sensitive to higher mass molecular species. This work has led to an excellent opportunity to transfer SIMS component technology to Evans.

In October 1994, the applications focus of the program was again redirected toward determination of Hg speciation. By December of 1994, speciation research using static SIMS was being conducted, and end users had been identified. The work on Hg speciation is described in Section 2 of this report.

The SIMS analysis program has also worked toward the development of transportable instrumentation, which has improved sensitivity and selectivity. To this end, a decision was made in FY93 to develop an ion trap SIMS instrument, because ion trap technology shows promise in meeting these requirements. A commercial ion trap mass spectrometer was ordered in FY-94. The instrument was received in late FY94, and was modified for SIMS in FY95. This modification is described in the present report (Section 4).

Technology transfer activities were initiated in FY93, which began to come to fruition in FY94, and were continued in FY95. Teledyne, Charles Evans & Associates, Inc., and Extrel are instrument manufacturers that have expressed an interest in SIMS components, and non-disclosure agreements were signed with all three firms. Later, instrument control and data acquisition software, which was developed to control INEL SIMS instrumentation, was licensed to Extrel for their internal use and evaluation. Additional detail describing the interest of the manufacturers is provided within this report (Section 5).

1.3 References

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[1] Groenewold, G. S.; Ingram, J. C.; Delmore, J. E.; Appelhans, A. D.; Dahl, D. A., *J. Haz. Mats.*, **1995**, *41*, 359-70.

[2] Groenewold, G. S.; Ingram, J. C.; Delmore, J. E.; Appelhans, A. D., *J. Am. Soc. Mass Spectrom.*, **1995**, *6*, 165 - 74.

2.0 Hg SPECIATION STUDIES USING SIMS

2.1 Introduction

Hg speciation is an important issue because environmental mobility is largely determined by the species of the metal. Examples of variable mobility among Hg species are HgO, which is known to strongly sorb on clay surfaces, and Hg chloride complexes, which do not sorb to clay surfaces, and hence have a high mobility in the environment. Highly mobile species present challenges to the health of the environment. Hg contamination is particularly acute at INEL and the Oak Ridge National Laboratory, where large quantities have been buried over the past 40 years, and present a threat to the aquifer. Despite this environmental importance, inorganic Hg speciation has not received a great deal of attention. Instead, most of the Hg speciation has been focused on the identification of organomercury species, primarily because of the high toxicity of methyl Hg compounds.

Static SIMS has the potential for identifying metal species extant on mineral surfaces, because the technique is capable of sputtering molecular species into the gas phase, where their masses can be measured, thus providing a means for identification. Since static SIMS is by nature nondestructive, the potential exists for relating observed gas-phase ions to the structures of species residing on the mineral surface. Static SIMS has been applied in our laboratory for the identification of gold complexes present on charcoal surfaces,[1] and also for the identification of complex salt species on salt cake samples simulating those encountered in Hanford waste tanks. In addition, the SIMS spectra of organophosphorus adsorbates was determined to be dependent on the oxidation state of Fe in a basalt matrix.[2]

A study was conducted to determine if organic or inorganic complex ions could be observed from Hg salts. If the salts could be differentiated based upon their SIMS spectra, then this would provide encouragement for pursuing this approach for Hg speciation studies on mineral surfaces.

2.2 Experimental

2.2.1. Static SIMS using a quadrupole instrument. The majority of the Hg complexation studies presented in this section were performed using a quadrupole-based SIMS spectrometer (Figure 2-1). This instrument has been described in detail previously;[3] it uses ReO_4^- at 10 keV as the primary bombarding particle, which is produced by heating a ceramic containing $Ba(ReO_4)_2$ in vacuum.[4] The ion gun was typically operated at 20 picoamps, although variations of +/- 20% were commonly observed over the course of a day's analyses. The focusing of the primary ion gun was adjusted so that the sample was just silhouetted on an image intensifier located behind the sample.

Thus, most of the primary ion beam is directed onto the target to which the sample was taped. A typical acquisition required 1320 seconds, and a typical sample had a geometric area of about 0.056 cm^2; therefore a typical dose was 2.8×10^{12} ions/cm^2. This dose is substantially less than the commonly accepted static SIMS limit.[5]

The secondary anions and cations were alternately extracted from the sample target region (pulsed extraction [3]), which mitigates charge buildup on the surface of the sample, and permits near simultaneous acquisition of the anion and cation spectra. The ratio of [time extracting cations] / [time extracting anions] was 1.5, and the total period for a single pulsed extraction sequence was 105 milliseconds, divided as follows: cation extraction, 60 milliseconds; electronic settle time, 2.5 milliseconds; anion extraction, 40 milliseconds; electronic settle time, 2.5 milliseconds. This sequence was repeated for each 0.2 amu step of the scan of the quadrupole mass spectrometer, which was scanned from 10 to 130 amu. The quadrupole was a 2 - 2000 u instrument, manufactured by Extrel (Pittsburgh, PA), and modified in our laboratory. The quadrupole was tuned for unit mass resolution and optimum sensitivity for *m/z* 198^+ in the SIMS spectrum of tetrahexyl ammonium bromide.[6]

2.2.2. Static SIMS using an ion trap instrument. Hg•cyclohexylamine complexes were investigated using an ion trap SIMS instrument.[7] A more detailed discussion of the ion trap is presented in section 4. Briefly, an ReO_4^- ion gun is located coaxially behind one end cap of a modified Finnigan ion trap mass spectrometer (Finnigan-MAT Corporation, San Jose, CA), and an offset electron multiplier is located next to the ion gun. The sample, attached to a probe, is located 3 mm from the opposite end cap and the ReO_4^- beam at 3.5 keV is focused on the sample through the ion trap. Ions in the mass range of interest were collected using filtered noise fields applied with a Teledyne system (Teledyne Electronics Technology, Mountain View, CA), and collision induced dissociation was performed using a supplementary RF field on the end caps.

2.2.3. Chemicals and sample preparation. Chemicals were obtained from commercial sources: mercuric oxide, mercurous nitrate monohydrate, mercurous chloride, mercuric iodide, mercuric sulfate, and mercuric chloride were obtained from J. T. Baker, Phillipsburg, NJ. Mercuric thiocyanate and formic acid were obtained from Fisher Scientific, Fairlawn, NJ. Mercuric sulfide was obtained from Cerac, Inc., Milwaukee, WI. Cyclohexylamine was obtained from Aldrich, Milwaukee, WI.

The Hg compounds were in powder or crystal form. For SIMS analysis, the powders or crystals were attached to a steel SIMS target using double-sided tape, and then analyzed. The Hg compounds were also exposed to gaseous complexing agents prior to analysis. This was accomplished by placing the exposed SIMS targets in the head space of a volatile, liquid complexing agent, in a covered jar at ambient temperature and pressure. Care was taken so that the

Hg compounds did not get wet with the complexing agent. Typical exposure times were 60 to 300 seconds.

2.3 Static SIMS Analysis of Unmodified Hg Compounds

The SIMS spectra of most Hg salts studied produced clear information on the counter anion, and little or no information which indicated the presence, or species of Hg which might be present. Exceptions to this trend were the two Hg chloride salts, and Hg sulfate.

Analyses of mercurous chloride (Hg_2Cl_2) and mercuric chloride ($HgCl_2$) contained no useful information in their cation spectra. The anion spectra were dominated by abundant Cl^-, as would be expected (Figure 2-2). For both salts, however, a low abundance ion cluster was observed from *m/z* 303^- to 309^-, which corresponded to $HgCl_3^-$ (Figure 2-3, 2-4). A cluster is observed because of multiple isotopes of Hg (198, 199, 200, 201, 202, and 204 are significant) and Cl (35 and 37 are significant). The relative abundances of the ions within the cluster were in good agreement with the theoretical abundances (represented by the bar chart in Figure 2-3). Thus the presence of Cl^- is clear, and Hg complexed with chloride is strongly suggested. In some spectra, a very low abundance cluster was observed from *m/z* 268^- to 274^-, which corresponds to $HgCl_2^-$. The formation of this Hg(I) species is not favored compared to $HgCl_3^-$, even when the starting compound is in the Hg(I) state.

The anion SIMS spectrum of mercuric sulfate showed very clear evidence for the presence of sulfate (Figure 2-5). The base peak in the spectrum was *m/z* 96^-, which corresponds to SO_4^-. HSO_4^- is also abundant, depending on the availability of protons. SO_3^-, SO_2^-, and SO^- are also observed, in decreasing abundance. Hg clusters were also observed in the anion spectrum (Figure 2-6): ions at *m/z* 310^- to 317^- were interpreted in terms of two clusters, which correspond to $^-O\text{-}Hg\text{-}OSO_3^{\bullet}$ and $HO\text{-}Hg\text{-}OSO_3^-$. The relative abundances of the two clusters were reproduced by calculating the theoretical abundances for a cluster consisting of 1.0 part $^-O\text{-}Hg\text{-}OSO_3^{\bullet}$ and 0.55 part $HO\text{-}Hg\text{-}OSO_3^-$ (the theoretical abundances are represented by the bar chart in Figure 2-6). It is of interest that a fifth oxygen atom is required for the observation of a Hg complex ion. Neutral $HgSO_4$ is probably sputtered from the surface of the salt, but observation of a charged species requires an additional oxygen atom. Addition of an oxygen atom results in the formation of a radical species (cluster beginning at *m/z* 310^-, Figure 2-7). The addition of a proton results in the formation of an even electron ion (cluster beginning at *m/z* 311^-).

Other salts tested included mercuric iodide, mercuric thiocyanate, mercuric nitrate, mercurous nitrate, mercuric oxide, and mercuric sulfide. In all cases except the oxide and the sulfide, abundant anions were observed which corresponded to the anion of the salt, but no Hg-bearing ions could be observed. Nitrate was observed as an abundant *m/z* 62$^-$ ion (NO_3^-), with a much lower abundance peak at *m/z* 46$^-$ (NO_2^-). This is in contrast to sodium nitrate, which contained an abundant NO_2^- ion. Thiocyanate (NCS^-) could be observed as an abundant ion at *m/z* 58$^-$, and iodide at *m/z* 127$^-$. No significant anions could be observed for the oxide or the sulfide.

2.4 Static SIMS Analysis of Hg Compounds Modified with Complexing Agents

Since Hg could not be observed for several of the compounds of interest, a suite of simple complexing agents were tested, to determine if Hg observability could be improved. The nitrate and oxide compounds were of particular interest, because these are species which may be encountered in field samples from contaminated sites at the Radioactive Waste Management Complex (RWMC).

2.4.1. Observation of Hg•formate complexes using a quadrupole SIMS instrument. It was found that a simple derivatization procedure could be used which would produce Hg•formate complexes that were easy to observe with the quadrupole SIMS instrument. This procedure only worked when starting with HgO. A small quantity of HgO was attached to double-sided tape on a SIMS target, and then placed in a jar containing approximately 0.5 ml of formic acid in the bottom, in such a manner that the HgO did not come into contact with the liquid formic acid (Figure 2-8). The jar was covered, and the HgO was allowed to interact with the formic acid vapor for 60 to 300 seconds, at which time the target was removed from the jar for analysis.

When the formic acid-exposed targets were analyzed, an abundant ion was observed at *m/z* 45$^-$, which corresponds to HCO_2^- (Figure 2-9). In addition, a lower abundance ion cluster appeared at *m/z* 247$^-$ to 253$^-$, which was measured with improved precision and signal/noise by performing a slow scan over the mass region of interest (Figure 2-10). In addition to the anion cluster, a cation cluster was also observed (Figure 2-11). The isotopic envelopes for the anion and cation clusters were in good agreement with the theoretical abundances calculated for $Hg{\bullet}HCO_2$. The anion cluster includes an ion at *m/z* 251$^-$, which is not part of the $Hg{\bullet}HCO_2$ cluster, but instead arises from $^{187}ReO_4^-$ deposition from primary ion bombardment; this explanation is supported by the observation that 251$^-$ and 249$^-$ ($^{185}ReO_4^-$) abundances increase with increasing dose.

The structure of the cation complex appears to be straightforward: the formate anion is attached to a Hg^{+2} cation. In contrast, a simple anion•cation attachment does not satisfactorily explain the Hg•formate anion, unless the metal is in the 0 oxidation state. If Hg is in the (II) state, then the best rationalization of the structure of the ion involves Hg insertion into a C-H or perhaps a C-O bond

(Figure 2-12). The fate of the mercuric oxide oxygen at the completion of the proposed complexation reaction is unknown.

We were unable to observe formate complexes starting with other Hg compounds. This was especially surprising for mercuric sulfide, which we anticipated would behave similarly to HgO. We speculate that the HgS is not basic enough to adsorb the formic acid.

2.4.2. Observation of Hg•CHA adduct ions using an ion trap SIMS instrument.

Hg complex ions could not be observed starting with mercuric (or mercurous) nitrate under any circumstances, using the quadrupole SIMS instrument. The quadrupole SIMS operates at low pressures in the region of the sample target, and thus few if any collisions take place after ions are sputtered into the gas phase. In contrast, the ion trap SIMS instrument operates at helium pressures in excess of one millitorr, which results in thousands of stabilizing collisions occurring after complex ions are sputtered into the gas phase. For this reason, it was felt that the ion trap SIMS instrument may offer a better possibility for observation of more fragile, but species-diagnostic adduct ions.

Mercuric nitrate was exposed to a number of complexing agents, in hopes that one would form a complex with the Hg which would be stable enough to withstand sputtering into the gas phase. 1,3-propanedithiol, 2,3-dimercapto-1-propanol, 1,2-benzenedithiol, 18-crown-6, ammonia, ethylenediamine, and methylphosphonic acid were used as complexing agents, but no Hg-bearing ions could be observed in the SIMS spectra. Instead, a Hg-cluster was observed from *m/z* 395^+ to 401^+ in several of the spectra (Figure 2-13), and the isotope distribution of the isotopic ions near *m/z* 399 strongly suggested Hg (Figure 2-14).

It was hypothesized that Hg was complexing with cyclohexylamine (CHA), which is a contaminant present in our laboratory atmosphere.[8] To test the hypothesis, CHA-$\underline{d}_{11}$ was deliberately added to the system, which resulted in the Hg-bearing ion cluster being shifted and partitioned into two groups of isotopic ions, at *m/z* 405^+ to 412^+, and 416^+ to 422^+ (Figure 2-15). These two groups approximately corresponded to CHA•Hg•CHA-$\underline{d}_{11}{}^+$, and Hg•(CHA-$\underline{d}_{11})_2{}^+$, respectively, and verified that adventitious CHA was responsible for the Hg-bearing isotopic ions observed in the unlabeled experiment.

What was surprising was that no $[\text{CHA+H}]^+$ was observed at *m/z* 100^+ or 111^+ in the unlabeled or labeled experiments (respectively); these ions normally comprise the signature for CHA adsorbed to protonating surfaces. Instead, *m/z* 98^+ was observed in the unlabeled experiment (as the base peak), and *m/z* 108^+ was observed in the labeled experiment (as the base peak), which clearly indicated that they were originating from CHA.

In the group of isotopic ions observed in the unlabeled experiment, it was surmised that the most abundant ion, *m/z* 399^+, in all probability corresponded to the most abundant Hg isotope, which is ^{202}Hg. The difference in mass between 399 and 202 is one amu less than the mass of two CHA molecules, and thus the Hg•CHA$_2$ isotopic ions must correspond to $(C_6H_{11}NH)Hg(C_6H_{11}NH_2)^+$, in some isomeric form. However, when the theoretical abundances of the isotopic ions were calculated for this composition and then compared with the measured abundances, the lower mass ions at *m/z* 393, 394 and 395 were poorly accounted for. A better fit was obtained by factoring in a second composition, which contained two less H atoms (Figure 2-14), and which is present at about half the abundance of $(C_6H_{11}NH)Hg(C_6H_{11}NH_2)^+$. This composition represents a second Hg•CHA structure present on the salt surface, or arising from the elimination of H_2 $(C_6H_{11}NH)Hg(C_6H_{11}NH_2)^+$ from in the gas phase.

The isotopic abundances measured for Hg•(CHA-$\underline{d}_{11}$)$_2$ were compared with calculated abundances (Figure 2-16). It was found that the best fit was obtained for a combination of $(C_6D_{11}NH)Hg(C_6D_{11}NH_2)^+$, and (as in the unlabeled case) a second cluster, which contained one less H *and* D atom.

M/z 98 and 300 ions were identified as daughter ions of the unlabeled cluster using the MS/MS capability of the ion trap SIMS instrument. *M/z* 395 - 400 was isolated using selective ion storage, and then excited to fragmentation: two significant ions were observed, one at *m/z* 98, and a second at *m/z* 300 (Figure 2-17). These ions are rationalized in terms of the structures suggested by the consideration of the isotopic abundances mentioned above (Figure 2-20).

When the mixed HgO•CHA / CHA-$\underline{d}_{11}$ adduct (*m/z* 410) was isolated and excited, both *m/z* 98 and 108 were observed as significant daughter ions, which confirms that both unlabeled and unlabeled CHA are present in this adduct (Figure 2-18). In addition, two low abundance clusters were observed at about *m/z* 300, and *m/z* 310. When the Hg•(CHA-$\underline{d}_{11}$)$_2$ adduct was isolated and irradiated, only *m/z* 108 was observed (no 98), together with low abundance ions was observed from *m/z* 307 - 310 (Figure 2-19).

The data are best interpreted in terms of Hg binding to the lone pair of one CHA to form a quaternary ammonium site, and displacing an amino proton of the second CHA (Figure 2-20). Displacement of a cyclohexyl proton is not favored, because this would result in a Hg•(CHA-$\underline{d}_{11}$)$_2$ adduct which would have an isotopic distribution in disagreement with what was experimentally observed (specifically, no significant *m/z* 421 would be expected, see Figure 2-16).

The favored adduct can then undergo three fragmentation reactions: 1) H_2 can be eliminated to form a daughter adduct which is partially isobaric with the parent adduct complex; 2) neutral CHA can be eliminated, to form $Hg{=}NH^+{-}C_6H_{11}$ (or some close isomer thereof); 3) H rearrangement from the cyclohexyl ring to the Hg atom, thus forming $C_6H_{10}NH_2^+$, and neutral C_6H_{11}-NH-Hg-H (or some isomer). We note that more complex explanations for the formation of *m/z* 98 may be imagined, but we prefer the explanation presented because of its simplicity and because it explains the *m/z* 108 ion observed in the deuterated experiment: this ion *is short one D, which originated from the cyclohexyl ring*.

