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REPORT OF INVESTIGATIONS/1991

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By Philip W. Holland

UNITED STATES DEPARTMENT OF THE INTERIOR



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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mA	milliampere
cm	centimeter	min	minute
cm ³	cubic centimeter	Ω	ohm
eV	electron volt	ppb	part per billion
g	gram	ppm	part per million
GΩ	gigohm	pF	picofarad
h	hour	psig	pound per square inch, gauge
KΩ	kilohm	s	second
MΩ	megohm	Torr	torr
μF	microfarad	Vac	volt, alternating current
μTorr	microtorr	Vdc	volt, direct current

A MASS SPECTROMETER METHOD FOR DETERMINING HELIUM IN THE PARTS-PER-MILLION TO 10-PERCENT RANGE

By Philip W. Holland¹

ABSTRACT

The U.S. Bureau of Mines has developed a mass spectrometer method for determining helium in the parts-per-million to 10% range to an accuracy of $\pm 1\%$. The method employs a mass spectrometer, an inlet system utilizing a chromatographic gas-sampling valve, and an activated coconut charcoal trap cooled with liquid nitrogen. Gravimetrically prepared standards of helium in nitrogen were used to demonstrate the linearity of the method over the concentration range of 10 ppm to 10.66% helium.

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INTRODUCTION

The Helium Act, Public Law 86-777, authorizes the Secretary of the Interior to maintain and operate Federal helium production facilities and to improve methods for helium separation, purification, and analysis. In pursuit of this mission, the Bureau of Mines investigates methods of helium purification, liquefaction, transportation, storage, and analysis.

The analytical method described in this report was developed to provide additional capability to analyze for helium² in the 10-ppm (0.001%) to 10% range. The method is presently used for determining the helium content of laboratory-prepared gaseous mixtures (excluding those containing percent-range hydrogen and/or neon). The method will be evaluated for determining the helium content of natural gas samples obtained in the Bureau's field survey program (1).³

Since the inception of the Government's helium program in 1917, analytical methods for determining helium have been developed and/or improved by the Bureau. In 1921, an apparatus and method for determining helium in natural gas were described by Seibel as part of Rogers' paper on helium-bearing natural gas (2). Seibel's method was an improvement of the method originally developed and reported by Cady and McFarland (3) of the University of Kansas. This method relied on the separation of helium utilizing the adsorptive property of activated coconut charcoal at liquid air temperature and subsequent measurement of the volume of helium obtained. The apparatus was later modified by Anderson (4).

In 1946, an improved apparatus and procedure for the determination of helium in natural gas were described by

Frost (5). The new apparatus also employed the adsorptive property of activated coconut charcoal at liquid air or liquid nitrogen temperature to effect separation of the helium; however, the percentage of helium present in the sample was determined by measurement of the helium pressure. The new apparatus reduced the time for an analysis from 40 min to less than 10 min, improved the minimum detectable limit for helium to a few thousandths of a percent, and was portable. With the Frost apparatus, as it was eventually called, an operator could analyze 50 or more samples in an 8-h day.

Use of the Frost apparatus for helium determinations in natural gas and gaseous mixtures containing up to 10% helium was replaced by the Bureau in 1975 with a gas chromatographic method. This method allows both helium and hydrogen to be determined in a single run lasting approximately 6 min. The separation is performed isothermally at 45 °C using Poropak Q and activated charcoal-molecular sieve series columns and argon as the carrier. The accuracy over the range of 0.1% to 10% helium is within $\pm 1\%$ when using gravimetric standards (6-7) for calibration and performing triplicate determinations of the sample. The minimum detectable limit for helium is 10 ppm.

The method described in this report is similar to previous Bureau-developed methods for determining helium in the 0.5- to 20,000-ppb range (8-9). The method utilizes a modified mass spectrometer and auxiliary inlet system to extend the helium analysis range from 10 ppm to 10%. The analysis time, which includes a single analysis of the sample and calibration standard, is 6 min.

ACKNOWLEDGMENT

The author expresses his sincere thanks and appreciation to Charles A. Seitz for modification of the mass spectrometer ion source, electronic circuitry, and other helpful suggestions in development of the analytical

method. Mr. Seitz is a chemist in the Section of Technical and Analytical Services, U.S. Bureau of Mines, Helium Field Operations, Amarillo, TX.

MASS SPECTROMETER SYSTEM

A schematic of the modified Du Pont⁴ 21-491B mass spectrometer is shown in figure 1. The following

modifications were made to the mass spectrometer: An auxiliary inlet system was added, consisting of an air-operated, sliding-piston, O-ring-sealed gas sampling valve and a 0- to 1,000-Torr (absolute) digital manometer system with a 5-1/2-digit display. The gas-sampling valve has a sample loop volume of 0.2 cm³ and is actuated by compressed air (25 psig) supplied through the solenoid valve.

