NASA CONTRACTOR
REPORT

NASA CR-2815

DESIGN AND FABRICATION
OF A BASIC MASS ANALYZER
AND VACUUM SYSTEM

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • APRIL 1977

1. Report No. NASA CR-2815	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Design and Fabrication of a Basic Mass Analyzer and Vacuum System		5. Report Date April 1977
		6. Performing Organization Code 1264
7. Author(s) Charles M. Judson, Conrad Josias, and James L. Lawrence, Jr.		8. Performing Organization Report No.
9. Performing Organization Name and Address Analog Technology Corporation 3410 E. Foothill Blvd. Pasadena, CA 91107		10. Work Unit No. 141-95-01-16
		11. Contract or Grant No. NAS1-13843
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546		13. Type of Report and Period Covered Contractor Report
		14. Sponsoring Agency Code

15. Supplementary Notes

Final report

Langley Technical Monitor: George M. Wood, Jr.

16. Abstract

A two-inch hyperbolic rod quadrupole mass analyzer with a mass range of 400 to 200 amu and a sensitivity exceeding 100 ppb has been developed and tested by the Analog Technology Corporation. This analyzer is the basic hardware portion of a microprocessor-controlled quadrupole mass spectrometer for a Gas Analysis and Detection System (GADS), currently being developed to satisfy specific analytical requirements of NASA, EPA, and DOD. The program is jointly supported by the NASA Technology Utilization Office; EPA/ESRL, Research Triangle Park, NC; USAF/AFWL, Kirtland AFB, NM; USAMC/HEL, Redstone Arsenal, AL, and USAM/BRDL, Ft. Detrick, MD.

The work described in this report covers the initial phase of the program, e.g., the development and testing of the hyperbolic-rod quadrupole mass spectrometer and associated hardware. The electronics, microprocessor, and memory for the system are being developed under a separate contract and will be detailed in a report following completion of the program.

17. Key Words (Suggested by Author(s)) mass spectrometry gas analysis pollution measurement quadrupole		18. Distribution Statement Unclassified – unlimited Subject Category 35		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified		21. No. of Pages 65	22. Price* $4.50

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DESIGN AND FABRICATION OF A BASIC

MASS ANALYZER AND VACUUM SYSTEM

Charles M. Judson, Conrad Josias, and James L. Lawrence, Jr.

Analog Technology Corporation

SUMMARY

A two-inch hyperbolic rod quadrupole mass analyzer has been developed and tested by Analog Technology Corporation. This analyzer constitutes the basis of a Gas Analysis and Detection System (GADS) that will satisfy specific analytical requirements of several agencies of the Government. The program is therefore jointly supported by the NASA Technology Utilization Office, EPA, and DOD, with the NASA Langley Research Center assuming contractual and technical direction responsibilities.

The first such system will be utilized by the USAF-AFWL, Kirtland AFB, NM, in a personnel safety and fire suppression application on board an airborne LASER laboratory. The second is to be applied by the EPA, Research Triangle Park, NC, in field monitoring of vinyl chloride and other hydrocarbon compounds. Additional systems will be delivered to the U.S. Army for field monitoring and for use in their high-energy LASER research program, and to NASA for several gas composition determination studies.

The work described in this report covers the initial phase of the program; e.g. the development and testing of the hyperbolic-rod quadrupole mass spectrometer and associated hardware. The electronics, microprocessor, and memory for the system are being developed under a separate contract and will be detailed in a report following completion of the program.

1.0 INTRODUCTION

The mass analyzer developed under this contract is derived from the Astronaut Breath Analyzer developed by Analog Technology Corporation under NASA Contracts NAS9-11307 and NAS9-12765. The Astronaut Breath Analyzer was conceived as a miniature quadrupole mass spectrometer complete with vacuum system and electronics and small enough to be carried by an astronaut for continuous breath analysis. Under these prior contracts, a miniature quadrupole was developed and fabricated by ATC, and prototype electronics were developed, but not miniaturized.

A vacuum system was constructed that, although not small enough to be carried by the astronaut, was small enough to form the basis for a portable instrument.

An unsolicited proposal by Analog Technology Corporation (ATC Proposal 74-741) to convert NASA-funded technology into commercial instrumentation was submitted on April 4, 1974 to the NASA Technology Utilization Office. That proposal was the original basis for the contract for which this report is written. In that submission, ATC proposed to utilize its NASA-funded Astronaut Breath Analyzer design as a key element in the development of a mass-spectrometer-based instrument for measurement of trace-gas constituents in air or other gases.

A modified version of the proposed instrument was described in a proposal supplement, which was submitted on September 17, 1974 to the Environmental Protection Agency in Research Triangle Park, North Carolina. The modified version provided a microprocessor to permit interference corrections to be made by a matrix calculation so that as

many as 38 constituents could be considered as possible interferences. This system would then permit trace-gas measurements to be made without requiring their prior separation in a gas chromatograph, which is commonly used for trace constituent measurements by mass spectrometry.

After consideration of this proposal and its supplement, NASA determined that it would fund the development of the system in stages. It was agreed that the first stage would be the development of the mass analyzer hardware. Hence, a proposal for the development of a basic mass analyzer for the trace-gas mass spectrometer system (ATC Proposal 75-811, March 5, 1975) was submitted to NASA Langley Research Center, Hampton, Virginia.

The purpose of the program was to develop a mass spectrometer patterned after the two-inch quadrupole mass analyzer used in ATC's Astronaut Breath Analyzer. The basic mass analyzer to be designed and fabricated was to consist of the mechanical portions of the mass spectrometer, including the vacuum system and the inlet system. The spectrometer would make use of a unique hyperbolic rod structure of pre-aligned unitary construction that had been previously developed by ATC. This was to be tested using laboratory electronics to the following specifications:

1. Mass Range: 4 to 200 amu.
2. Detection Limit: 0.1 ppm except for peaks present in pure air and in the absence of adjacent peaks.
3. Maximum Interference from Adjacent Peaks: 10^{-3}
4. Dynamic Concentration Range: 10^{5}
5. Measurement Time: Programmable, 10 seconds maximum.
6. Precision and Accuracy: 5% for concentrations above 2 ppm.

Complete mass-spectrometer systems using such a design would be constructed in follow-on contracts after successful completion of a feasibility demonstration. It was expected that the first complete instrument would be constructed for the Air Force to monitor gas mixtures that would not necessarily be air with only trace impurities. It thus appeared that there would be two versions of the instrument, the requirements of which would differ at least with respect to the composition of the bases to be analyzed.

The elements required for the basic mass analyzer were defined as follows:

1. A hyperbolic-rod quadrupole mass filter;
2. An ion source;
3. An electron-multiplier detector;
4. A vacuum envelope in which these elements would be mounted;
5. An ion pump; and
6. An inlet system for introducing gas into the system.

The program was to be initiated by a parametric design study, and completed by a demonstration of performance and a final report.

2.0 DESCRIPTION OF THE INSTRUMENT

The requirements of the present mass spectrometer differ from those of the Astronaut Breath Analyzer in that the object is to measure trace rather than major constituents, and that the upper end of the mass range is increased from 44 to 200 amu. Furthermore, the present instrument requires the addition of an electron multiplier, modification of the ion source and the mass-filter entrance to provide high sensitivity over a wider mass range, and a vacuum system that provides a sufficiently low background level.

Figure 1 shows the system that was constructed, the laboratory electronics used in testing the system, and a gas-sample inlet that is also part of the test system. The system itself consists of an analyzer mounted within a vacuum tee and a 30-liter/second ion pump. There is baffling in the ion-pump connection line that completely eliminates any detectable noise at the electron multiplier resulting from ions or metastable molecules from the ion pump.

Figure 2 shows a closer view of the vacuum tee. This is a standard commercial tee, 6.3 cm in diameter, 21 cm long, with 11.4 cm diameter flanges. The mass filter is mounted to the wall of the envelope, with an electrical connection through the envelope so that the rf electronics can be located sufficiently near the filter to minimize the power required. The ion source and gas entrance are mounted on one flange, and the electron multiplier on the opposite flange. The ion pump is mounted below on the third flange. The ion source, electron multiplier and ion pump can each be independently removed and replaced without removing the mass filter. Alignment of the ion source and the electron
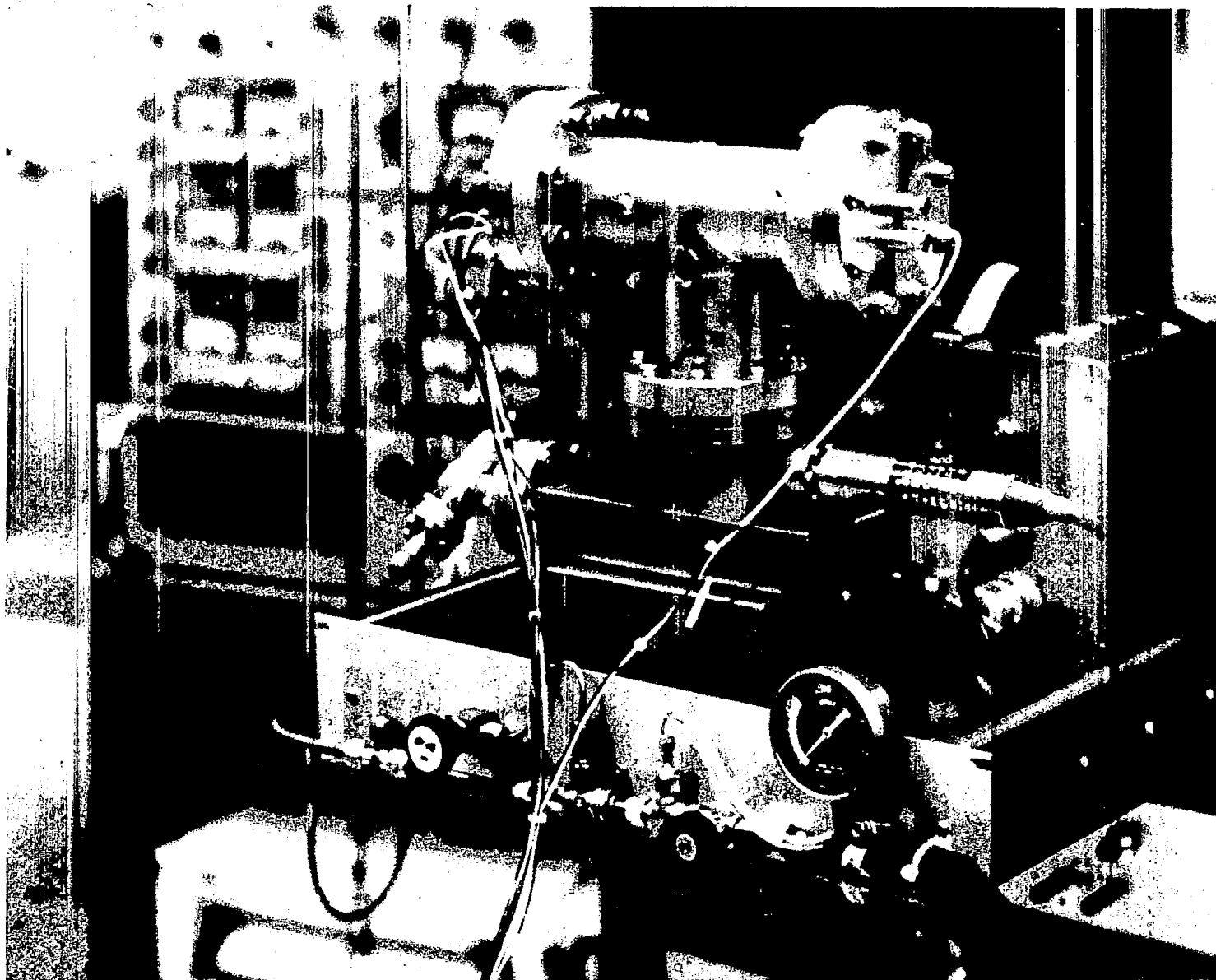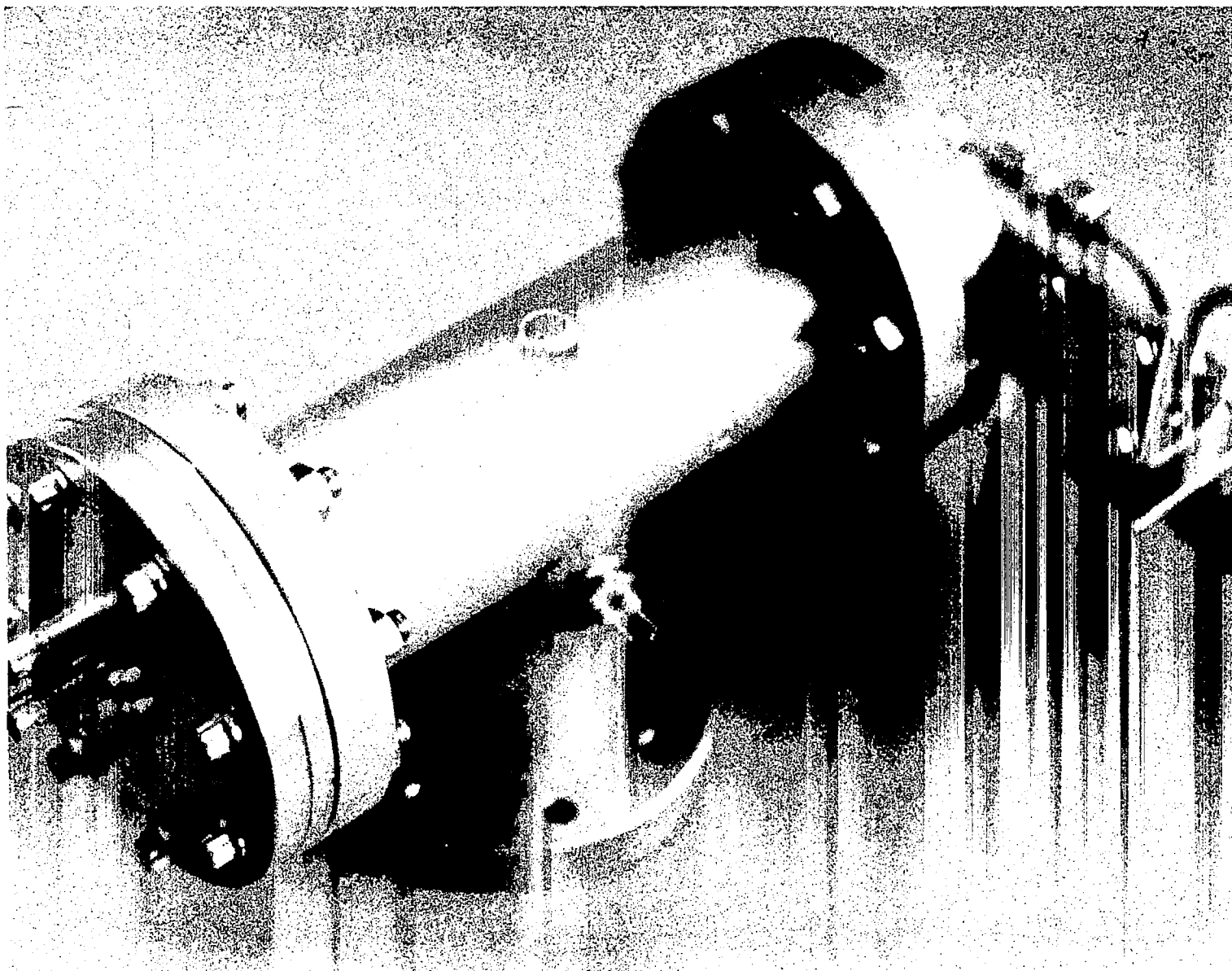
Figure 1 Mass Spectrometer with Laboratory Test Setup