2.5 Scheme for Identification of Hg Species

The anions and the Hg-bearing complex ions may be assembled into a qualitative scheme for identifying Hg species present on sample surfaces (Figure 2-21). This scheme would allow one to assign Hg species starting from nothing but the static SIMS spectrum. The scheme presently has the following limitations:

1. Detectability of complexes on mineral surfaces has not been established.
2. Identification of Hg carbonates, silicates, and aluminates has not been established. These species are anticipated to be significant species in the environment.
3. Hg was not detectable for thiocyanate or iodide.

2.6 References

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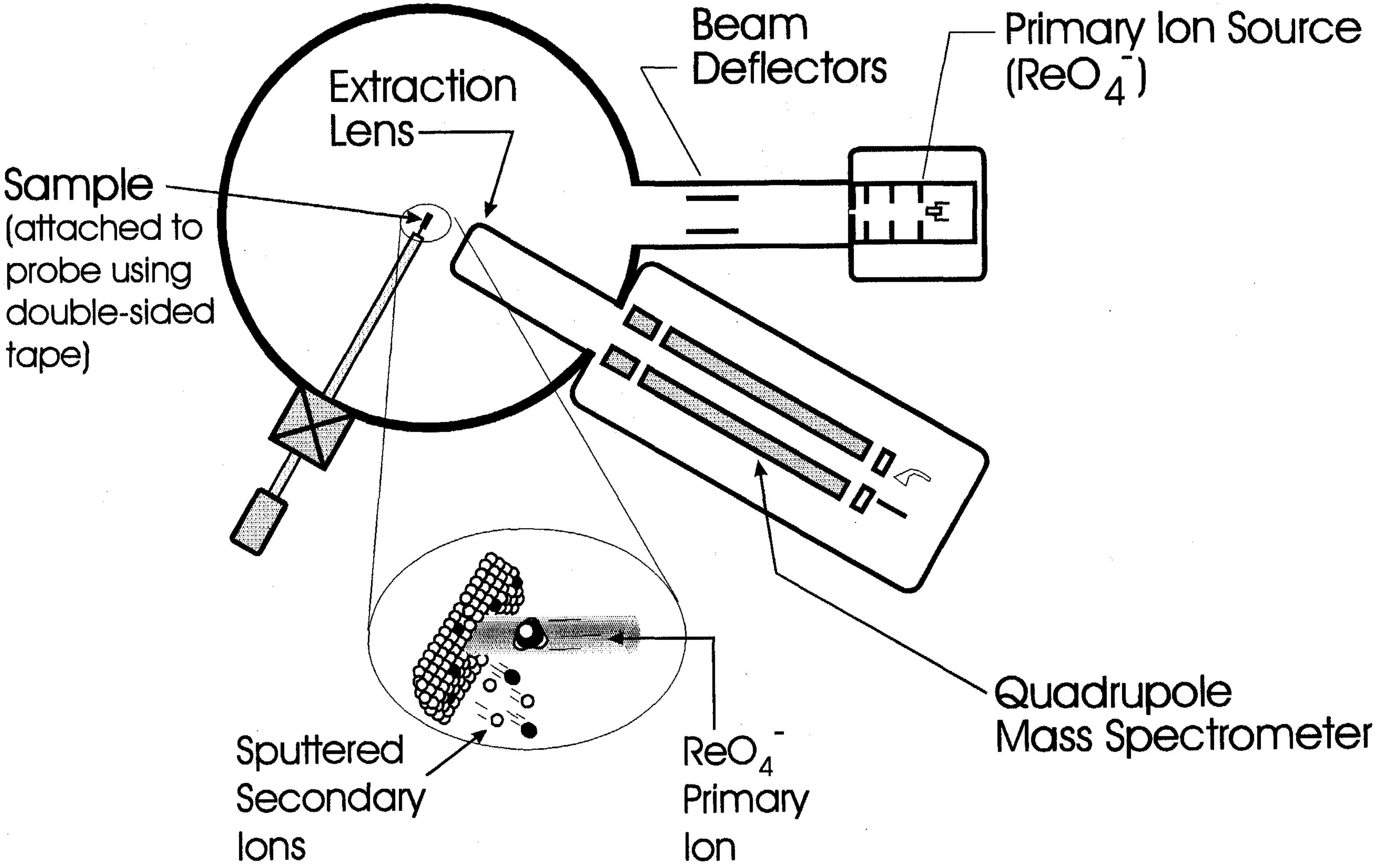


Figure 2-1. Schmatic diagram of the quadrupole SIMS instrument

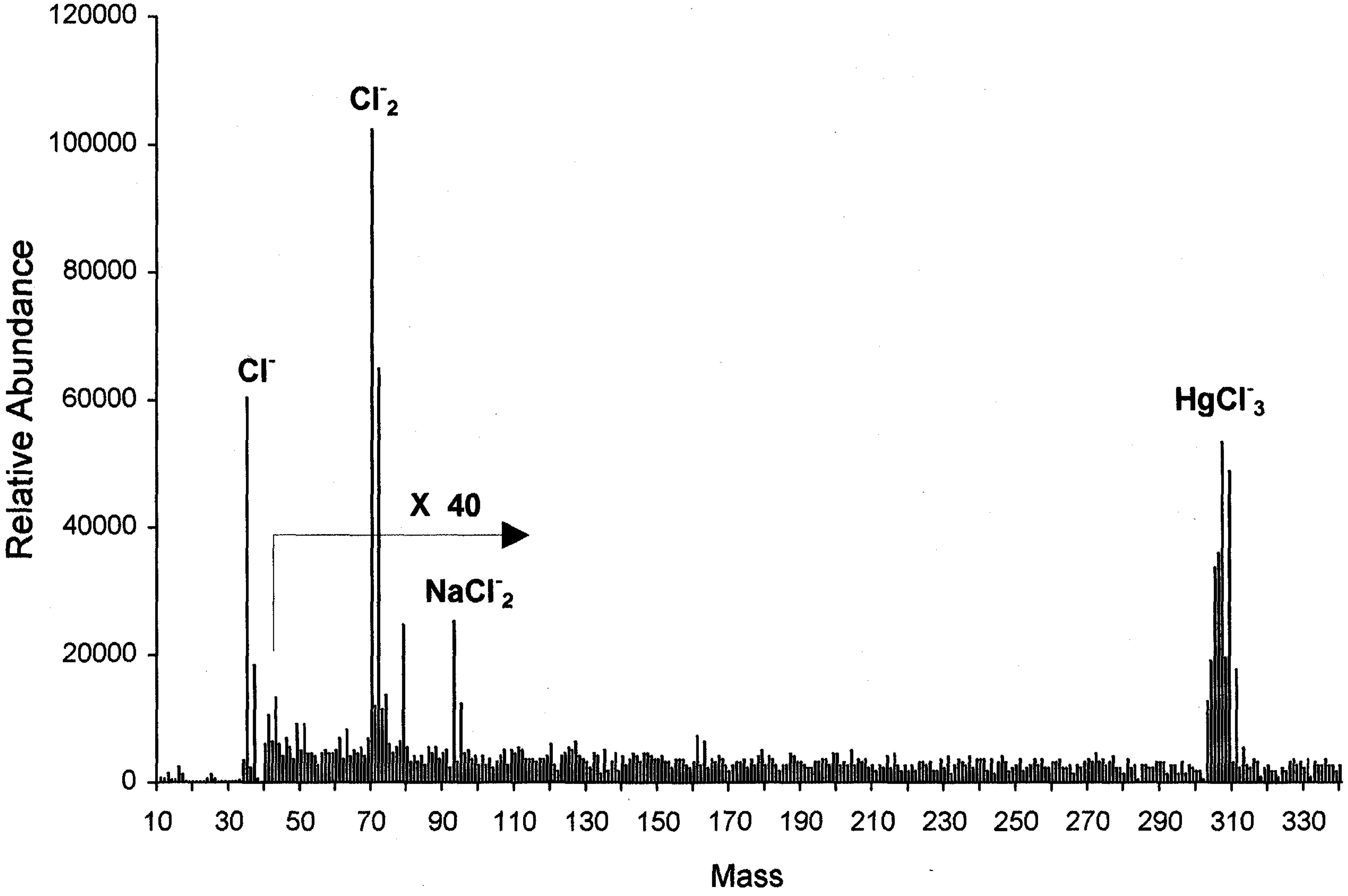
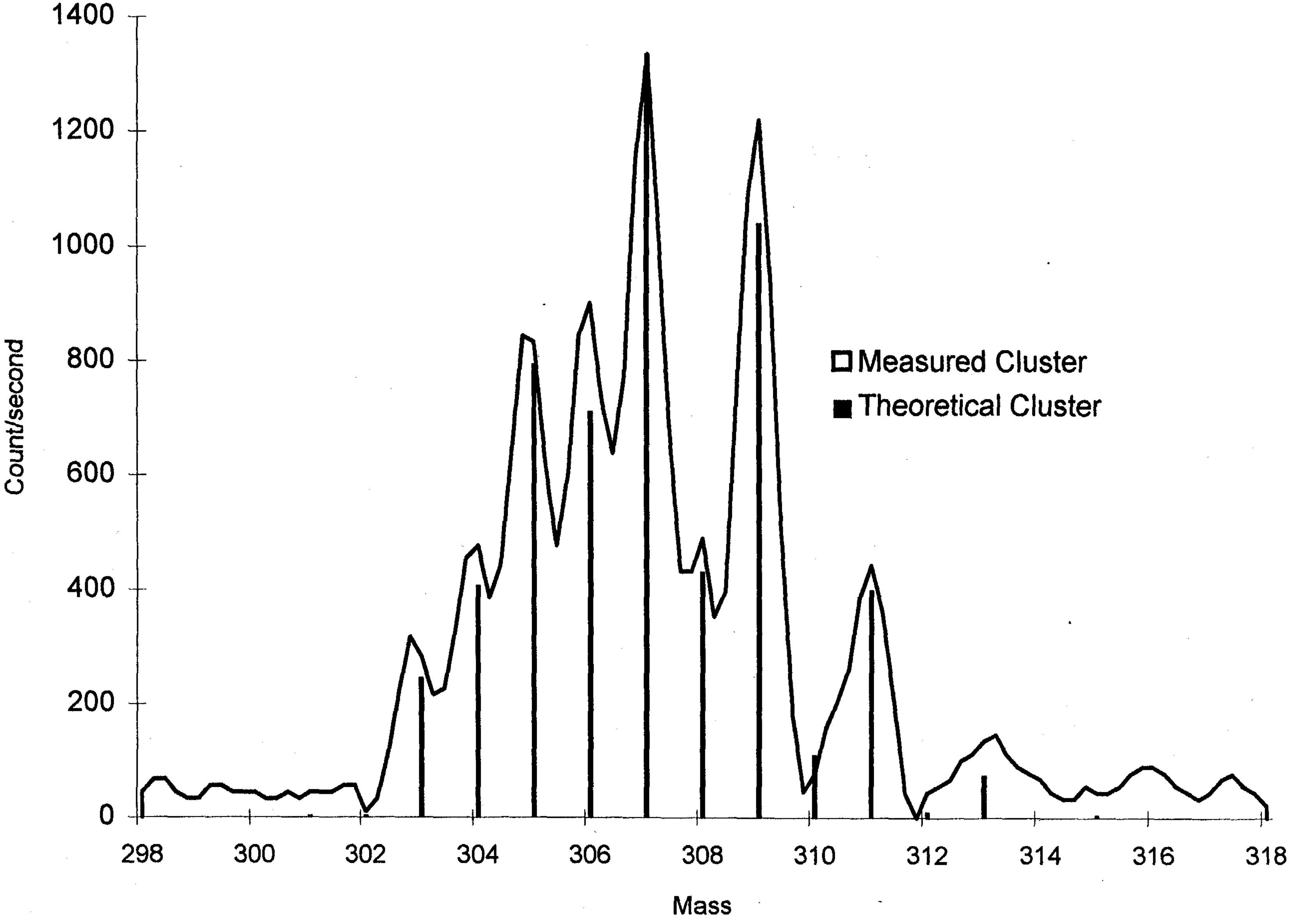


Figure 2-2. Anion SIMS spectrum of $HgCl_2$, acquired using the quadrupole SIMS instrument.



Figrue 2-3. Anion SIMS spectrum of the $HgCl_3^-$ cluster, acquired using the quadrupole SIMS instrument. Bar chart is the calculated isotopic abundances for the cluster.

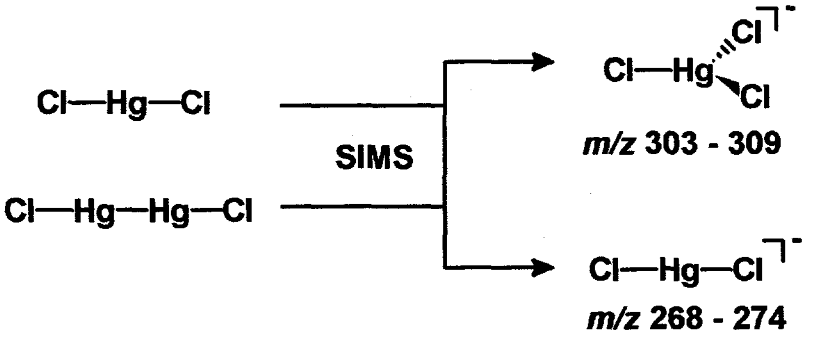


Figure 2-4. Reaction schematic of the formation of mercury chloride cluster ions under ion bombardment.

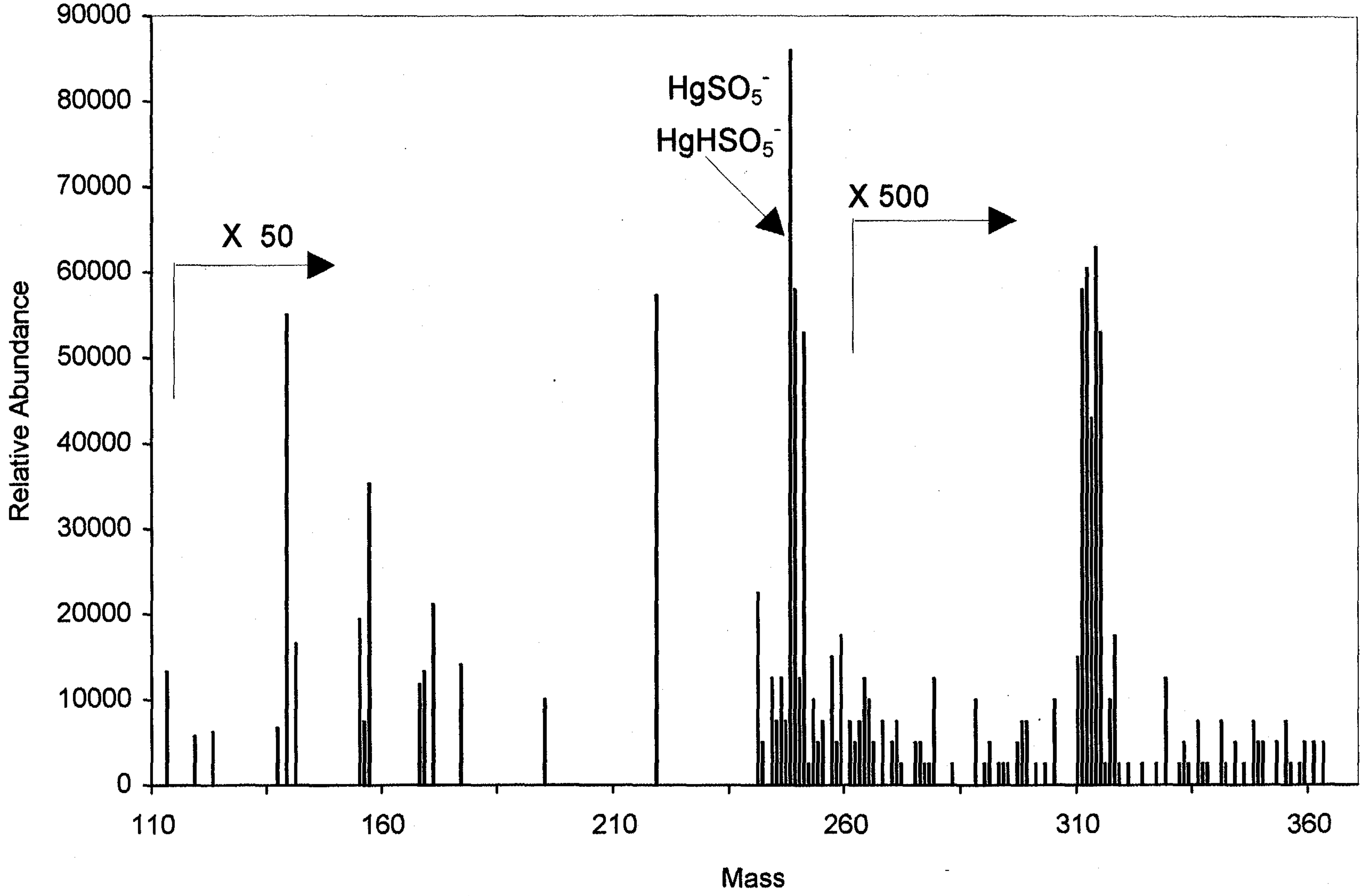


Figure 2-5. Anion SIMS spectrum of $HgSO_4$, acquired using the quadrupole SIMS instrument.

