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BY MODULATED MOLECULAR BEAM MASS SPECTROMETRY

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February 1968

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ABSTRACT

A system for mass spectrometric analysis of trace constituents in gases utilizing a molecular beam inlet system was built and tested. Modulation of the sampling molecular beam permitted the use of phase sensitive detection methods, which improved the signal-to-noise ratio and reduced the interference due to background gases in the vacuum chamber. The system was tested by analyzing natural oxygen gas for the various isotopic combinations. The 1.5 ppm $O^{17}O^{18}$ isotope was measured with an accuracy of 5%. The ultimate sensitivity of the technique is believed to be ~0.1 ppm.

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INTRODUCTION

The sensitivity of mass spectrometric analyses of trace constituents in gases is often limited by the pressure of the background gas in the vacuum envelope, or by system noise due to stray electromagnetic fields or inherent in the associated electronics. In the conventional method, the gas to be analyzed is added by an inlet line to the ion source region of the mass spectrometer. This method requires careful attention to reduce the background gases in the vacuum system at the m/e values of interest well below the concentration of the components in the gas being analyzed. The maximum ion source pressure at which most mass spectrometers can be operated is about 10^{-5} torr. Higher pressures may damage the filament or alter the ionization process by ion-molecule reactions. If it is desired to detect a 1 ppm constituent in a gas at 10^{-5} torr in the ion source, the background at the m/e of the trace constituent must be 10^{-11} torr or less.[1] To attain such a low background requires ultra high vacuum techniques, a very clean system, and repeated bakeout of the entire system. Blum and Torney[2] have investigated the use of a cold cathode ionizer to reduce the substantial contribution of the hot filament and ionizer housing to the background.

Background contamination in isotopic analysis is further aggravated by the "memory effect". In routine analyses of uranium hexafloride using a conventional inlet system, UF_6 adsorbed on the inlet line walls and on the ionizer structure from previous runs continues to outgas during subsequent analyses of gases of different isotopic composition and can falsify the measured abundance ratios. Brunnée[3] has succeeded in reducing the memory effect by introducing the UF_6 as a narrow molecular beam which passes through the ion source without striking the walls.

In the work reported here, in addition to admitting the gas to the ion source as a collimated molecular beam, the beam is mechanically modulated prior to entry into the mass spectrometer. By amplifying only the ac component of the signal from the spectrometer (which is of the same frequency as the chopper) the dc background signal is virtually eliminated. In addition, the predominantly white noise of the electronic devices and the 60 cycle pickup from stray electromagnetic fields is substantially reduced by narrow band amplification.

The beam is detected on the first pass through the ionizer and is effectively demodulated after striking the walls of the vacuum chamber. Since the collimated beam does not strike the spectrometer or the vacuum chamber walls before it is detected, chemically active gases, or even free radicals can be analyzed as easily as stable gases.

The only part of the system which must be kept extremely clean if very high precision is desired, is the inlet system which constitutes the source of the molecular beam. The need for extreme cleanliness in the inlet system can be reduced by using high source pressures (up to 15 torr in this study) or by continual fast flushing of the gas through the inlet system if sufficient gas is available.

The application of phase sensitive analysis to detect weak modulated signals from a mass spectrometer in the presence of background gas was pioneered by Fite and coworkers[4] and Datz et al.[5] These authors, however, used the technique to detect the main constituent of the beam after scattering off of a solid surface. Recently, Pyper, Newbury and Barton[6] have utilized the modulated beam technique to measure the molecular isotope ratios in water. Since deuterium enriched water was employed, detection of trace constituents was not a problem.

In the present work, we tested the modulated molecular beam technique on the molecular isotopes of natural O_2 in order to determine the accuracy and precision of components present in the ppm range.

DESCRIPTION OF APPARATUS

The experimental apparatus consists of three chambers: the source chamber, the roughing chamber, and the experimental chamber. The major components of the apparatus are shown in Fig. 1 and in the photograph of Fig. 2. The source chamber contains the gas to be analyzed and is equipped with a variable leak and forepump for setting the desired source pressure. The source chamber is connected to the roughing chamber by a glass source with a single orifice forming the molecular beam. The roughing chamber contains the chopping motor and chopper. More than 99% of the gas load from the source chamber is evacuated by the six-inch oil diffusion pump attached to the roughing chamber. The roughing chamber is separated from the experimental chamber by a 1 mm diam. collimating aperture which serves to form the molecular beam. The experimental chamber houses the mass spectrometer and is pumped by a 500 lit/sec ion pump.

The vacuum tank is made of aluminum and the bellows, flanges, and ion pump are stainless steel. The aluminum O-ring flange in which the glass source is mounted also supports the chopping motor and contains the electrical feedthroughs for driving the motor. Two small viewing ports in the roughing chamber are situated on line with the chopper to allow the use of a light-photo diode arrangement to produce a reference signal of the same frequence as the modulated beam. This was found to be unnecessary, however, as the reference signal could be obtained directly

from the amplifier which supplies the power to the chopper motor. The aperture separating the experimental and roughing chambers is screwed into the chamber wall allowing easy change of the aperture size.

The mass spectrometer is mounted on a rotatable flange on top of a bellows. This arrangement allows the ion source to be aligned with the collimating aperture. The alignment is done with a telescope sighted on the collimating orifice through the viewing port on the end of the ion pump. This view of the ion source and the collimating orifice is shown in Fig. 3. The small black spot inside the large circle is the 1 mm diam. collimating orifice and the ion source is the rectangular structure surrounding the spot.

A diaphragm pressure gauge (Wallace Tiernan Model FA 129 160) is used to read source pressures from atmospheric to 1 torr and a calibrated thermocouple gauge is used for pressures from 1 torr to 10^{-3} torr. The inlet system is constructed of 1/4-in. copper tubing with a copper bellows the last 10 in. to allow the source a small degree of movement. The copper bellows is attached to a stainless steel male tapered 24/40 fitting which is in turn mated to the female 24/40 of the glass source. The glass source fit into a double O-ring fitting welded to an aluminum flange which fit into the outer wall of the roughing chamber. To insure that the center-line of the O-ring fitting in the aluminum flange on the outer wall was coincident with the collimating orifice on the inner wall, the holes in the inner and outer walls were drilled after the two chambers had been welded together and without removing the piece from the milling machine table.