Figure 2   Mass Spectrometer in Vacuum Housing Plus Leak Assembly

multiplier with respect to the mass filter is maintained by pins that fit into matching holes in the mass-filter mounting structure.
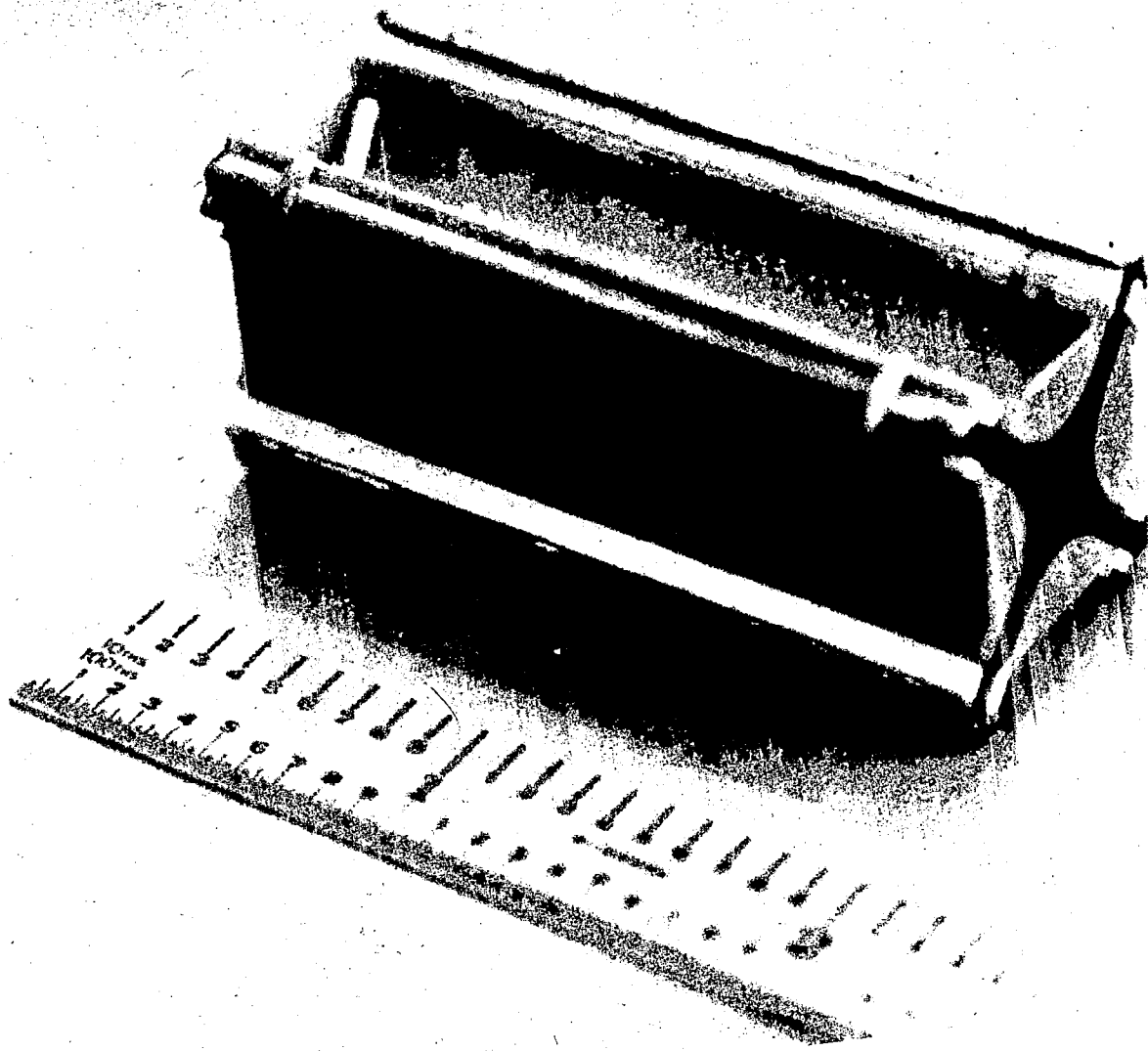
The electron multiplier is a commercial high-current continuous-dynode multiplier. The multiplier is offset from the mass-filter axis so that there is no line-of-sight path from the ion source to the multiplier.

The flange whose face is seen in this view is the multiplier end. There is seen at the opposite end a variable-leak valve that serves in the test system to both control the leak rate and to close the gas entrance line when the system is not in operation. The final instrument will have a fixed-orifice leak valve that can be operated in a closed position or in a single, fixed open position.

The mass filter (Figure 3) is 5.1 cm long, with tungsten hyperbolic electrodes having a radius of 0.381 cm. The filter is manufactured by chemical vapor deposition onto a mandrel with the effect that the dimensions of the electrode are determined by the dimensions of the mandrel. This process for manufacturing the mass filter was the invention of James L. Lawrence, Jr., and Frederick R. Pickett of Analog Technology Corporation, and the process was developed by the Company prior to initiation of the contract.

In the end view of the mass filter shown in Figure 4, it can be seen that the deposited analyzer is a single rigid structure of four mass-filter electrodes, with eight insulators connecting these mass-filter electrodes to four ground-plane electrodes.

Figure 5 shows a drawing of the ion source used in this mass spectrometer. The inside of the source is a cylinder 0.76 cm in diameter and 0.76 cm high. Provision was made for a repeller
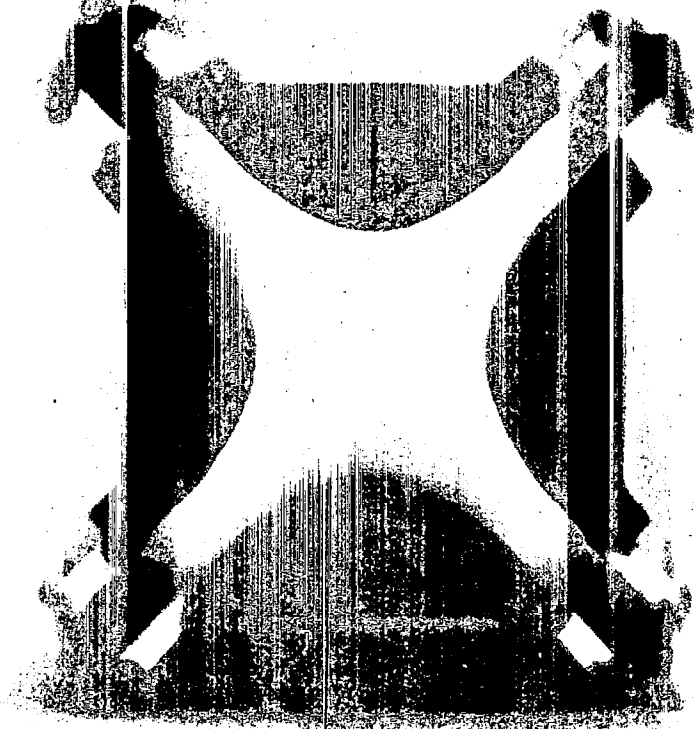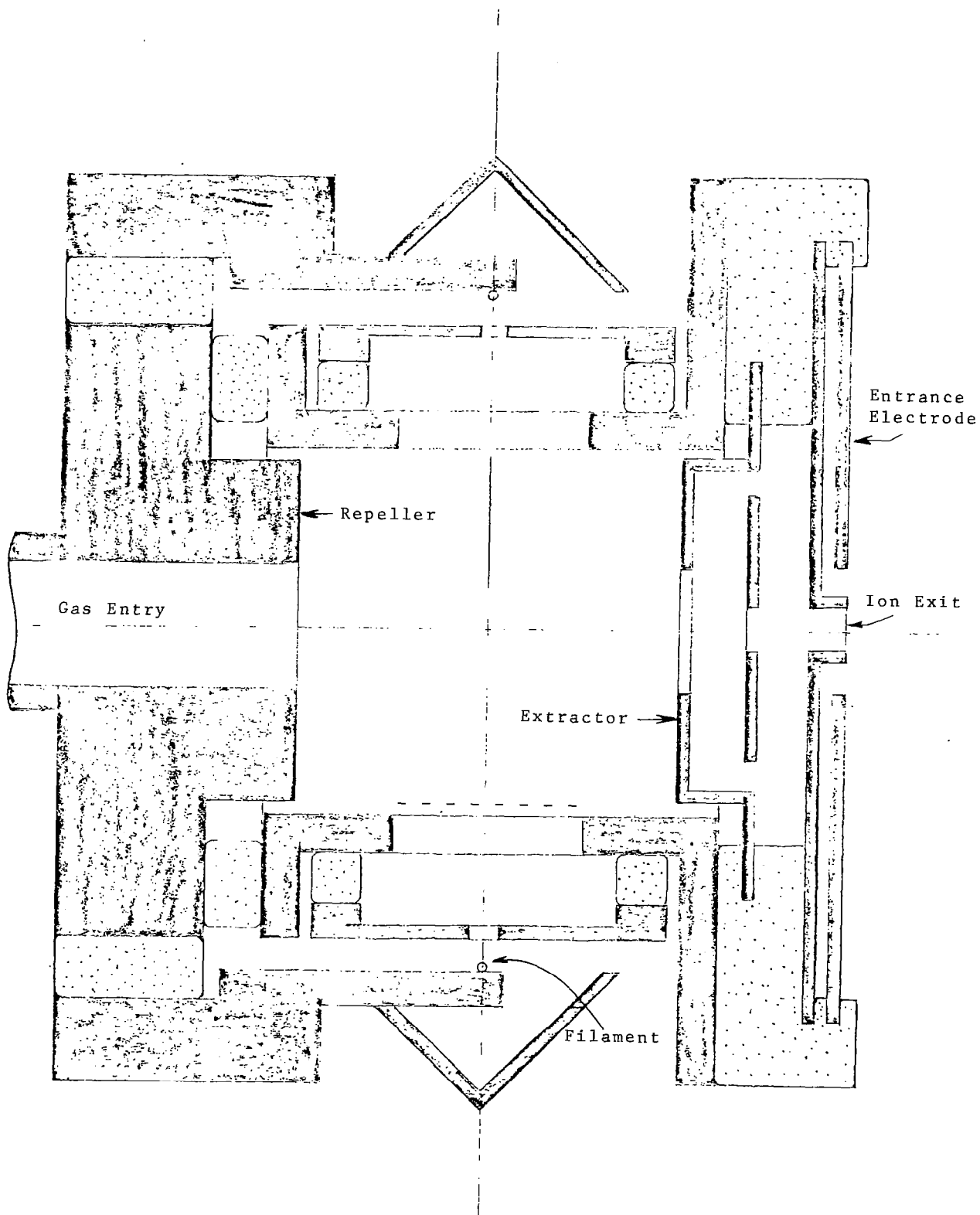
Figure 4   End View of Mass Filter

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Entrance
Electrode

Ion Exit

Repeller

Gas Entry

Extractor

Filament

Figure 5   Ion Source

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and an extractor, each of which can be maintained at a voltage different from the voltage applied to the walls of the ionization box. Provision was also made for two apertured electrodes between the extractor electrode and the mass filter, both of which were operated negative with respect to the mass-filter axis.

