NASA TECHNICAL MEMORANDUM

NASA TM X-3112

IN SITU MASS ANALYSIS OF PARTICLES
BY SURFACE-IONIZATION MASS SPECTROMETRY

by William S. Lassiter and Allen L. Moen

Langley Research Center
Hampton, Va. 23665

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • NOVEMBER 1974

1. Report No. NASA TM X-3112	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle IN SITU MASS ANALYSIS OF PARTICLES BY SURFACE-IONIZATION MASS SPECTROMETRY		5. Report Date November 1974
		6. Performing Organization Code
7. Author(s) William S. Lassiter and Allen L. Moen		8. Performing Organization Report No. L-9675
9. Performing Organization Name and Address NASA Langley Research Center Hampton, Va. 23665		10. Work Unit No. 176-21-31-05
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Technical Memorandum
		14. Sponsoring Agency Code

15. Supplementary Notes

Allen L. Moen is Head of the Department of Physics, Central College, Pella, Iowa.

16. Abstract

A qualitative study of the application of surface ionization and mass spectrometry to the in situ detection and constituent analysis of atmospheric particles was conducted. The technique consists of mass analysis of ions formed as a result of impingement of a stream of particles on a hot filament where, it is presumed, surface ionization takes place. Laboratory air particles containing K, Ca, and possibly hydrocarbons were detected. Other known particles such as Al_2O_3, $Pb(NO_3)_2$, and Cr_2O_3 were analyzed by detecting the respective metal atoms making up the particles. The fact that, in some cases, mass numbers indicative of compounds making up the particles were detected shows that surface ionization of particles sometimes leads to chemical analysis as well as to elemental analysis. Individual particles were detected, and it was shown that the technique is sensitive to Al_2O_3 particles with a mass of a few nanograms.

17. Key Words (Suggested by Author(s)) Surface ionization Mass spectrometry Aerosols Aerosol elemental analysis	18. Distribution Statement Unclassified – Unlimited STAR Category 13

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 15	22. Price* $3.00

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MASS SPECTROMETRY

By William S. Lassiter and Allen L. Moen*
Langley Research Center

SUMMARY

A qualitative study of the application of surface ionization and mass spectrometry to the in situ detection and constituent analysis of atmospheric particles was conducted. The technique consists of mass analysis of ions formed as a result of impingement of a stream of particles on a hot filament where, it is presumed, surface ionization takes place. Laboratory air particles containing K, Ca, and possibly hydrocarbons were detected. Other known particles such as Al_2O_3, $Pb(NO_3)_2$, and Cr_2O_3 were analyzed by detecting the respective metal atoms making up the particles. The fact that, in some cases, mass numbers indicative of compounds making up the particles were detected shows that surface ionization of particles sometimes leads to chemical analysis as well as to elemental analysis. Individual particles were detected, and it was shown that the technique is sensitive to Al_2O_3 particles with a mass of a few nanograms.

INTRODUCTION

Recent studies indicate a need for measurements of atmospheric particulate matter (refs. 1 and 2), including composition and size distribution, as well as a need for determining sources from which the particles originate. Of concern is the effect of particles on atmospheric chemistry and on the Earth's radiation budget. Present-day standard techniques for the elemental or chemical analysis of atmospheric particles involve collection by filters or impactors and subsequent transport of the collection devices to a laboratory for analysis. Such techniques can lead to contamination of the particles as well as to alteration of their properties by interaction with the collection devices. Thus a means for analyzing the particles as they exist, that is, an in situ analysis, is needed. Existing data indicate that in some environments, such as the stratosphere, particles consist of a solid core surrounded by a liquid or by a frozen liquid (refs. 3, 4, and 5). In such cases collection followed by subsequent handling and subjection to environments other than the one from which the particles originate could

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*Head, Department of Physics, Central College, Pella, Iowa.

easily alter their properties and composition. A technique which appears attractive for analyzing particles in situ is surface-ionization mass spectrometry suggested by Davis in reference 6. Davis has shown that this technique detects individual particles of $CaNO_3$, $SrCO_3$, Cr_2O_3, and CuO and that the size estimated from the responses agrees reasonably well with that estimated from Stokes' law for the rate of settling in air. Development of such a technique for field and possibly flight use would allow real-time in situ detection and constituent analysis of particles and would minimize the contamination problem.

The report presents laboratory studies of setting up the surface-ionization mass spectrometry technique and of expanding its detection capability to species not studied by Davis.

SYMBOLS

e	electronic charge
g^+	statistical weight of positive ions
g_o	statistical weight of neutrals
I	ionization potential
k	Boltzmann constant
N^+	number of positive ions leaving the hot filament per unit area per second
N_o	number of neutral atoms leaving the hot filament surface per unit area per second
p	pressure in intermediate chamber
p_c	pressure in the 20-ft^3 vacuum chamber
T	temperature
ϕ	work function of filament material

TECHNIQUE

The technique of determining the composition of particles by surface-ionization mass spectrometry is depicted in figure 1. Atmospheric air containing particles enters a vacuum environment through an aperture with the expanding stream incident on a hot filament. The particles, which adhere momentarily to the filament, subsequently evaporate into their component molecules and/or atoms. Assuming to first order that the process obeys the Saha-Langmuir equation (ref. 7)

$$\frac{N^+}{N_0} = \frac{g^+}{g_0} \exp\left[\frac{e(\phi - I)}{kT}\right] \tag{1}$$

a fraction of the molecules or atoms leave the filament in a positively ionized state, depending on the temperature-time history, the work function and temperature of the filament, the ionization potential of the molecule or atom, and the statistical weights of the ionic and atomic states. Other processes, such as charge transfer at the surface or in the vapor phase and surface or vapor-phase chemical reactions, are neglected. The ions are then focused by electrostatic lenses into a mass spectrometer, which can identify and quantitatively measure the ions according to their mass to charge ratio.