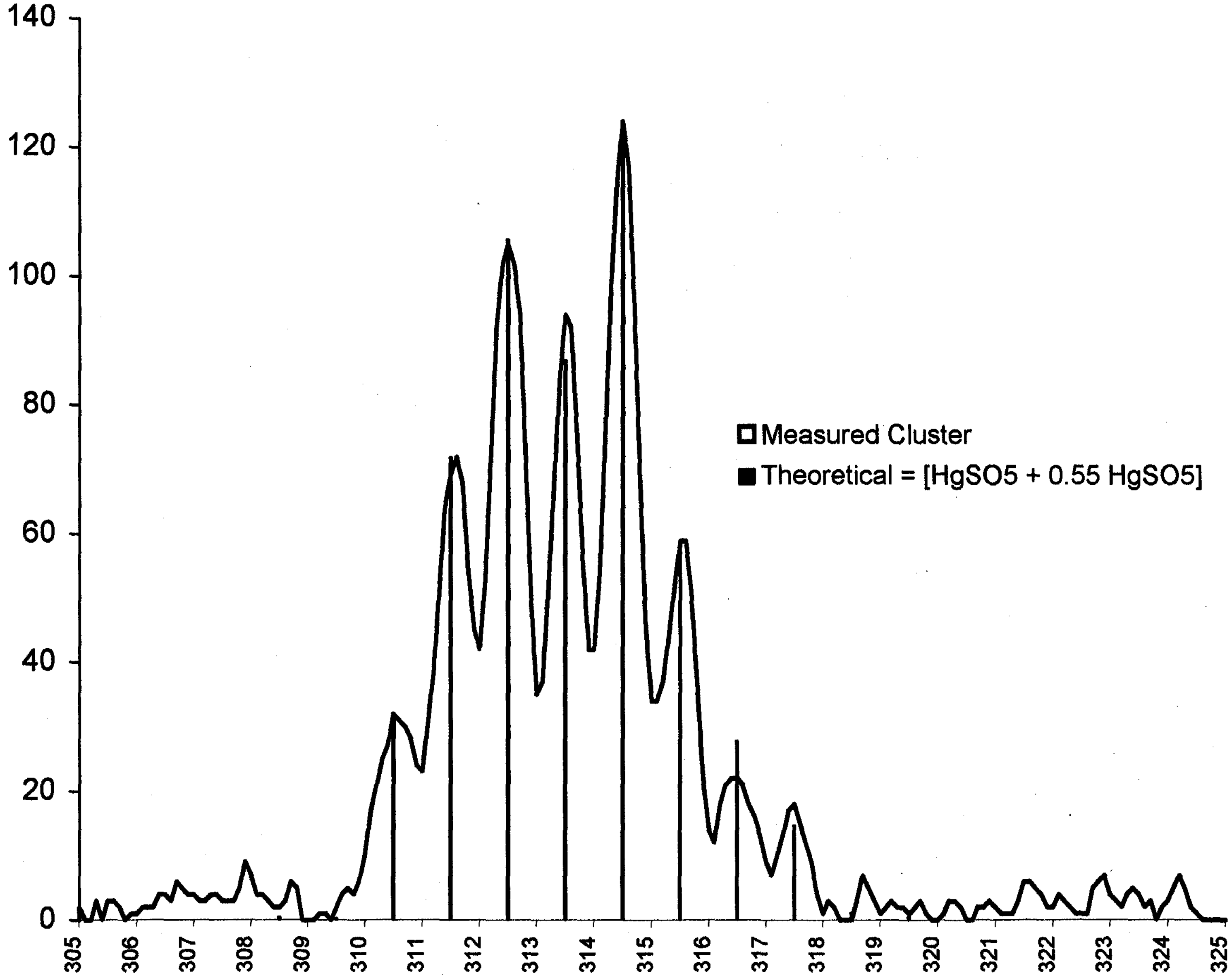


Figure 2-6. Anion SIMS spectrum of $HgSO_4$, O-Hg-OSO_3^- region. The spectrum is superimposed on a bar chart representing the isotopic pattern calculated for a linear combination of $HgSO_5^-$ + (0.55)$HgSO_5^-$.

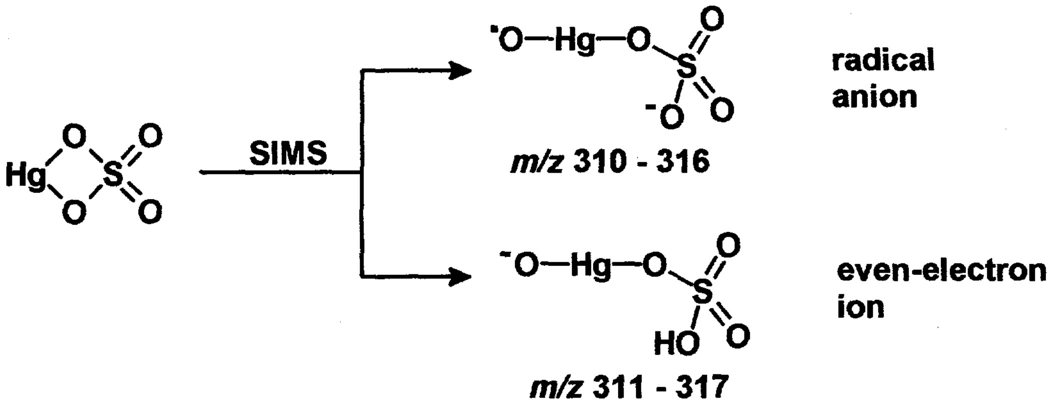


Figure 2-7. Reaction schematic of the formation of mercury sulfate cluster ions under ion bombardment.

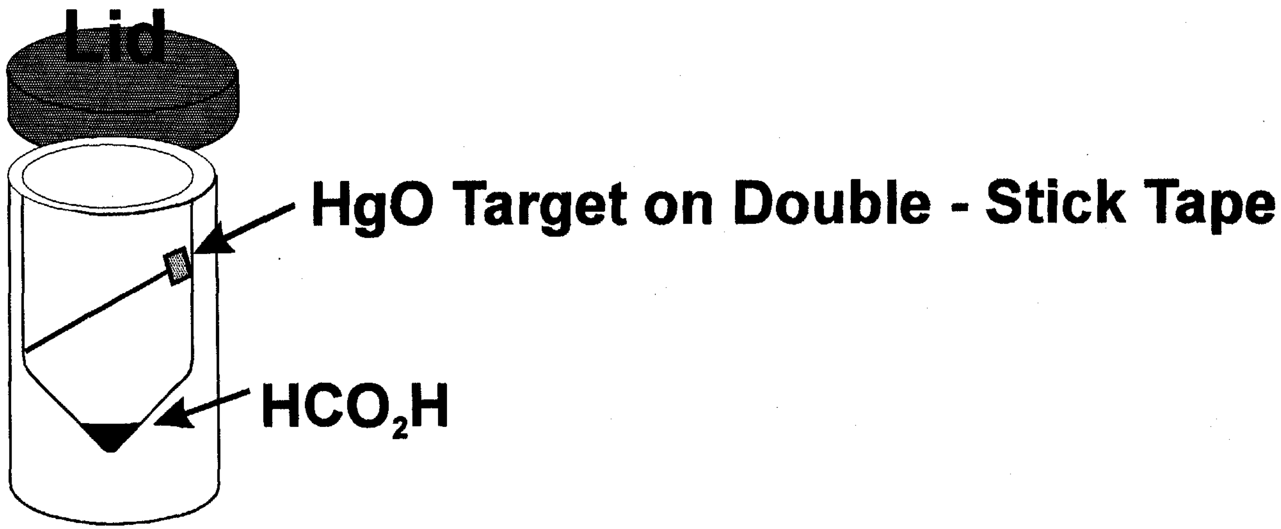


Figure 2-8. Diagram of HgO attached to a SIMS target exposed to HCO_2H vapor. HgO does not come into contact with liquid HCO_2H.

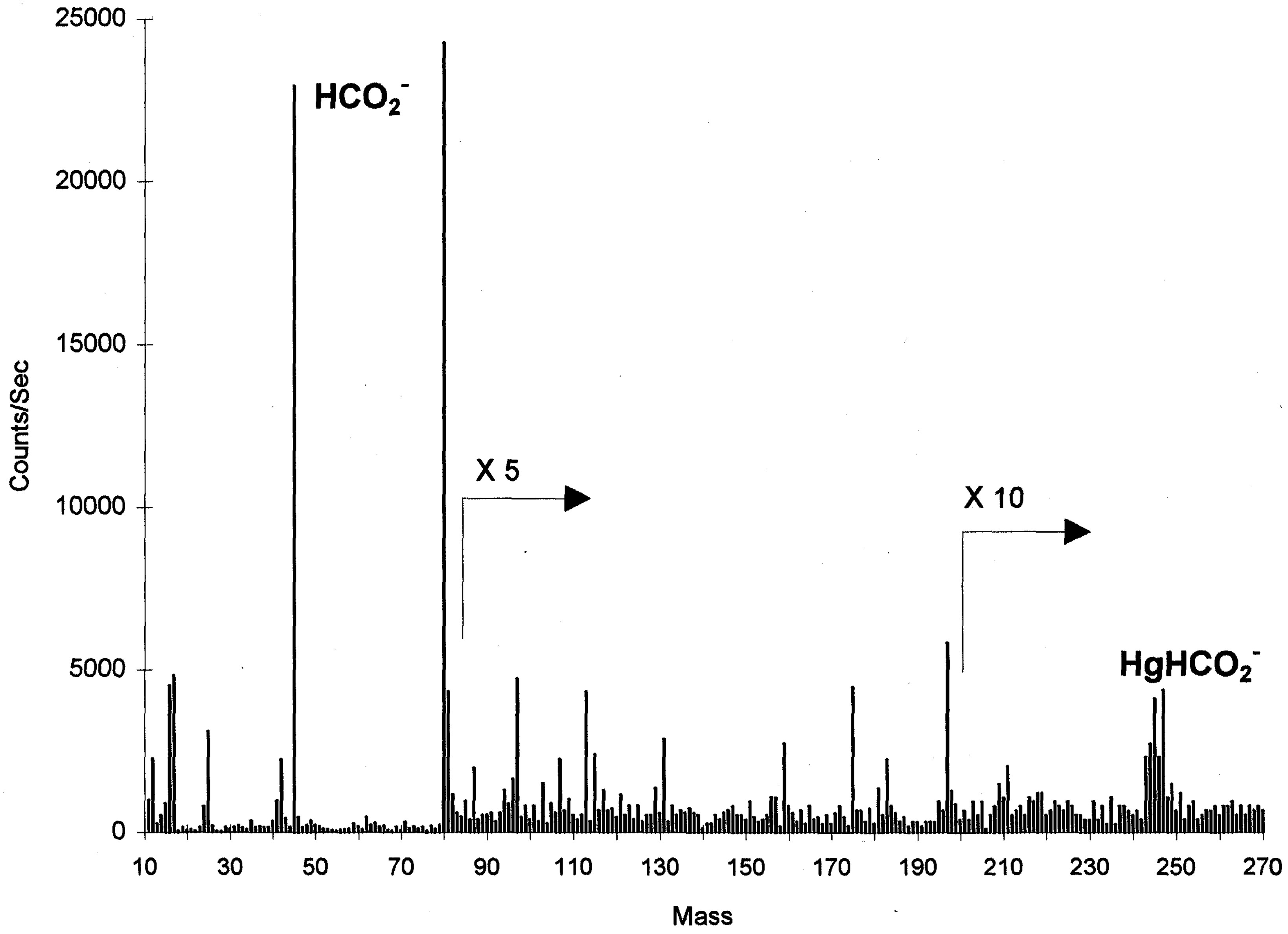


Figure 2-9. Anion SIMS spectrum of HgO exposed to formic acid, acquired using the quadrupole SIMS instrument.

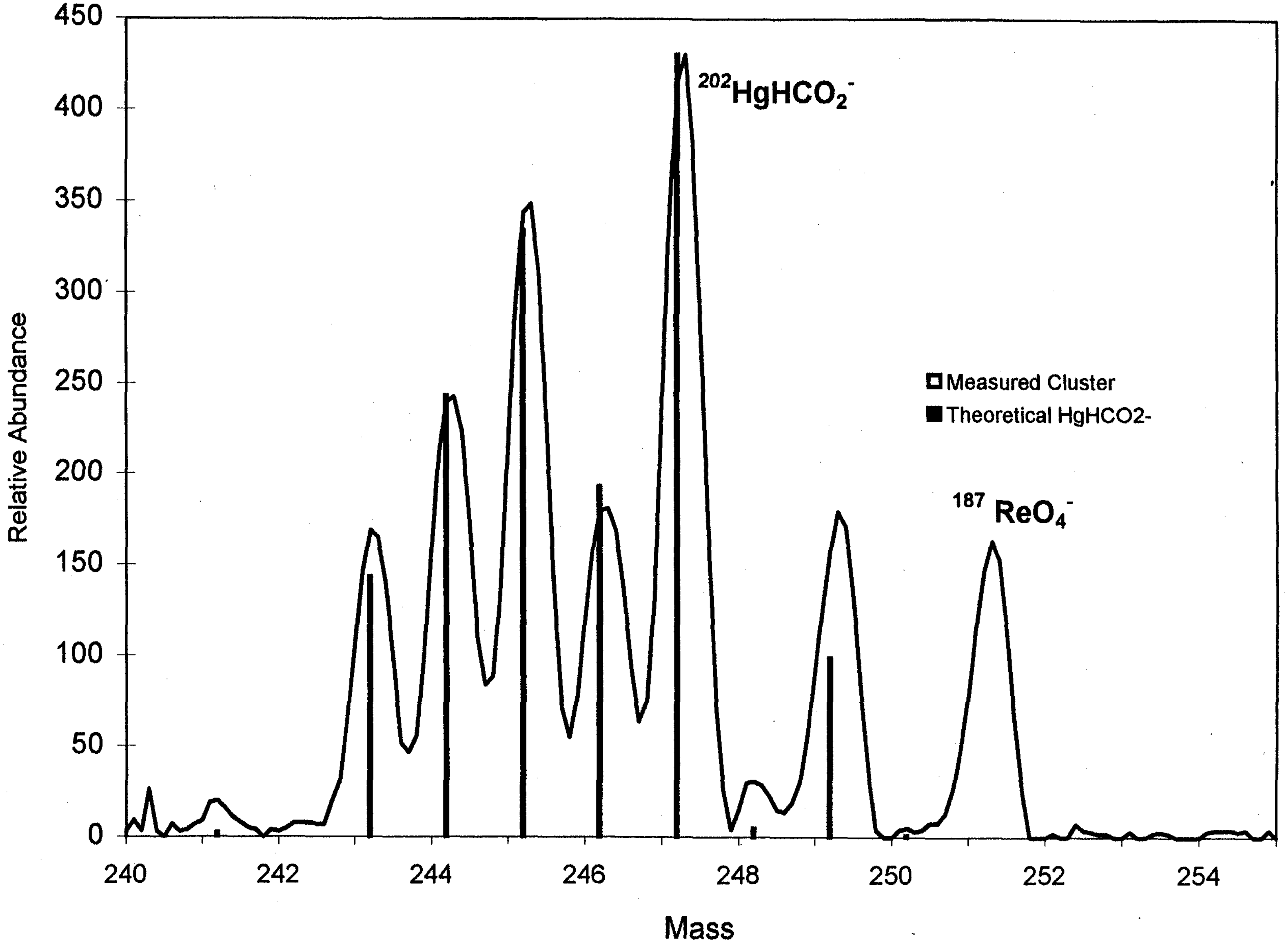


Figure 2-10. Anion SIMS spectrum of HgO· HCO_2^-, plotted with bar graph representing theoretical isotopic distribution. Spectrum was acquired using the quadrupole SIMS instrument.

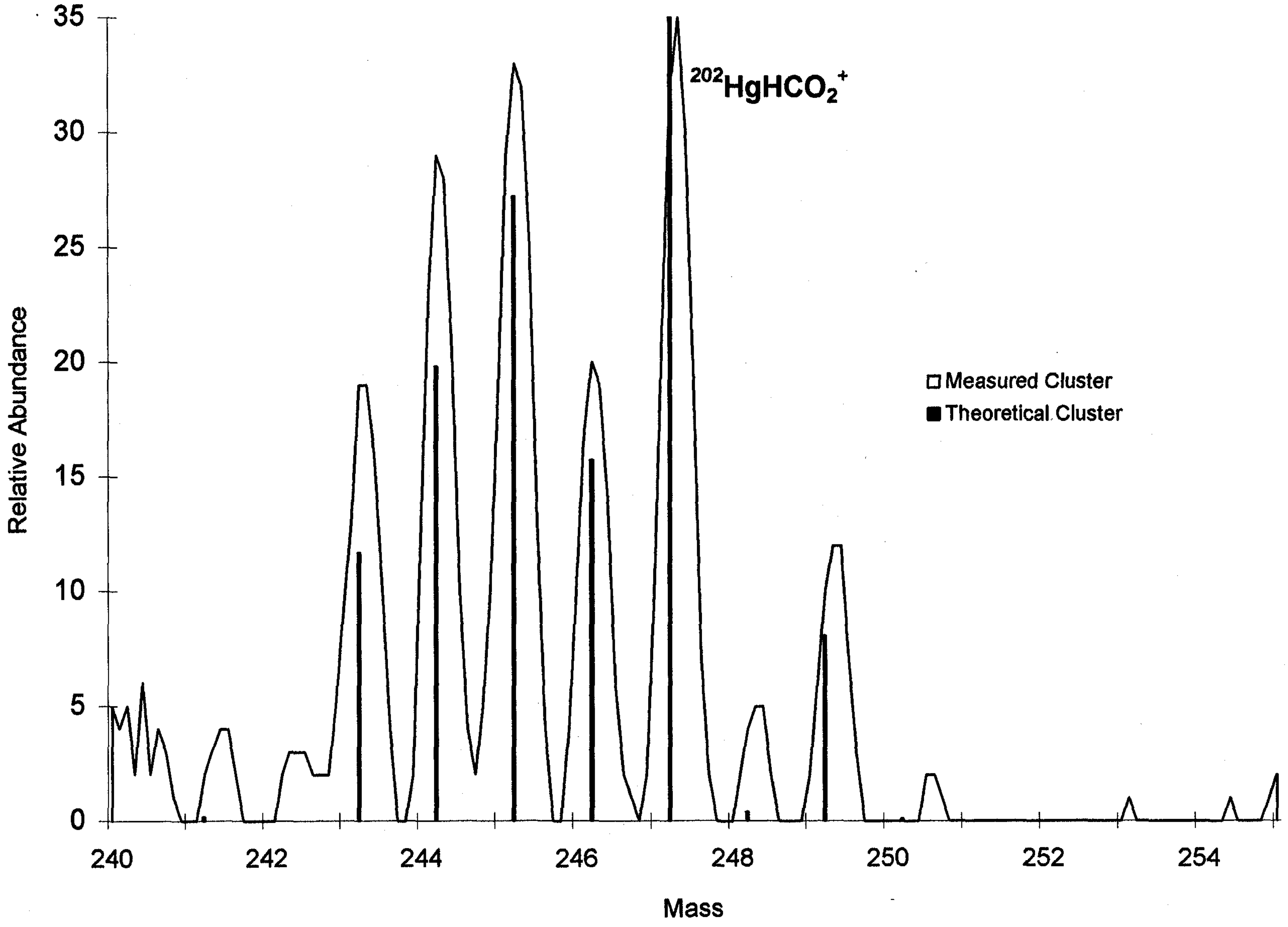


Figure 2-11. Cation SIMS spectrum of HgO HCO_2^+, plotted with bar graph representing theoretical isotopic distribution. Spectrum was acquired using the quadrupole SIMS instrument.