²"Helium" in this report refers to the isotope helium-4.

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

⁴Reference to specific manufacturers or trademarks does not imply endorsement by the U.S. Bureau of Mines.

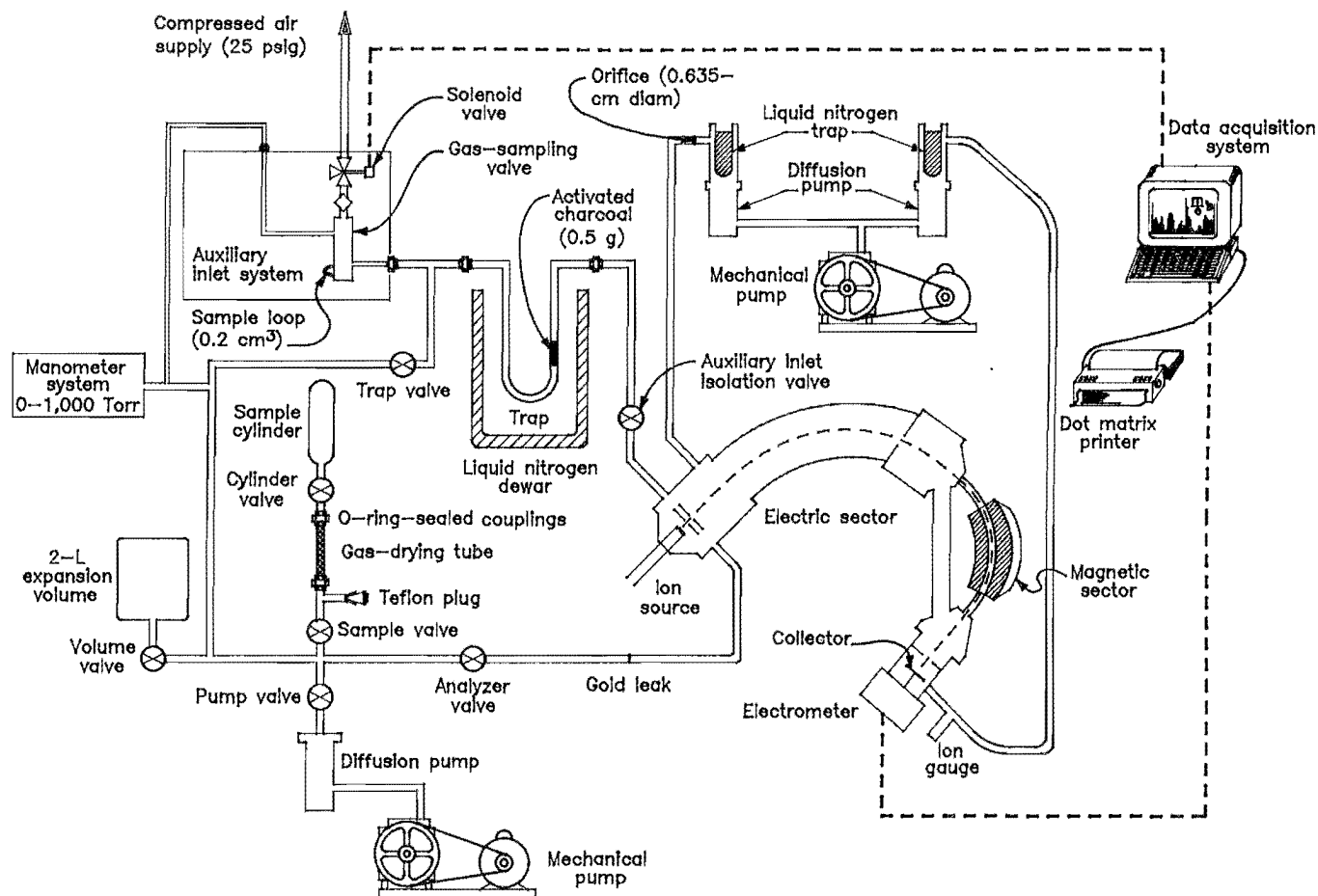


Figure 1.—Schematic of modified Du Pont 21-491B mass spectrometer.

The solenoid is switched on command using a Teknivent model 1050 mass spectrometer data acquisition system and the relay circuit shown in figure 2. The data acquisition system is interfaced to an IBM-AT personal computer which performs data processing with Teknivent Vector One mass spectral software and a special BASIC language program.