The source shown in Fig. 4 was produced by drawing the end of the glass tube and cutting it off at the desired inside diameter. A glass collar was then fused onto the source to mate with the O-ring fittings holding it into the system.

The beam was modulated by a two-bladed chopper constructed by cutting a slot in the end of 1/4 in. diam. aluminum rod. The chopper was driven by a two phase, two pole ac synchronous motor (Globe Industries Model 158 A100-2). The motor was powered by an audio oscillator and amplifier and could be run at frequencies between 40 cps and 300 cps. Below 40 cps the motor did not consistently track the driving frequency and above 300 cps it overheated. Since the motor was two pole and the chopper had two blades, the driving frequency and the beam chopping frequency were the same. This permitted the reference signal to be taken directly from the amplifier and eliminated the need for an auxillary photo-diode. The mass spectrometer was well shielded from stray electromagnetic fields from the motor by the intervening vacuum chamber wall which was pierced only by the 1 mm diam. orifice. A modulation frequency of 145 cps was used in all experiments.

The molecular beam was mass analyzed by a quadrupole mass spectrometer (EAI Model QUAD 200). The quadrupole rod structure was 7-1/2 in. long with a special ion source to permit unobstructed passage of the molecular beam perpendicular to the axis of the rod bundle. An electron multiplier with a measured gain of 5×10^5 was used to collect the ions and amplify the signal. Three methods were used to detect the signal coming from the multiplier: an oscilloscope attached to the mass spectrometer control was used for strong signals. A lock-in amplifier or digital noise averaging computer was employed for weak signals.

The lock-in amplifier is a Princeton Applied Research Model HR-8, with type A preamplifier. The signal first goes through an intermediate amplifier where the entire spectrum of frequencies is amplified, then through the signal-tuned amplifier which limits the signal to a narrow bandwidth centered on the desired frequency. The signal is then mixed with the first harmonic of the reference signal to produce a rectified ac signal which passes through an integrating circuit to produce a dc output for the recorder. The input impedance of the lock-in amplifier is 10 megohms and contains a blocking capacitor. A 10 megohm resistor was placed in parallel with the input to provide a ground path for the charge collected on the last stage of the electron multiplier. The resulting 5 megohm input impedance is reduced by $(2/\pi)(1/\sqrt{2})$ to account for the fact that the lock-in responds only to the fundamental mode of the square wave input and takes the RMS average of the rectified ac signal from the mixer. A peak-to-peak voltage should appear 2.25 times as large on the lock-in as on the 1 megohm input impedance oscilloscope.

The noise averaging computer which can be used in place of the lock-in is a Technical Measurement Corporation Digital Computer Unit Model CN-1024 with a CAT Logic Unit Model 202 plug in. A signal is fed into the CAT and is converted from analog-to-digital representation. There are 1024 addresses with a minimum scan time of 31.25 μsec per address. A reference signal with the same frequency as the modulated beam is supplied to the CAT directly from the oscillator. With each sweep of the addresses the desired signal is summed while the random noise cancels out. The results can be monitored on a built-in scope or read out on punched tape. It was necessary to amplify the signal from the mass

spectrometer before putting it into the CAT. The first three amplifiers of the lock-in were used for this purpose. Use of the output from the signal monitor on the lock-in amplifier as the input of the CAT not only amplified the signal but also narrowed the bandwidth of the random noise before digital noise averaging.

PERFORMANCE OF THE MOLECULAR BEAM SOURCE

In order to permit absolute calibration of the system sensitivity, the equivalent pressure of the molecular beam in the ion source must be known. This requires knowledge of the centerline beam intensity as a function of driving pressure in the source chamber. The beam intensity can be determined from measurements of the total leak rate and angular distribution of the emitted molecules. Methods for experimentally determining these two characteristics of a molecular beam source have been described by Giordmane and Wang,[7] Hanes,[8] and Johnson et al.[9] The apparatus used to measure the emission characteristics of the glass source used in the present study is described in ref. 10.

The total leak rate as a function of source pressure (or source conductance) was determined by following the pressure decay of a large ballast tank connected to the source tube. The conductance of the source shown in Fig. 4 for oxygen was 1.0 cc/sec at source pressures below 8 torr and increased to 1.5 cc/sec at ~15 torr.

The same apparatus used to determine the source conductance was also used to measure the angular distributions at various source pressures. The sharpness of the angular distribution is most conveniently described by a "peaking factor", which is the ratio of the centerline beam intensity

for the source to that from an ideal thin-walled orifice with the same total leak rate. Theoretical estimates of peaking factors for long channels are presented in refs. 7 and 8. Peaking factors for long channels as large as 10 have been measured.[7,8]

The intensity of the molecular beam at a distance d cm along the axis of the source can be written in terms of the total leak rate and the peaking factor X as:

$$I = X\,(\ell/\pi d^2) \qquad (1)$$

where I is the centerline beam intensity in molecules/cm^2-sec and ℓ is the total leak rate. A plot of the angular distribution from the source at a source pressure of 18 torr is shown in Fig. 5 along with a cosine distribution from an ideal orifice of the same strength. The peaking factor is the ratio of the magnitudes of the intercepts of these curves with the $\theta = 0°$ axis. The maximum emission rate occurs 13° off the axis, undoubtedly because the source was drawn from wide bore tubing by hand. The molecular beam is skimmed from a narrow solid angle about $\theta = 0°$, where the peaking factor is approximately 1.2. For our purposes, Eq. (1) will be simplified by setting X equal to unity for all source pressures. With the leak rates calculated from the source conductance and d equal to the distance between the tip of the source and the center of the ion source in the mass spectrometer apparatus (4.5 cm), the intensity of the neutral beam in the ion source can be calculated. The rate of ionization depends upon the number density or equivalent pressure of the beam in the ion source. The latter is[11]

$$P_{MS}(\text{torr}) = \frac{1}{4}\,\frac{\sqrt{MT}}{3.51\times10^{22}}\,I \qquad (2)$$

where M is the molecular weight of the gas and T is the absolute temperature.

If the mass spectrometer has a sensitivity of $\mathcal{S}$ amp/torr, the measured amplitude of the modulated signal can be converted to an equivalent pressure by the formula:

$$S(\text{volts}) = \mathcal{S} R p_{MS} \qquad (3)$$

where S is the peak-to-peak output voltage on the oscilloscope or the dc output voltage from the filtering network of the lock-in amplifier. The input impedance of the detection equipment is denoted by R; for the lock-in system, the corrections for rejection of higher modes of the square wave and RMS averaging discussed previously must be included in R.