As shown, the extractor electrode has an aperture of 0.254 cm diameter and the two filter entrance electrodes have apertures of 0.0762 cm diameter. The source was constructed so that these apertures could be varied in order to determine experimentally the optimum dimensions.

The construction of an ion source having an extractor electrode operated at a voltage different from that of the ionization box requires that the insulators that mount the extractor be located so that the fields in the ion source are not affected by charge build-up on these insulators. This is accomplished in this design by locating the insulator completely away from the ion source, as shown in the drawing. The electrode that follows the extractor appears in the drawing to be unsupported, but is mounted in a similar way in the plane perpendicular to the drawing.

The ion source has two filaments, located symmetrically opposite to each other, and in back of each filament there is a shield that was operated at the potential of the negative side of the filament.

Electrons enter the ionizing region through an electron slit that can be operated at a positive potential with respect to the ionization box. The filament-slit dimensions can be and have been varied, but have been generally set at 0.127 cm square. There is a screen attached to the wall of the ionization box that is at ionization-box potential and minimizes

any penetration into the ion source of the field from the voltage applied to the electron accelerating slit.

The filaments used have been rhenium wire, 0.0076 cm in diameter and 0.76 cm long. The ion current from this filament saturates at about 2 mA of emission under typical conditions, and has generally been operated at an emission level of about 1 mA. Filament current is controlled to maintain constant total emission, although there is provision to measure trap current using the structure associated with the opposite filament as an electron trap.

Magnetic collimation of the electron beam was tested, but was not used further because in the tests run it did not improve performance.

Gas enters the ion source through a tube with a length long compared to the diameter, entering on the axis through the repeller. Calculations indicate that the density of molecules in the ionizing region can be increased over the density present due to the average pressure in the ion source by using a small-diameter beaming-tube entrance such as is provided here. Experiments performed using this geometry did not show the expected improvement in sensitivity and were not pursued further.

There are also entrance electrodes in quadrupole symmetry present at the mass-filter entrance that are used to obtain delayed-dc entrance fields. Two of the four electrodes are shown in Figure 5, and are shielded from the entering ion beam, as are the others, by a lip on the entrance aperture.

Figure 6 shows these entrance electrodes from an end view. Their construction is thin and circular, and they are located closer to the mass-filter axis than are the mass-filter electrodes. These electrodes are constructed in essentially the same way as they were in the Astronaut Breath Analyzer. This structure was designed to be used with the application of dc voltages of polarity opposite to that applied to the adjacent mass-filter electrode. The opposite-polarity dc voltages reduce the dc field in the entrance and have an effect similar to that obtained when the rf voltage in phase with the adjacent mass-filter electrode is applied to the entrance segment of a segmented-rod structure.

These entrance electrodes were operated with dc voltages in the manner in which they were designed to be used, and also with rf voltages. In the latter case, it was required that the rf voltage applied to the entrance electrodes be attenuated because of the shorter distance of these electrodes from the axis.

Figure 6 also shows the alignment holes in the end of the ion source, which fit onto pins on the mass-filter mounting structure, thus ensuring that the ion source is aligned to the mass-filter axis.

Figure 7 illustrates the ion source, mass filter, and electron multiplier mounted within the vacuum tee. This drawing shows the design in its original form. The present version, for which performance results are reported, differs mechanically in some minor details from that shown (e.g. in ion pump baffles, multiplier offset, etc.), but the location of the components and the way in which they are mounted remains as shown in this drawing.

Figure 6   "Delayed-DC" Entrance Electrodes

A Ion Source
B Ion-Source Mounting Structure
C Gas-Entry Line
D Mass Filter
E Electron Multiplier
F Electron Multiplier Offset
   Electrodes
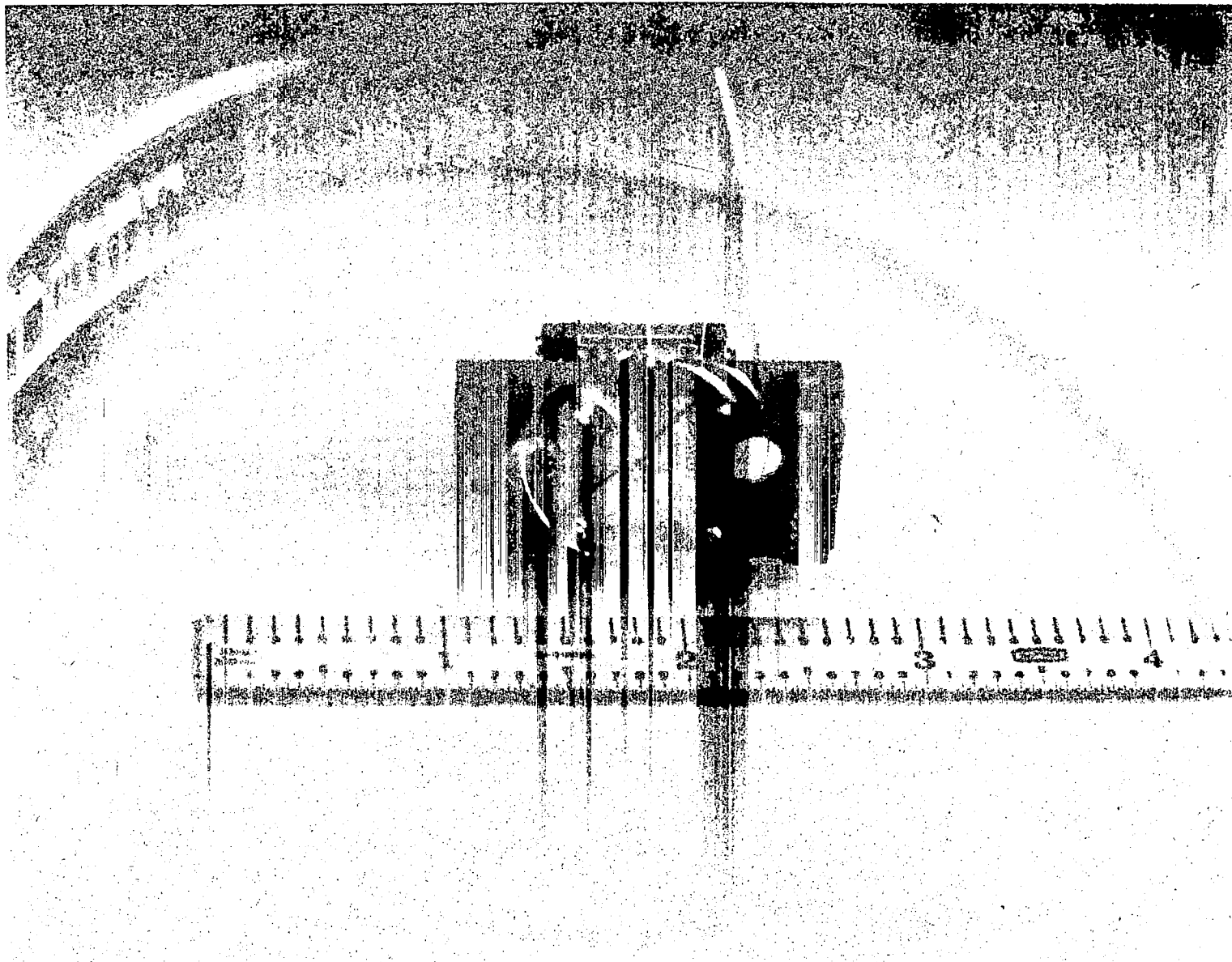G Ion-Pump Entrance Baffles

Figure 7   Sectional View of Mass Spectrometer and Vacuum Housing

The ion source is shown as a block at A, without any details of the ion source structure or of the electrical connections to the ion source. There is shown at B an ion-source mounting structure that provides a spring-loaded mounting by which the ion source is made to fit into the mass-filter assembly. The gas entry line is shown at C, entering transversely to the mass-filter axis. This was later changed to provide gas entry on the axis. The mass-filter assembly is shown at D, with two of the parallel mass-filter electrodes being seen. The electron multiplier is shown as a block at E. Offset electrodes at the entrance to the electron multiplier are shown at F, although the construction of the offset entrance shown differs in detail from that actually used. Baffles in the ion-pump entrance are shown at G, although again the structure shown is not exactly that used.

The system was designed to operate at a radio frequency on the order of 2 MHz, an ion energy on the order of 2 V, and a filament emission on the order of 1 mA. The system was further designed to operate with a gas flow at the leak-valve less than 10^{-4} torr-liters/second in order to allow use of a relatively small 30-liter/second ion pump under conditions of reasonably long pump life.

3.0 DESIGN OF COMPONENTS AND ASSEMBLY OF THE SYSTEM

3.1 Parametric Study

Before individual components were designed, a parametric study was conducted in order to set specifications for the components. Some of the results of this study are discussed in this subsection.

3.1.1 Dimensions of the Mass Filter

The mass filter used in the Astronaut Breath Analyzer had a length of 5.1 cm and a radius (distance from the axis to the mass filter electrodes) of 0.19 cm. After the advantages and limitations of using a mass filter of greater length and/or radius were considered in some detail, it was decided that it would be advantageous to increase the mass filter radius from 0.19 cm to 0.38 cm.

The primary reason for using a larger radius was to reduce the required dimensional tolerance, which is a major factor in limiting the resolution of a mass filter. From the basic equation for the mass filter, which is given by

$$V = k M R^2 F^2,$$

where V is the rf voltage required for a particular mass M in a filter with radius R at frequency F, it can be seen that

$$\Delta M/M \sim 2 \; \Delta R/R$$

The dimensional tolerance required for a specified resolution is a fixed fraction of the radius, and thus the absolute value of the tolerance increases with increasing radius.

Assuming that the voltage or power of the rf power supply is limited, use of a larger radius leads to use of a lower frequency. Whether use of a larger radius and a lower frequency would be expected to lead to an increased or reduced sensitivity depends on the model assumed for the way in which

radius and frequency affect sensitivity. It is probably poss-
ible to obtain an increase in sensitivity with a larger radius
and a correspondingly lower frequency, but this is at best a
minor justification for use of a larger radius in this in-
strument.

One definable adverse effect of using a larger radius
and a correspondingly lower frequency is that the maximum
allowable ion energy is reduced. In order to provide a speci-
fied resolution, the ions must remain in the filter for a
sufficient number of cycles to be resolved. According to
an experimental criterion reported by Paul, the required num-
ber of cycles depends on resolution with a relationship

$$n = 3.5 \sqrt{\frac{M}{\Delta M}}$$

In terms of length of the filter and excitation frequency,
this leads to an equation for the maximum allowed ion energy

$$V_A = \frac{\Delta M}{2} \left(\frac{F \ L}{3.5} \right)^2$$

where the ion energy, V_A, is in volts the frequency, F, is
in MHz, and the length, L, is in cm. For the present case,
with a frequency of 2 MHz and a length of 5 cm, the calcu-
lated energy for a peak width ΔM equal to 1/2, is 2.0 volts.

With a radius reduced by 1/2 and a frequency increased
by 2, the allowed energy would be increased to 8 volts. An
increased ion energy might be expected to provide an increased
sensitivity and also to reduce the problem of entrance fringe
losses. However, a four times increase in ion energy accom-
panied by a four times reduction in filter cross section
actually provides very little, if any, increase in sensitivity.

The advantage in using a smaller radius and an increased frequency is that the fringe loss is reduced. To avoid fringe losses in the entrance, the time of passage through the fringe should be less than 2 cycles of the excitation frequency. Assuming that the fringe region has a length approximately equal to the filter radius, the number of cycles in the fringe region is

$$n_F = 2 \ R \ F \ \sqrt{\frac{2V_A}{M}}$$

where R is the filter radius. Substituting the allowed ion energy, V_A, previously derived for the maximum to obtain a specified resolution, it is seen that the number of cycles in the fringe is

$$n_F = 3.5 \ \frac{R}{L} \ \sqrt{\frac{M}{\Delta M}}$$

In order to obtain $\Delta M = 1/2$ at mass 200, with the filter used for which R/L = 0.075, the number of cycles in the fringe is 5.2.

In order to reduce the number of cycles in the fringe to 2.0 by use of a smaller filter radius, it would be necessary to reduce the filter radius by a factor of 2.6. It was considered more desirable to keep the larger radius with its lesser requirements for dimensional tolerance, and to provide electrodes for correction of the entrance fields, rather than to attempt to eliminate the need for entrance corrections by use of a smaller radius.