A sample is admitted to the mass spectrometer from the gas-sampling valve through a 0.64-cm-diam (0.10-cm-wall) by 44-cm-long stainless steel U-tube containing 0.5 g of minus 40- plus 60-mesh activated charcoal on the downstream side of the tube (fig. 1). The charcoal is held in place with stainless steel and glass wool packing. At liquid nitrogen temperature, gases other than helium are adsorbed by the charcoal. Thus, use of the trap allows a larger volume of sample to be admitted to the mass spectrometer for increased helium output and a lower minimum detectable limit.

The vacuum system of the mass spectrometer was modified by installing a 0.635-cm-diam orifice (fig. 1) in the

line to the diffusion pump that is adjacent to the ion source. The orifice reduces the pumpout rate from the ion source, which results in a more consistent helium peak shape for quantitation and a lower minimum detectable limit (9).

The mass spectrometer ion source and associated circuitry were modified as depicted in figure 3. The modifications were made to provide direct control of the ionizing current. Before these modifications were made, the ionizing current was controlled indirectly by controlling the total emission of the filament. The ionization chamber "block" was drilled with a 0.152-cm-diam hole opposite the filament to allow the emitted electrons to be collected by an anode constructed of 0.127-cm-thick by 0.48-cm-wide stainless steel stock. Synthetic sapphire spacers were used to isolate the anode from the ionization chamber. The anode is operated at a voltage that is 150 Vdc more positive than the filament. The modified ion source provides constant ionizing current (anode current), which is adjustable from a minimum of 15 μ A to a maximum of 80 μ A.

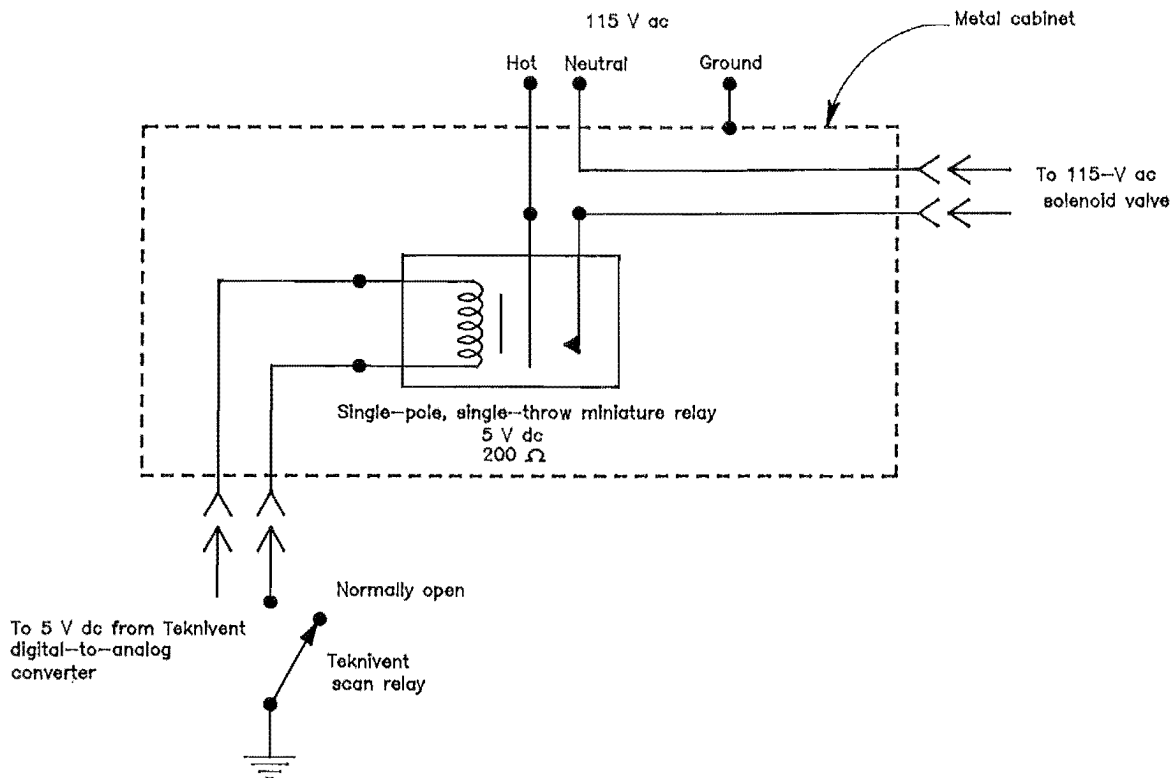


Figure 2.—Schematic of relay circuit used to switch solenoid valve.

