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Mass Spectrometer Method for Determining Parts per Billion Helium-3 in Helium

UNITED STATES DEPARTMENT OF THE INTERIOR

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MASS SPECTROMETER METHOD FOR DETERMINING PARTS PER BILLION HELIUM-3 IN HELIUM

by

David E. Emerson[1] and Elmer T. Suttle[2]

ABSTRACT

The Bureau of Mines has developed a mass spectrometer method for determining the helium-3 content of high-purity helium. The work was performed to evaluate experimental methods for removing helium-3 from high-purity helium and to better determine the composition of pure helium used in research. This was accomplished by increasing the inlet sample pressure, ionizing current, and amplification of the current produced by the ions collected on a conventional mass spectrometer that had been modified. With these modifications, the helium-3 content was determined in the parts-per-million and parts-per-billion range in helium-4.

INTRODUCTION

There is a continuing effort to improve the capability to analyze Bureau of Mines helium. Helium-3 is present in Bureau of Mines helium in the 200-parts-per-billion (ppb) range. To determine the helium-3 content of production helium and to evaluate experimental methods used to remove helium-3 from the helium-4 product, an analytical method for determining the helium-3 content was developed. The method can be used to analyze for helium-3 in the parts-per-million (ppm) to less than the 1-ppb range. A conventional mass spectrometer was modified so that it was more sensitive and stable.

In 1939, Alvarez and Cornog (4)[3] proved that helium-3 existed in nature. They utilized a 60-inch cyclotron and found that there was approximately 12 times as much helium-3 in helium obtained from the atmosphere as in the helium obtained from a natural gas well that they analyzed.

Le Pair, Van Laar, and Loopstra (6) determined the composition of a helium-3-helium-4 mixture by measuring the transmission of thermal neutrons. Their minimum detectable limit was above 50 ppb.

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[1] Chief, Unit of Technical Services.

[2] Supervisory chemist.

[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Mass spectrometry has been the most common method for determining the isotopic composition of the stable isotopes of elements. Aldrich and Nier (1-3) determined the helium-3-helium-4 isotopic ratio of several natural gas samples by mass spectrometry. They showed that the helium-3 content of natural gas varies with the source of natural gas.

Coon (5) determined the isotopic abundance of helium-3 in one sample of natural gas and atmospheric helium by detecting the He^3 (n,p)H^3 disintegration induced by thermal neutrons.

Previous measurements by Aldrich and Nier have indicated that helium-3 is present in helium extracted from natural gas in the order of 1 part in 10^7, and that the abundance ratio varies depending on the source of natural gas (2). Previous authorities have reported a minimum detectable limit of approximately 30 ppb (3). The present work extends the analytical range to less than 1 ppb with a 2σ accuracy of ±15 percent, by using a modified mass spectrometer, increased sample pressures, and weighed primary standards (7) in the same range as the unknown samples.

ACKNOWLEDGMENT

We express our sincere thanks and appreciation to George M. Lucich, electronics engineer, Unit of Technical Services, Helium Operations, Bureau of Mines, Amarillo, Tex., for his assistance in the modification of the electronic circuitry of the mass spectrometer.

APPARATUS DESCRIPTION

A Consolidated Electrodynamic Corp. (CEC)[4] mass spectrometer Model 21-102, which is a 180°-type, single-focusing, 5-inch-radius instrument and scans by varying the ion-accelerating voltage, was used. It was modified with the following equipment: CEC 21-104 analyzer assembly with external adjustable slit width (0-20 mils), CEC electron multiplier and Wien filter, improved power supply for the electron multiplier, 2-pen recorder with 10 range selections of 1 millivolt (mv) to 1 volt on each pen, and a 0- to 30-torr Barocel No. 1014 electronic pressure gage for the sample inlet system.