DESCRIPTION OF SYSTEM

A block diagram of the apparatus is shown in figure 2. A 20-ft^3 vacuum chamber pumped by a 10-inch diffusion pump with a liquid-nitrogen trap produced the vacuum environment. The inlet system consisted of a copper tube approximately 3.7 m in length with an outside diameter of 6.3 mm. A needle valve near one end of the copper tube controlled the inlet flow.

The copper tube penetrated the vacuum chamber and attached to a stainless steel intermediate chamber located inside the vacuum chamber. The intermediate chamber was a stainless steel cross capped with flanges and having an outside diameter of 38.1 mm. A hypodermic needle with a length of 25.4 mm and an inside diameter of 0.23 mm (conductance of about 0.4 ml/sec at 40 torr[1]) was positioned in a flange of the cross opposite from but concentric with the inlet tube. This needle served as a means of collimating the particles onto the hot filament. A 0.08-mm-diameter hole in a 6.3-mm-thick flange was also used to collimate the particles. The intermediate chamber was pumped by a mechanical roughing pump. Another tube attached to the intermediate chamber led to a Bourdon gage positioned outside the large chamber. The Bourdon gage monitored the

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[1]1 torr = 133.3 Pa.

pressure inside the intermediate chamber. Pressure inside the 20-ft^3 vacuum chamber was measured by an ionization gage. Figure 3 is a photograph of the vacuum chamber and inlet system.

A zone-refined 99.995 percent pure rhenium ribbon filament, 3.2 mm by 22.2 mm by 0.01 mm, was positioned in the vacuum chamber in line of sight with the hypodermic needle and oriented so that the center line of the hypodermic needle made an angle of 45$^\text{o}$ with respect to the filament surface. Positioned 90$^\text{o}$ with respect to the hypodermic needle center line and thus 45$^\text{o}$ with respect to the filament surface was an EAI QUAD 1100 quadrupole mass spectrometer. The spectrometer was positioned so that the horizontal plane containing the needle center line extended into the ionization region of the spectrometer. Figure 4 is a photograph showing the geometry of the intermediate chamber, the filament, and the mass spectrometer. An optical pyrometer positioned outside the vacuum chamber was used to determine the rhenium filament temperature.

Two stainless steel rings with an outside diameter of 31.8 mm and an inside diameter of 6.3 mm served to accelerate and to focus the ions produced at the filament surface into the mass spectrometer. These rings were positioned concentric with the mass-spectrometer center line between the filament and the mass spectrometer. Positioning of the rings resulted in a spacing of 4.8 mm between the two and about 6.3 mm between the filament and adjacent ring.

<center>PROCEDURE</center>

Initial objectives were to develop a procedure for analyzing the particles subjected to an environment simulating the lower stratosphere, that is, a temperature of -40$^\text{o}$ C, a pressure of 40 torr, and a range of particle density from 0.1 to 1 particle/cm^3. Problems with the apparatus prevented thermal simulation, so that the procedure presented is only for pressure simulation which yielded between 40 and 50 torr in the intermediate chamber. The pressure in the intermediate chamber could be controlled by adjusting the needle valve which altered the flow rate into the system.

The vacuum chamber was pumped to a residual pressure of about 5×10^{-8} torr while the mechanical roughing pump lowered the pressure in the intermediate chamber to about 1 torr. The rhenium filament was thermally activated and the quadrupole mass spectrometer was operated with its electron source filament off. Research grade oxygen was then let into the intermediate chamber to investigate the effect of oxygenation of the rhenium filament on the detection of filament impurities and background constituents in the system. The mass spectrometer was scanned over the mass range of about 1 to 90 amu. Then, the intermediate chamber was evacuated, the needle valve was opened to fill the chamber with air to about 48 torr, and the mass spectrometer was again

scanned over the mass range of about 1 to 90 amu to determine whether any aerosols in laboratory air could be detected. (Mass-spectrometer scans with the rhenium filament operating are hereafter referred to as ion scans.)

Various types of particles were transported into the intermediate chamber by inserting the inlet tube into a glass bottle containing the particle of interest in powder form. The mass-to-charge ratios corresponding to elements and compounds making up the particles with ionization energies within detection limits were investigated at enhanced resolution by narrowing the ion-scan range to cover only the mass-to-charge ratio of interest. The filament temperature and voltages on the extraction lenses were adjusted so that the response was enhanced. A positive voltage ranging from about 5 V to 15 V on the lens closest to the filament suppressed secondary electron emission from the filament. A negative voltage ranging from about -20 V to -100 V on the other lens attracted the positive ions into the mass spectrometer.

RESULTS AND DISCUSSION

Two types of apertures were used to collimate the particles from the intermediate chamber to the filament: a 0.08-mm-diameter hole in a 6.3-mm-thick flange and the 25.4-mm-long hypodermic needle, described previously. No significant differences were observed in the performance of each aperture except that some oil appeared to have accumulated in the needle. This oil probably originated from back streaming of the mechanical pump on the intermediate chamber.