The mass filter length was maintained at the 5.1 cm used in the Astronaut Breath Analyzer. A mass filter of two or three times this length would provide an advantage of increased sensitivity due to use of higher ion energy, and would

also provide a reduced fringe entrance loss, both improvements being obtained without requiring any change in filter radius. The advantage of a small increase in length are, however, quite modest. A 10- or 15-cm mass-filter length was considered to be a distinct compromise of the requirement for a compact instrument. Considerations of physical size, minimum rf excitation power, and ease of fabrication favor the shorter mass filter that has been used.

3.1.2 Gas-Flow Considerations

Review of existing commercial ion pumps indicated that pumps with a pumping speed in excess of 30 liters/sec are significantly larger and more expensive than pumps with pumping speed in the 20-30 liter/sec range.

Since a 50-60 liter/sec pump would appear to provide only a minor improvement in background with a disproportionate increase in size and weight, it was determined that a portable 30-liter/sec ion pump would be adequate.

It was determined that the components of the analyzer could be located inside a 6.4 cm OD envelope with all components at least 0.3 cm from the envelope wall. Under these conditions, the only pumping conductance restrictions that can be expected to affect spectral background are the restrictions at the exits from the ion source, the mass filter, and the multiplier housing.

The mounting assemblies for the mass filter and the electron multiplier were designed so that the exit pumping conductances were greater than 3 cm^2. This is approximately 50 times the exit conductance from the ion source and approximately equal to the 30-l/sec speed of the pump. Under these conditions, the effect of slow pumping out of the mass filter and multiplier housings should be negligible.

A conventional closed source with a differentially pumped filament and a source exit conductance on the order of 1 to 5 liters/second was determined to be suitable for this instrument. It was concluded that the desired source pressure would be in the 10^{-5} torr region, being limited by pressure linearity considerations and by the gas load to the pump.

Based on the source conductance and source pressure specified above, the inlet leak rate would be on the order of 1 to 5 x 10^{-5} torr-liters/sec.

The proposed system requires that gas be transported to the mass spectrometer from a distance, and then be introduced into the mass spectrometer through a leak. To move gas over some distance in a reasonably short time requires a relatively high flow of gas. Only a small part of this gas is admitted through the leak to the mass spectrometer; the major part by-passes the mass spectrometer leak and goes to a pump.

One decision that was considered in regard to the inlet system design was the choice of pressure of the gas at the entrance to the mass spectrometer leak. It was desired in this system that the leak admitting gas to the mass spectrometer have an associated valving capability such that the combined leak-valve element be able to control the flow of gas when the valve is open and also shut off the flow completely when the valve is closed. The construction of such a leak-valve was such as to permit the control of flow through the use of a small orifice.

For air-monitoring applications, the gas entering the mass spectrometer is essentially air at all times and has a constant viscosity. In that case, the mass spectrometer ion

currents can be used to calculate concentrations of the various trace gases present with either molecular or viscous flow at the entrance.

In the Air Force applications, for which the initial instrument was being constructed, the gas would not always be air and would not have a constant viscosity. In that case, a mass spectrometer analysis of the entering gas requires that the flow through the leak be molecular. Use of a reduced pressure at the entrance to the leak greatly simplifies the construction of a molecular-flow orifice. It was therefore determined that the initial instrument to be constructed for the Air Force would use a reduced pressure (on the order of a few torr) at the leak entrance, and that the inlet system would require pumping to move gas from the sample point to the mass spectrometer and to reduce the pressure to the level of a few torr. This might be accomplished with a single pump, or it might be found that the system would be simpler if separate pumps were used to move gas to the mass spectrometer and to reduce pressure.

For the air-monitoring version of the instrument, it would not be necessary to reduce pressure. The same leak-valve design could be used, as in the case of the Air Force instrument, with gas entering at atmospheric pressure through a smaller orifice.

3.1.3 Detection Limit

The proposal specified that a sensitivity of 10^{-9}A of ion current would be obtained for 100% nitrogen (the ion-source operating pressure to be used was not specified), that this would be obtained with intensities stable to 5% or better, and that a constituent with a sensitivity of 1/100 of that for nitrogen could be detected at 0.1 ppm concentration.

This required a capability to detect an ion current of 10^{-18}A, or 6 ions/second, plus an analyzer sensitivity of 10^{-9}A for nitrogen.

The design requirements for such performance were reviewed at the beginning of the program. A sensitivity of 10^{-9}A for 100% nitrogen with the calculated ion-source pressure, which was on the order of 3×10^{-5} torr, is 3×10^{-5}A/torr. This appeared to be a modest specification in view of the sensitivity reported for existing designs. However, sensitivity of this magnitude had not been experimentally demonstrated for either a short filter, or for a mass filter capable of producing peaks with flat tops such as were obtained in the Astronaut Breath Analyzer. It was desired to obtain such flat-topped peaks and to obtain such peaks over the full mass range of the instrument in order to minimize the stability requirements of the rf/dc power supply, thus permitting the use of a simpler and lower cost rf/dc excitation system. It was not, however, essential to the specifications of the instrument that flat-topped peaks be obtained, only that the peaks have sufficiently steep sides to obtain low adjacent-peak contributions.

The various factors restricting the detection limit were considered, with the following conclusions:

1.   A current-detection limit of 10^{-18}A is required. With a multiplier gain of 10^{5}, which is a conservative value, the multiplied current required is 10^{-13}A. The current-to-frequency converter, a standard product manufactured by the contractor, has a noise current of 3×10^{-14}A, rms for 1-second samples, and can be used.

2. For detection of 6 ions/second, a measurement time
   approaching one second is required by statistical
   considerations.

3. Achievement of non-spectral noise levels on the order
   of 6 ions/second requires low levels of non-spectral
   background, including possible background signals from
   events arising in the ion pump, in the electron multi-
   plier, and in the ion source. It was concluded that
   the greatest difficulty in achieving a limitation of
   6 events/second at the multiplier of non-spectral noise
   would be the problem of non-spectral events arising in
   the ion source. It was clear that use of an offset
   electron multiplier would be essential for reduction
   in non-spectral noise from the ion source. However,
   there was not available at the beginning of this con-
   tract any definitive data as to the background level of
   this non-spectral ion source noise that might be reached
   by using an offset multiplier.

4. It was concluded that obtaining spectral background
   limits of 6 ions/second appears to be more difficult
   than obtaining non-spectral background limits of this
   magnitude. Without attempting to predict the back-
   ground levels that might be achieved for any specific
   constituents, the precautions required to minimize
   non-spectral background were defined. The walls of
   the transport system should be heated. Provision
   should be made to bake the analyzer envelope (and possibly
   to heat the analyzer envelope continuously). Because
   gas previously pumped is re-emitted from an ion pump,
   the extent to which any gas to be measured is admitted
   to the system should be minimized, both with respect to
   the concentration admitted and the length of time.

Calibrations should be made with low concentrations and with brief periods of admission.

3.2 Major Components Designed by ATC

The major components designed by ATC were the mass filter, the ion source, the leak-valve, and the vacuum envelope. The considerations involved in the design of these are reviewed in this subsection.

3.2.1 Design of the Mass Filter

Prior to the start of this contract, a method of fabricating a mass filter as a single unitary structure by chemical vapor deposition was developed and tested. In this process, mass filters of highly reproducible structure are fabricated by chemical vapor deposition onto a mandrel so that the dimensions of the mass filter are determined by the dimensions of the mandrel. In this process it is just as easy to construct a mass filter with hyperbolic rods as with round rods. Further, the insulators that separate the electrodes are bonded to the electrodes in the deposition process, thus avoiding the problems of reproducibly mounting the electrodes to the insulators.

A mass filter structure was fabricated prior to the contract to reduce the invention to practice. However, this structure was not mechanically perfect, and a second filter with a more nearly perfect match to the specified dimensions was constructed during the contract.

The insulators are embedded in the mass filter at the time the electrodes are deposited. The metal that overlays the insulators must then be removed to permit the four electrodes to be insulated from each other.

In constructing the initial filter, the insulators were uncovered by grinding away the undesired tungsten. In constructing the second filter, the removal of the metal covering from the insulator surface was accomplished by electro-chemical grinding.

3.2.2 Design of the Ion Source

Alternative ion-source designs were considered in some detail, with particular attention given to three basic configurations. These were:

1. A conventional source of the type sometimes referred to as a Nier source in which the electron beam is transverse to the analyzer axis;

2. A source in which the electron beam is co-axial with the ion beam; and

3. A source with a physical construction resembling an ion gage.

In the latter, the ionization region is surrounded by a cylindrical grid, the filament is located outside of the grid, and electrons are present in a space-charge-controlled cloud, rather than in a beam.

Consideration of a source of the ion-gage type with a filament outside of a cylindrical grid led to the following conclusions: (a) Such sources appear to provide the highest available sensitivity for detection of low partial pressures; (b) There is no evidence that such sources have been demonstrated to provide ion currents that are linear with concentration and independent of the other species present; and (c) There is doubt about the possibility, even with a major

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development program, of achieving quantitative operation for
mixture analysis in such a source except at low total pres-
sures. This leads to doubt that the use of such a source
for quantitative mixture analysis would actually provide
increased sensitivity over a conventional source with a trans-
verse electron beam.

Review of the information available about ion sources
with co-axial electron and ion beams led to two conclusions
as follows: (a) It is not clear whether such an ion source
has an advantage or a disadvantage in sensitivity over a
source with a transverse electron beam; and (b) Such sources
are less well understood than sources with a transverse elec-
tron beam. The literature provides very little information
about them beyond a description of the construction. The
further conclusion was that development of such a source for
the present instrument would almost certainly be a more com-
plex project than development of a source with a transverse
electron beam.

A second alternative choice with respect to the design
of the ion source was whether to use a closed source in which
the molecule density in the ionizing region is determined by
the balance of flow in and out of the source, or to use an
open source with a molecular beam of the gas to be analyzed,
in which a high molecular density is created by a molecular
beam. It is reasonably obvious that a source can be con-
structed that, with minor changes in the way in which gas
enters and leaves the source, can be operated either as a
closed source or as an open molecular-beam source. It can be
seen further that a molecular beam source can be closed, and
such sources have been described in the literature. Calcu-
lations indicated that maximum sensitivity would probably be

achieved in such a source using a molecular beam in a closed source.

The source design selected was, therefore, a closed source with a molecular-beam entrance. If the molecule density is determined by the density in the beam, the restricted exit conductance of the closed source does not materially act to increase the sensitivity, but does act to reduce the partial pressure of constituents present in the analyzer due to re-emission of material adsorbed on the walls of the analyzer, or due to re-emission from the ion pump.

A dual filament structure was adopted to minimize the problems of limited filament life. The two filaments were located opposite to each other in a conventional manner for dual-filament ion sources.

A filament shield was placed behind the filament to act as an electron repeller. The shield was constructed to operate at negative filament voltage for simplicity of structure but could be modified to operate with a negative bias.

An insulated electron-accelerating slit was provided that could be operated positive with respect to the ionization box in order to test the possible advantages of such construction over the simpler construction in which the electron slit is at ionization-box potential.

Provision was made to operate one filament as an electron source and the opposite filament, filament shield, electron-accelerating slit as an electron trap. Operation with trap-controlled emission could then be compared with operation with control of total emission.

Capability of collimating the electron beam with a pair
of small fixed magnets located directly behind each filament
was also provided.

Both the back and front walls of the ionization box
were insulated from the box so that either the back wall
could be used as a repeller or the front wall could be used
as an extractor. It was anticipated that it would probably
not be necessary to have both the repeller and the extractor
operated at a voltage different from the box potential.
However, a configuration permitting operation with either a
repeller or an extractor as an electrode to control the field
within the source was selected in order to test the two alter-
natives.

Two apertured electrodes were provided between the ex-
tractor electrode of the ion source and the mass filter.
These electrodes permit control of the ion beam as it enters
the mass filter, either by aperturing the beam or by focussing
it.

Quadrupole ion-source designs in which the entrance to
the mass filter is controlled by an entrance aperture commonly
use an entrance at ground potential. The Astronaut Breath
Analyzer provided an entrance aperture electrode operated at
a negative potential with respect to ground that served,
along with the delayed-dc entrance electrodes, to minimize
the loss of ions at the entrance. The present ion source
was designed to permit such operation of the entrance elec-
trode at a negative potential.

Focussing between the ionization box and the mass filter
was provided by a simple structure, a single thin electrode

symmetrically placed between the extractor and the filter entrance. It was recognized that a more sophisticated focussing system could be used to provide increased sensitivity. However, there was sufficient information about sensitivity obtainable with the structure used to be reasonably certain that the required sensitivity could be obtained. The goal of the design was to obtain the specified sensitivity with peaks having steep sides and flat tops. It was believed that focussing systems producing increased ion-beam intensities at the entrance to the mass filter would tend to cause deterioration of peak shape. It appeared then that the ion source for the proposed mass spectrometer would probably not be improved by use of a more sophisticated focussing system.