Tests were made to compare the equivalent pressures calculated from the leak rates by Eqs. (1) and (2) with those obtained from the measured output signals and Eq. (3). The average mass spectrometer sensitivity was determined in the usual way for the non-modulated background and found to be 17 amps/torr. The sensitivity was measured several times over a period of two months, and was unaffected by changing a burned out filament in the ion source. The modulated mass 32 signal was measured on the oscilloscope, for which R = 1 megohm. The comparison is shown in Fig. 6. In the interval between the two sets of experiments shown in the plot, the source tube was removed to replace the collar, which had cracked. At source pressures less than ~5 torr, the equivalent pressures measured from the output signals were approximately a factor of four lower than the curve determined by the leak rates in Eqs. (1) and (2). This discrepancy is attributed to the smaller electron-neutral interaction volume in the ion source when a molecular beam is analyzed rather than a non-directed gas.

The electrons from the filament traverse the ionization chamber as a narrow sheet whose small dimension is perpendicular to the plane of the photograph of Fig. 3. If the axis of the source tube and the collimating orifice is properly centered in the ionization cage, the volume of interaction of the beam with the electrons is proportional to the diameter of the molecular beam at the center of the ion source. The tip of the source tube is 2 cm from the 1 mm diameter collimating orifice and the center of the ionizer is an additional 2.5 cm from the collimating orifice. Approximating the source as a point, the diameter of the beam at the center of the ionizer is ~2.3 mm. For a non-directed gas filling the ion source, the volume of the electron-neutral interaction is proportional to the width of the ionizer cage, which in our spectrometer is ~10 mm. Approximately four times as many ions are created in a non-directed gas filling the ion source than in the collimated molecular beam when both are at equal pressures. This difference is the most probable source of the discrepancy of Fig. 6, but the close agreement between the observed factor and that predicted by simple geometrical considerations is in part fortuitous. The extraction efficiency for ions created in the center of the ion source where the molecular beam is concentrated is greater than that for ions created in a random gas near the filament or electron collector ends of the ion source. This effect reduces the expected factor below four, but is partially compensated by the impossibility of insuring that the electron sheet crosses the molecular beam exactly at its center. Even slight misalignment would reduce the interaction length from a diameter to an off-center chord.

For source pressures less than 5 torr, the equivalent pressures (or beam intensity) varied linearly with the total leak rate, whereas the theory[7,8] predicts a square root dependence. This behavior was also observed in the insensitivity of the measured peaking factors to source pressure. The square root dependence of beam strength on leak rate was probably not observed because of the variable cross section of the source channel and the high source pressures used. Above 0.2 torr the oxygen mean free path is smaller than the diameter of the source orifice.

At oxygen pressures in the source tube greater than 5 torr, the equivalent pressure in the beam obtained from the modulated output signal was as much as an order of magnitude lower than expected. At a source pressure of 15 torr, the pressure at the diffusion pump end of the roughing chamber was $\sim 7\times10^{-5}$ torr, which corresponds to a net pumping speed of ~300 lit/sec. Since the pump is rated at 500 lit/sec, the pressure around the source tube was probably $\sim 10^{-4}$ torr. Cloud formation in the rather congested region between the chopper and the collimating orifice may have sufficiently increased the pressure here to have caused attenuation of the beam by gas phase collisions. This is a reasonable source of the low signals observed with strong beams.

If the factor of four introduced by the difference in ionization volumes is considered, the comparison of Fig. 6 indicates that the amplitude of the modulated output signal is a reliable measure of the equivalent pressure of the molecular beam in the ion source.

The maximum oxygen source pressure employed was 15 torr, which produced an equivalent beam pressure at the ion source of $\sim 6\times10^{-7}$ torr. Because of the differential pumping arrangement, the background pressure in the ex-

perimental chamber under these conditions was 6×10^{-8}torr. The base pressure (no beam) in the experimental chamber was about 9×10^{-9}torr. The system was never baked.

SIGNAL MEASUREMENT

To detect weak signals, the spectrometer was maintained on the m/e of interest until the lock-in amplifier produced a steady dc output signal or until the digital noise avefager had executed a sufficient number of sweeps to permit satisfactory measurement of the amplitude of the output voltage waveform.

Measurements were taken with both the oscilloscope and the lock-in detector whenever possible. The digital noise averager was used infrequently. It was found that the signal from the lock-in detector was 2.0±0.1 times the signal read on the scope. This factor is quite close to the expected value of 2.25. The factor 2.0 was used to convert readings from the scope to the lock-in. Any signal greater than 500 mv on the scope was too large for the lock-in and any signal level below about 1 mv on the lock-in could not be read on the scope because of noise.

Figure 7 shows a typical signal from a strong modulated beam as seen on the scope, along with the reference signal taken from the output of the audio amplifier driving the chopping motor. Figure 8 shows a typical recorder output taken from the lock-in amplifier with an oxygen beam and m/e = 35 (corresponding to the isotope $O^{17}O^{18}$) and the signal obtained by resetting the spectrometer to the baseline between m/e = 35 and m/e = 34. The significance of this baseline signal is discussed later.

When using the digital noise averager in place of the lock-in detector, the system was allowed to run until the wave form heights of ~1 in. grew on the scope. By measuring the peak height (with a ruler) and the analysis

time required to reach that height, the ratio of the concentrations of any two species could be determined. A baseline signal was also taken for each run by setting the spectrometer between two adjacent mass peaks.

MOLECULAR ISOTOPES IN NATURAL OXYGEN

The sensitivity of the system was tested by measuring the concentrations of the isotopic combinations in natural oxygen and comparing the data with the values predicted from the known atomic abundances of O^{16}, O^{17} and O^{18}. Measurements were made at source pressures from 0.05 to 15 torr with the lock-in detector and at 0.2 and 3.0 torr with the digital noise averager. Masses 32 through 36 were monitored. The isotopic fraction was taken as the ratio of the signal at a particular mass to the mass 32 signal. The results are shown in Table I. All of the isotopes were detected at source pressures from 0.2 to 15 torr. At a source pressure of 0.05 torr, masses 35 and 36 could not be detected. The baseline levels listed in the last column of Table I were obtained by setting the spectrometer between peaks. These readings were directly proportional to the beam strength as measured by the mass 32 signal except for source pressures below 1 torr. Here the baseline signal was just slightly greater than the 0.3 μv background level of the detection system with no beam. The signal levels reported in Table I are above the baseline values.