The ionizing current circuitry of the mass spectrometer was modified as shown in figure 1. Using this circuitry, ionizing currents of 7 to 775 microamperes (μa) can be obtained as required. A 0- to 2,000-μa filament emission meter, as shown in figure 2, was installed to indicate the filament emission. Slower scan rates for the mass spectrometer were obtained by use of the modified scan rate control circuitry shown in figure 3.

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[4] Reference to specific equipment is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

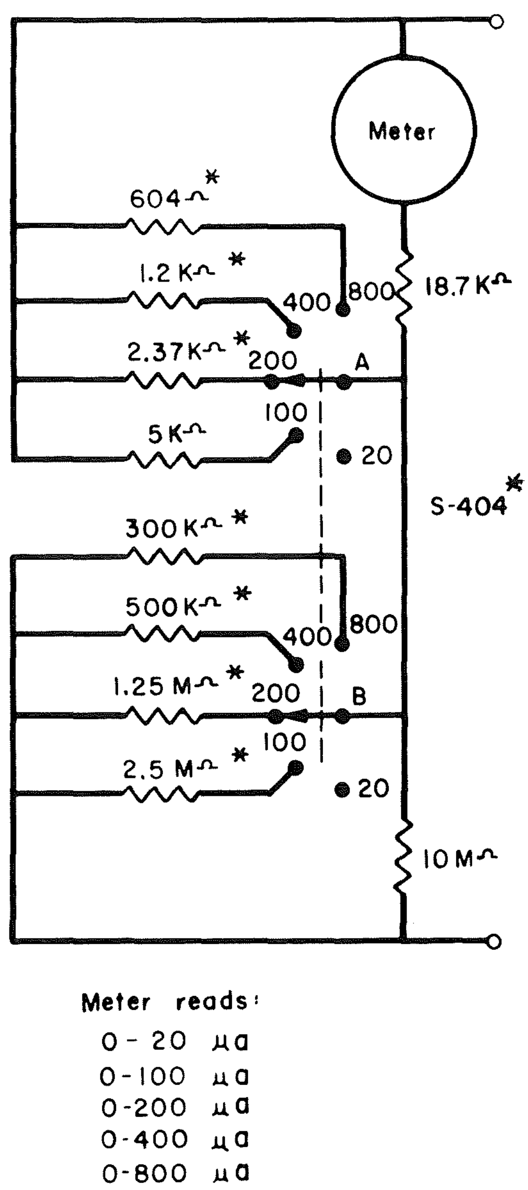

FIGURE 1. - Ionizing current control.

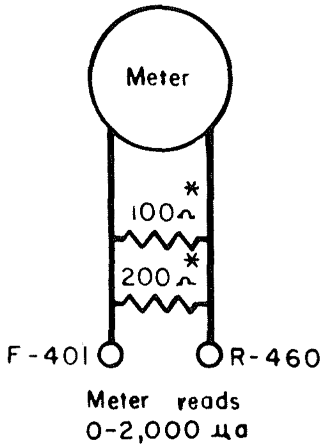

FIGURE 2. - Filament emission circuit.

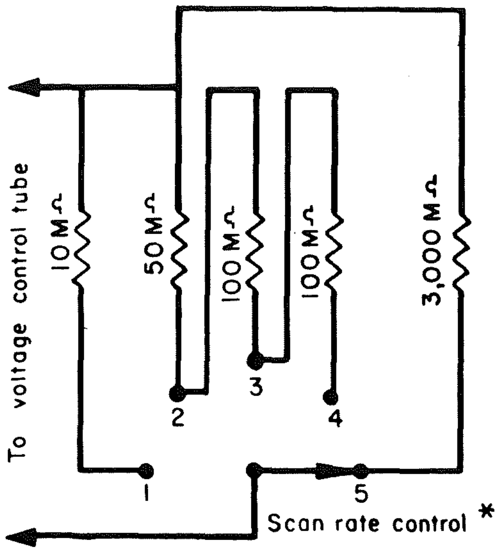

FIGURE 3. - Scan rate control circuitry.

* Indicates additions or modifications to original circuit.