The response of the system to background impurities and laboratory air was investigated. Figure 5 shows ion scans taken with a filament temperature of 800° C and a scan rate of 0.017 Hz. Figure 5(a) shows an ion scan made with the intermediate chamber evacuated to its residual pressure of about 1 torr. No particles were detected under these conditions. Figure 5(b) shows an ion scan after letting oxygen into the intermediate chamber to a pressure of about 48 torr. The peaks appearing at mass-to-charge ratios 23 amu and 39 amu are attributable to Na and K, respectively. The peaks at 58 amu, 59 amu, 84 amu, and 86 amu have not been identified. It was initially believed that these peaks were due to back streaming of the pump oil, but spectra obtained by other researchers with different mass spectrometers operating in the ion-bombardment mode indicate no relationship (ref. 8). The appearance of all peaks in figure 5(b) is attributed to an increase in the surface ionization for the species corresponding to these peaks resulting from an increase in the filament work function due to oxidation. (See eq. (1).) Thus it appears necessary for the rhenium filament to be in an oxidized state for detection of these species to be possible.

The oxygen was pumped out of the intermediate chamber, and the filament was flashed for a few seconds to remove impurities. Laboratory air was then let into the intermediate chamber to a pressure of about 47 torr. Figure 5(c) shows an ion scan with laboratory air incident on the filament. The decrease in the Na peak is attributed to the fact that the filament was partially cleaned by the flashing process. This scan also indicates an increase in the K peak, as well as increases in peaks at 58, 59, 84, and 86 amu. A peak at 72 amu is also evident in this scan but has not been identified. These unidentified peaks could be due to hydrocarbons in laboratory air. Thus it is concluded that laboratory air particles containing K and possibly hydrocarbons were detected with a rhenium filament temperature of about 800° C. The natural constituents of air $\left(O_2, N_2, Ar, etc.\right)$ were not detected because of their high first ionization potential.

Another ion scan of laboratory air was taken but at a higher filament temperature of 1600° C, as shown in figure 6. The peak at 23 amu confirms the presence of Na, but it is not known whether any of the peak originates from laboratory air. The 27-amu peak is attributable to Al from the Al_2O_3 powder that had previously been inlet; some of the Al_2O_3 had adhered to the walls of the inlet tube and was slowly coming off. The 39-amu and 41-amu peaks are the stable isotopes of K. The 40-amu, 42-amu, and 44-amu peaks are attributable to Ca in the laboratory air. It was not determined in what form the Ca existed in the air.

Figure 7 shows a continuous recording of the Ca mass number as a function of time while laboratory air was inlet. The discrete peaks are attributed to collisions between individual particles containing Ca and the rhenium filament. The variations in the peak heights indicate that different-size particles were hitting the filament, and the maximum time lag between particle responses appears to be of the order of seconds. Careful attention to the time lag and the ion-scan rate was necessary so that the mass-to-charge ratio of interest was not scanned between particle hits.

Powders were introduced into the system by inserting the inlet line inside the mouth of the glass bottle containing the powder. The response to each powder introduced into the system is shown in table I by the mass-to-charge ratio that was detected. Also shown are the ions believed to correspond to the particular mass-to-charge ratio detected. Of the elements detected, Pb has the highest first ionization potential. Inasmuch as the work function of unoxidized rhenium (about 5 eV (ref. 9)) is rather low compared with the first ionization potentials of Pb and Cr (7.4 eV and 6.76 eV, respectively), detection of these two elements would not be expected. (See eq. (1).) Thus the detection of these elements indicates an increase in the work function of the rhenium filament caused by oxidation of the filament when subjected to laboratory air and oxygen. These findings are in agreement with Davis (ref. 6), who observed an increase in the work function of rhenium to 7.5 eV after exposure to small quantities of air, and with other studies (refs. 9 and 10).

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TABLE I.- ANALYSIS OF POWDERS INTRODUCED

Powder	Ion detected	Mass-to-charge ratio detected, amu
$CsNO_3$	Cs^+	133
Li_2Cl_3	Li^+	7
$Pb(NO_3)_2$	Pb^+	208
$PbCl_2$	Pb^+	208
Cr_2O_3	Cr^+	52
Al_2O_3	Al^+	27
La_2O_3	LaO^+	155
Gd_2O_3	GdO^+	174
$(NH_4)_2SO_4$	$(NH_4)_2SO_4^+$	132

The detection of the ions LaO^+, GdO^+, and $(NH_4)_2SO_4^+$ indicates low ionization potentials for these compounds and shows that the technique is capable of not only elemental analysis but, in some cases, chemical analysis. Evidently a significant number of molecules of these chemical compounds were ionized and drawn away from the filament before complete pyrolysis could occur. Further work is needed in this area to establish an inventory of species and corresponding sensitivities.

The oxide Al_2O_3 was detected at a filament temperature of 1600^0 C as mass-to-charge ratio 27 amu, which is the ratio corresponding to Al^+. The mass-spectrometer electronics were then adjusted for high resolution and tuned to the 27-amu peak. Individual particle collisions with the filament were observed, as when Ca was detected in laboratory air. A size-distribution measurement of a sample of the Al_2O_3 powder used was performed with the Millipore ΠMC Particle Measurement Computer System. The measurement showed that 75 percent of a 500-particle sample had diameters between 4 μm and 16 μm. Assuming that the single-particle events observed were due to collisions of 16-μm-diameter particles with the filament, calculation of the mass detected for one of these particles shows that the technique is sensitive to a few nanograms of Al_2O_3.