Finally, as in the Astronaut Breath Analyzer, four ion-entrance electrodes in quadrupole symmetry were located on the mass-filter side of the filter entrance aperture. These electrodes were to be used as "delayed-dc" entrance electrodes to control the entrance and thereby optimize the peak shape. The particular structure selected for control of the entrance field was not regarded as the best possible structure, but as the least problematical to use, because its construction was simple, and it had been previously tested in the Astronaut Breath Analyzer.

3.2.3 Design of the Leak-Valve

A new, commercially available piezo-electric leak-valve was purchased and was found to not provide stable control of gas flow except at flow rates higher than was intended for the present application. It was concluded that a leak-valve suitable for this application could not be purchased and would have to be designed.

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A commercial variable-leak-valve was purchased for use in the test vacuum system and was successfully used in testing the mass spectrometer and the vacuum system. This valve has the advantage of being easily adjustable over a wide range of flow rates. However, it is a manually operated valve and does not have the desired feature of being capable of automatic closure on loss of power or other emergency condition.

It was decided that the new leak-valve that was to be designed would be a commercial valve with a fixed orifice. Measurements of mass spectrometer performance using the commercial variable-leak-valve described above would be used to determine the optimum conductance for the new fixed-conductance design.

A leak-valve was then designed by modifying a commercial valve. This unit (Figure 8, expanded view of Figure 9) uses a fixed-aperture gold-foil leak with a minimum dead volume between the foil and the valve seal and seat, so that only a very small amount of gas enters the mass spectrometer after the valve closes. The valve was tested to verify the leak conductance in the open position and the leak-tight closure of the valve.

3.2.4   Design of the Vacuum Envelope

It was found that the ion source, mass filter, and the electron multiplier would fit within a commercial vacuum tee, 6.4 cm in diameter and 21 cm long, with 11.4-cm diameter flanges. A design for mounting the components within the flange was developed that permitted mounting the ion source
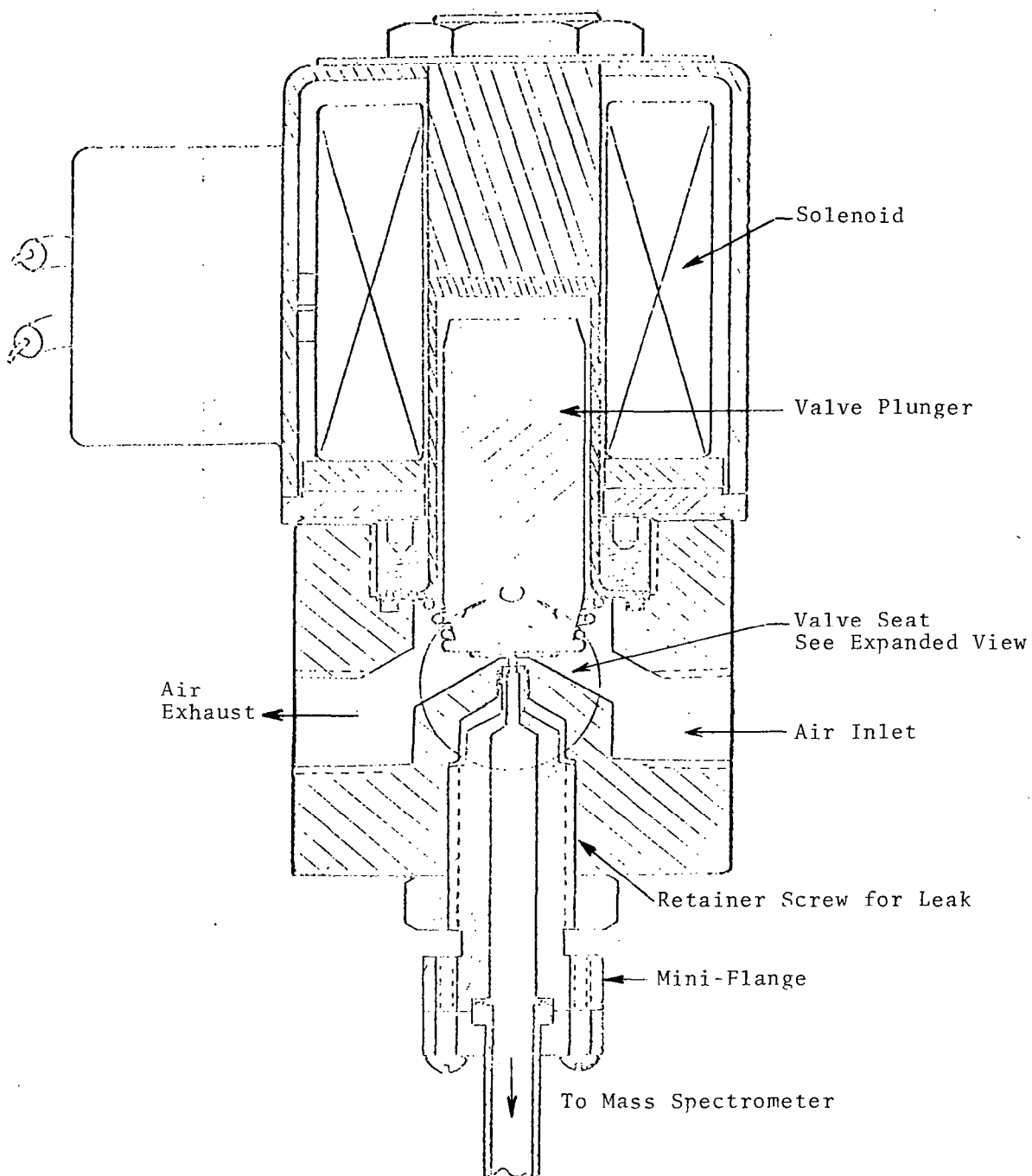
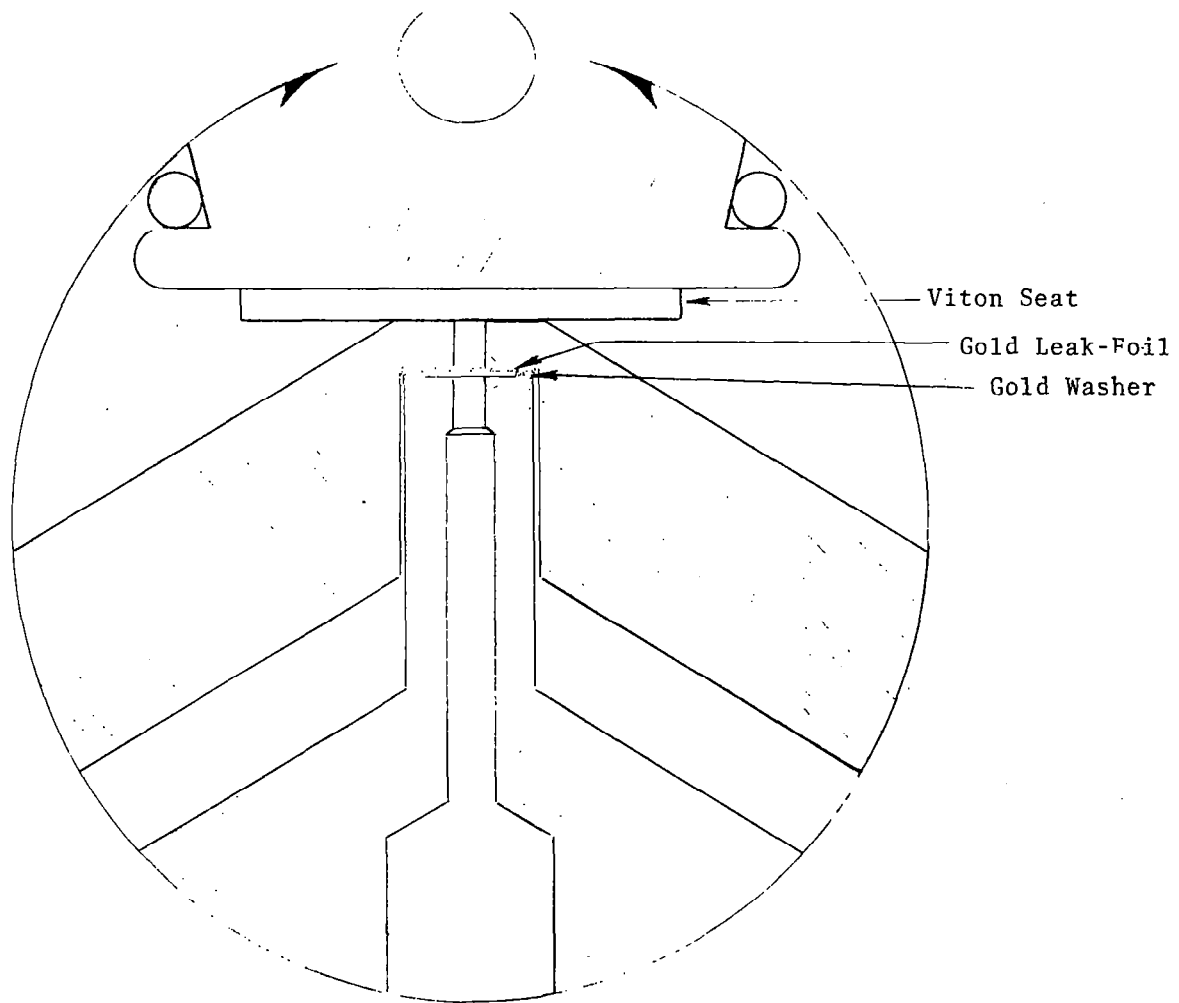Figure 8   Valve With Molecular Leak

Figure 9   Expanded View of Leak Valve

to one flange, and the electron multiplier to the opposite
flange. The mass filter was then attached to the envelope,
and provision was made so that the alignment of the ion source
and of the electron multiplier to the mass filter was main-
tained by pins that fit into matching holes when the system
was assembled.

Construction of the vacuum system also required design
of a housing for the electron multiplier, and a connection
of the tee to the ion pump, including a baffle in the ion-
pump connection.

In order to minimize any possible noise events at the
multiplier entrance and at the same time maintain a good
vacuum inside the multiplier housing, the multiplier housing
was constructed to provide a closed box around the multiplier
with the entrance aperture facing the mass filter, and with
pumping apertures located in the housing at the base end
away from the multiplier entrance.

An ion exit aperture was also attached to the multiplier
housing, and this was insulated so that a negative bias volt-
age could be applied to this aperture to accelerate ions
through the fringe field at the exit in the same manner as
they are accelerated through the entrance fringe field.
While it would be expected that there would be field penetra-
tion from the multiplier high voltage that would accelerate
ions through the exit aperture, it seemed useful to test the
application of a bias voltage at the exit aperture.

In the final design, there was a screen across the exit
aperture. In the earlier version, which had a smaller exit

aperture, there was no screen. There has not been an experimental determination of any advantage or disadvantage resulting from the use of this screen.

A baffle was placed in the section of the tee attached to the ion pump. This baffle consists of three plates with staggered apertures such that a particle must undergo four wall collisions to pass through. There is also a grounded screen on the pump side of this baffle which prevents penetration of the flow discharge from the ion pump.

A manually operated vacuum valve for connection of a rough pump to start the ion pump, a gas inlet line, and the necessary electrical connections comprised the remainder of the vacuum assembly.

Two connectors for the rf/dc voltage were provided on the wall of the envelope immediately adjacent to the mass filter. These connectors were provided at this point so that the rf/dc power supply could be located immediately adjacent, thus permitting a minimum capacity in the connection and a minimum power requirement for this power supply.

Two shielded electrical connectors were provided at the exit flange for the electron-multiplier high voltage and the electron-multiplier output current. A four-pin connector was also provided at the exit flange. Two connections were required for the multiplier-entrance offset voltage and the filter-exit voltage. A third terminal was used to make the electron-multiplier ground connection outside the vacuum to facilitate measurement of unmultiplied current at the multiplier input.

Two ten-pin connectors were provided at the entrance
flange for ion-source voltages and for heaters and thermo-
couples used to control the temperature of the ion source
and the gas line entering the ion source.

A stainless-steel gas entrance line was welded to the
entrance flange, connecting the leak-valve to the ion source.
A short section of this line was made up of insulating material
so that the ion source could be operated at a negative potential.

3.3 Selection of Major Purchased Components

Two major components of the system were to be purchased
commercial products: the ion pump and the electron multiplier.
The ion pump selected was a triode 30-liter/second pump de-
signed for high pumping speed with noble gases.

The electron multiplier selected was a high-current,
continuous-dynode multiplier. A continuous-dynode multiplier
was used primarily because of its compact structure, rather
than because of any known superior performance characteristics.
Initially, an offset construction fabricated by ATC was used
to provide non-line-of-sight passage of ions from the ion
source to the multiplier. Later, when it was found that a
multiplier was commercially available with a built-in offset
construction, that model was substituted. Both versions of
the offset construction substantially reduced the non-spectral
noise from the ion source, but neither construction reduced
the non-spectral noise to negligible levels.