Extensive background corrections were unnecessary, since the spectrum of the modulated beam is much cleaner than the ordinary background spectrum in the vacuum chamber. Mass 37, however, was detected in the modulated beam. This was attributed to the heavier isotope of chlorine. The contribution of Cl^{35} to the mass 35 peak was obtained from the measured mass 37 signal and the natural abundances of the two chlorine isotopes. This correction amounted to at most 20% of the total mass 35 signal.

Table I. Summary of results of experiments with isotopes of molecular oxygen.†

Detection Equipment Used	P_{source} (torr)	m/e = 32		m/e = 33		m/e = 34		m/e = 35**		m/e = 36		
		S_{32}	S_{32}/S_{32}	S_{33}	S_{33}/S_{32}	S_{34}	S_{34}/S_{32}	S_{35}	S_{35}/S_{32}	S_{36}	S_{36}/S_{32}	$S_{baseline}$
Scope and lock-in	14.5	19v	1	14mv	7.4×10^{-4}	72mv	3.8×10^{-3}	26μv	1.4×10^{-6}	72μv	3.8×10^{-6}	18μv
"	0.058	160mv	1	119μv	7.4×10^{-4}	600μv	3.7×10^{-3}	---	--	---	--	--
"	14.5	17.4v	1	13mv	7.5×10^{-4}	66mv	3.8×10^{-3}	28μv	1.6×10^{-6}	67μv	3.8×10^{-6}	11μv
"	0.050	120mv	1	--	--	0.45mv	3.7×10^{-3}	---	--	---	--	0.4μv
"	14.8	23.6v	1	18.8mv	7.9×10^{-4}	94mv	4.0×10^{-3}	31μv	1.3×10^{-6}	86μv	3.8×10^{-6}	23μv
"	0.19	420mv	1	280μv	6.7×10^{-4}	1.52mv	3.6×10^{-3}	0.5μv	1.2×10^{-6}	1.5μv	3.6×10^{-6}	0.4μv
"	1.5	3.8v	1	2.55mv	6.7×10^{-4}	13.6mv	3.6×10^{-3}	4.2μv	1.1×10^{-6}	12.4μv	3.3×10^{-6}	3.5μv
Scope,* CAT	3	--	1	--	7.0×10^{-4}	--	--	---	1.2×10^{-6}	---	2.9×10^{-6}	--
CAT	0.2	--	1	--	5.4×10^{-4}	--	3.5×10^{-3}	---	2.5×10^{-6}	---	5×10^{-6}	--

† Signals are reported as lock-in amplified dc output voltages; baseline readings have been subtracted from the signals at each mass number.

* In this run the main oxygen beam was too large to put into the CAT, hence for m/e = 32 the signal was taken from the scope. The signal for m/e = 34 was taken with both the scope and CAT. The isotope ratios were then calculated by:

$$\text{ratio} = S_i(\text{CAT})/S_{34}(\text{CAT}) \times S_{34}(\text{Scope})/S_{32}(\text{Scope})$$

** Mass 35 signals have been corrected for Cl^{35} contributions using the mass 37 signal and the isotopic composition of chlorine.

Table II shows the accuracy and precision of the three measurements made at a source pressure of 15 torr utilizing the lock-in detector. Both the precision and accuracy of the data are approximately ±5%. The 1.5 ppm $O^{17}O^{18}$ isotope was measureable at source pressures as low as 0.2 torr.

The measurements made with the digital noise averager were considerably less accurate than those obtained with the lock-in amplifier. This is undoubtedly in large part due to the measurement of the peak heights directly from the small built-in oscilloscope on the unit with a ruler. The performance of this device could be improved if the counts in the channels containing the peaks and valleys of the output waveform were punched out and suitably averaged by a computer program. However, the fact that this additional data processing is necessary limits the utility of the digital noise averager when compared to the relative ease of operation of the lock-in system.

ULTIMATE SENSITIVITY

The smallest concentration measured in the oxygen tests was that of the 1.5 ppm $O^{17}O^{18}$ isotope. Experimental demonstration of higher sensitivity could not be obtained with oxygen, because of the absence of molecular isotopes in the 0.1-1 ppm range. However, we believe that the detection limit of the system is considerably below 1.5 ppm. In the recorder trace shown in Fig. 8, the mass 35 isotope produced a 26 μv signal on top of the 18 μv baseline.[12] The recorder trace varied by approximately ±1 μv about these values. We estimate that a 2 μv signal could have been detected above the 18 μv background, although with a loss of precision. A 2 μv

Table II

Isotope ratios of molecular oxygen for high source pressure runs.

Isotope	m/e	S_i/S_{32}	Predicted*	Accuracy %
$O^{16}O^{16}$	32	1	1	--
$O^{16}O^{17}$	33	$(7.6\pm0.22)\times10^{-4}$	7.4×10^{-4}	+2.7
$O^{16}O^{18}$	34	$(3.9\pm0.10)\times10^{-3}$	4.0×10^{-3}	-2.5
$O^{17}O^{18}$	35	$(1.43\pm0.13)\times10^{-6}$	1.5×10^{-6}	-4.7
$O^{18}O^{18}$	36	$(3.8\pm0.0\ )\times10^{-6}$	4.0×10^{-6}	-5.0

* The predicted molecular isotope abundances are calculated by assuming a statistical combination of the atomic abundance of O^{16}, O^{17}, and O^{18} [Handbook of Chemistry and Physics, 45th Edition, (Chemical Rubber Company, Cleveland, Ohio, 1966)].

trace constituent signal in a 20 v main component signal corresponds to a detection limit of ~0.1 ppm. The capability of the system of measuring signals of this order was demonstrated by the experiment at 0.2 torr source pressure. Here a 0.5 μv mass 35 signal was detected above a baseline of 0.4 μv, and the $O^{17}O^{18}$ isotope abundance was within 20% of the true value.

According to Eq. (3) (with R = 2 megohms for the lock-in amplifier), a 2 μv signal corresponds to a partial pressure of 6×10^{-14} torr in the ion source. For an electron multiplier gain of 5×10^{5}, the same signal results from the collection of ~12 ions/sec at the first dynode.