When Al_2O_3 particles were inlet, it was discovered that the particles were sticking to the copper inlet tube. With the inlet needle valve closed, the inlet tube was shaken, and a large burst of pulses occurred at mass-to-charge ratio 27. Such data suggest that a short inlet line with line of sight from inlet to filament is more desirable.

CONCLUDING REMARKS

It has been shown that a technique involving vaporization of particulate matter by impingement on a hot filament followed by surface-ionization mass spectrometry can elementally analyze particles for elements with low ionization potentials. The data also show that the technique can be used to derive chemical information from particles by ionizing and detecting molecular species composed of more than one element which are vaporized and which have low ionization potentials. Potassium, calcium, and mass-to-charge ratios 58, 59, 72, 84, and 86 amu were detected when laboratory air was inlet. A much higher filament temperature was required for the detection of Ca than for K. The ability to detect elements with high ionization potentials, namely, Pb and Cr, by introducing particles containing these elements indicates a work-function increase due to oxidation of the rhenium filament by the laboratory air.

The data show that the surface-ionization technique is sensitive to laboratory-air single-particle impacts with the hot filament. Single particles of Al_2O_3 with masses of a few nanograms and particles in laboratory air containing Ca were detected.

Langley Research Center,
    National Aeronautics and Space Administration,
        Hampton, Va., September 30, 1974.