3.4 Test Equipment

In addition to the construction of the mechanical portions
of the proposed mass spectrometer, the contract required that
test equipment be assembled to permit verification of perform-
ance to the required specifications. The test equipment, which

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consisted primarily of electronics required to operate the system, was as follows:

1. RF/DC Power Supply - A variable-frequency rf/dc power supply commercially manufactured for operation of quadrupole mass filters was purchased. This power supply permitted testing of the ATC mass filter for operation over a range of frequencies.

2. Ion-Pump Power Supply - An ion-pump power supply was purchased with the ion pump.

3. Electron-Multiplier Power Supply - A 3-KV dc power supply was purchased to provide stable and adjustable voltages for operation of the electron multiplier.

4. Miscellaneous Power Supplies - A set of dc power supplies, which was available in the ATC laboratory, was used to provide the required ion-source voltages. One of these was modified to serve as an emission regulator.

5. Signal-Processing Electronics - A wide-range current-to-frequency converter manufactured commercially by ATC was used to measure ion currents. This converter has both digital and analog outputs and can be used either with a standard chart recorder or with the MAD (memory, analyzer, and display) system manufactured by ATC in which a spectrum can be stored in memory and displayed on a CRT.

6. Mass Programmer - The purchased rf/dc power supply did not have any built-in capability for voltage selection or voltage scanning. Therefore, a digital programmer was constructed that permitted selection of mass with a resolution of 0.1 amu, and scan from a selectable starting mass at a selectable scan rate.

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In addition to providing electronic test capability, a method of preparing gas mixtures for testing the instrument's capability to measure trace constituents was also required. A system for mixing gases continuously at low concentrations was defined using a rotameter for measuring flow at high rates and a calibratable leak for low flow rates. The leak was available in the laboratory, and required rotameters were purchased.

4.0 DESIGN OPTIMIZATION

Performance optimization tests and the resulting system modifications are described in this section.

4.1 Sensitivity and Peak Shape

Modifications of the system after its initial assembly were primarily for the purpose of obtaining optimum peak shapes at the required sensitivity. The general approach was to maximize sensitivity to the extent that this could be accomplished without degrading peak shape, and then to attempt to improve peak shape further.

The ion source was originally assembled with gas entry transverse to the mass-filter axis, with the three aperture plates between the ionizing region and the mass filter having aperture diameters of 0.254 cm, 0.254 cm, and 0.0762 cm, starting with the aperture nearest the ionizing region. There was an electron collimating magnet in the plane of the electron beam. The source did not operate as expected, saturation of ion current being observed at unreasonably low electron currents. The filter-entrance aperture was increased from 0.0762 cm to 0.254 cm, and the problem disappeared. Results of later tests, using a small filter entrance aperture, suggest that the initial problem was not due to the use of a small filter-entrance aperture. The cause of the problem is not known. However, later tests indicated that removal and reassembly of the collimating magnet could cause large differences in performance, and this may have been the problem.

Adequate sensitivity was achieved after the filter-entrance aperture was increased to 0.254 cm, but the failure to obtain the desired peak shapes at higher masses was disappointing. Application of field-correction voltages (either filter-entrance-aperture bias voltage or "delayed-dc voltages" at the entrance electrodes) was found to increase the slope on

the low-mass side of the peak at relatively low masses or resolutions, or at any mass with relatively low resolutions, but provided very little effect on the slope at masses above 100 with resolutions required for low adjacent-peak contributions.

The filter-entrance aperture was reduced again to 0.0762 cm in an attempt to improve the peak shape at high mass, but there was no major improvement in peak shape. However, it was found that when the system was operated with a negative bias at the filter-entrance aperture, the sensitivity changed very little, independent of whether the filter-entrance aperture was 0.0762 cm or 0.254 cm. This indicated that the small filter-entrance aperture could be used without any large loss in sensitivity, but did not demonstrate any advantage of using small filter-entrance apertures. Retaining the small filter-entrance aperture of 0.0762 cm, the electron collimating magnets were then removed. The maximum electron current at which the ion current is saturated was higher without collimating magnets, and the sensitivity was also increased. However, the increase in the ion current was not as large as the increase in the electron current. Performance without the magnets was apparently better.

Performance with an original electron aperture of 0.127 cm x 0.382 cm was then compared with performance using a 0.127 cm x 0.127 cm electron aperture. There was little difference in the sensitivity, indicating that the smaller aperture, with its correspondingly smaller exit conductance for gas, is probably preferred.

The next modification was the substitution of an axial molecular beam for the original transverse molecular beam. The result was an increase in sensitivity by a factor of 3 at mass 28 and a factor of 10 at mass 127. There had been

concern that the axial molecular beam would lead to a greatly increased background because of excited molecules beamed along the axis. No such problem was encountered. There was no increase in the ratio of background-to-peak ratio with the axial beam. In the absence of any background problem, it was concluded that the axial beam would be preferred. Not only was the sensitivity increased, but the voltage adjustments appeared to be less critical.

The comparison of operation with and without electron collimation was repeated with an axial molecular beam. Operation without electron collimation was again found to be more easily reproduced, and the problem in obtaining reproducible data with collimating magnets present was found to be particularly great when small exit apertures were used. It was concluded that, at least with the present design of the collimating magnets, performance was better without the magnets and that they would not be used.

Reduction of the beaming-tube diameter from 0.254 cm to 0.0762 cm for operation with an 0.0762 cm filter entrance aperture would be expected to increase the sensitivity, but the expected increase was not observed. This experiment failed to confirm that the ion source sensitivity is determined by the density of molecules in the beam as defined by the diameter of the beaming tube. While this result was not understood, the experiment was not pursued further. Instead, the structure was returned to the larger diameter tube with the expectation that alignment problems would be less critical with the larger-diameter tube.

The mass-filter entrance aperture was then reduced to a diameter of 0.0254 cm with no improvement in peak shape over that obtained with a diameter of 0.0762 cm. It appears clear

that a small filter-entrance aperture by itself does not pro-
vide the desired peak shapes.

It was concluded at this point that the peak shape might
more likely be improved by changes in the design of the
delayed-dc entrance electrodes than by changes in the design
of the ion source.

The delayed-dc ramp mode of operation originally used
in this instrument was a version having dc voltages applied
to electrodes located 1/3 of the distance from the axis to
the mass-filter electrodes. These dc voltages were of polar-
ity opposite to those of the dc voltages applied to the ad-
jacent mass-filter electrodes. Voltages thus applied cause
an effect similar to that obtained when ac voltages are
applied to entrance electrodes in the segmented-rod version
of the delayed-dc entrance correction.

The present structure was retested with ac voltages
applied to the entrance electrodes. In this case, the ac
voltages applied had the same phase but 1/3 of the amplitude
of the voltage applied to the adjacent filter electrodes.
The slope on the low-mass side of the peak was clearly im-
proved over that obtained with dc voltages applied to the
entrance electrodes. However, the peak shapes were still
deficient with respect to the goal of obtaining flat tops at
masses approaching 200 with 0.1% adjacent-peak contribution.

The filter exit aperture diameter used up to this
point was 0.381 cm, or 1/2 of the distance between filter
electrodes. Published experiments in which flat-topped peaks
were produced for relatively high resolutions were run with
a filter exit aperture equal to the distance between filter
electrodes. Performance with a larger filter exit aperture
(0.762 cm in diameter) was tested, but the increased filter
exit diameter did not lead to the desired sharper peak rise
on the low-mass side. Although no advantage was demonstrated
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for the larger aperture, this configuration was used for the experiments that followed.

The filter entrance was then collimated, providing two successive 0.0762-cm diameter apertures. There was no marked improvement with respect to reduced peak tails or increased peak slopes. Having previously found that a small filter entrance aperture did not provide improvement, the tentative conclusion was drawn that neither a small aperture nor collimated apertures by themselves would provide the desired peak shape.

The entrance electrodes to which the delayed-dc voltages are applied were originally thin electrodes protected by a lip, the theory regarding the use of dc voltages at the entrance electrodes indicating that such a lip is desirable. When rf entrance voltages were applied, the lip was removed in accordance with the conventional view as to the action of rf fields as entrance correction fields. Subsequently, the thickness of the electrodes was increased from 0.0254 to 0.0762 cm, with no improvement observed. Finally, it was considered that the presence of unshielded entrance electrodes nearer to the axis than the filter electrodes might be undesirable, and the electrodes were returned to the original 0.0254 cm thickness protected by a lip. Again, no change in peak shape was observed. The presence or absence of a lip to shield the entrance electrodes is apparently not critical, at least when rf entrance voltages are applied.

At the conclusion of this contract, the sensitivity obtained was significantly greater than that required in the specifications. While the specification of 0.1% adjacent peak contribution over the full mass range might be met by the configurations tested during this contract by using triangular peaks and re-

quiring that the rf/dc power supply be sufficiently stable
to accurately measure such triangular peaks, it is desired
that the peaks over the full mass range have both flat tops
and steep sides so that the stability requirements of the
rf/dc power supply will be less critical.

Plans for continuation of these optimization experiments
are considered in the Appendix.

4.2 Non-Spectral Background

Several modifications of the initial structure were made
for the purpose of minimizing non-spectral background.

It was initially found that there was a detectable back-
ground due to events at the ion pump. This background was
detected when the ion pump was turned on, but was absent when
the ion pump was briefly turned off. After the baffle in the
ion pump connection was modified to the structure described
in section 3.2.4, the background from the ion pump was not
detectable.

Having eliminated the background from the ion pump, the
only detectable non-spectral background seen with the filament
off was the background due to events at the multiplier. This
background, as expected, varies with the multiplier voltage.

The observed background when the mass spectrometer fila-
ment was off was at most a few particles per second and was
negligible compared to the background arising from events
in the ion source that appeared when the filament was turned
on.

The background from the ion source was expected, and a
multiplier that was offset so that there was no line-of-sight

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path from the ion source to the multiplier had been used to minimize this background.

The construction of the electrodes between the mass-filter exit and the multiplier entrance as originally installed was according to a design developed by ATC. Several modifications of this offset structure were tested with the objective of minimizing the ratio of non-spectral background to signal detected. Later a multiplier commercially available with an offset construction was used.

With either structure, the background current appearing when the filament was turned on with the air entering the mass spectrometer was at least 10 million times less than the current measured for mass 28.

At one point during the testing, a structure was installed in which a portion of the wall constituting the box around the electron multiplier was omitted so that the region of the multiplier entrance was open on the side. An excessive background was observed when the filament was turned on, but this problem was eliminated when the walls were closed off in accordance with the original design.

4.3 Selection of Operating Conditions

Operation at 2.0- and 2.5-MHz frequencies for the mass-filter rod voltage was compared, with no indication of improved performance at the higher frequency. It was arbitrarily decided on the basis of these tests to use 2.0 MHz in the rf/dc power supply to be constructed for operation of this mass filter.

The effect of varying the voltages applied to the ion source was studied in some detail, and a considerable amount of information obtained. Final decisions as to the voltages

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to be used were not made, pending final determination of the
ion-source structure to be used to optimize peak shapes.
However, the following conclusions were tentatively drawn:

● The use of a repeller at a voltage different from that
of the ionization box does not appear to be useful when an
insulated extractor electrode is available.

● Sensitivity is increased by use of an extractor aperture
at a voltage negative with respect to the ionization box, and
is further increased by use of one or more negative apertures
between the extractor and the mass filter.

● Use of excessive negative voltages on any of the elec-
trodes between the ionization box and the mass filter causes
deterioration of the peak shape.

● Use of a biased electron entrance does not provide in-
creased sensitivity but may be beneficial by allowing use of
lower filament current, thus providing the possibility of
longer filament life.

● No evidence was found to support any advantage of con-
trolling trap current rather than total emission current in
this instrument. Because ion current ratios are measured,
it is not required that the ionizing electron current be con-
stant. Further, the trap current in an uncollimated ion
source is not necessarily a good measurement of the effective
ionizing current. Finally, the trap current appears to be
a reasonably constant fraction of the total emission for a
specified filament under specified operating conditions.

The final decision regarding the mass-filter entrance
electrodes will be made as part of the structure optimization,

but it appears that the filter entrance will be biased negative and that ac voltages will be applied to the delayed dc electrodes.

Use of a negative bias voltage at the filter exit was not found to provide a significant increase in sensitivity. It was, however, found to be desirable to use a positive bias voltage slightly greater than the ion energy at the multiplier entrance aperture.

Tests of the mass filter in the continuous-scan mode were conducted by scanning across a single peak with a constant dc voltage on the mass-filter electrodes. It was shown that, under some conditions, this led to improved peak shapes over those obtained conventionally with both rf and dc voltages scanned. This method requires that the dc voltage be stepped to an increased value at approximately the half-mass point. The technique is probably useful only within some limited mass range, but could perhaps be used in the present instrument. However, that method was not examined in detail because it has no application to step scanning, which is the primary operating mode of the instrument being developed.

The system was operated with an inlet gas flow of approximately 3×10^{-5} torr-liters/second for test purposes. The effect of varying inlet gas flow on sensitivity and on spectral background after introduction of specified gases was not examined.