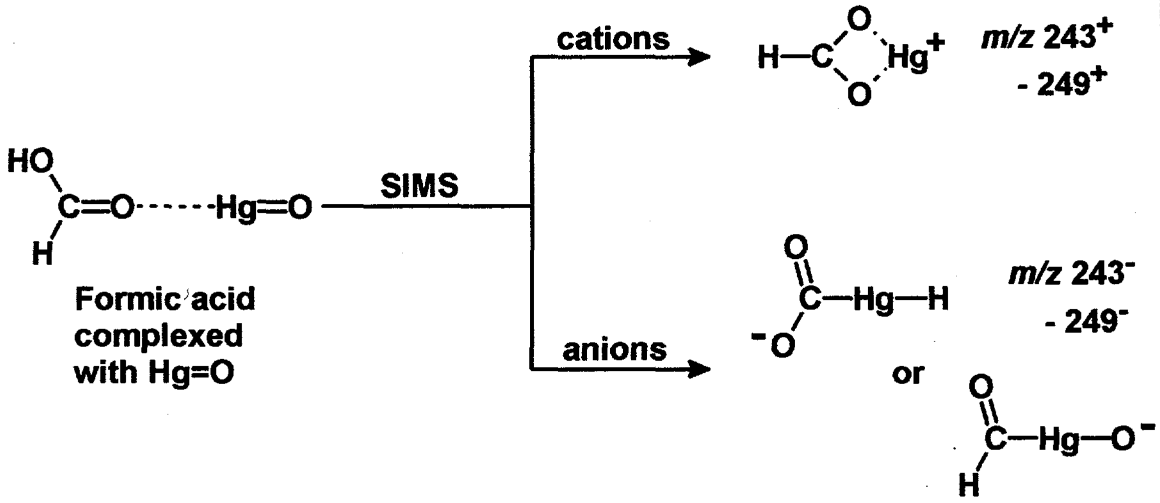


Figure 2-12. Proposed structures for the Hg•formate complexes, anion and cation.

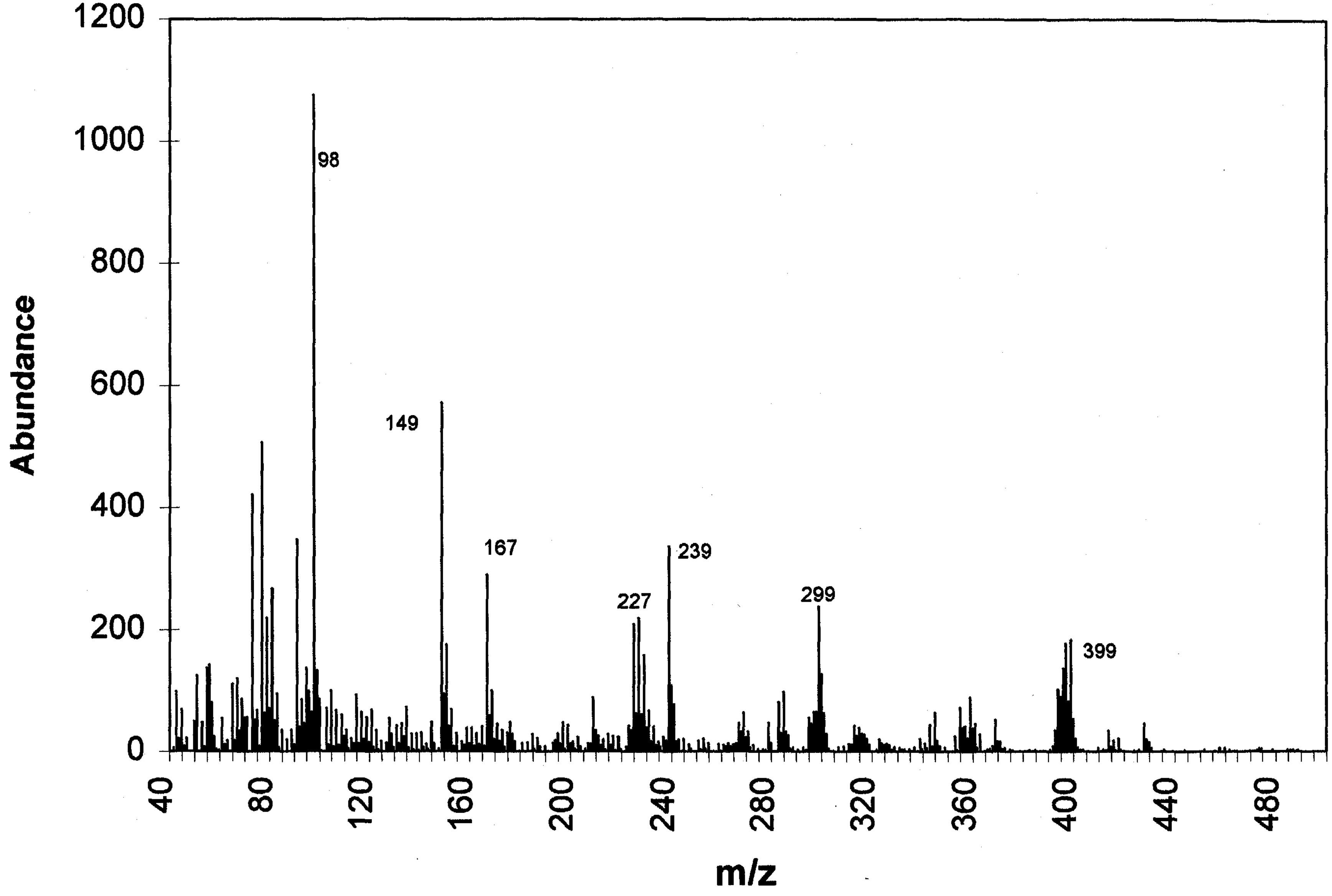


Figure 2-13. Cation SIMS spectrum of $Hg(NO_3)_2$ exposed to CHA. Acquired using ion trap SIMS instrument.

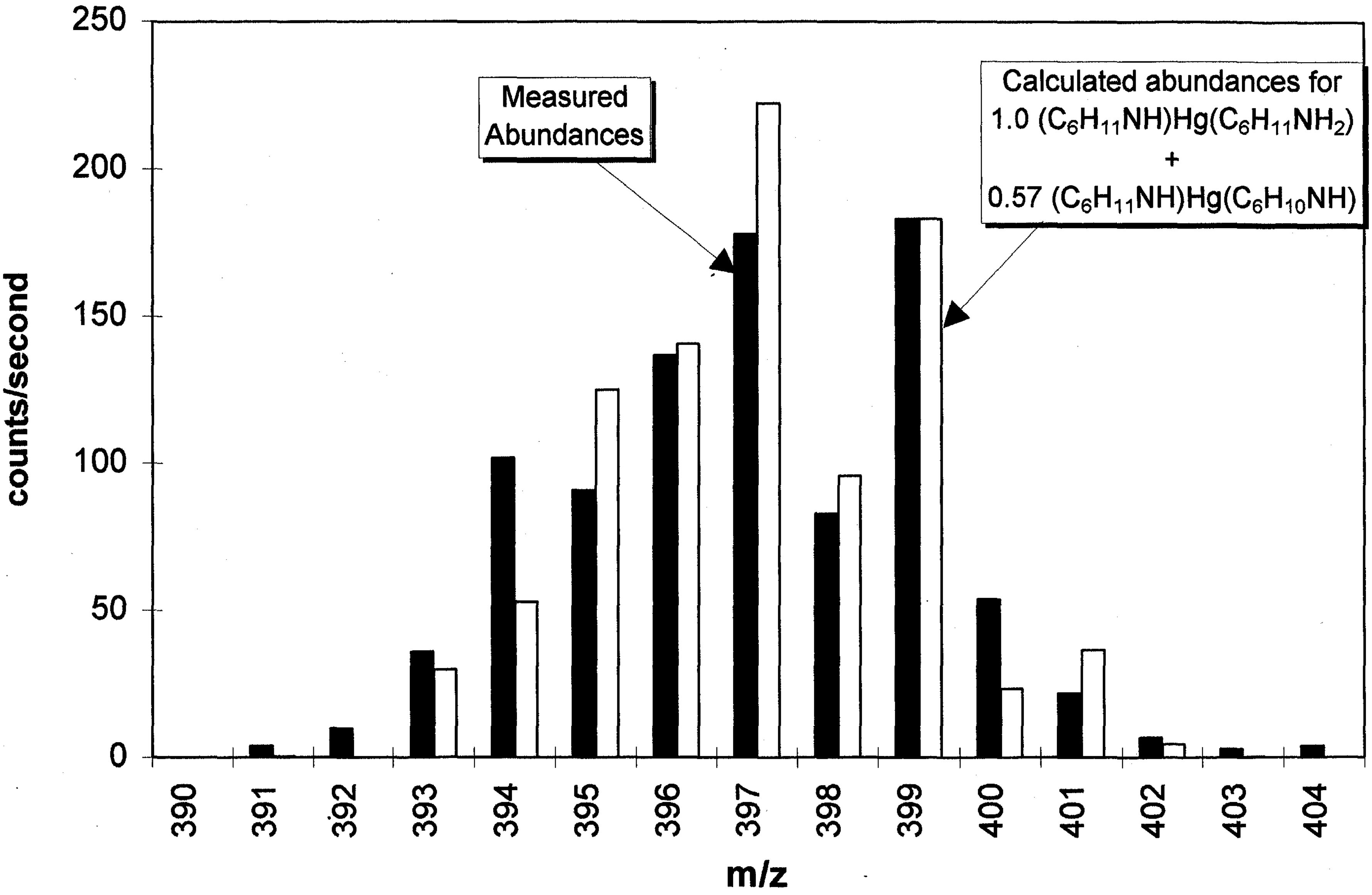


Figure 2-14. Isotopic ions for $Hg(CHA)_2$, plotted with theoretical abundances calculated for a combination of two compositions differing in mass by 2 amu

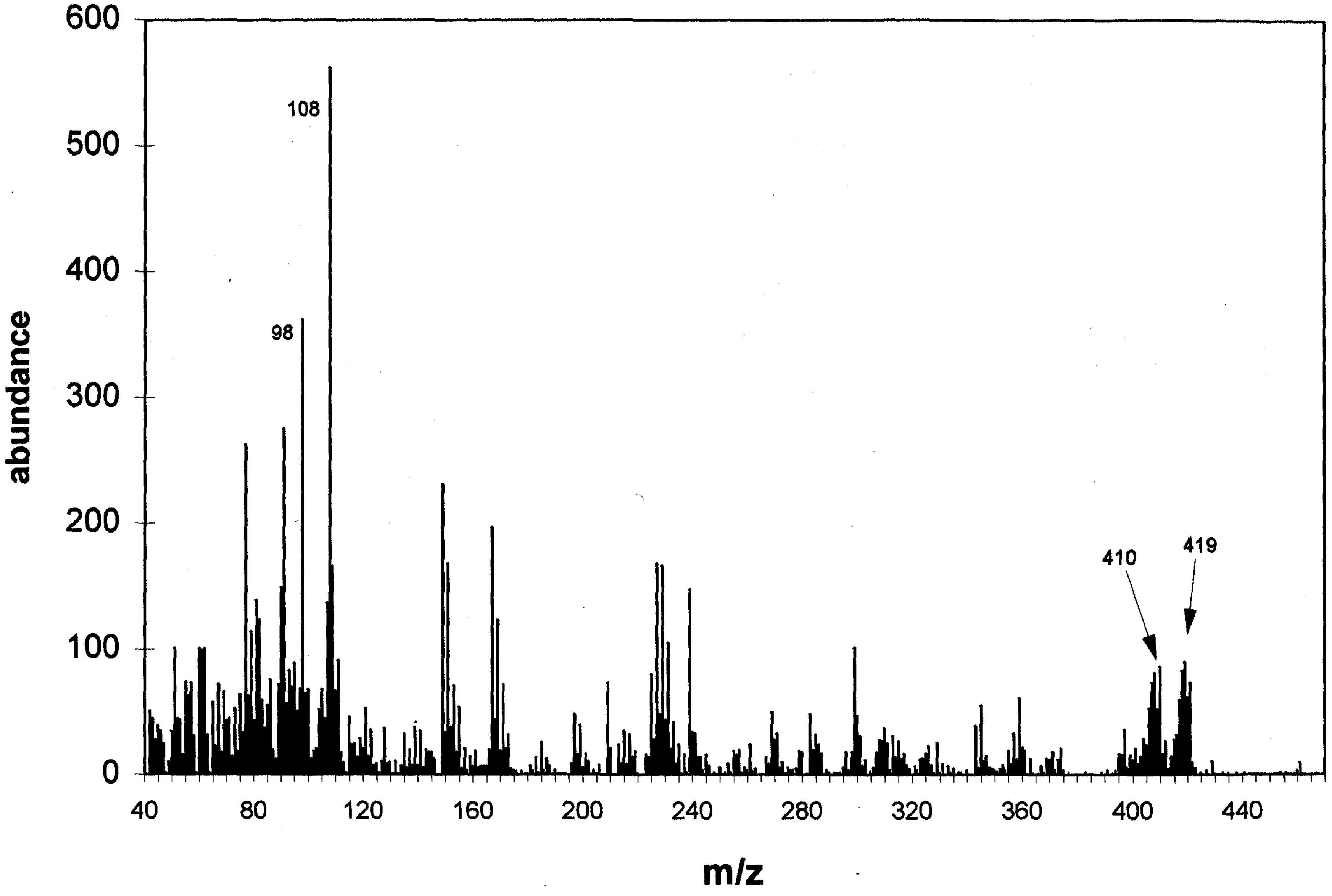


Figure 2-15. Cation SIMS spectrum of $Hg(NO_3)_2$ exposed to CHA-$\underline{d}_{11}$ and adventitious CHA. Acquired using ion trap SIMS instrument.

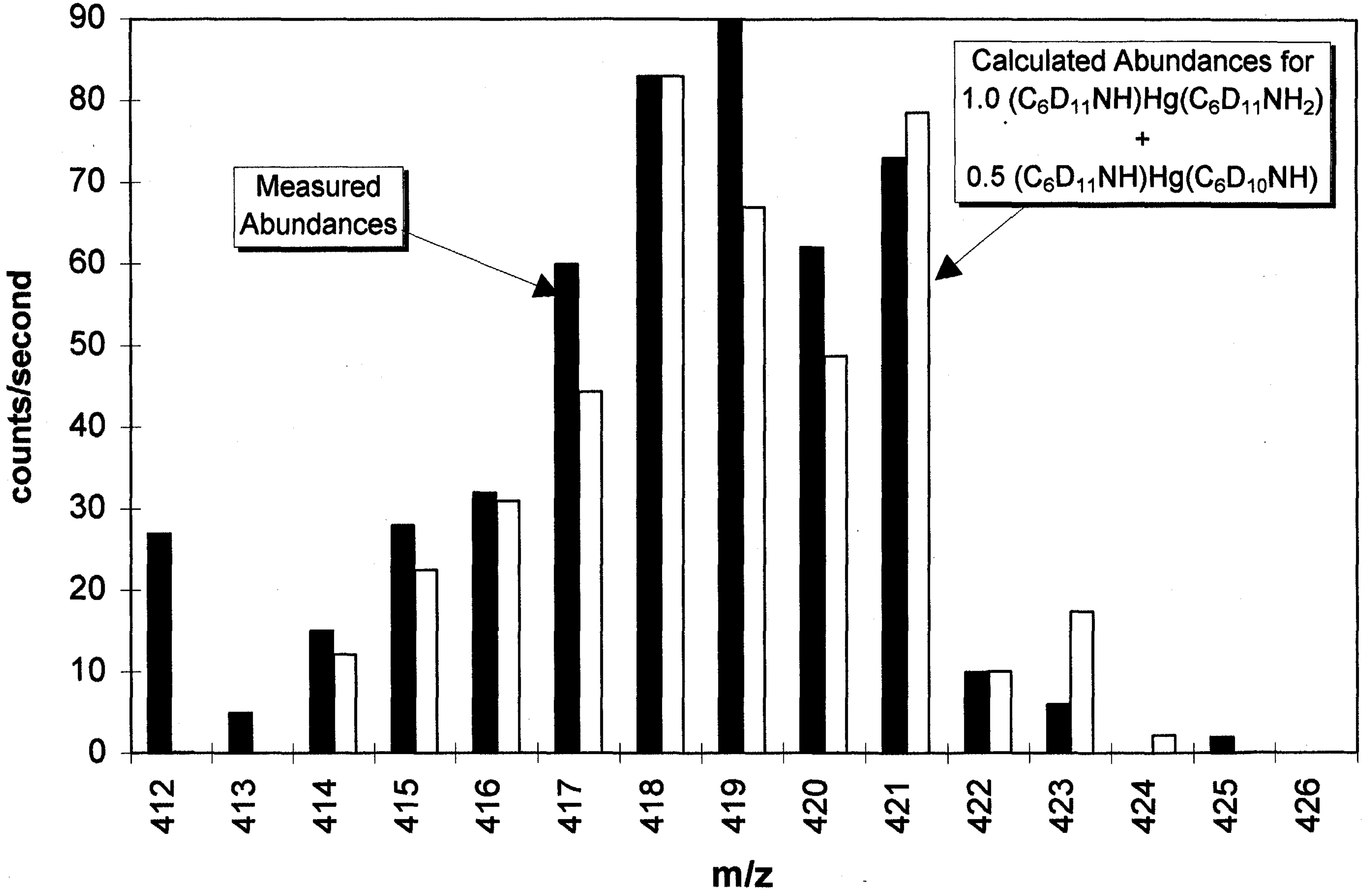


Figure 2-16. Isotopic ions for Hg(CHA-$\underline{d}_{11}$)$_2$, plotted with theoretical abundances calculated for a combination of two compositions differing in mass by 3 amu.