The mass spectrometer metal inlet system was modified for high-pressure work by installing a 0- to 50-torr absolute manometer pressure gage D next to valve 1 as shown in figure 4. The manometer connection normally furnished on the auxiliary metal inlet valve assembly was cut off near valve 8 and fitted with a stainless steel connection C. Pressure gage B was added for checking residual pressure and leaks in the inlet sample connections. A plexiglass sheet was placed on the inlet cabinet in front of the 3-liter sample volume for operator protection.

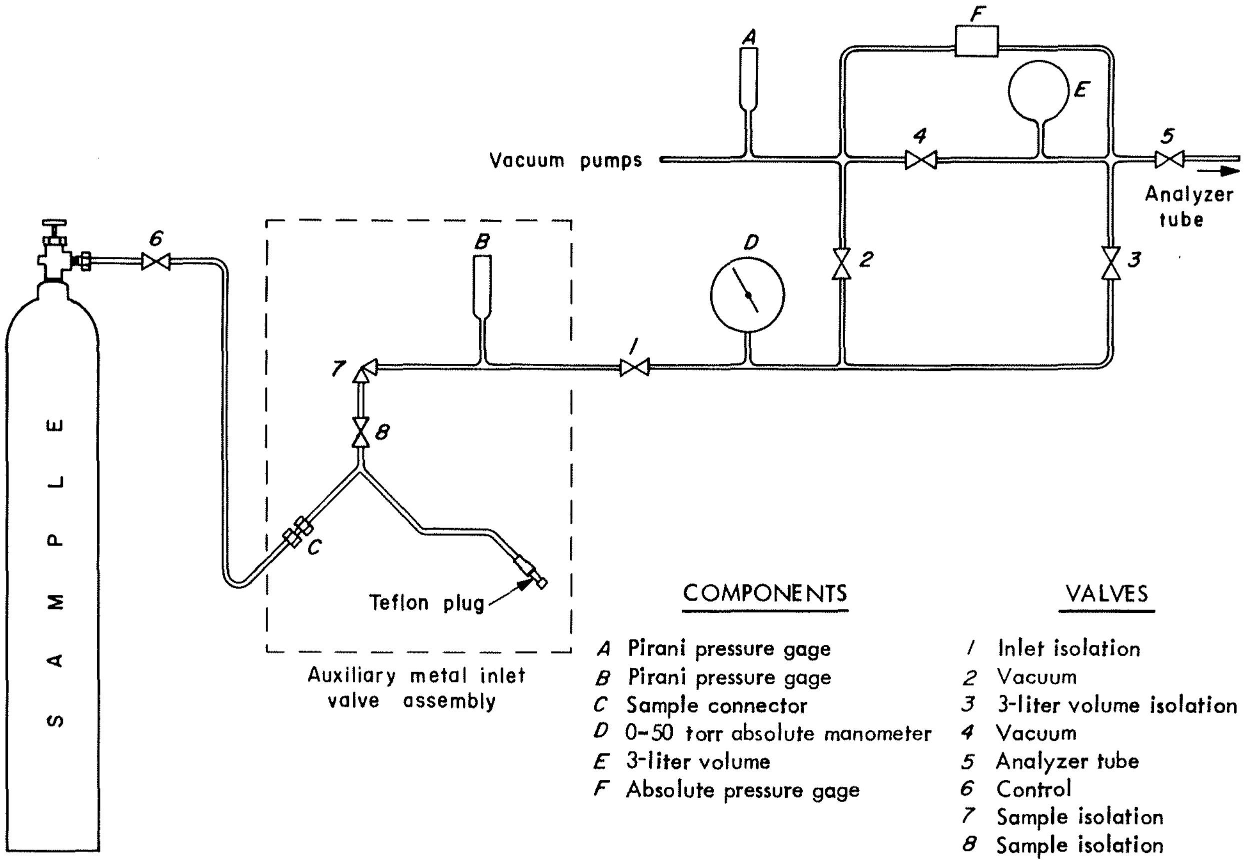

FIGURE 4. - Modifications to mass spectrometer inlet system.