The 18 μv baseline signal, however, constitutes a modulated "background" equivalent to 5×10^{-13} torr. This signal was independent of mass number and resolution and was proportional to the beam strength for high source pressures. These symptoms suggest that the baseline signal was due to ions from the primary modulated beam which reached the electron multiplier without mass analysis. Ions injected into the "blind spot" at the center of the rod structure of the quadrupole analyzing section experience no electric field and hence are not mass analyzed. If this blind spot were eliminated, the minimum detectable signal should be on the order of 0.5 μv, and the maximum sensitivity could be increased by a factor of four.

Stronger beams than those used here could be generated by multichannel sources with higher peaking factors than the single tube used in these experiments. However, the stronger beam would produce larger baseline signals, and the detection limit would not decrease as rapidly as the beam strength increased.

CONCLUSIONS

The primary advantage of a modulated molecular beam inlet system is the ability to accurately detect ppm concentrations of trace constituents without the ultra high vacuum conditions which conventional mass spectrometric gas analysis requires. The results of this study suggest that the detection limit, which is set by the performance of the mass spectrometer rather than the vacuum system, may be as low as 0.1 ppm.

The major disadvantage is the time required to perform a complete mass analysis. A "scan" of the spectrum of a modulated molecular beam requires approximately one hour. Because the gas is continually flowing into the vacuum system during the analysis, larger quantities of gas are consumed with the modulated beam method than with conventional inlet systems.

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11. Equation (2) is derived from $I = n_{MS}\bar{v}$, where $\bar{v}$ is the mean speed of the beam molecules ($\sqrt{8kT/\pi m}$), and n_{MS} is the number density in the beam (p_{MS}/kT).

12. Approximately 4 μv of the mass 35 signal shown in Fig. 8 was due to Cl^{35}.

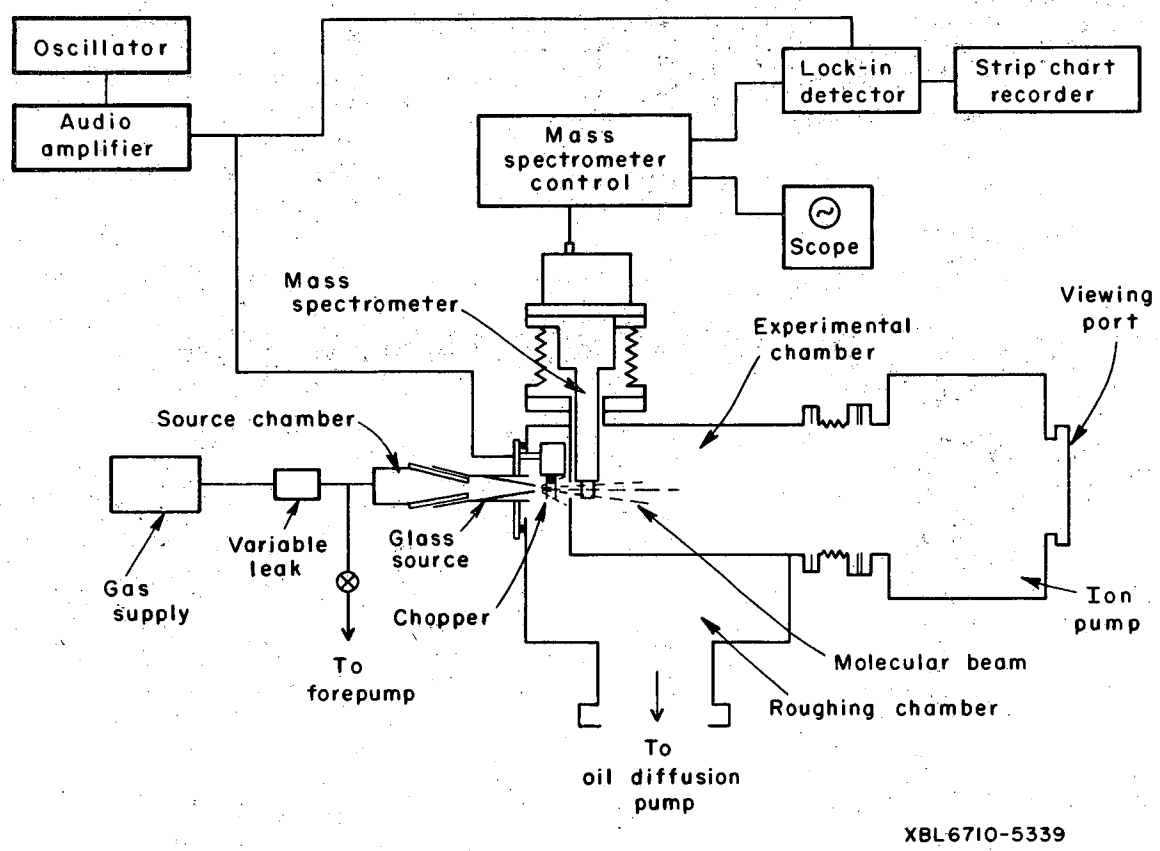

Fig. 1 Modulated molecular beam gas analysis apparatus.