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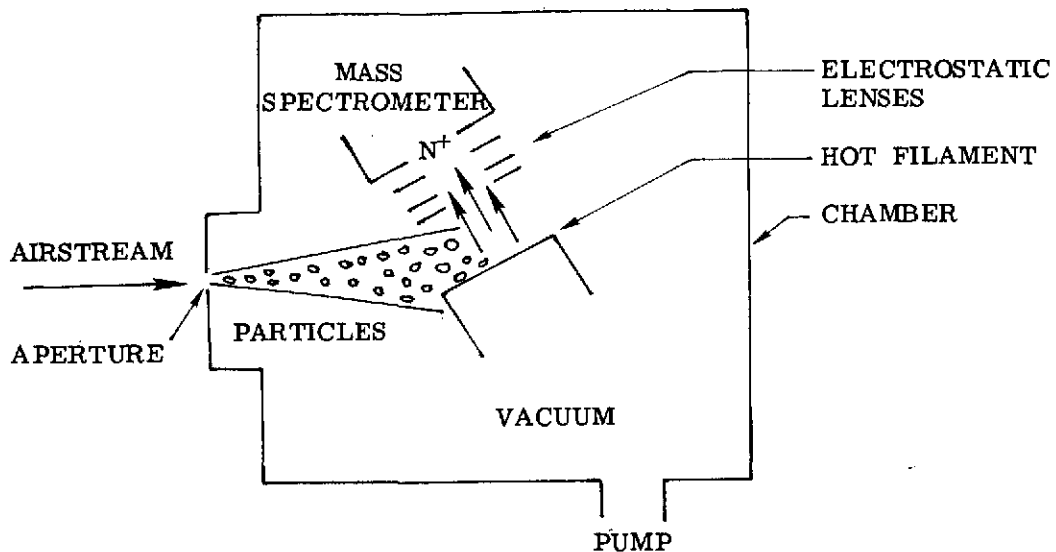
Figure 1.- Schematic of detection process of particle analysis by