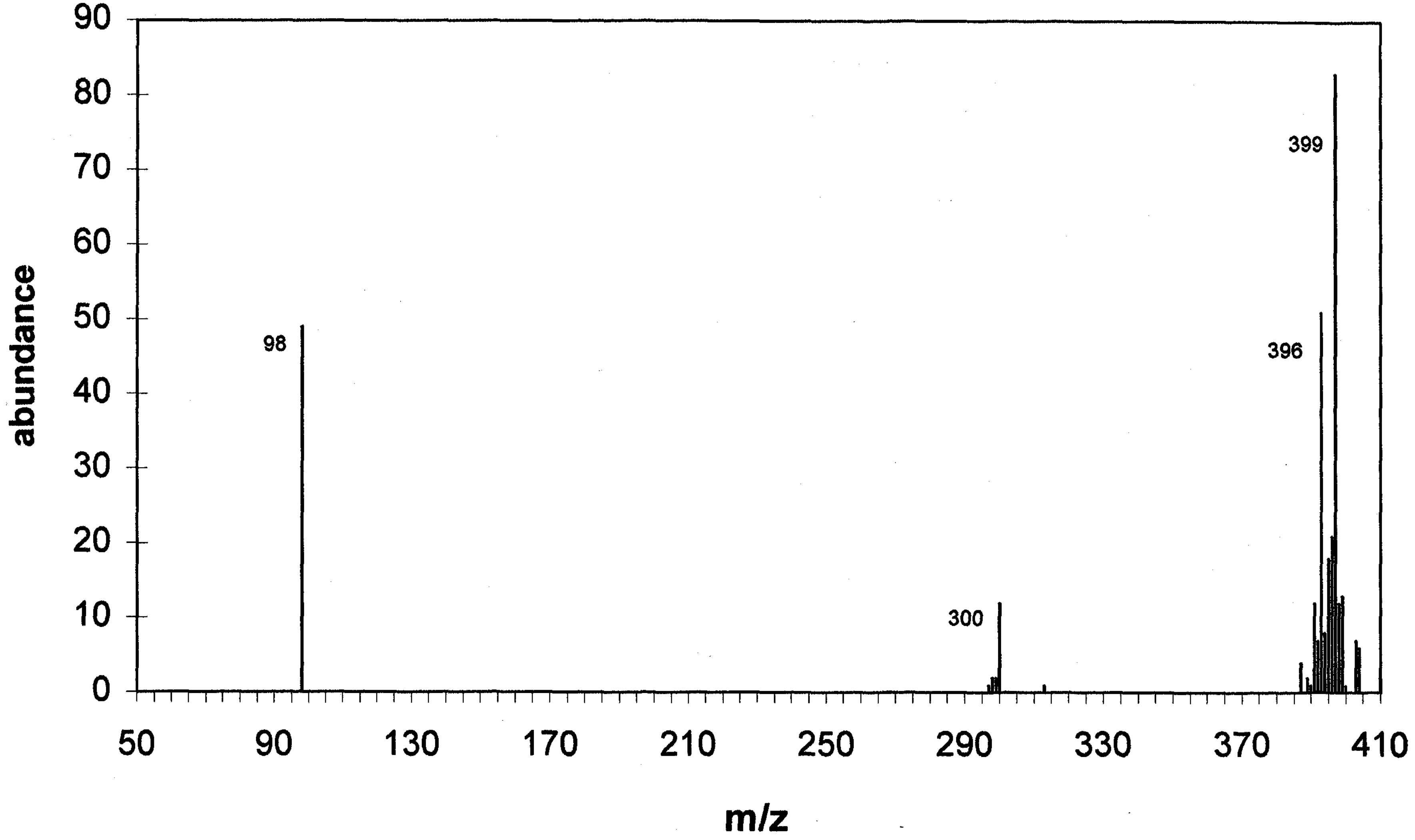


Figure 2-17. SIMS/MS of CHA adsorbed to $Hg(NO_3)_2$, *m/z* 399 region isolated and fragmented.

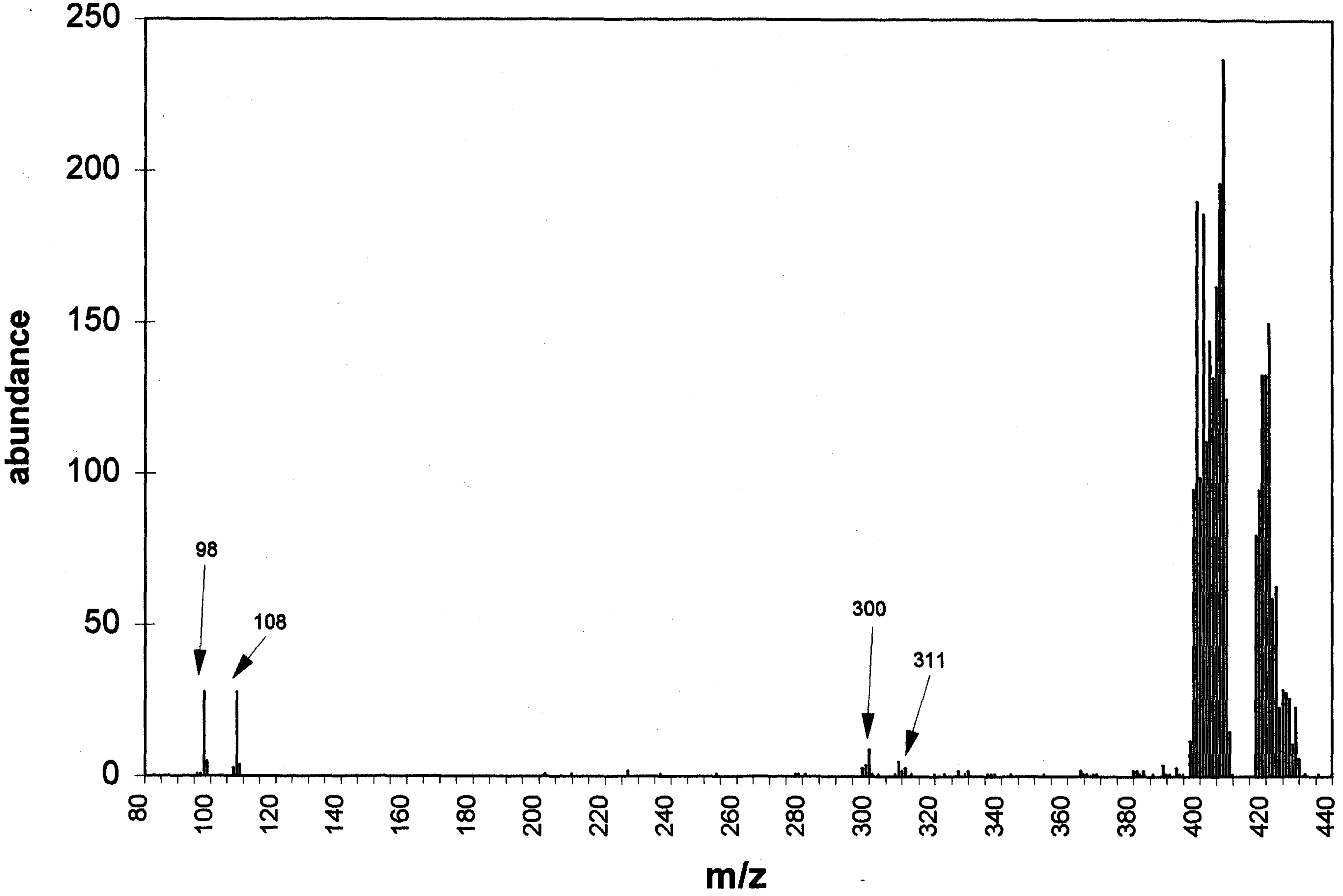


Figure 2-18. SIMS/MS of CHA-$\underline{d}_{11}$ adsorbed to $Hg(NO_3)_2$, *m/z* 410 region isolated and fragmented.

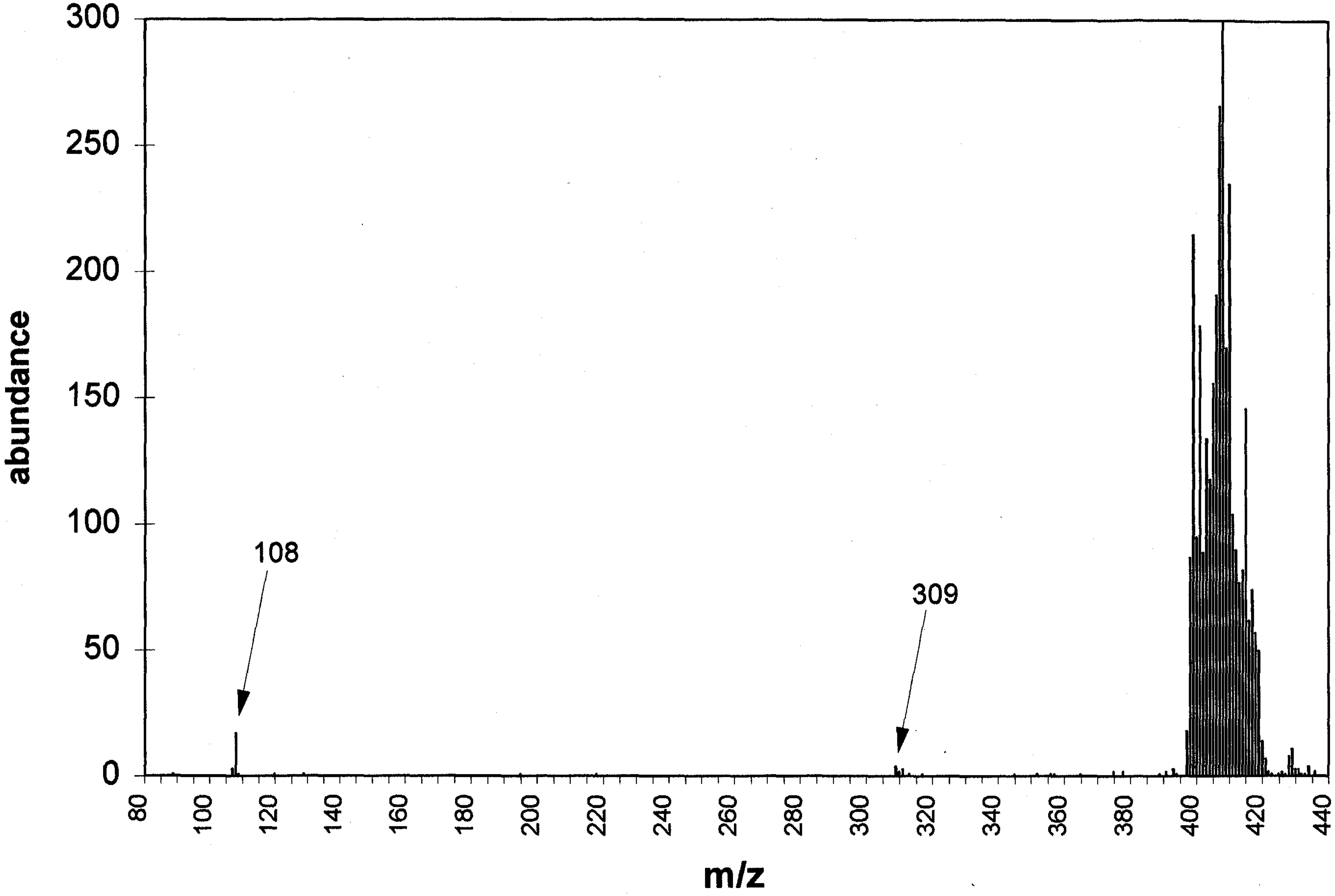


Figure 2-19. SIMS/MS of CHA-$_d$11 adsorbed to Hg(NO3)2, m/z 421 region isolated and fragmented.

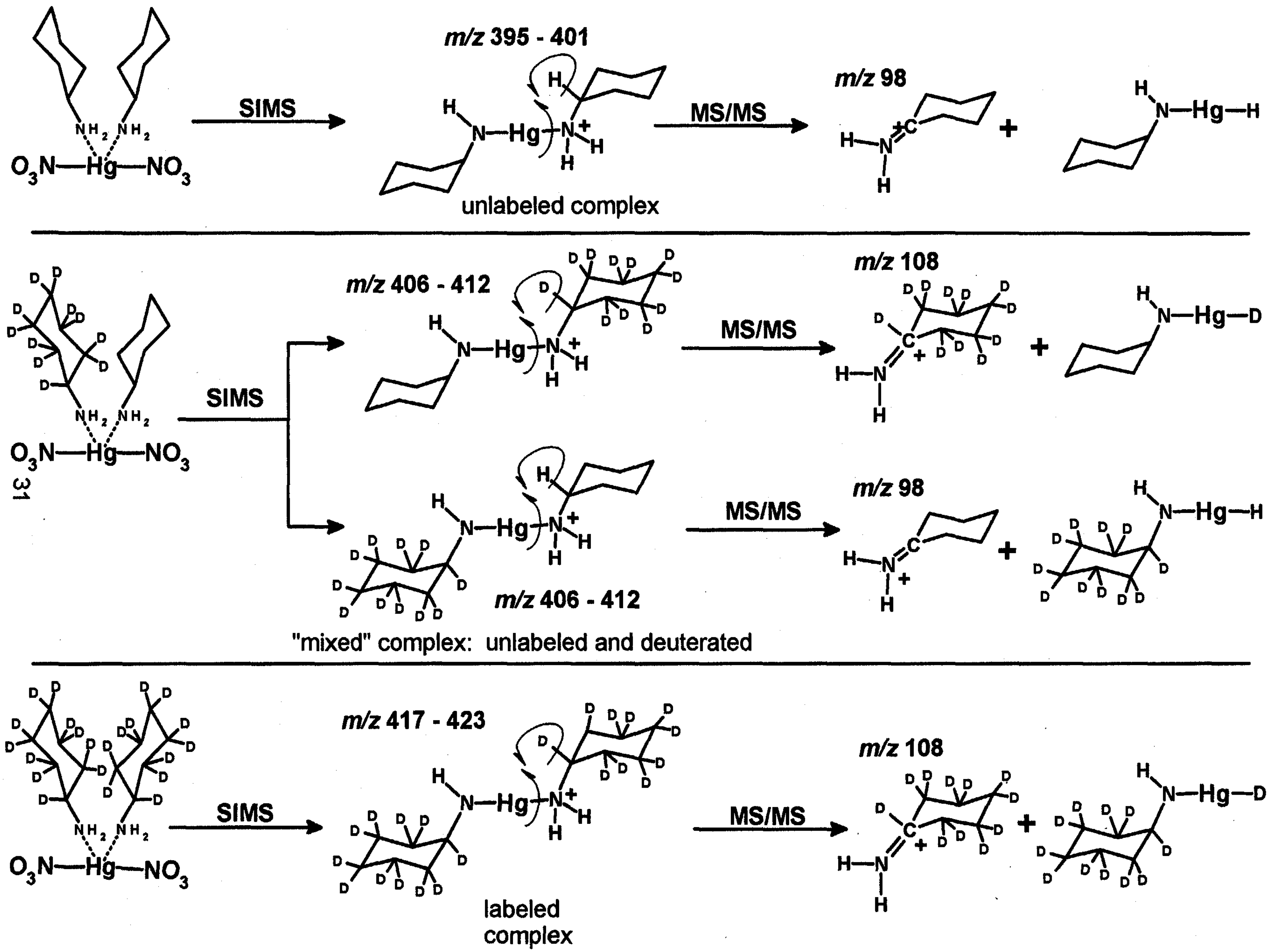


Figure 2-20. Proposed structures and fragmentation for $Hg(CHA)_2$ adducts observed in the static SIMS spectrum of CHA adsorbed to $Hg(NO_3)_2$.

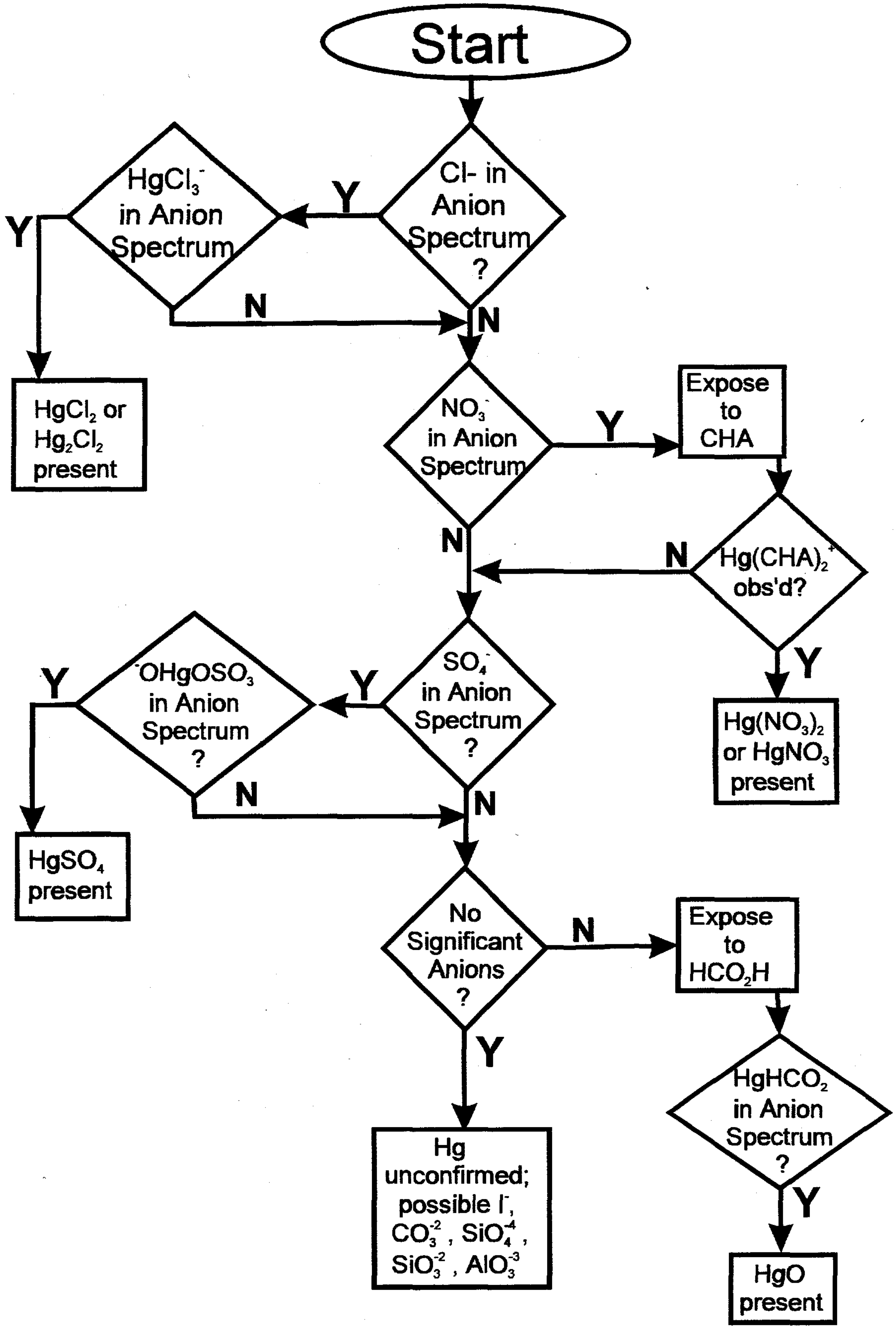


Figure 2-21. Qualitative scheme for identification of Hg surface species using static SIMS.