PROCEDURE

To determine the helium-3 content accurately, it is necessary to obtain a representative sample and analyze it under the same conditions as a weighed primary standard. The sample cylinders were connected by the use of a standard stainless steel cylinder connection and control valve _6_ (vacuum to 3,500 psi) as shown in figure 4. The control valve outlet was fitted with a stainless steel line to the auxiliary metal inlet valve assembly as was reported earlier by Suttle, Emerson, and Burfield (_8_).

The inlet line is evacuated to the sample cylinder by opening valves _2_, _1_, _7_, _8_, and _6_ in that order. After a high vacuum is attained, valve _6_ is closed and the sample cylinder valve is opened.

The system is purged with the sample gas in the following sequence: Close valve _2_ and open valve _6_ slowly, admitting the sample gas into the inlet system. Pirani pressure gage _B_ will indicate the increased pressure. When the pressure exceeds the readability of _B_, the pressure is observed on the absolute manometer _D_. After the pressure is at least 5 torr, valve _6_ is closed and valve _2_ is opened to evacuate the system. This completes the purging of the inlet system.

To admit the sample, valve 3 is opened and pressure gage F is nulled on zero; then F is preset to 1 torr, valve 2 is closed, and valve 6 is slowly opened until a null reading on F is observed. Valve 6 is closed and the sample is isolated by closing valve 3. A final pressure reading is made on F

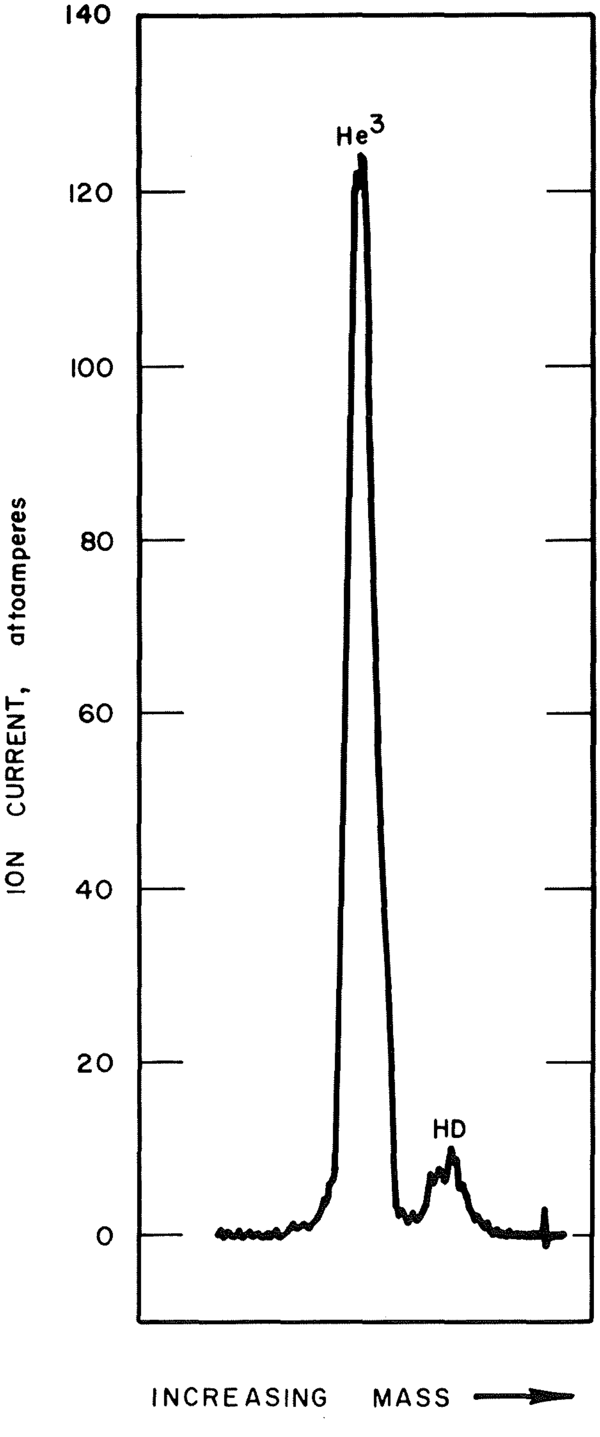

FIGURE 5. - Mass spectrometer scan of weighed primary standard containing 109 ppb helium-3 at 1-torr sample pressure and 180-μa ionizing current.