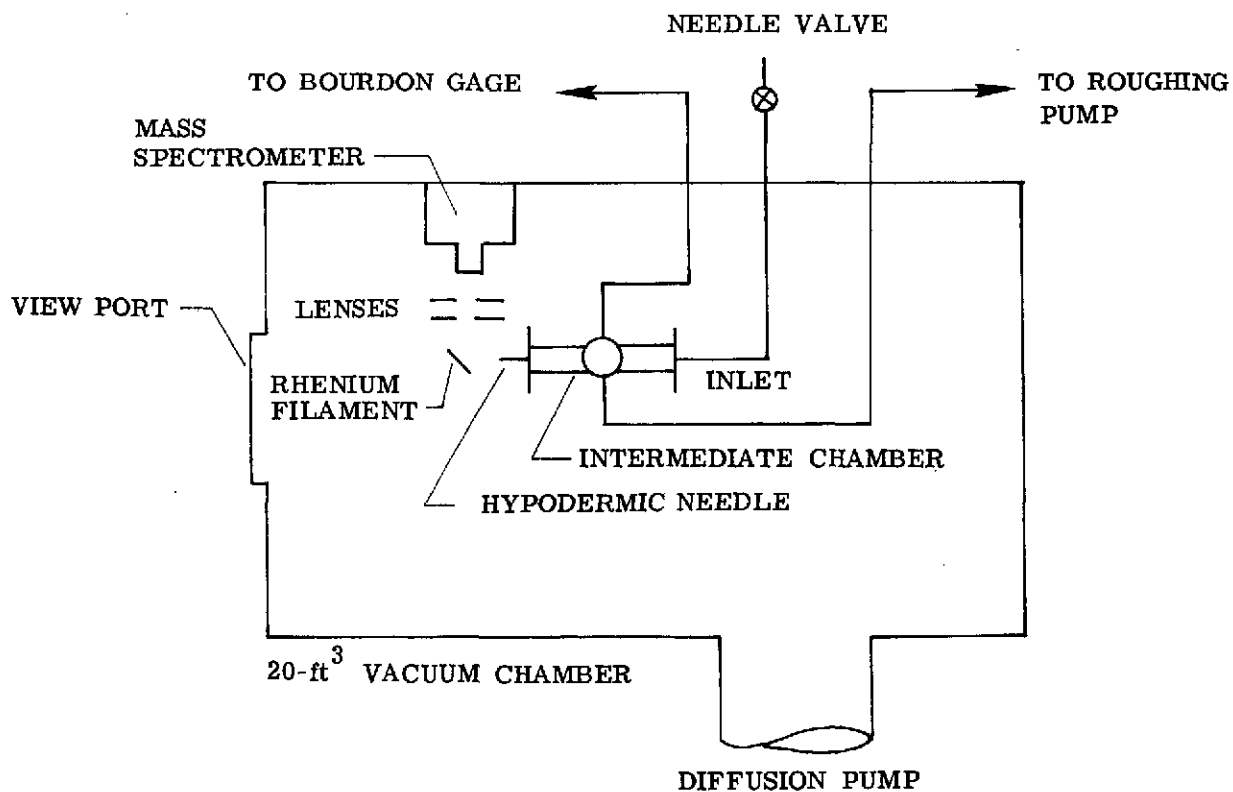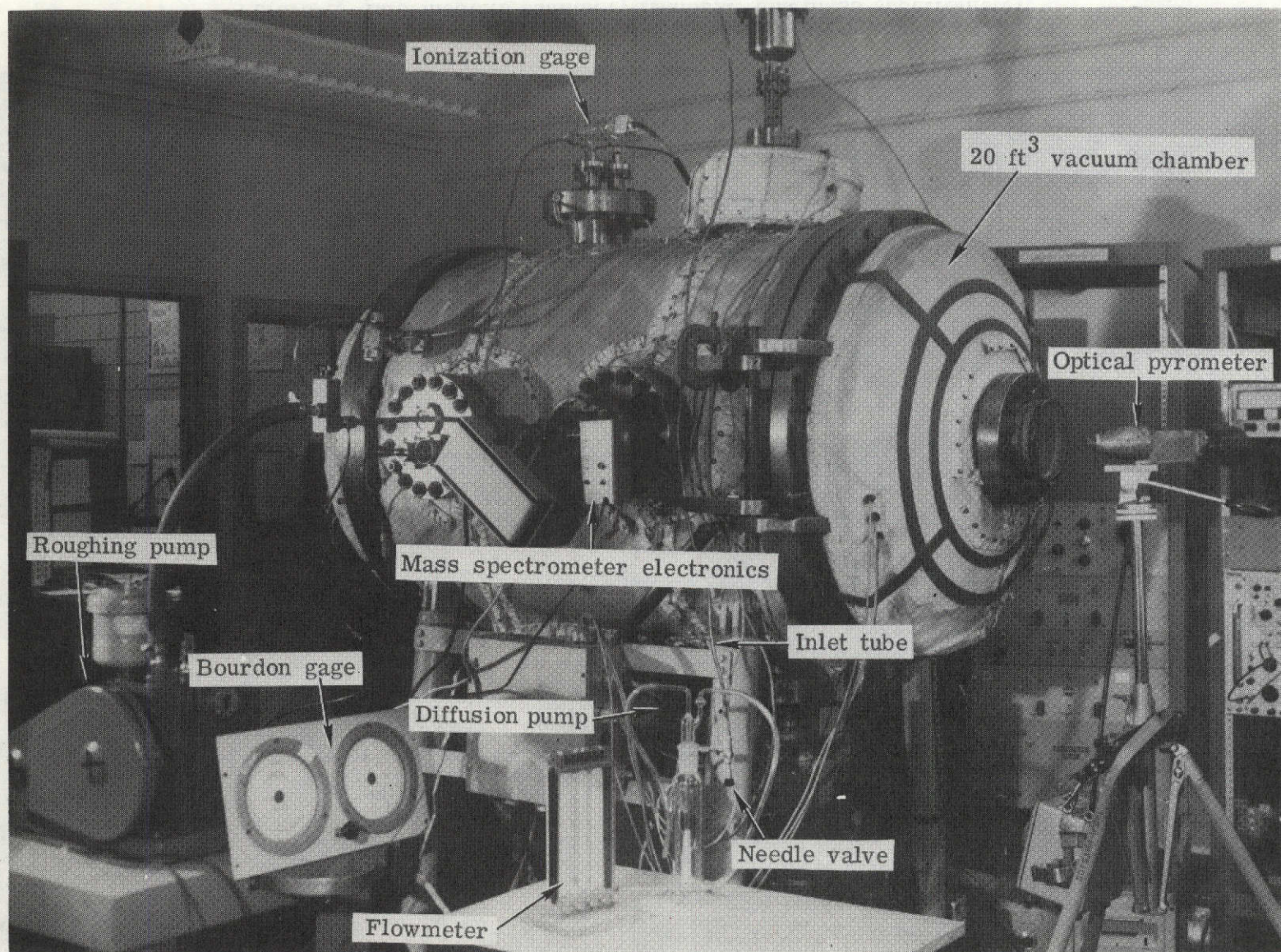surface-ionization mass spectrometry.