3.0 EDTA ANALYSIS USING LASER DESORPTION ION TRAP MASS SPECTROMETRY

3.1 Introduction

The purpose of this investigation was to explore the feasibility of using laser desorption ion trap mass spectrometry for the analysis of ethylene diamine tetraacetic acid (EDTA) in environmental soil samples. EDTA is a common contaminant in DOE waste disposal sites, and the compound is known to efficiently complex with uranium and other radioactive elements. The complexed elements are mobilized in the subsurface, because they are not effectively sorbed. For this reason, methods for detection and speciation of EDTA are sought. At the present time, the analysis of EDTA costly and time consuming: the compound must be extracted from the matrix, then derivatized, and finally analyzed by gas chromatography. Since laser desorption mass spectrometry has been demonstrated for the volatilization of highly ionic compounds, the technique might be suitable as a preliminary screening method for EDTA in soil samples. Recent research has focused on interfacing laser desorption with ion trap mass spectrometers; if successful, the end product might be applicable to DOE characterization scenarios. Dr. Luke Hanley of the University of Illinois at Chicago is the leading expert in this area, and for this reason, a study was contracted to his laboratory to explore the possibility of using laser desorption ion trap mass spectrometry for characterizing EDTA.

3.2 Experimental Details

3.2.1. Instrumentation. The experimental apparatus is shown in Figure 3-1. The core experimental configuration (without SWIFT or 212 nm laser pulses) has been described previously.[1]

Solid samples were introduced into the vacuum chamber on the end of a solids probe. They were vaporized and ionized by 212 nm laser pulses produced by 5th harmonic generation from a Nd:YAG laser. The ions were held inside the ring electrode of the ion trap by a low amplitude radio frequency voltage, then mass-selectively ejected into the dynode/channeltron detector. The ion trap was filled with ~10^{-4} torr of He buffer gas during the experiments, unless otherwise noted.

Since the last description of this apparatus[1], we have added the capability to eject unwanted ions prior to the final mass sweep by use of the SWIFT technique[2,3]. SWIFT pulses were constructed using MathCad software, then downloaded to the LeCroy LW410 arbitrary waveform generator (AFG). The AFG was fired by a computer based data acquisition board (National Instruments PC-TIO-10). The laser, AFG, and radio frequency pulse sequences used in these experiments are shown in Figure 3-2.

An example of the utility of the SWIFT method is shown in Figure 3-3. The top spectrum (A) shows negative carbon clusters produced by laser ablation of graphite.

The middle spectrum (B) depicts the same carbon cluster spectrum after all ions below m/z 80 have been ejected by a SWIFT pulse. Low mass ejection was used frequently in EDTA analysis (see below). The lower spectrum (C) in Figure 3-3 shows isolation of a single mass carbon cluster at m/z 60 by use of a different SWIFT pulse.

By reversing the high voltage polarity on the dynode, either positive or negative ion spectra could be recorded.

The entire experimental apparatus, laser desorption scheme, and SWIFT methodology were implemented in our laboratory prior to the receipt of this INEL subcontract, using funds from non-INEL sources. The above information has been included here as background for the analyses and methodologies discussed below.

3.2.2. Sample Preparation. Aqueous solutions of Na_2EDTA and Mg_2EDTA salts were prepared and dried onto aqua regia etched stainless steel or mechanically polished basalt surfaces. Where noted, roughly equal amounts of $NaNO_3$ or $NaNO_2$ were added to these solutions to enhance the EDTA ion signals. The pH of these solutions was varied by the addition of NaOH or HNO_3. The Raritan soil samples were finely ground with dry Na_2EDTA, wetted with $NaNO_2$ solutions, then pressed into the surface of a piece of aluminum foil.

All experiments and most of the data analysis were performed by Oleg Kornienko. Preliminary results were obtained by Sean Brynjelsen. Support for both of these graduate students was provided by INEL funds.

3.3 Results and Discussion

A few general trends appear from the spectra presented below. Intact ions of EDTA salts were not observed. No ions of m/z > 140 were observed either. Instead, both positive and negative ion spectra displayed several "fingerprint" ions which can be used to identify the presence of EDTA in unknown samples. Attempts have made to chemically identify these characteristic ions, but definitive assignments would require tandem mass spectrometry experiments which are currently beyond the capability of our instrument (due to insufficiencies in the buffer amplifier following the AFG).

Figure 3-4 displays the positive ion spectra from a mixture of Na_2EDTA and $NaNO_3$ dried onto stainless steel from solutions having pH = 2, 7, and 12. SWIFT pulses were used to eject most ions of m/z < 40. Strong ion signals were observed at m/z 44, 54.5, 62, 63, 91, 111, and 129. The ion at m/z 44 may be CO_2^+, or alternatively $O{=}C{=}NH_2^+$; both ions could easily be derived from EDTA. The assignment of CO_2 is supported by the observation that *m/z* 45^+ was prominent in the spectrum of the acidic solution, which likely indicates the formation of CO_2H^+. The ions at m/z 62 and 63 almost certainly correspond to Na_2O^+ and Na_2OH^+, and are derived from $NaNO_3$; these ions are also observed in the SIMS spectra of unmodified $NaNO_3$ and NaOH. The ion at m/z 129^+ is

$Na_3CO_3^+$, which results from fixation of CO_2 by a basic surface. The ion may be EDTA-derived, but this explanation is not favored because the ion can also be observed in the spectra of basic solids like NaOH. For neutral pH samples, the fingerprint ions for EDTA were assigned as m/z 44, 54.5, 91, and 111.

Figure 3-5 displays the negative ion spectra from a mixture of Na_2EDTA and $NaNO_3$ dried onto stainless steel at solution pH = 2, 7, and 12. SWIFT ejection of m/z < 35 did not affect the spectrum since there are few ions in this mass range other than m/z 26. The strongest negative ions observed are m/z 26 and 42. The former is certainly due to CN^- and the latter probably results from NCO^- or $N(CH_2)_2^-$. The relative intensities of these two ions were unaffected by solution pH. The m/z 75 ion could be assigned to $Na(CN)_2^-$ or $NH_2CH_2COOH^-$. The m/z 91 ion could result from CN loss from $H_2NCH_2CH_2NHCH_2CO_2^-$. The m/z 107 ion could be assigned to $(H_2N)_2NCH_2CONa^-$ or $Na(CNO)_2^-$. The fingerprint ions for EDTA + $NaNO_3$ are m/z 26, 42, 91, and 107 (the m/z 75 ion tends to be of lower intensity).

Figure 3-6 displays the negative ion spectra of pH = 7 solutions of (a) neat Na_2EDTA, (b) Na_2EDTA + $NaNO_2$, (c) Na_2EDTA + $NaNO_3$, and (d) Mg_2EDTA + $NaNO_2$. In addition to the m/z 26, 42, 91, and 107 ions depicted in Figure 3-5, the m/z 124 ion also appears in all of these spectra. M/z 124^- most likely corresponds to $Na_2(CN_3)^-$. Addition of $NaNO_2$ or $NaNO_3$ salts increased the ion signals by a factor of two to fivefold. Similar enhancements were observed for the positive ion spectra (data not shown). No ions from $NaNO_3$ were observed in these EDTA spectra, although they could be formed from the pure nitrate salts. The similarity of the sodium and magnesium salt spectra indicate that Mg did not contribute to the gaseous ion complexes, although Na-bearing ions observed in the spectra of the Mg salts might be derived from the added $NaNO_2$. Presumably, it is expected that EDTA complexes with other non-alkali metal ions would not affect the ions observed in 212 nm laser desorption mass spectra.

Additional negative ion spectra were recorded with deuterium substituted for the helium buffer gas in the trap. No shifts in masses were observed, although the negative ion signal increased significantly. This implies a lack of gas phase protonation in the negative ion spectra.

Figure 3-7 displays Na_2EDTA spectra from basalt surfaces. Spectrum (a) indicates a detection limit of 200 pmole (64 ng EDTA) and the predominance of the m/z 26, 75, and 124 ions. Spectrum (b) was collected for a sample containing ~1400 pmole (450 ng), and m/z 42 and 91 ions are observed in addition to those ions mentioned earlier. The amount of sample desorbed was estimated by consideration of the laser spot size and the concentration of EDTA solution deposited on the surface. The 200 pmole limit of detection estimate should be considered only approximate.

Figure 3-8 depicts the positive and negative ion spectra of 1% by weight Na_2EDTA in Raritan valley soil, mixed with $NaNO_2$. Both the positive and negative ion spectra display most of the fingerprint ions discussed above, although they also show significant signal from other ions originating from the soil (e.g., K^+ at m/z 39 in the positive ion spectrum).

The basalt surfaces and the Raritan soil samples were recorded to simulate actual environment soil samples contaminated with EDTA salts or complexes. It is clear that either positive or negative ion spectra could be used to identify EDTA in such samples, although the degree of uncertainly would be reduced by utilizing both types of spectra. However, the limit of detection for EDTA by this method might require further improvement. Furthermore, the sensitivity clearly varies strongly with the type of soil sample. Instrumental considerations dictate that sensitivity to EDTA will also depend upon the type of mass spectrometer employed. Any practical application of this method to EDTA analysis in soils must be precluded by careful calibration with clean and EDTA spiked samples of the soils of interest using the same mass spectrometer which will be employed for the unknown analysis.

3.4 Conclusions

We have demonstrated that 212 nm laser desorption ion trap mass spectrometry can be used for the direct analysis of EDTA salts on stainless steel surfaces, basalt surfaces, and soil samples. Analysis must be accomplished by the identification of several fingerprint ions since no intact molecular ions are observed. While either could be used for analysis, the most reliable method would be to record both the positive and negative ion spectra for a given sample. Limits of detect are as low as 200 pmole, but depend strongly on sample preparation. Addition of $NaNO_2$ or $NaNO_3$ enhanced the ion signals by two to fivefold. Further experiments are required to develop 212 nm laser desorption ion trap mass spectrometry into a reproducible and quantifiable method for the analysis of EDTA in soils. However, it is clear that this methodology is feasible for this type of environmental soil analysis.

3.5 References

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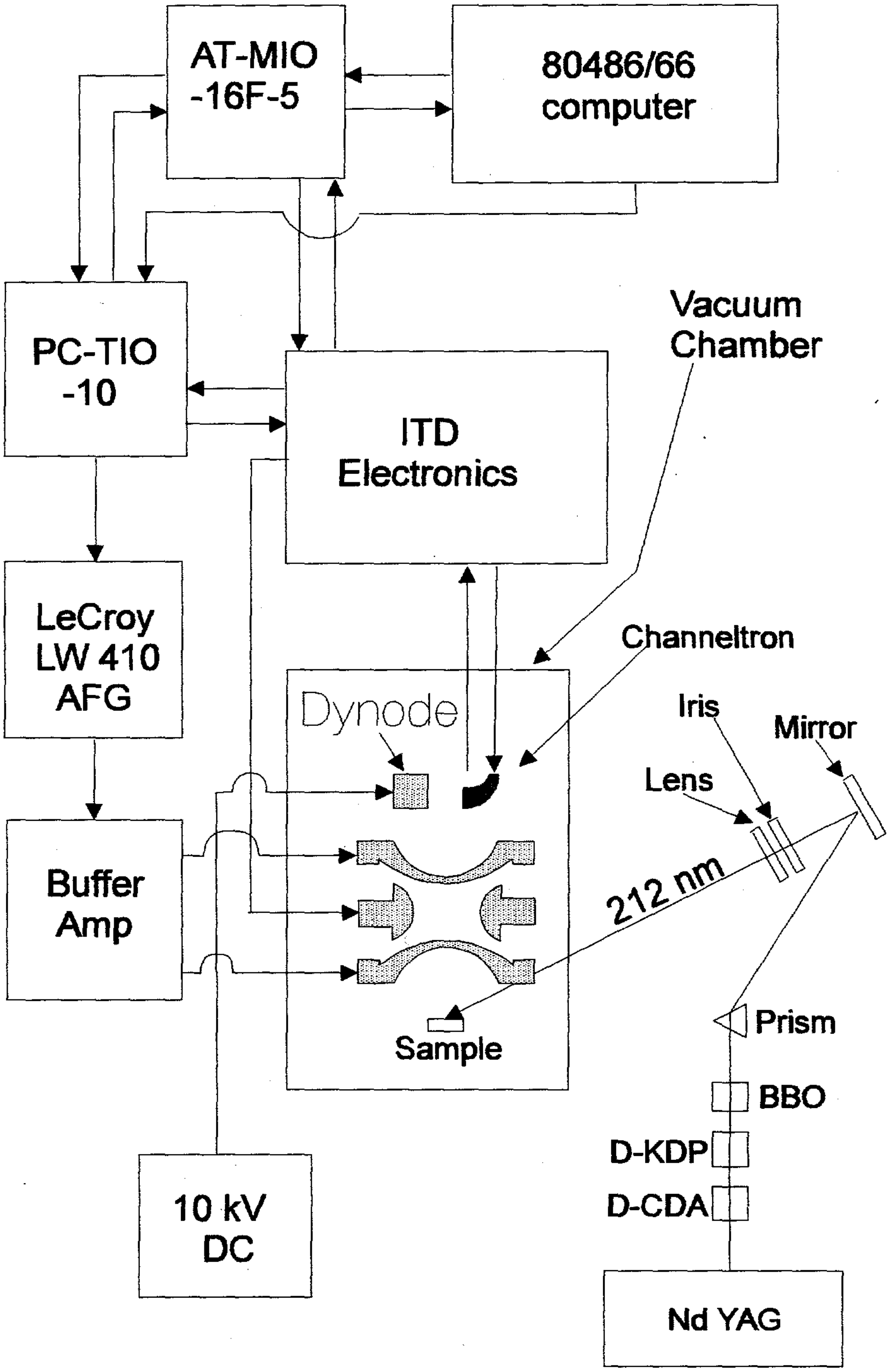

Figure 3-1. Schematic diagram of laser desorption ion trap mass spectrometer

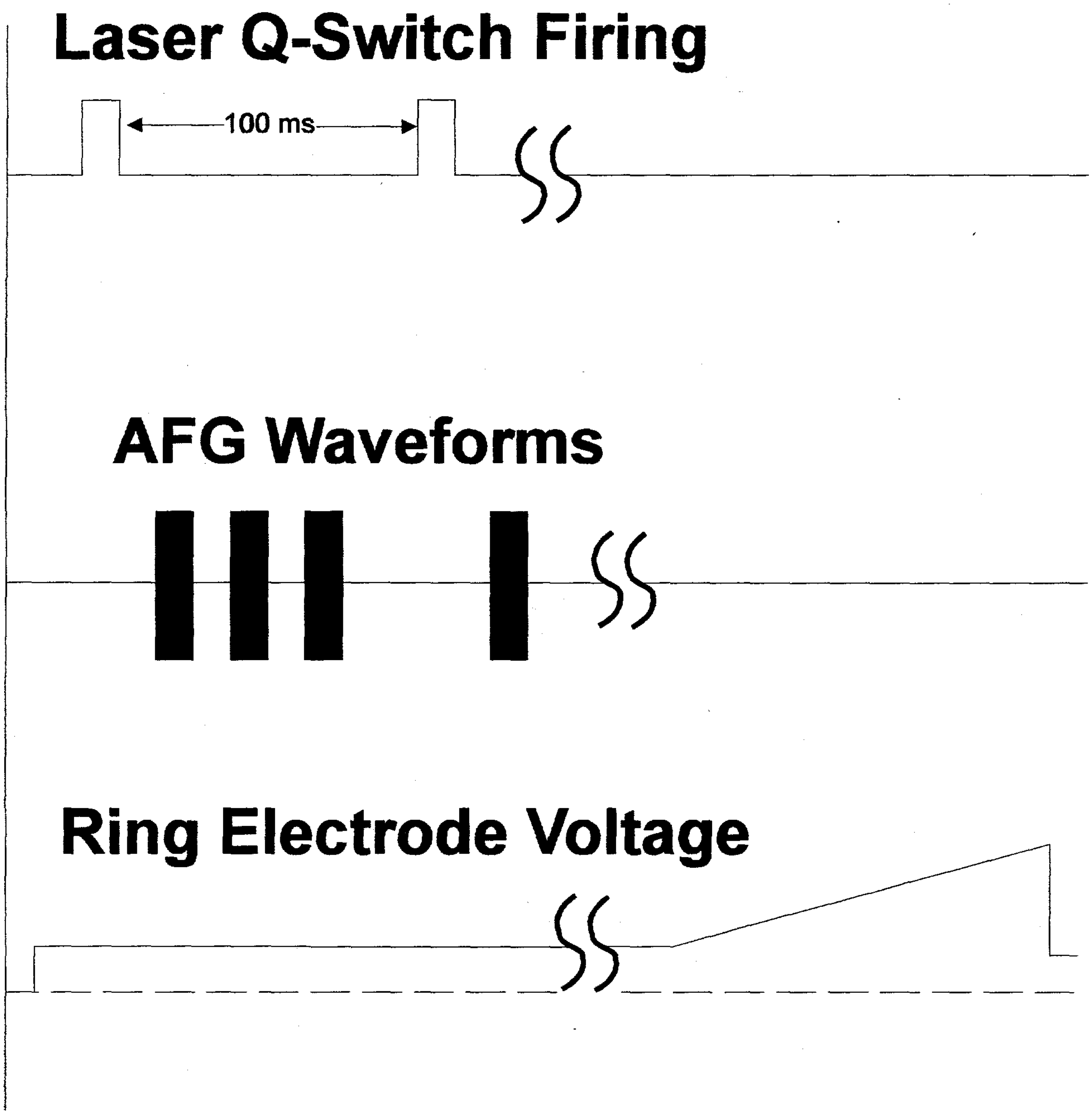

Figure 3-2. Laser, AFG, and radio frequency pulse sequences used in laser desorption experiments.