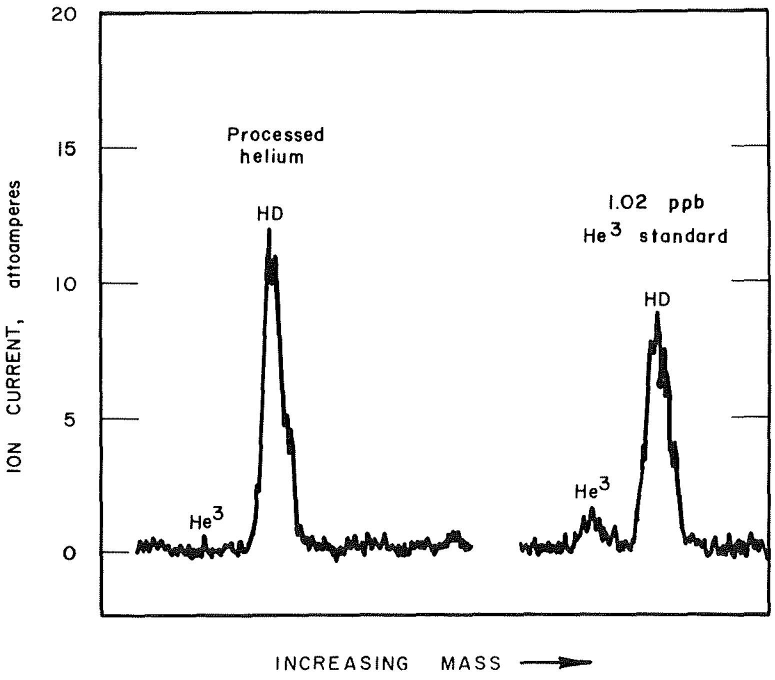

FIGURE 6. - Mass spectrometer scan of processed helium-4 (zero helium-3) and 1.02 ppb helium-3 samples at 1-torr sample pressure and 180-μa ionizing current.

and recorded. Valve 2 is opened to remove the sample between valve 6 and valve 3.

The mass spectrometer operating settings are made as listed in table 1, then the gas sample is admitted to the analyzer by opening valve 5. The recorder and sweep switch are turned on. The ion accelerating voltage is monitored by a digital voltmeter to determine the voltage when the helium-3 peak appears on the scan. This voltage has been predetermined by analyzing a mixture of helium-3 in helium-4 in the same range as the unknown to be analyzed. The total time required to analyze a standard and unknown sample is 50 minutes. Typical mass spectrometer scans for helium-3 are shown in figure 5 (weighed primary standard containing 109 ppb helium-3 in helium-4) and figure 6 (sample of processed helium-4 containing no detectable helium-3 and a weighed primary standard containing 1.02 ppb helium-3 in helium-4).

TABLE 1. - Mass spectrometer operating settings

Magnet current................................ampere..	0.1838
Ion accelerating voltage......................volts..	1,900 to 1,880
Ionizing current...................................μa..	180
Analyzer slit width............................mils..	5.0
Ionizing voltage...............................volts..	70
Input resistor (preamplifier)..................ohms..	5×10^{10}
Electron multiplier.................volts per stage..	130
Scan rate (about 3 minutes)........................	Position 5
Focus-nonfocus switch..............................	Nonfocused
Recorder 2 pen.....................................	Variable (1 mv to 1 v)
Chart speed.........................meter per hour..	1
Inlet sample pressure..........................torr..	1

DISCUSSION OF RESULTS

To determine the optimum sensitivity of the helium-3 peak, the ionizing current and inlet sample pressure were progressively increased.