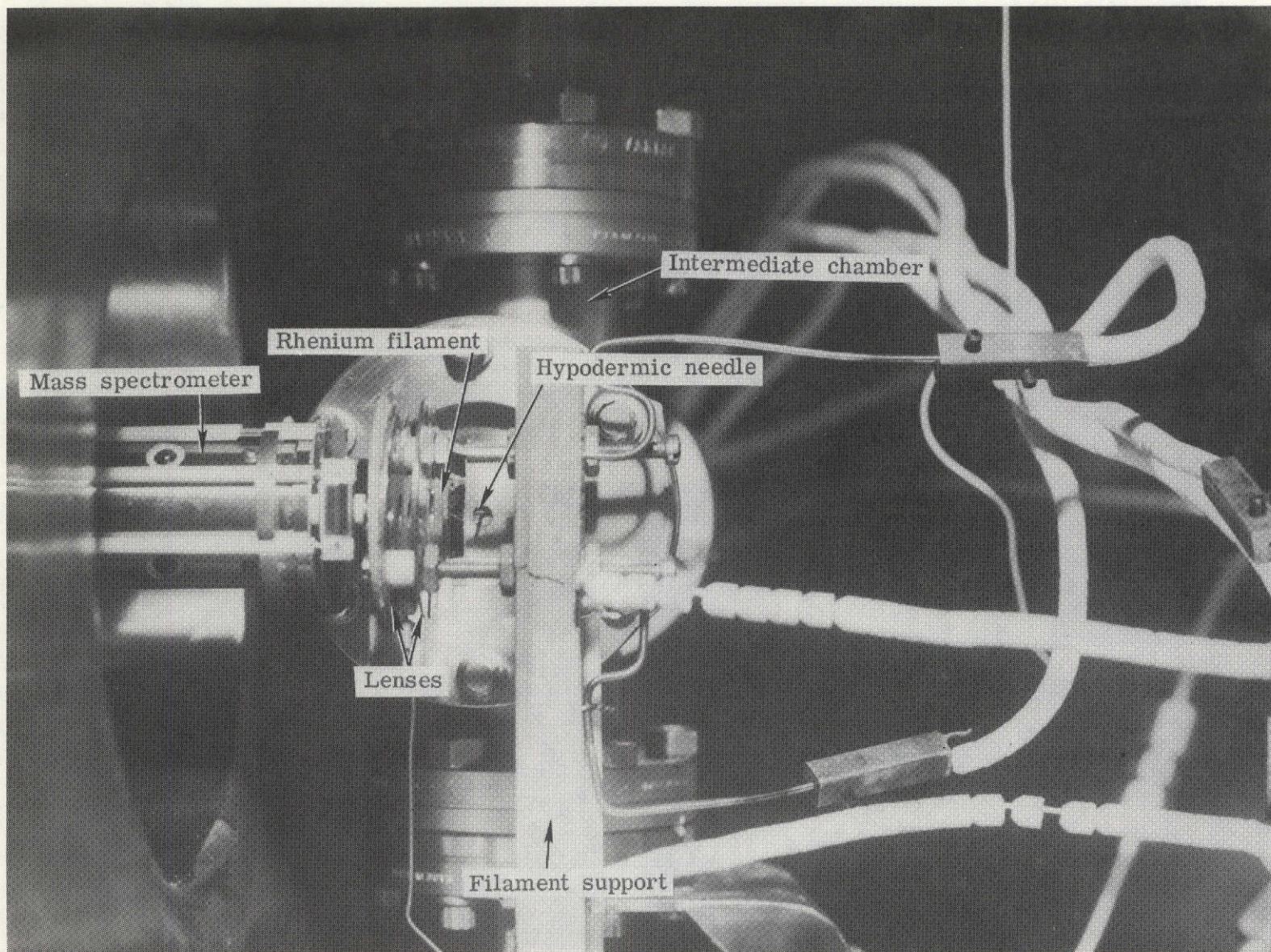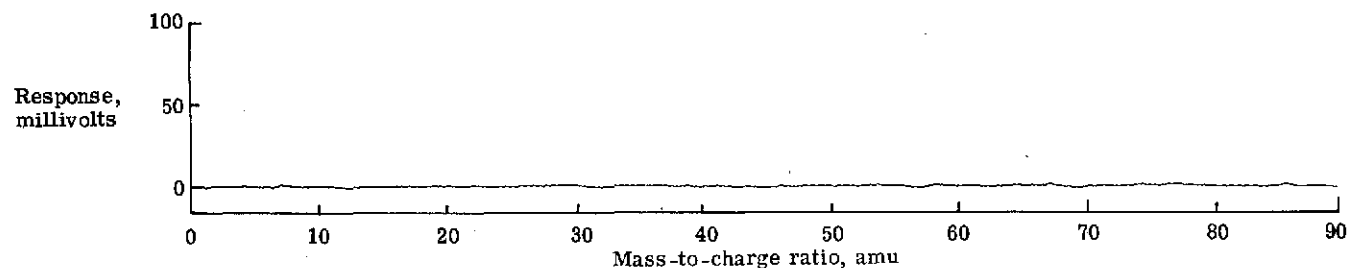Figure 2.- Schematic of apparatus.
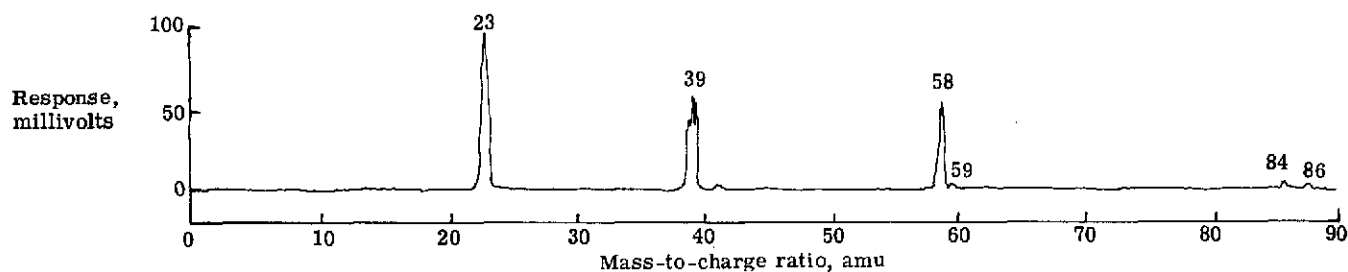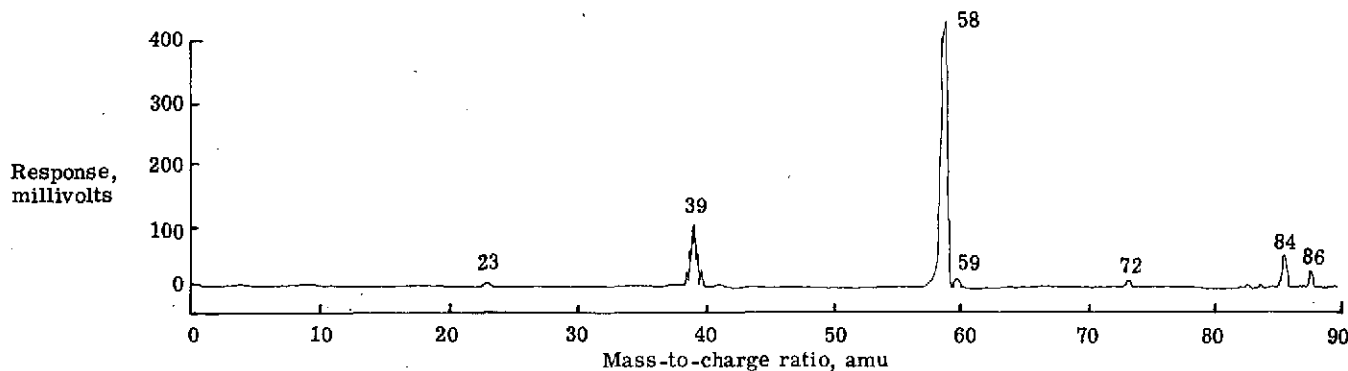
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Figure 3.- Vacuum chamber and inlet system.