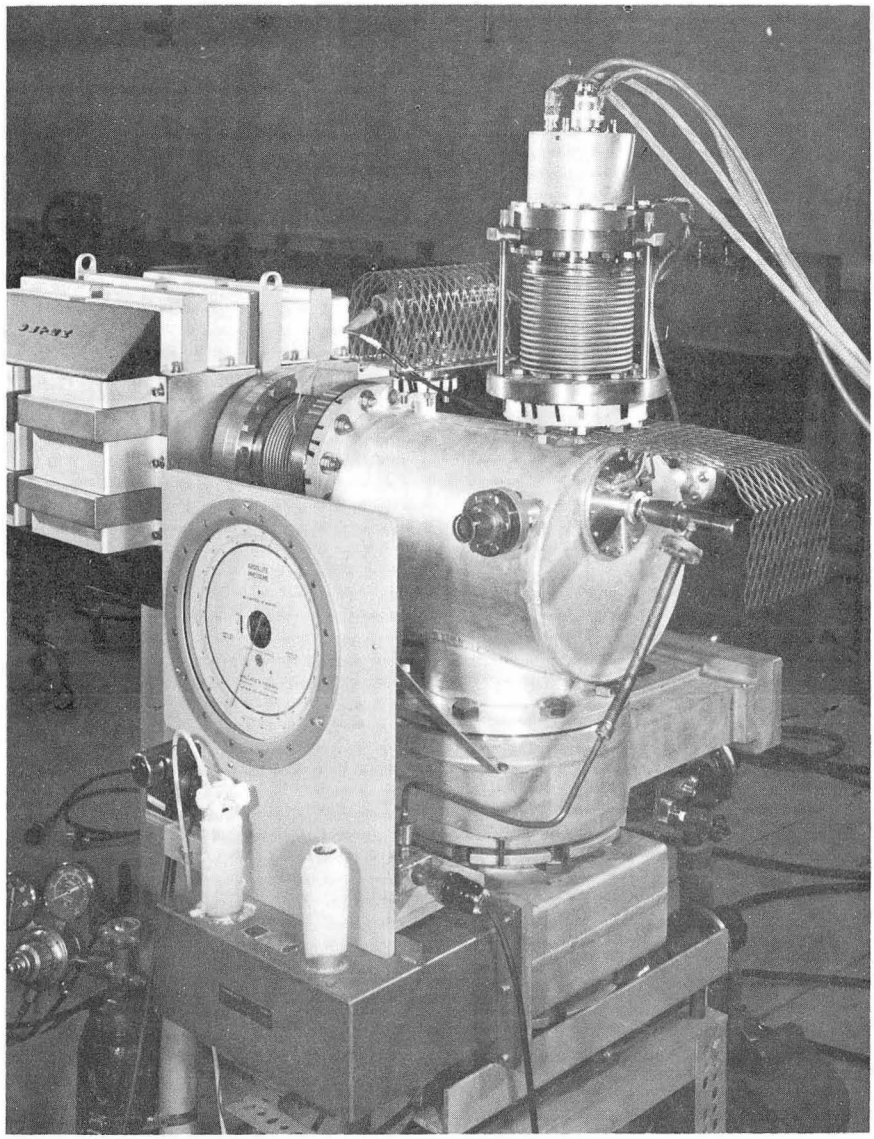

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Fig. 2 Photograph of apparatus.

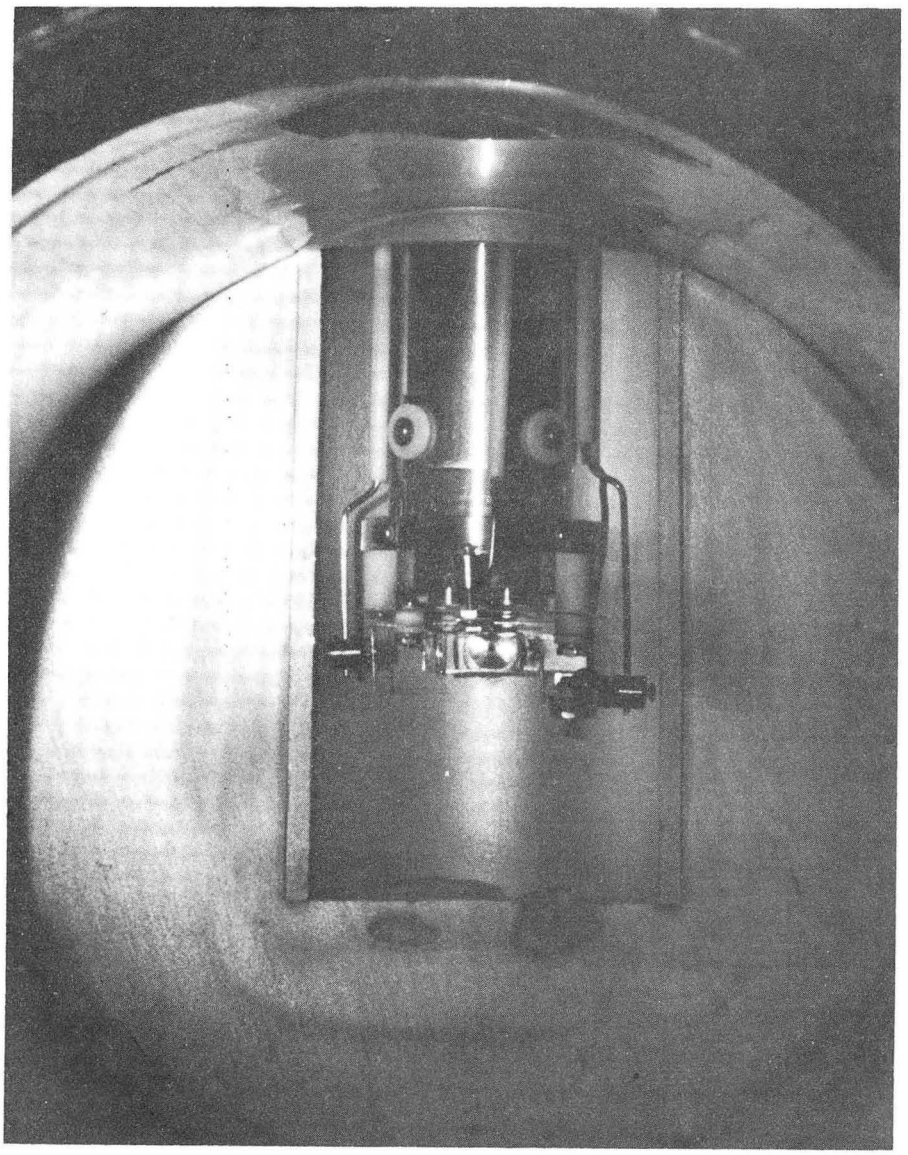

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Fig. 3 View of mass spectrometer in experimental chamber showing molecular beam entry into the open ion source.

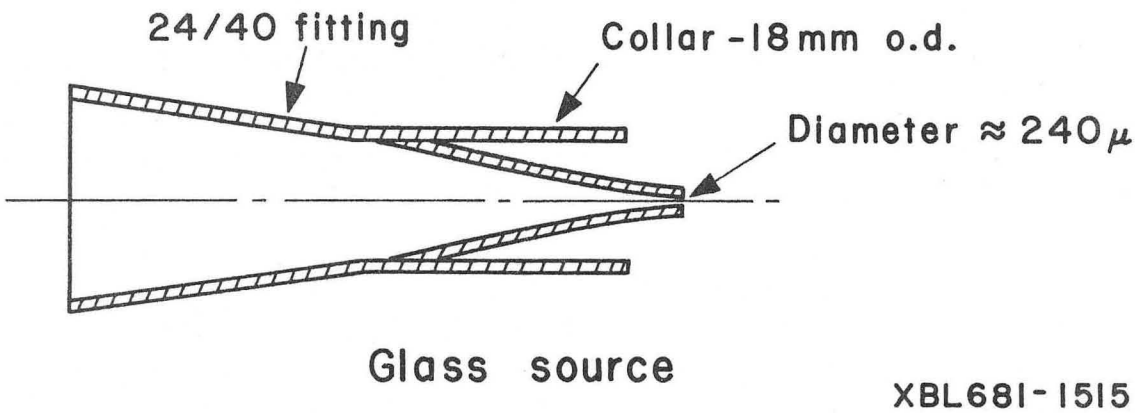

Fig. 4 Glass molecular beam source tube.