The effect of inlet sample pressure and ionizing current on the helium-3 sensitivity is shown in figure 7. The sensitivity of the helium-3 peak increases with increased sample pressure up to about 4 torr, and increases with increased ionizing current up to 300 μa. The inlet sample pressure was varied from 0.5 to 9 torr in the 3-liter volume at 100, 180, 250, 300, 400, and 500 μa ionizing current.

The settings of 1 torr inlet sample pressure and 180 μa ionizing current were selected for routine operation because the sensitivity was adequate for determinating helium-3 in Bureau operations. Previous experience at these settings resulted in a minimum of filament failures and instrument downtime.

To insure that helium-3 rather than some other ion was analyzed, the following pertinent information and procedures were noted and followed:

1. There was no detectable background peak on the helium-3 peak setting when analyzing processed helium (zero helium-3).

2. The resolving power completely separates the helium-3 peak from the hydrogen deuteride (HD) peak.

3. Weighed primary standard mixtures of helium-3 in helium-4 were analyzed and compared. The results were linear from the parts-per-million range down to the 1-ppb range. These data are shown in table 2.

TABLE 2. - Mass spectrometer linearity of helium-3 from 1.02 ppb to 10.3 ppm

Weighed primary standard	Peak height, attoamperes	Peak height, attoamperes/ppb
1.02 ppb..................	1.2	1.2
10.2 ppb..................	11.2	1.1
109 ppb...................	124.0	1.1
1.06 ppm..................	1144.0	1.1
10.3 ppm..................	10965.0	1.1

To calibrate the mass spectrometer for helium-3 analysis, weighed primary standards were prepared by a gravimetric method that is accurate in the parts-per-billion range to ±7 percent (7). The helium-3 used for preparing the calibration standards was obtained from Mound Laboratory where it is refined from gases obtained from nuclear reactions. The weighed primary standards were prepared by successive dilution of helium-3 with helium-4 until a concentration in the parts-per-million or parts-per-billion range desired was achieved. The helium-4 used for the dilution was the processed helium-4 (zero helium-3), which is shown in figure 6.