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Figure 4.- Intermediate chamber, filament, and mass spectrometer.

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(a) Intermediate chamber evacuated to $p \approx 1$ torr; $p_c = 8 \times 10^{-8}$ torr.

(b) Intermediate chamber backfilled with oxygen to $p \approx 48$ torr; $p_c = 2 \times 10^{-5}$ torr.

(c) Intermediate chamber backfilled with laboratory air to $p \approx 47$ torr; $p_c = 2 \times 10^{-5}$ torr.

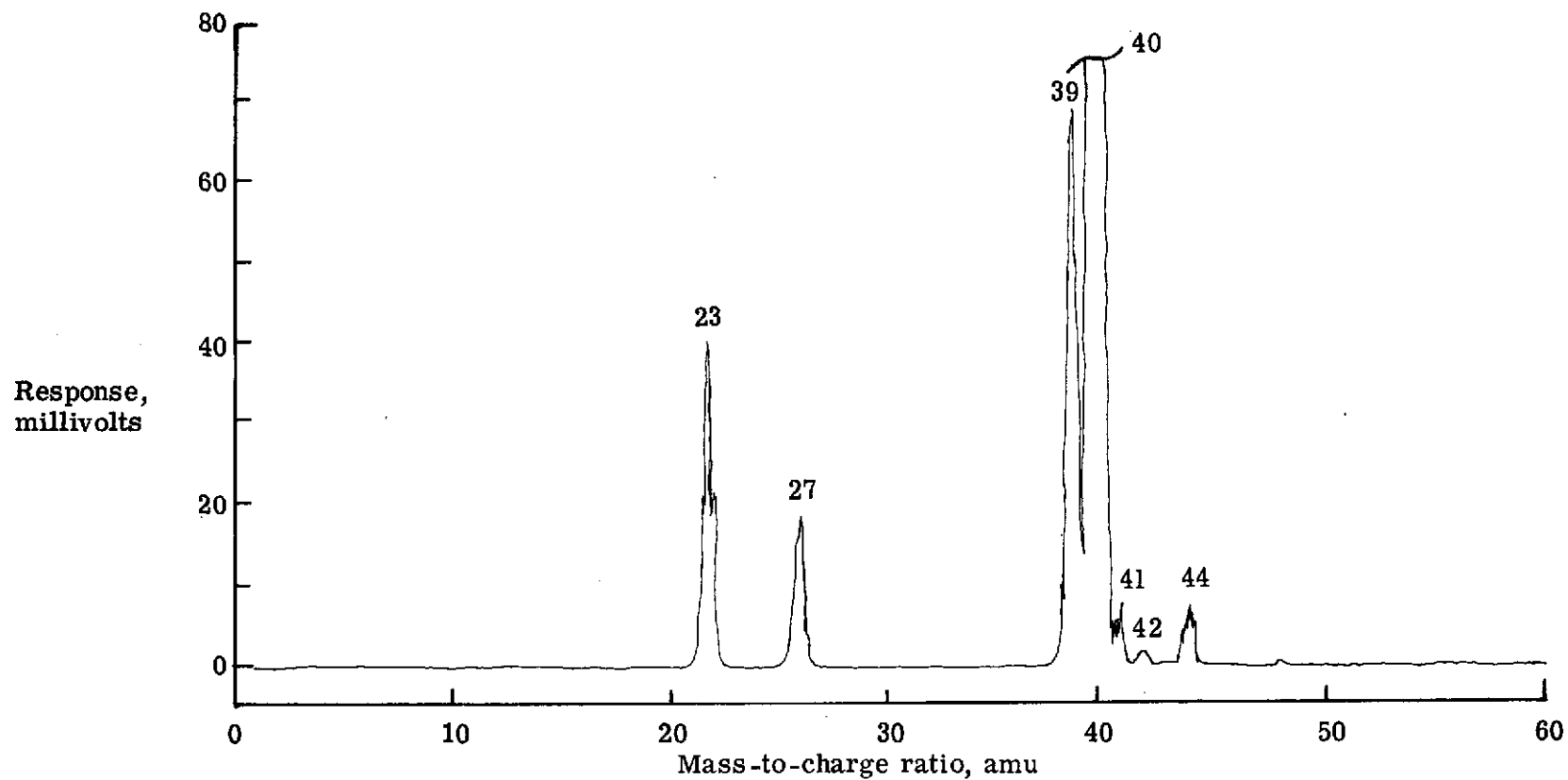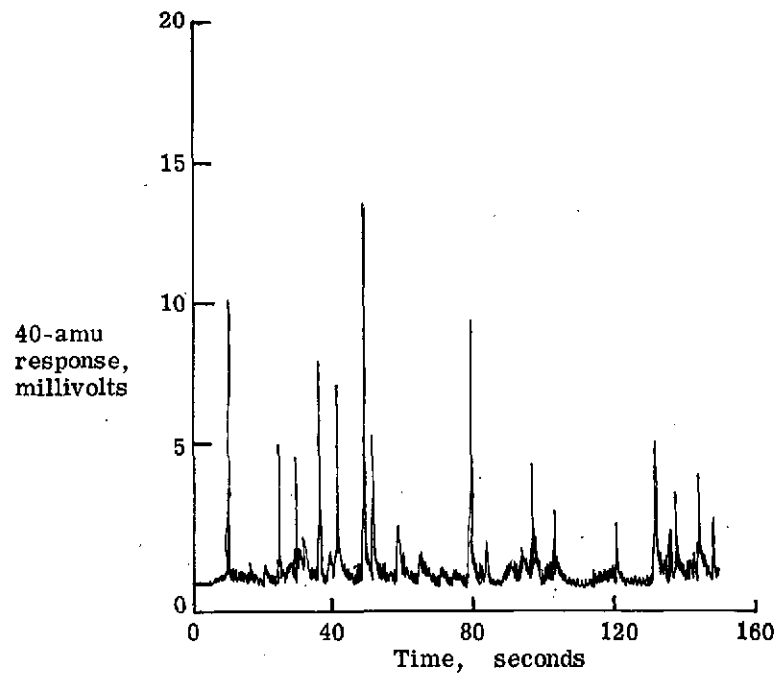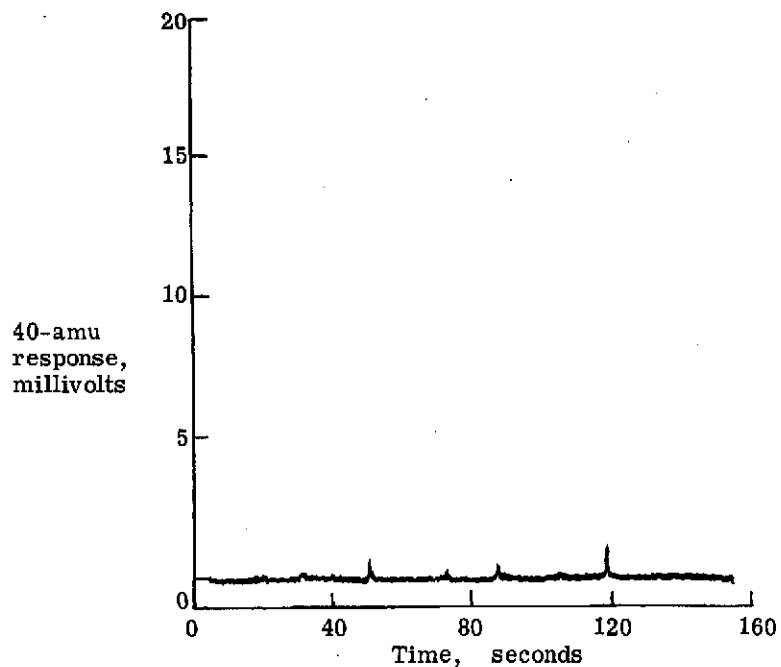Figure 5.- Ion scans at a scan rate of 0.017 Hz and with the rhenium filament at about 800° C.

Figure 6.- Ion scan of laboratory air at a filament temperature of 1600° C, intermediate chamber pressure of 41 torr, and scan rate of 0.017 Hz. p_c = 2.4 × 10^{-5} torr.

(a) Intermediate chamber at residual pressure of 0.8 torr. (b) Laboratory air inlet with intermediate chamber at

$p_c = 8 \times 10^{-8}$ torr.   pressure of 41 torr. $p_c = 2.2 \times 10^{-5}$ torr.

Figure 7.- Time history of the 40-amu mass-to-charge ratio.