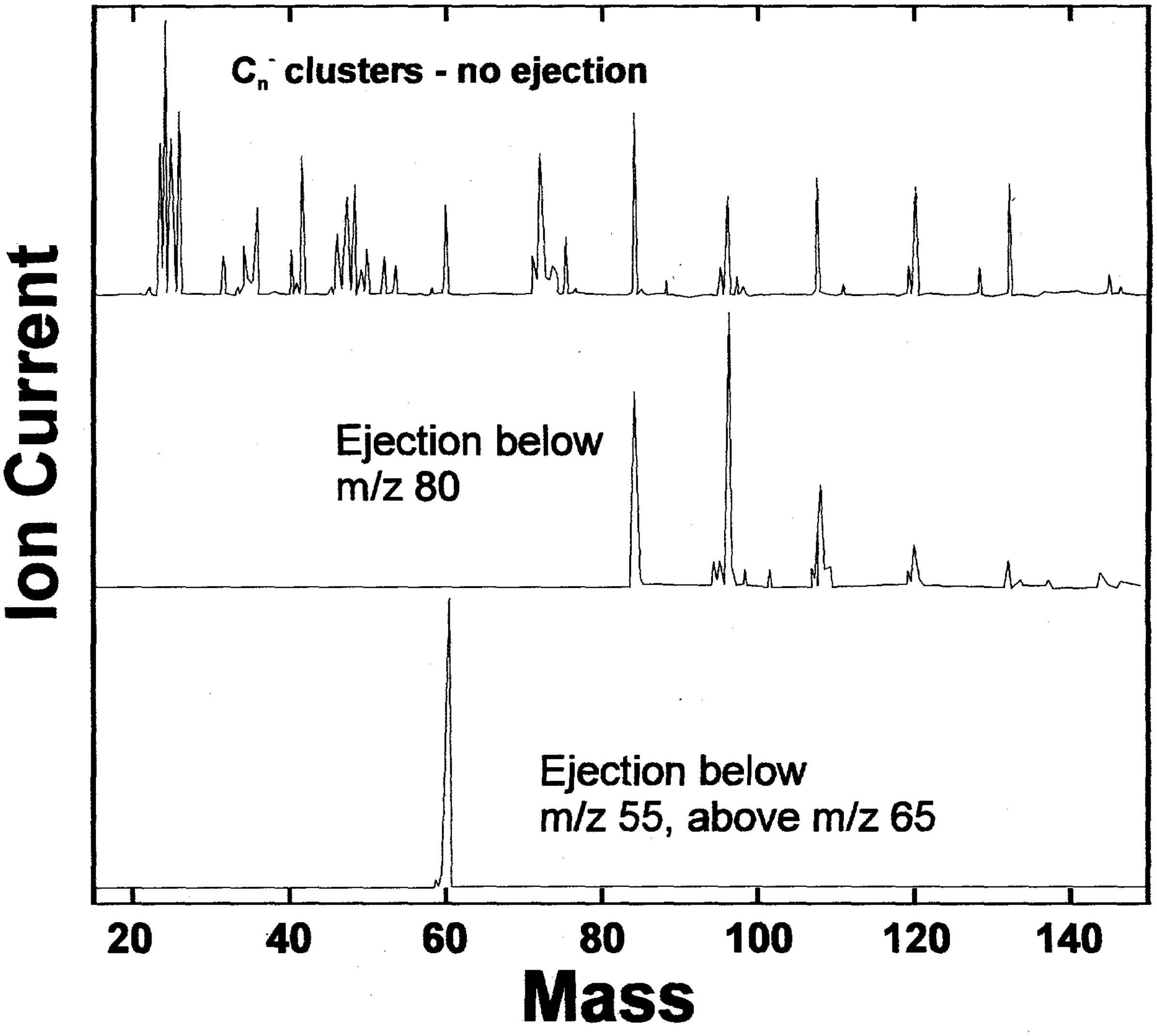

Figure 3-3. Demonstration of SWIFT ejection of carbon clusters from ion trap.

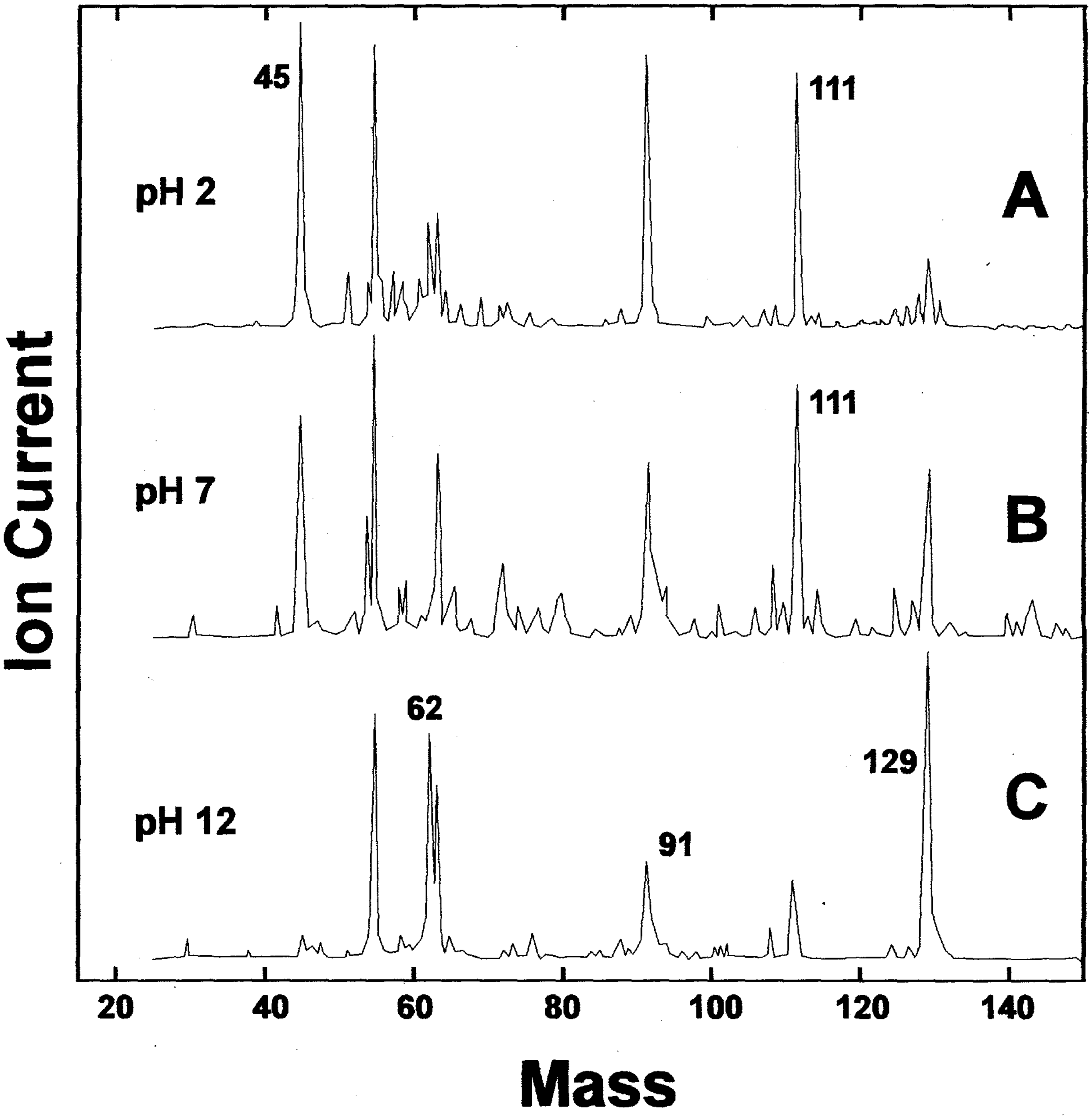

Figure 3-4. Positive ions from Na_2EDTA + $NaNO_3$ on stainless steel at pH = 2, 7, and 12.

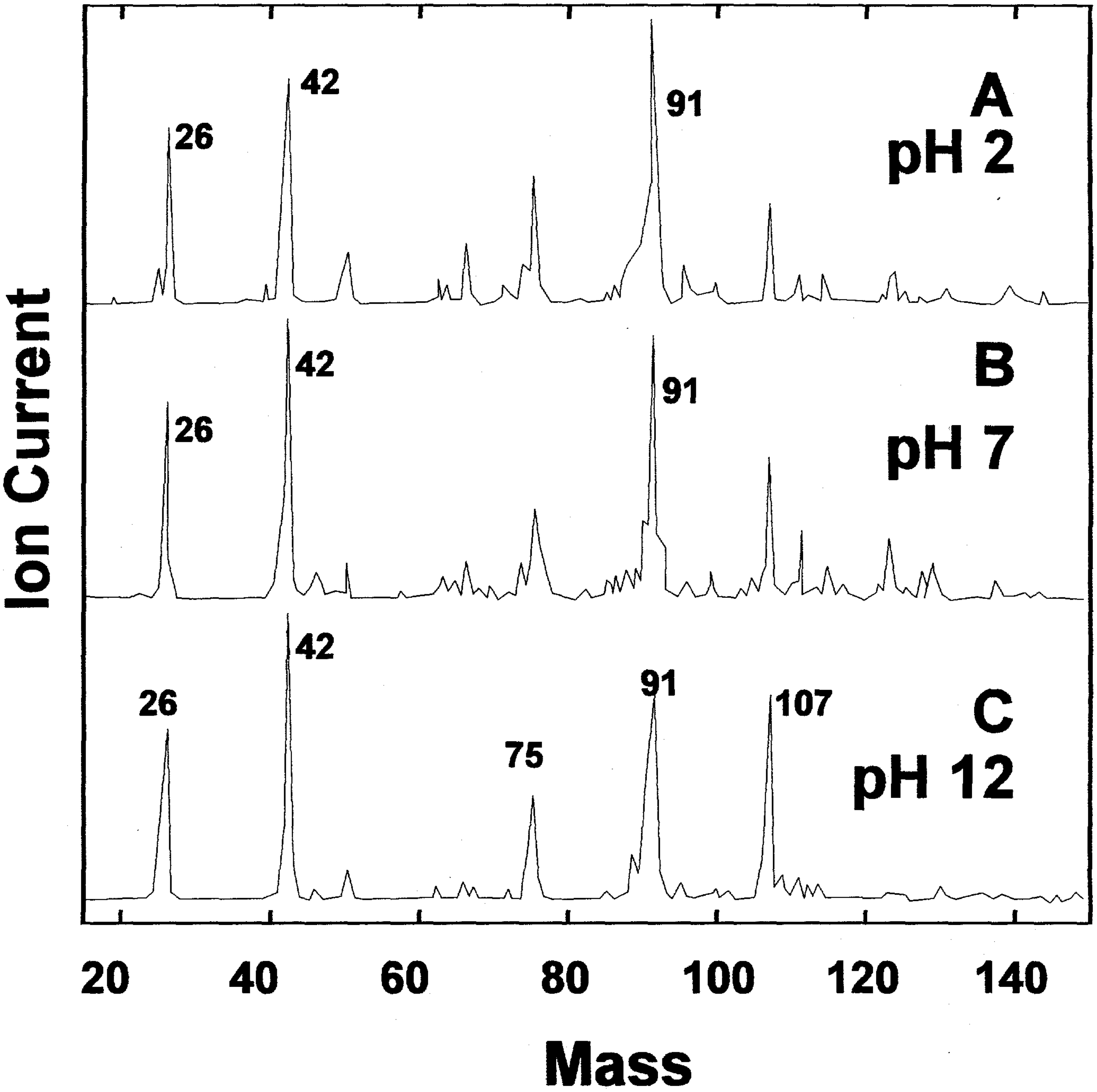

Figure 3-5. Negative ions from $Na_2EDTA + NaNO_3$ on stainless steel at pH = 2, 7, and 12.

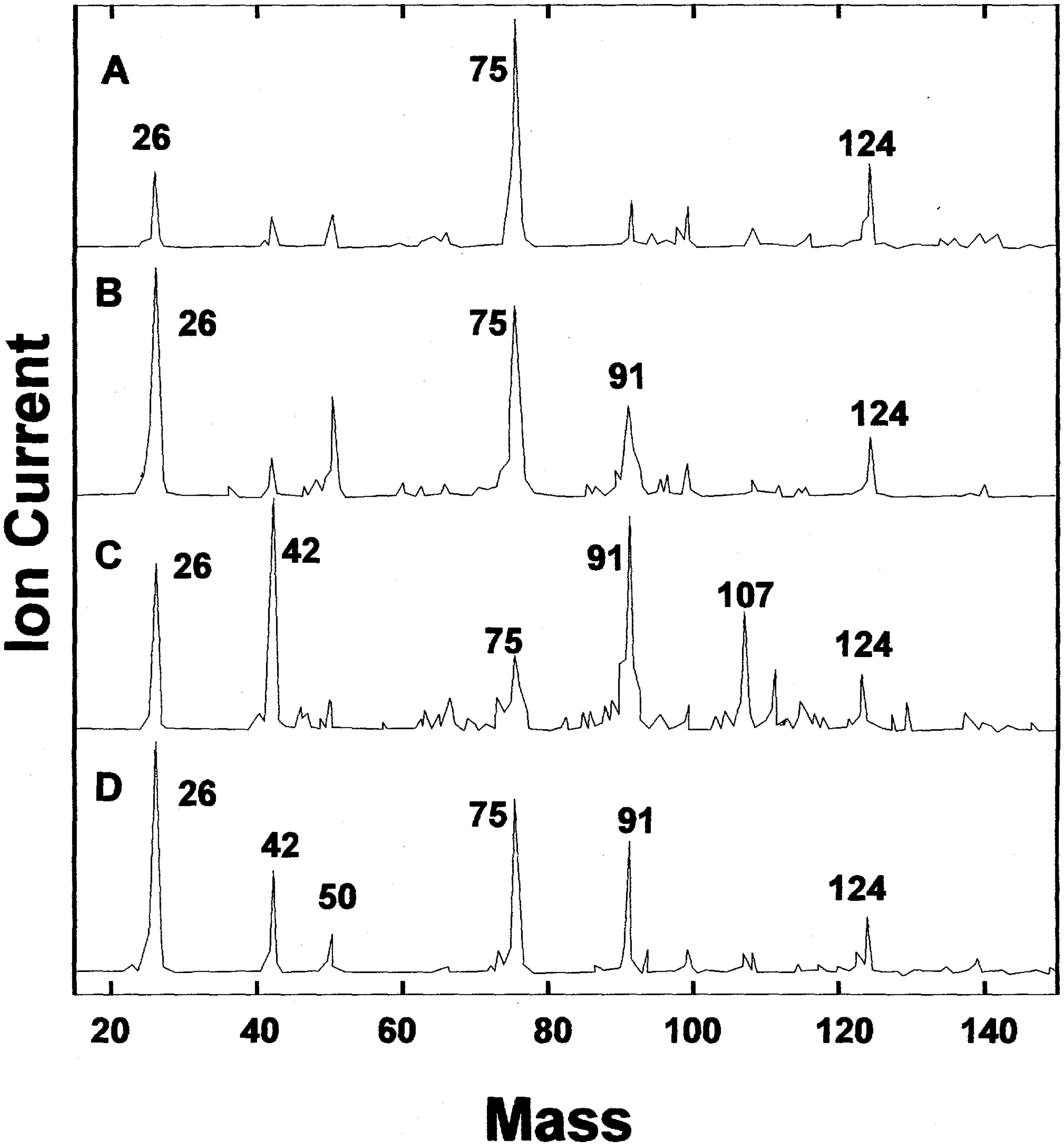

Figure 3-6. Negative ion spectra from pH = 7 solutions of (a) neat Na_2EDTA, (b) $Na_2EDTA + NaNO_2$, (c) $Na_2EDTA + NaNO_3$, and (d) $Mg_2EDTA + NaNO_2$.