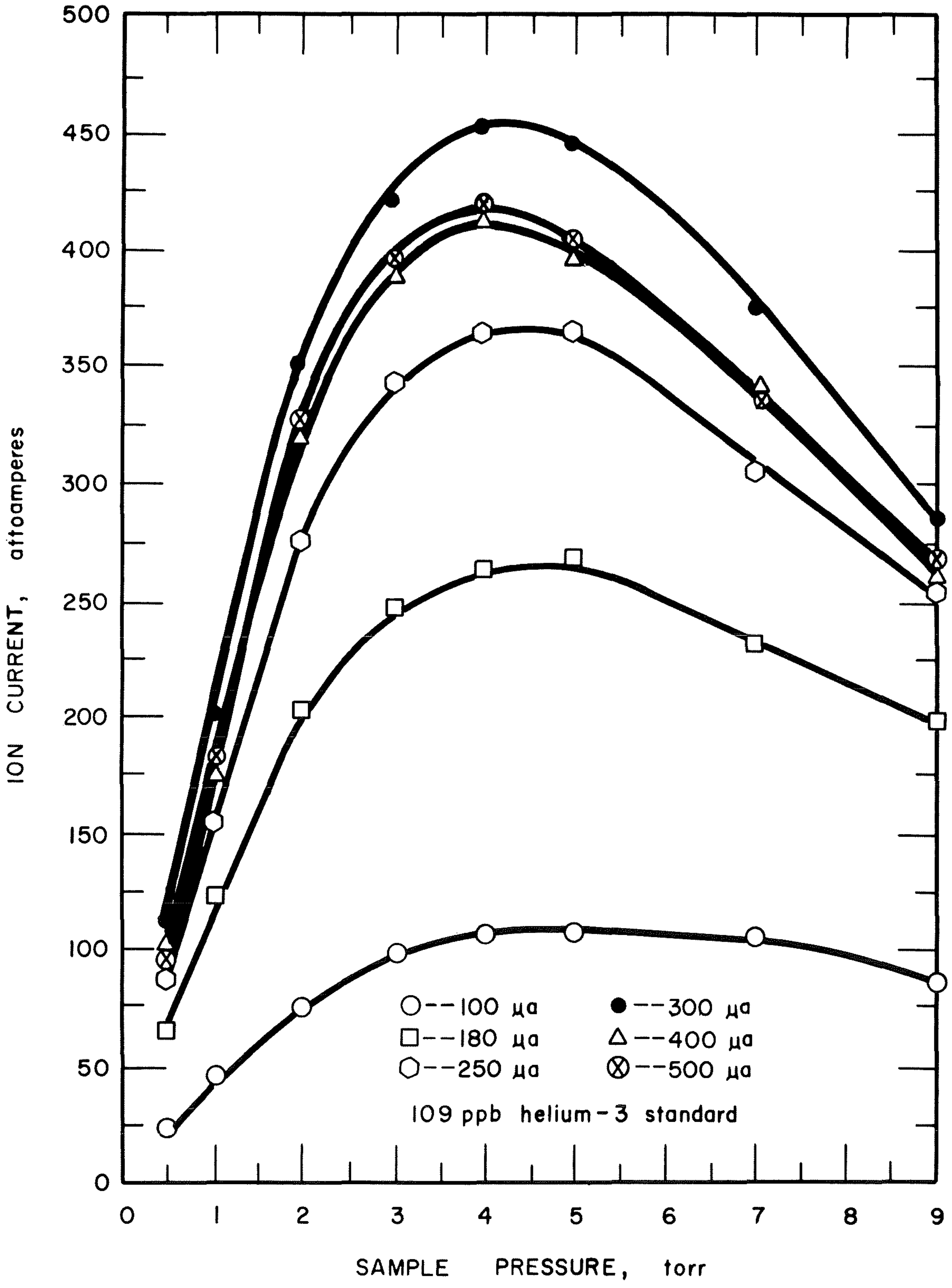

FIGURE 7. - Sensitivity at 100- to 500-μa ionizing current and inlet sample pressure from 0.5- to 9-torr.

The reproducibility of this method was checked by analyzing four samples 10 times. The results are given in table 3.

TABLE 3. - Precision of method[1]

Sample	Helium-3 content, ppb	Standard deviation, ppb
1..................	10.1	0.4
2..................	23.1	1.3
3..................	79.7	4.1
4..................	215.0	9.1

[1] The accuracy of this method is better than ±15 percent at the 95-percent confidence level in the ppm and ppb range.

CALCULATIONS

The sensitivity or peak height of helium-3 at the same inlet sample pressure and mass spectrometer settings will vary slightly each day. To correct for these slight variations, a helium-3 weighed primary standard or a certified standard in the same range as the unknown is analyzed before each unknown sample. The helium-3 content in the sample is calculated as shown in equation 1.

$$He_u \ D_s = He_s \ D_u \tag{1}$$

or

$$He_u = \frac{He_s \ D_u}{D_s}, \tag{2}$$

where He_u = ppb helium-3 in unknown sample,

D_u = peak height (attoamperes) of helium-3 from unknown sample,

He_s = ppb helium-3 in weighed primary standard,

and D_s = peak height (attoamperes) of helium-3 from weighed primary standard.

CONCLUSIONS

The mass spectrometer procedure outlined provides a precise and reliable method for determining the helium-3 concentrations in helium-4. The detection limits attainable allow further experimentation in methods for removing helium-3 from helium-4. Better mass spectrometer stability will be required to extend the minimum detectable limit to the parts-per-trillion range.

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