5.0 PERFORMANCE RESULTS

The results of tests on the performance of the mass spectrometer are summarized in this section. Since the performance optimization program will continue under the contract for the prototype instrument (to be delivered to the Air Force), the results described here, though representative of those expected of the prototype, should be regarded as being of an interim nature.

5.1 Sensitivity

The sensitivity goal for this instrument (10^{-9}A for nitrogen at mass 28) was easily achieved, with good peak shape.

5.2 Mass Discrimination

The reduction in sensitivity between mass 28 and 127, as measured with constant peak width, indicates that sensitivity varies approximately as $1/M$. It had been expected that the discrimination against high mass might be greater than was actually found.

5.3 Peak Shape

There are two considerations of essential concern with respect to peak shape. One is that it is desired to have a low adjacent-peak contribution, and the other is that it is desired to have flat peak tops, so that precise measurements of peak intensity can be made with less restriction on stability of the rf/dc voltages than would otherwise be required. Both of these considerations require steep peak sides, although it is customarily difficult to achieve a steep rise on the low-mass side.
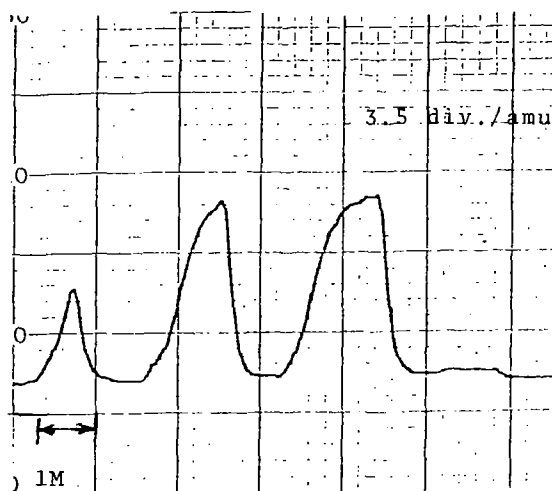
One of the particular objectives in the evaluation of this mass analyzer and in the experimental optimization of

its design was to obtain flat-topped peaks at masses in the 100- to 200-amu region with good resolution. Peaks with reasonably flat tops were obtained in the Astronaut Breath Analyzer with a peak width at half-mass of 0.6 amu. The adjacent peak contribution under these conditions was 0.01%. There are experiments reported in the literature showing similar performance at a higher mass with a ten-inch mass filter having a segmented-rod structure. There has not, however, been any previously recorded attempt to obtain such performance at masses above 50 amu with a short filter or with the relatively simple version of the delayed-dc entrance used in the present instrument.
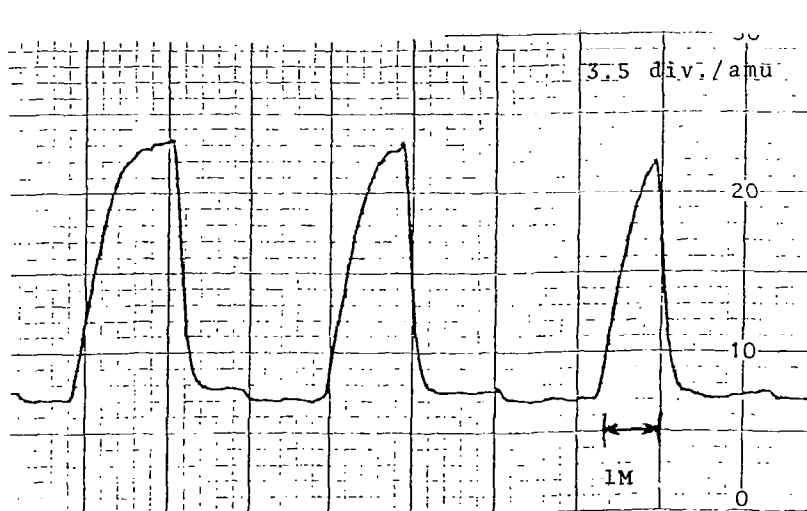
To evaluate the performance achieved at higher masses, measurements were made with the mass-127 peak of SF_6, a compound easily handled in gaseous form.

Peak shapes are shown in Figure 10 for the mass-127 peak with no voltage at the entrance electrodes (these electrodes being grounded) and with dc voltages applied to these electrodes. Three peaks are shown in each case with resolution being varied by change in the rf/dc ratio. A modest increase in the steepness of the low-mass (left-hand) side of the peak is shown when dc voltage is applied to the entrance electrodes. Better peak shapes are obtained when rf voltages are applied to the entrance electrodes (Figure 11). Peak C of Figure 11 approaches having a flat top, and this is obtained with a peak width at half-height of approximately 0.7 amu. One of the goals of the optimization program was to produce peaks with flatness at least as good as that shown here up to mass 200, and with sides having sufficiently good shapes as to limit adjacent-peak contribution to 0.1%. Although this performance was not achieved, it appears to be within reach.

3.5 div./amu

a.   No Entrance Voltage

3

3.5 div./amu

20

10

1M

0

b.   With dc Entrance Voltage

Figure 10   Shapes of Peaks at Mass 127 for 1-V Ions
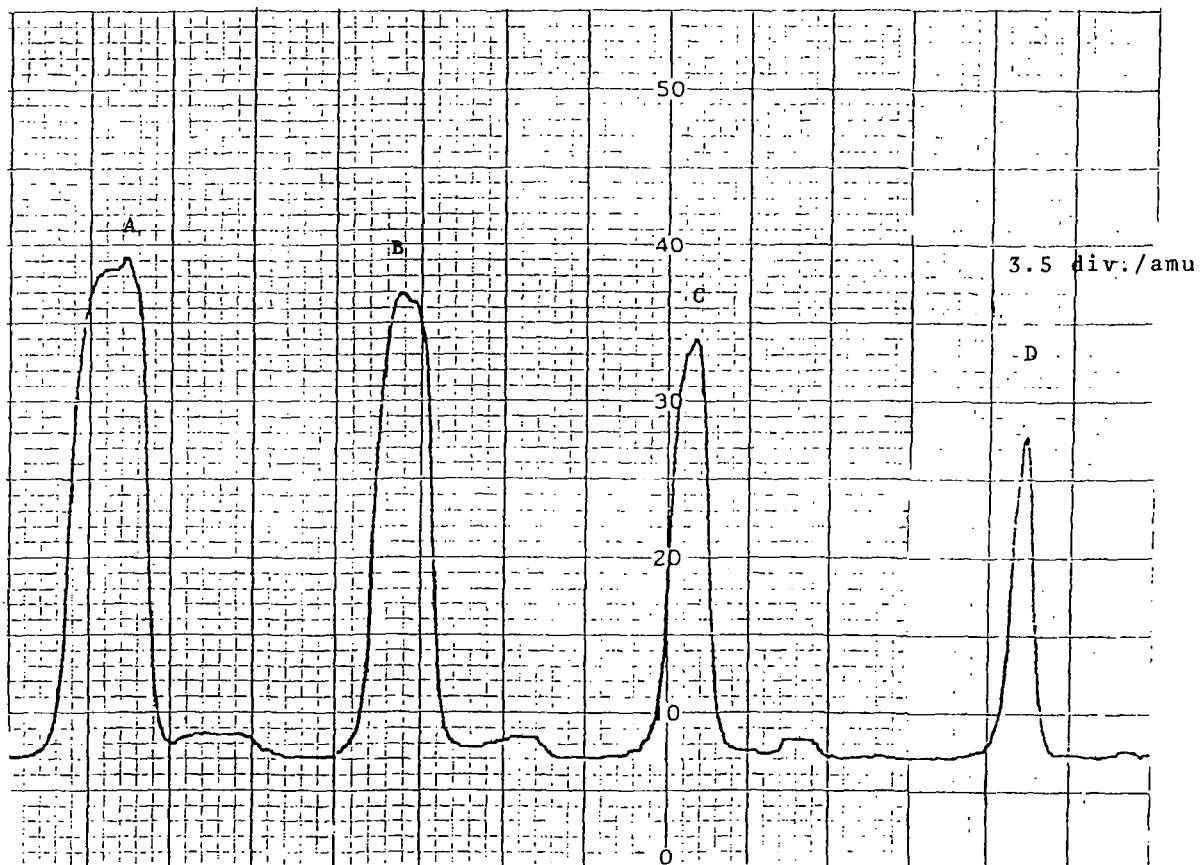With and Without DC Entrance Voltages

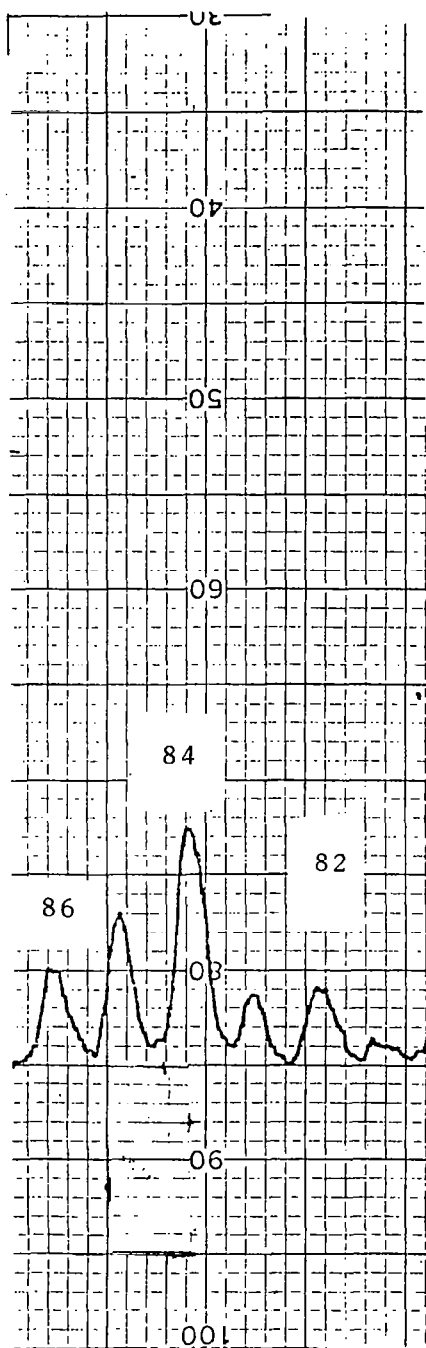Figure 11   Shapes of Peaks at Mass 127 for 1-V
Ions With AC Entrance Voltages

Peak C of Figure 11 has a peak tail such that the adjacent-peak contribution is on the order of 1%, rather than 0.1%. An adjacent-peak contribution of 0.1% can be obtained at lower masses with this peak width, or at this mass with a narrower peak.

At the conclusion of the work described in this report, it appeared that the following further tests would be desirable in a continuing program to improve peak shape:
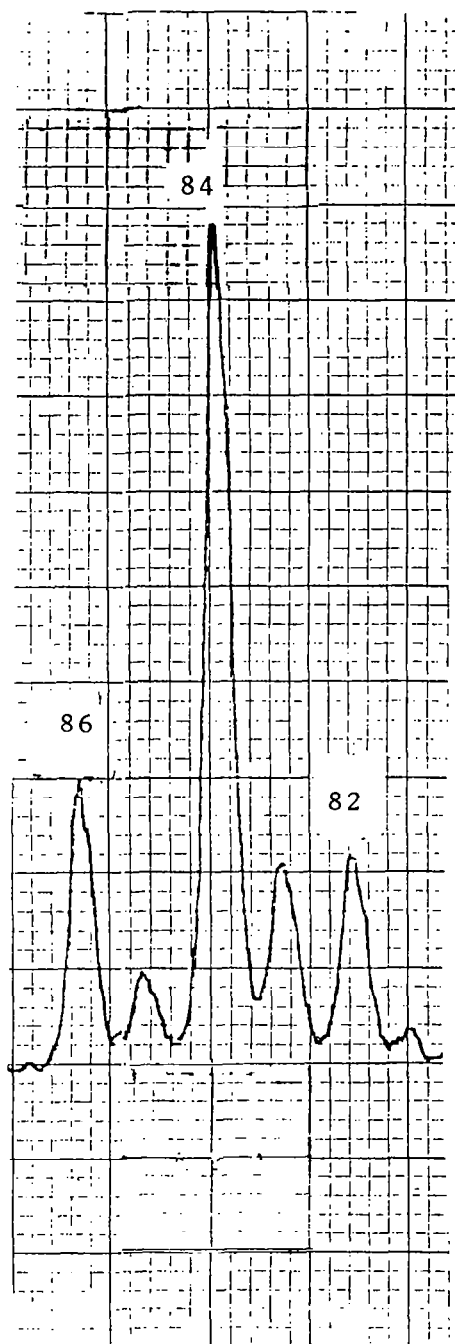
1. Additional measurements of peak shape with varying mass-filter entrance-aperture dimensions, in particular, with an entrance aperture larger than 0.076 cm;

2. Testing of the effect of variations in the mass-filter exit aperture, and of the presence or absence of a grid at the mass-filter exit on peak shape; and

3. Examination of various possible sources of asymmetry in the voltages applied or in the mechanical alignment of the system on peak shape.