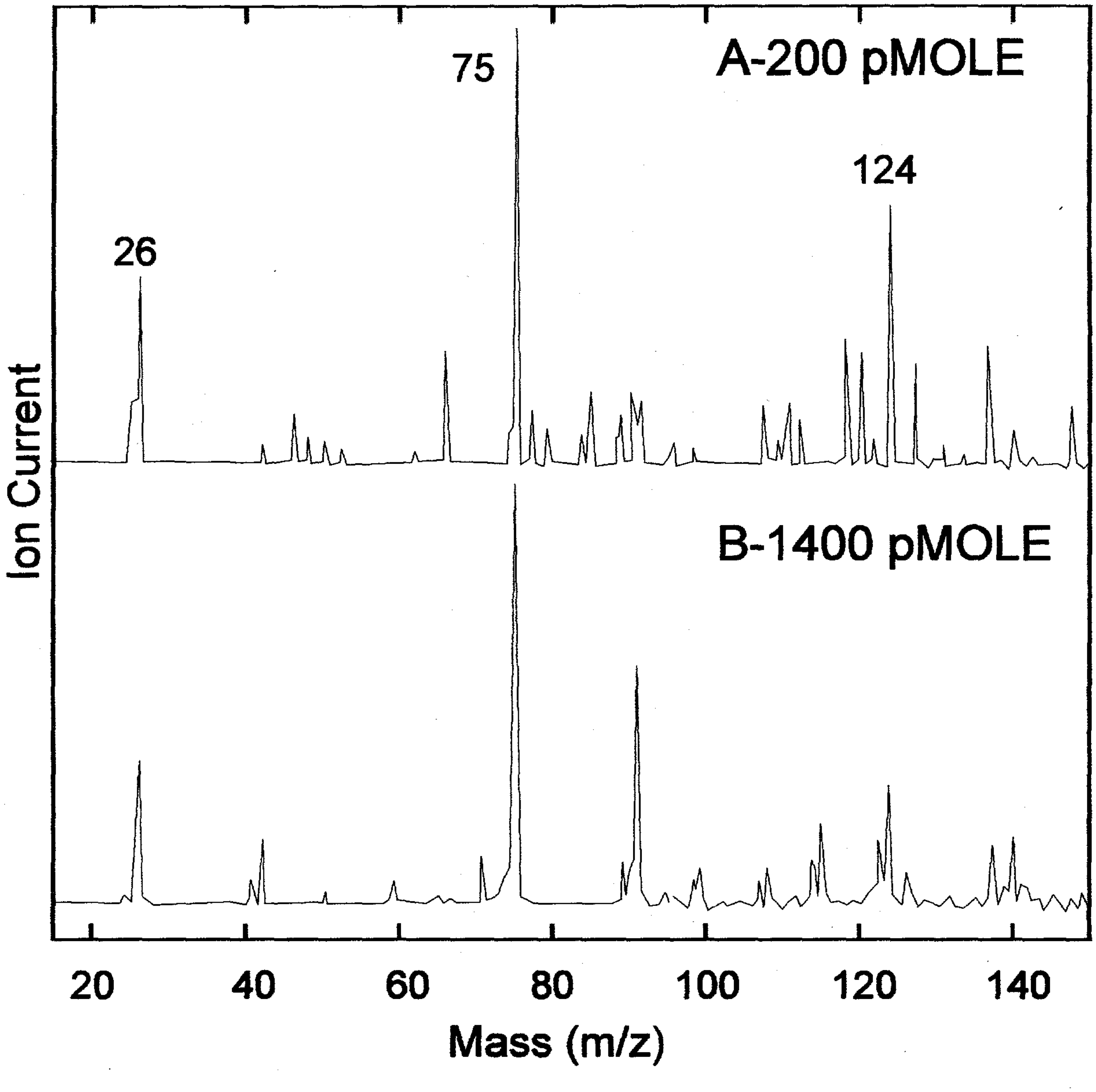

Figure 3-7. Negative ion spectra from (a) 200 pmole and (b) 1400 pmole of Na_2EDTA on a polished basalt surface.

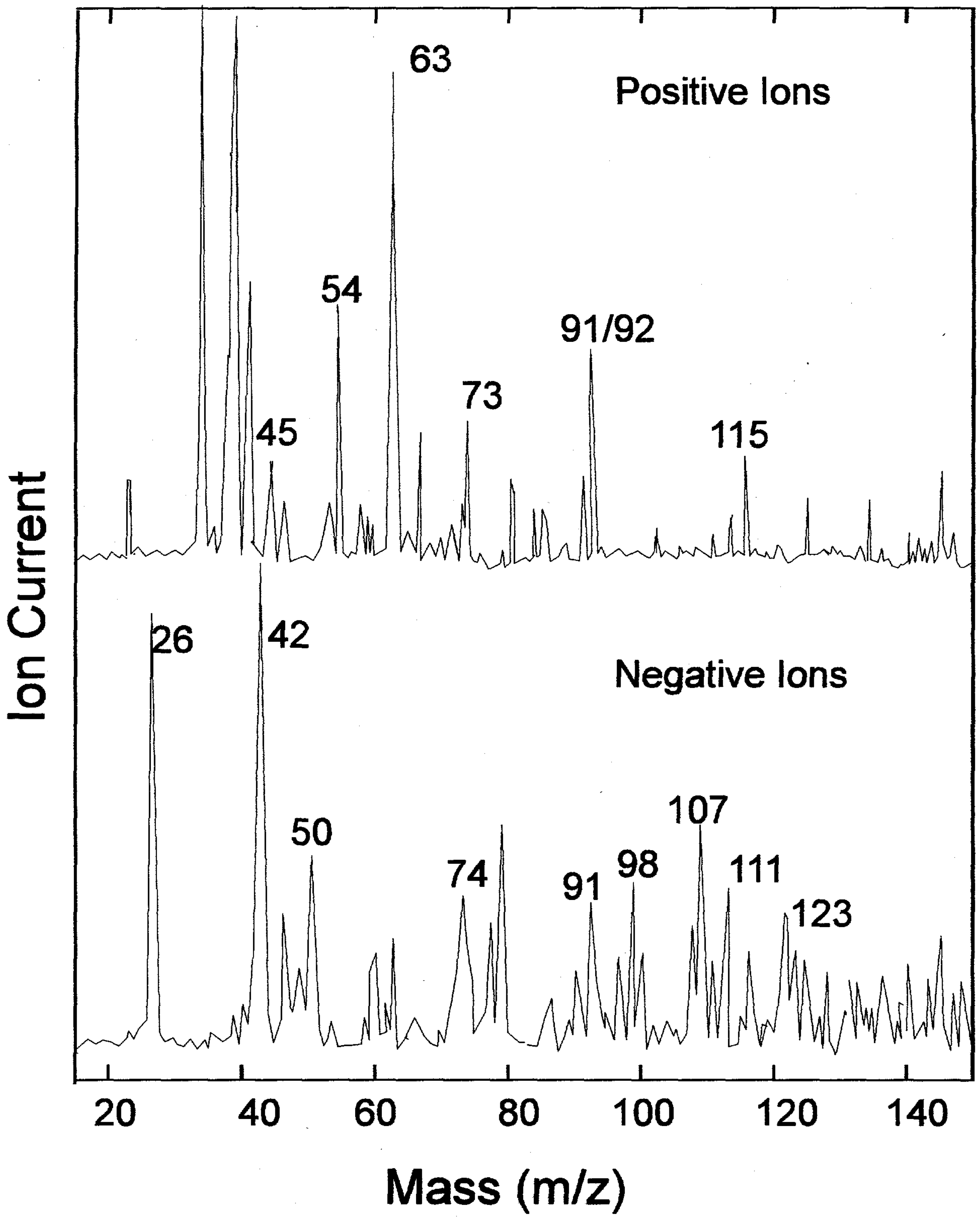

Figure 3-8. Positive and negative ion mass spectra of 1% by weight Na_2EDTA in Raritan soil, mixed with $NaNO_2$.

4.0 Ion Trap SIMS Development

An ion trap mass spectrometer was purchased from the Teledyne Corporation and modified with an ReO_4^- ion gun and an offset detector system. Electronics for controlling the offset detector optics and the ion gun pulsing were fabricated and tested. A delay in receipt of the ion gun power supply unit has delayed final testing of the ion gun, however fabrication of the supply has been completed by the manufacturer and is due to arrive the third week of September. The system has been tested in the electron impact mode of operation (the standard operating mode). A photograph of the system is shown in Figure 4-1. All components have been mounted on a rolling electronics cart, including the He bath gas. This makes the system transportable within the laboratory and demonstrates that a field-transportable system could be designed for operation at waste remediation sites.

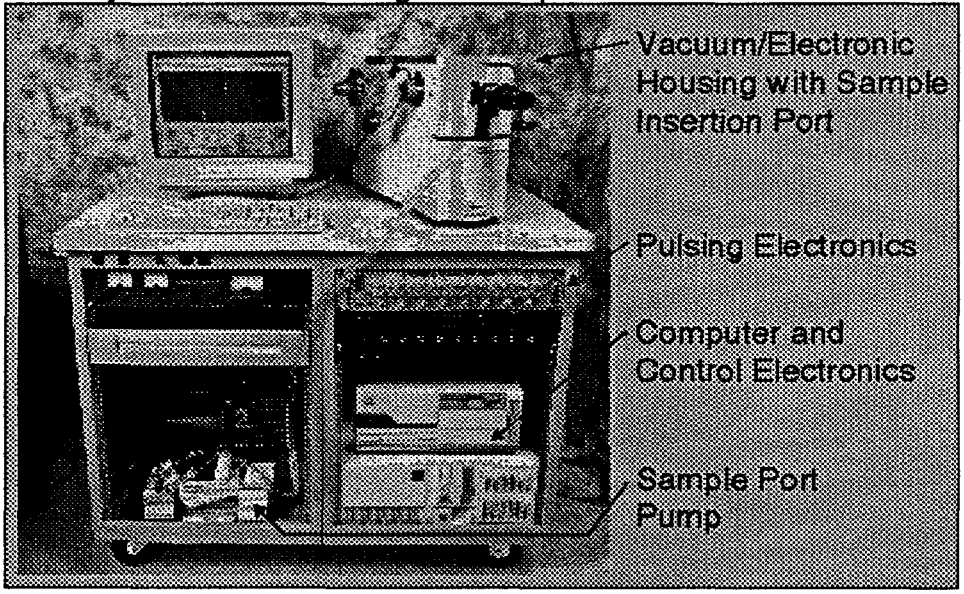

Figure 4-1. Teledyne ion trap mass spectrometer modified for secondary ion mass spectrometry.

A photograph of the internal components of the system is shown in Figure 4-2, which shows the ion gun, offset detector system, the ion trap mass spectrometer, and the sample inlet port. A schematic diagram of the system is shown in Figure 4-3. The ReO_4^- ion gun has been designed to be small, rugged, and require only a single power supply unit for operation. It produces a 2 mm beam with up to a nanoamp of current on target, and produces essentially no gas load on the pumping system. The gun is mounted on a gimbal assembly to permit alignment with the ion trap. The detector system is designed to allow the ReO_4^- ion beam to pass through the detector region during sampling, and to divert the secondary ions that are ejected out of the ion trap during mass analysis to the detector during the measurement period. This system includes a mirror lens that accomodates for the wide energy spread in the secondary ions as they are ejected out of the ion trap. Figure 4-4 shows a SIMION model of the ion trajectories. The system is designed to detect both positive and negative ions, although the current software only allows only one polarity to be collected at a time.

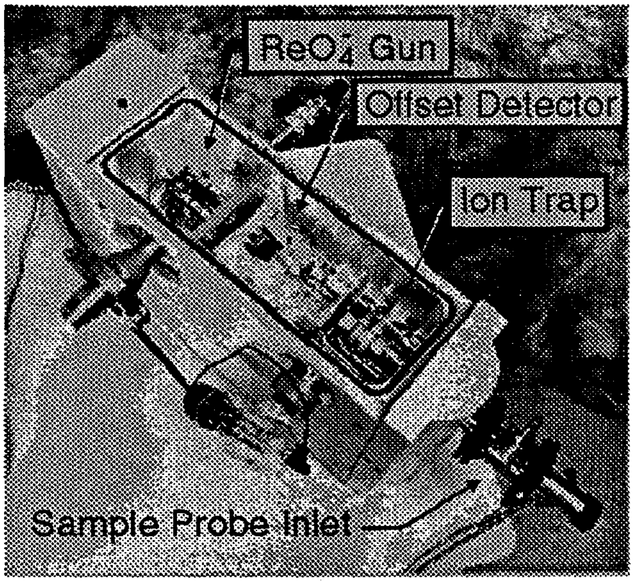

Figure 4-2. Top view of ion trap mass spectrometer showing the ion gun and offset detector components added inside the vacuum system, and the sample probe inlet assembly.

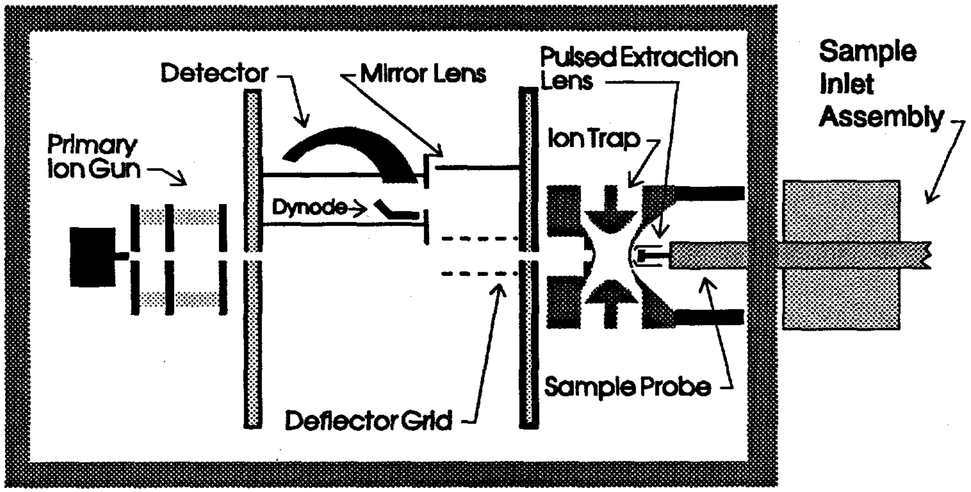

Figure 4-3. Layout of system modified for SIMS.

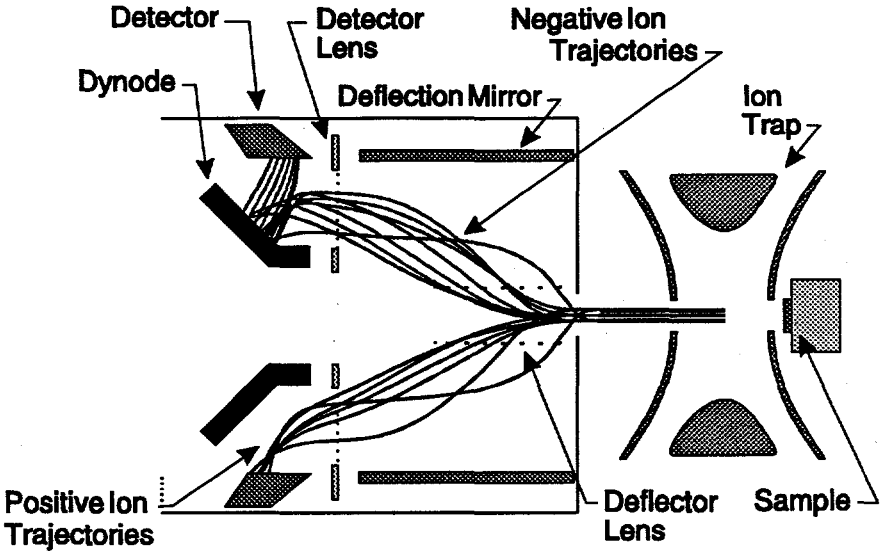

Figure 4-4. SIMION calculated ion trajectories for the offset detector system.

The ion trap mass spectrometer was modified by enlarging the apertures in the end caps to better accomodate the transmission of the ReO_4^- primary beam through the ion trap (and onto the sample). The sample insertion port was designed so that it mounts directly to the original vacuum system without any modifications required; it simply replaces the electron impact ion source, and the two can be interchanged in about 10 minutes. A small oil-free diaphram pump is used for rough-out of the sample probe inlet system. The installation of all components had only a marginal effect on the vacuum in the system, raising the base pressure from 8×10^{-7} Torr to 3×10^{-6} Torr. This will not effect the performance of the instrument.

5.0 TECHNOLOGY TRANSFER OF SIMS COMPONENTS

5.1 Private Industry

Transfer of technology components of INEL SIMS instrumentation to private industry was continued in FY95. It is worthwhile mentioning that in FY94, INEL licensed instrument control and data acquisition software, which can be used for SIMS (or other types of mass spectrometry), to Extrel-Millipore (a manufacturer of quadrupole mass spectrometer instruments).

In FY 95, work continued on attempts to transfer SIMS ion gun components to Phi-Evans, Inc. Phi-Evans is a spin-off company of Charles Evans & Associates, Inc. Phi-Evans is interested in acquiring the INEL ReO_4^- source for testing, but had concerns relating to the "brightness" of the ReO_4^- source. Specifically, Phi-Evans required an ion gun which could operate at a primary ion current of a nanoamp, and this was a concern since the INEL ReO_4^- was typically operated at less than 100 picoamps. This problem was addressed by redesigning the ion gun in FY95, and a prototype of this gun was demonstrated to be capable of generating a primary ion current of > 1 nanoamp.

Subsequent to this development, Dr. Bruno Schuler of Phi-Evans visited INEL in July of 1995. During this visit, concerns relative to surface damage caused by ReO_4^- were addressed. It was found that the damage cross section for ReO_4^- impacting poly(ethyleneterphthalate) was substantially less than that observed using Ar^+, Xe^o, or Xe^+, and was about the same as Ar^o. This was encouraging, because it indicated that ReO_4^- was, if anything, less destructive than most atomic primary particles. At the present time, Phi-Evans is deciding which instrument in their product line would be best suited to accommodate the ReO_4^- ion gun.

Transfer of detector and ion gun components to Teledyne continued in FY95. Interest at Teledyne has been sparked by difficulties the company encountered with their detector design. Teledyne personnel contacted INEL SIMS personnel for assistance with this problem, and this rekindled interest in transfer of the detector and gun components. Thus transfer of components to Teledyne remains a realistic possibility.

5.2 Technology End Users

*DOE Users.*Technology end users at the INEL Central Facilities Area 674 pond, and the Radioactive Waste Management Area acid pit remediation were identified in FY95. Samples were received in FY95 from both sites. Garbage samples from the acid pit were determined to have no Hg contamination. Speciation methods were not sufficiently developed in FY95 to aggressively pursue identification of species present in the soil samples, but this activity will be continued in FY96 using internal funding.

Non-DOE Users. The technology was also transferred to non-DOE users, specifically the Army Chemical Materiel Destruction Agency, and DOE NN-20. Both of these applications efforts are continuing in FY96.

6.0 FUTURE AND DIRECTION

DOE-OTD funding for the SIMS Development program is scheduled to terminate at the end of FY96, and only technology transfer activities are funded for this fiscal year. It is expected that transfer of ion gun components to Phi-Evans will occur during this year. Transfer of components to Teledyne is less certain, but remains a good possibility.

Work initiated to demonstrate Hg speciation will likely be continued in FY96, using internal INEL R&D funding. The continuation of the project was motivated by the encouraging progress that was made under the DOE-OTD SIMS Development program and by the critical need that exists for Hg species information from real world samples.

The development of transportable ion trap SIMS and quadrupole SIMS instruments will continue in FY96. The U.S. Army is an end user that is especially interested in development of transportable SIMS instruments, because of the demonstrated effectiveness of SIMS for the detection of nerve agent degradation products.