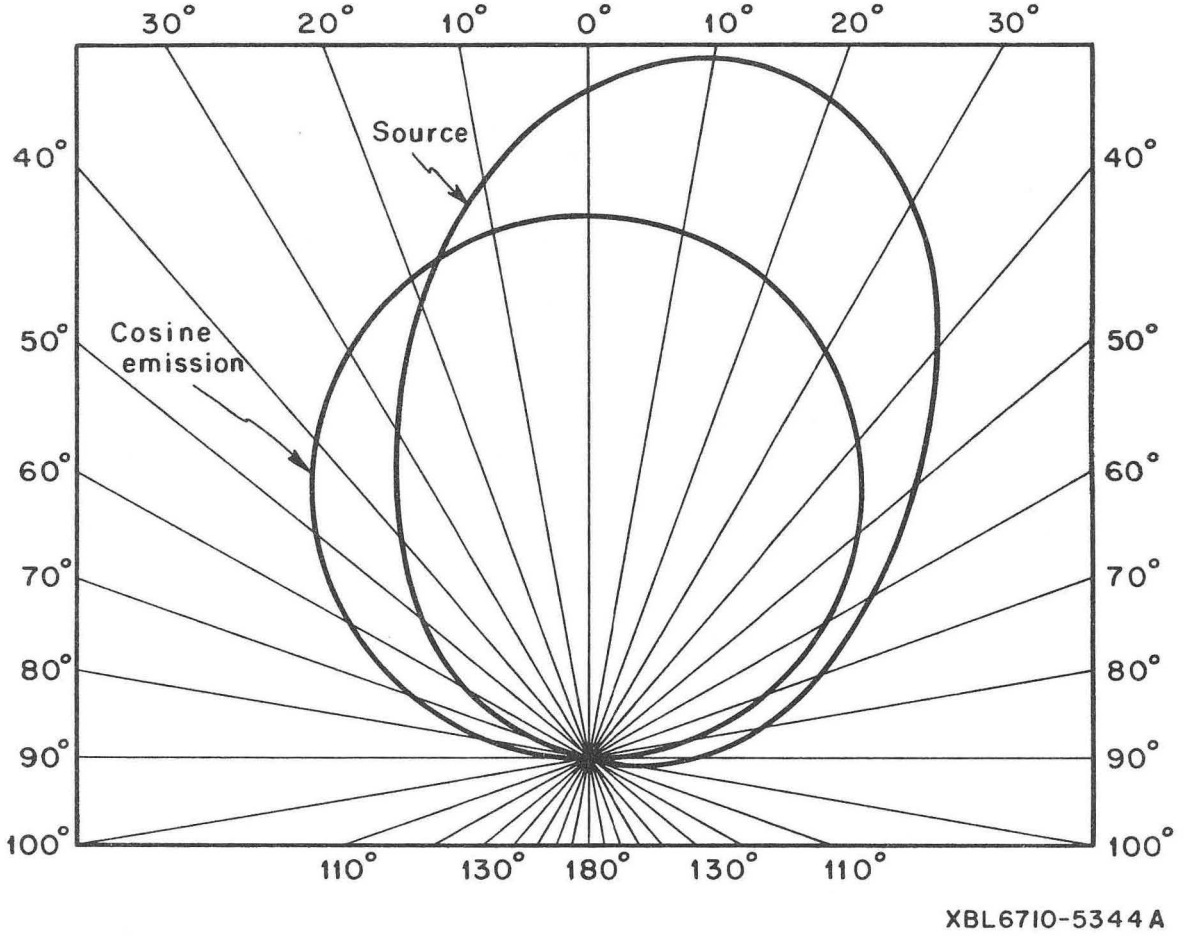

Fig. 5 Angular distribution from molecular beam source at an oxygen source pressure of 18 torr.