5.4   Detection Limit

A detection limit of less than 0.1 ppm was demonstrated by measurement of the krypton isotopes present in normal air. Spectra of the krypton isotopes in air and in pure nitrogen are shown in Figure 12. The spectrum for pure nitrogen represents a background signal. The krypton isotopes at masses 82, 83, 84, and 86 are seen to be considerably enhanced in the air sample. The peak at mass 85 is not enhanced and is background due to something other than krypton. The mass-82 and -83 isotopes are present in normal air at a concentration of approximately 0.1 ppm and are easily detected in these spectra.
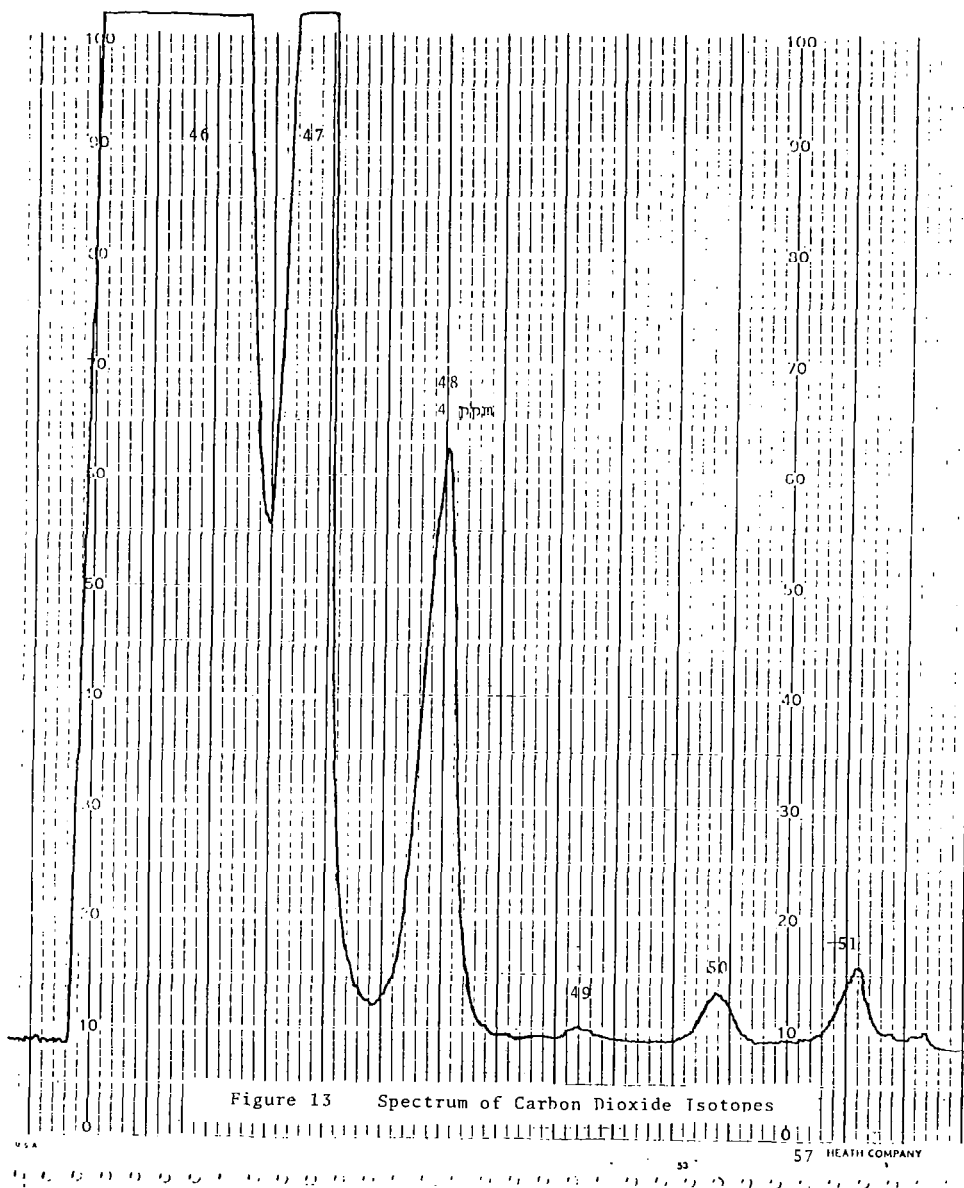
a. In Nitrogen   b. In Air

Figure 12   Spectra of Krypton Isotopes

A detection limit better than 0.1 ppm was also demonstrated by measurement of the mass-48 isotope of carbon dioxide, present at 4 ppm in pure carbon dioxide. Figure 13 shows a spectrum with this peak present at 100 times the noise between peaks, indicating a detection limit of 40 ppb.

The detection limit for a particular species depends on the sensitivity for that species, and on the background signal, which consists of components from both spectral and non-spectral sources.

Non-spectral background may be present as a result of events in the ion pump, events at the electron multiplier, and events in the ion source. When the ion pump is baffled, background from events in the ion pump is less than one event/second and is not measurable. Background from the multiplier (appearing when high voltage is applied to the multiplier) is measurable but is negligible compared to background from the ion source. Non-spectral background is, for practical purposes, entirely due to events in the ion source. This background represents a current at the electron multiplier output that appears when the filament is turned on, but with no accelerating voltage applied to the ion source. Such background events are due to arrival of photons at the multiplier or other secondary events of some kind, but not primary events involving ions formed in the ion source and transmitted through the mass filter to the multiplier. The level of this background varies with the ion-source structure and, in particular, varies with the mass-filter entrance aperture. The selection of an optimum mass-filter entrance aperture remains to be made and will involve considerations of peak shape, as well as signal-to-background ratio. However, a background of 10^{-16}A can be achieved with a mass-filter entrance aperture of 0.0762 cm under conditions in which the nitrogen sensitivity is 10^{-9}A. This background level is sufficiently small to

Figure 13   Spectrum of Carbon Dioxide Isotones

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ensure a detection limit of 0.1 ppm for a constituent having a sensitivity equal to that for nitrogen. For a constituent having a sensitivity less than that for nitrogen, detection of 0.1 ppm may require subtraction of background. The detection limit achievable will then be determined by the precision of the measurement, which will depend on the length of time taken for the measurement as considered in section 5.6.

The system can be baked so that spectral background for most masses is sufficiently low as to permit detection of 0.1 ppm constituents, provided that the system has not been subjected to previous entry of large concentrations of the species to be measured. It is planned that calibrations will be made with low concentrations introduced for a short period of time, and it is not expected that there will be any significant effect on detection limit as a result of background changes after calibration. However, experimental tests remain to be made of the possible increase in detection limit for a particular species when trace concentrations are measured some short time after measuring an analytical sample with high concentrations of that species.

5.5 Dynamic Concentration Range

The specification for the dynamic concentration range of the system is 10^5, which is primarily applicable to the measurement system. The inherent dynamic concentration range of the mass analyzer is at least 10^7 as indicated by the demonstrated detection limit of 0.1 ppm.

5.6 Measurement Time

The specification in the contract for measurement time is 10 seconds. This is the time for measurements at the detection limit. The demonstrated detection limit of 0.1 ppm for isotopes of krypton in air was achieved with a measurement time of 1/2 second per point measured.

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It was a goal of the proposal that a constituent with a sensitivity of 1/100 of that of nitrogen would be detected at 0.1 ppm concentration in a measurement of 10 seconds. Detection limits of constituents of low sensitivity have not been experimentally measured in this instrument. Calculations can be made as to the detection limit for a ten-second measurement time if the limitation is the precision with which non-spectral background can be subtracted. The non-spectral background is approximately 600 events/sec. This can be measured in 10 seconds with a probable error of 5 events/sec. This is approximately equal to the signal calculated to be obtained at 0.1 ppm with a sensitivity 1/100 of that for nitrogen. The goal is achieved if the dominating background is the non-spectral background.

The limitations of spectral background achievable at various masses, and the determination of sensitivities at which constituents can be detected in the presence of spectral background remain to be studied.

5.7 Precision and Accuracy

Precision and accuracy are specified at 5% for concentrations in excess of 2 ppm. The 2-ppm lower limit for this precision is based on the assumption that the signal must be 20 times the detection limit for 5% precision to be achieved. Precision and accuracy are specifications primarily relevant to the total system and are particularly concerned with stability of the rf/dc voltages. However, measurements of precision have been made using this analyzer with the test electronics, measuring the ratio between mass-28 and mass-14 peaks using 1-second step-scan measurements. A short-term precision of better than 5% was easily demonstrated. No measurements of long-term stability were performed, and accuracy will depend on long-term stability.

An accuracy of 5% can be achieved if recalibrations are made with sufficient frequency to correct for long-term drifts in the measured peak ratios.

5.8 Mass Range

The mass analyzer was operated over a mass range from 4 to about 185. No problems of peak shape at high or low mass were encountered except for the expected fact that there is a maximum mass at which flat-top peaks are obtained with a specified peak width. There is no doubt that the mass range can be extended down to mass 2 and up to about mass 200. The limitations to mass range of the system will be in the dynamic range of, and in the upper mass attainable with, the rf/dc power supply and in the upper mass at which some specified peak shape can be obtained. This limitation in peak shape at high mass is the only mass-range limitation that depends on the design of the mass analyzer. The continuing mass-analyzer optimization program is addressed specifically to determination of this limit.

6.0 CONCLUSION

A miniature mass spectrometer based on a 5.1-cm-long mass filter was constructed. This mass analyzer included an ion source, a mass filter, and an electron-multiplier detector, all of which were mounted in a vacuum envelope, plus an ion pump.

This system, designed as an analyzer for trace constituents in air, was tested and demonstrated to have the capability of 0.1 ppm detection of trace impurities in air.

Using a delayed-dc entrance correction, peaks with nearly flat tops are obtained with 1% adjacent peak contributions at mass 127. It is anticipated that with further refinements of the operating conditions, the adjacent peak contribution at mass 127 can be reduced to the specified 0.1%.

The extent to which the performance of this instrument will be affected by some upper mass limit remains to be determined. This limit will depend, in part, on the design of the rf/dc power supply that excites the mass-filter electrodes and, in part, on the results of the mass-spectrometer optimization experiments that are currently being brought to completion. The instrument can certainly be operated up to the specified mass range of 200 amu, and very probably to a considerably higher mass. It has not yet been determined over what mass range it will be possible to simultaneously achieve a low adjacent-peak contribution and a highly stable measurement of peak intensity.

APPENDIX

The ion source optimization work under the follow-on contract was in progress at the time this report was being written. Peaks with flatter tops and smaller tails were obtained at mass 127 with no significant loss in sensitivity, as shown in Figure 14. Improvement was obtained with the same source structure used to obtain the peaks shown in Figure 11, but with two changes made in the voltages applied to the source. One change was that the filament aperture was operated at ion-box voltage, where previously it had been operated at a positive voltage with respect to the ion box. The second change was that the final source-exit aperture (the mass-filter entrance aperture) was operated at -10V where previously it had been operated at -20 to -50V.

The development of a system using this mass analyzer is continuing through the construction of the electronics required for operation of the mass analyzer, of a microprocessor for control of the operation and processing of the data obtained, and of a multiple-sample inlet system. This system, although designed for trace-gas analysis over the mass range from 4 to 200 amu, using a fixed-orifice leak as the inlet, and having computer-controlled operation and data processing, can be modified for other approaches to trace-gas analysis or for different, unrelated applications. A particularly simple modification would be the substitution of a membrane separator inlet for the fixed-orifice leak, thus providing enrichment of the trace constituents with lower detection limits for trace-gas analysis.
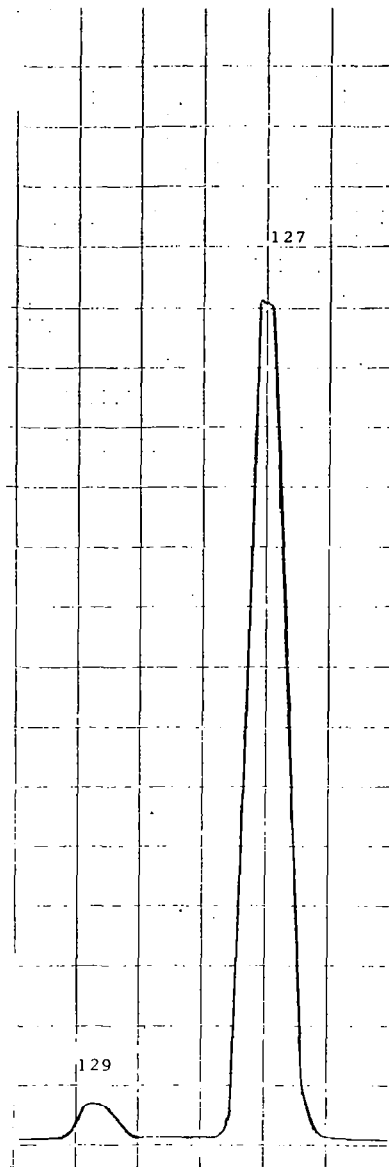
Figure 14   Peak Shape at Mass 127 With Modified
             Aperture Voltages and With AC Entrance Voltages