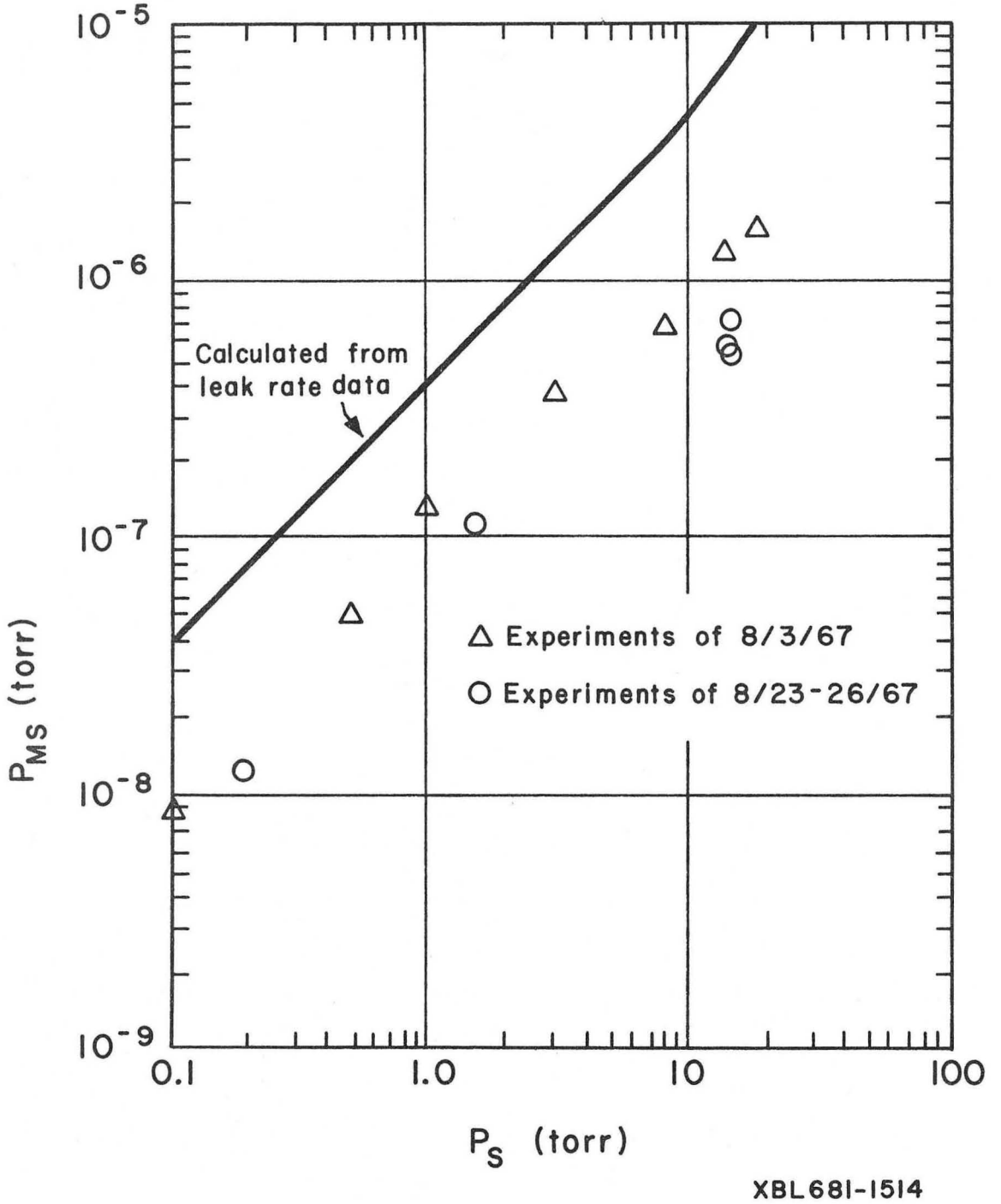

Fig. 6 Comparison of equivalent pressures of the modulated molecular beam in the ion source. Line: calculated from oxygen leak rate and Eqs. (1) and (2); Points: measured from amplitude of modulated mass 32 signal on oscilloscope and Eq. (3).

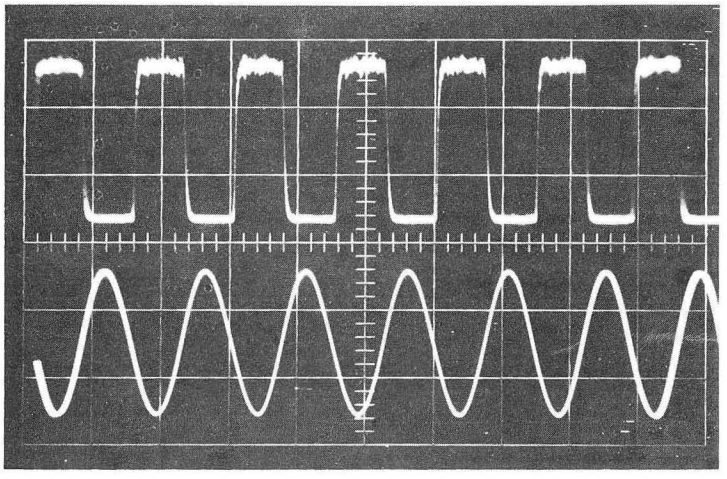

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Fig. 7 Oscilloscope trace of 145 cps modulated oxygen beam and reference signal from audio amplifier.

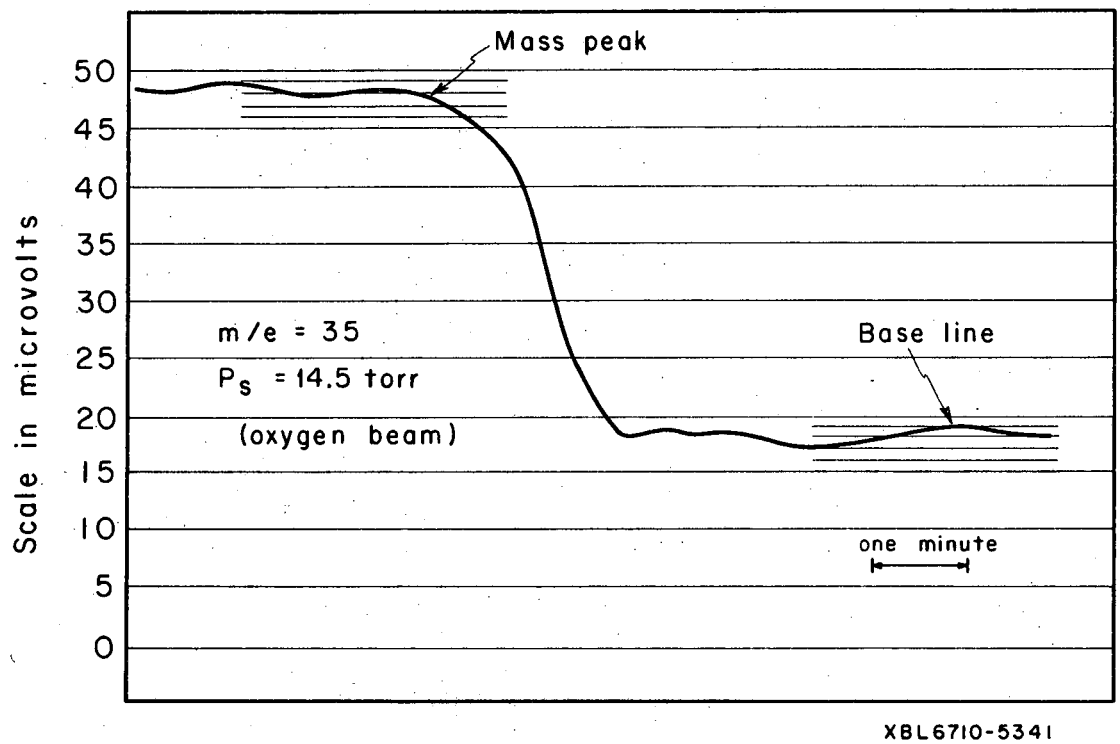

Fig. 8 Recorder trace of dc output of lock-in amplifier. Mass 35 and baseline signals for a beam of oxygen generated by a source pressure of 14.5 torr.

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