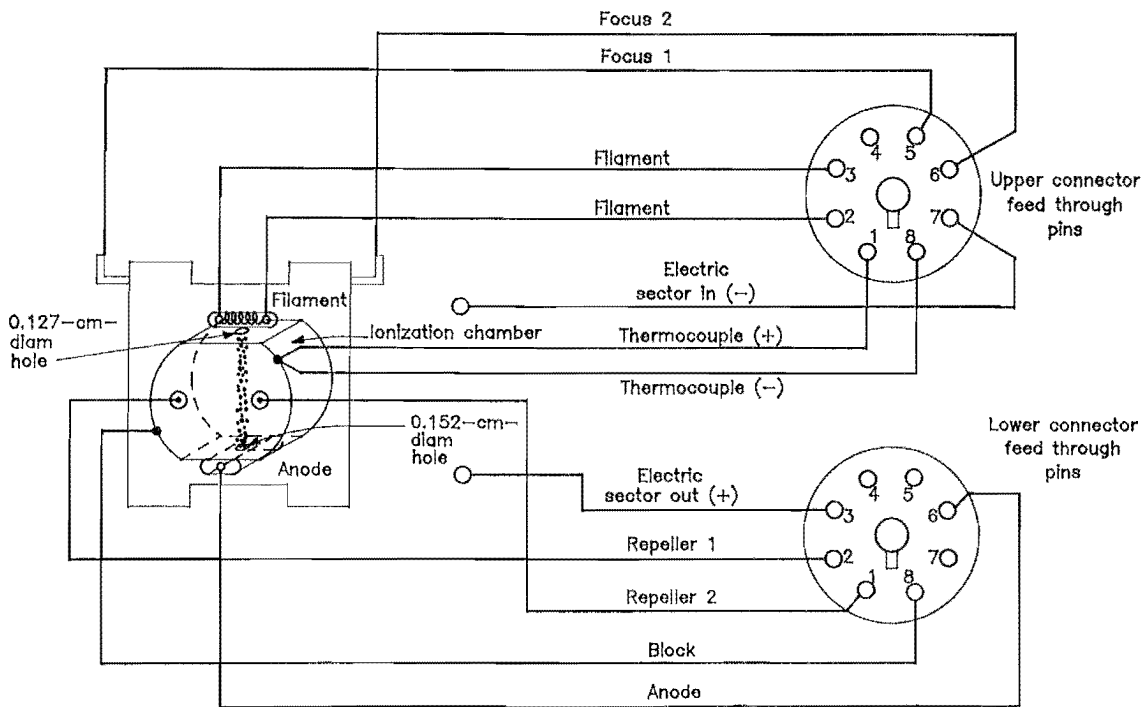


Figure 3.—Modified Du Pont 21-491B mass spectrometer ion source and associated circuitry.

The electrometer circuit depicted in figure 4 utilizes an operational amplifier (Analog Devices 549) for ion current amplification. The electrometer provides both current and voltage gain with a maximum output of about 10 Vdc.

The circuit was housed in a carbon steel case to shield it from electromagnetic radiation and to minimize drift caused by ambient temperature fluctuations.

LINEARITY

The linearity of the analytical system for helium concentrations ranging from $0.001006\% \pm 0.000001\%$ to $10.6569\% \pm 0.0002\%$ was checked by comparing laboratory-prepared helium-in-nitrogen gravimetric standards. Linear regression plots of the peak area versus helium concentration curves are shown in figures 5 through 7. The plotted peak areas are the averages obtained for three runs of each standard. The correlation coefficients for the

curves are 0.9999, 0.9998, and 0.9999, respectively. Sample pressures of 300, 30, and 15 Torr were employed to correspond to the concentration ranges of 0.001% to 0.53% helium, 0.53% to 5.05% helium, and 1.34% to 10.66% helium, respectively. Reduction of sample pressure with increasing helium concentration is required to prevent overload of the data acquisition system's integration capacity.

ANALYTICAL PROCEDURE

The following mass spectrometer parameters are adjusted to prepare the instrument for use in this method. The magnet current and accelerating voltage potentiometers are adjusted to produce a maximum response at mass 4 while admitting a $300\text{-}\mu\text{Torr}$ sample of

0.5% helium in nitrogen to the "gold leak" from the conventional batch inlet system. The nominal magnet current and accelerating voltage values are 160 mA and 1,400 Vdc, respectively. The ionizing current is set at 15 μA , and the ionizing voltage is set at 70 eV.

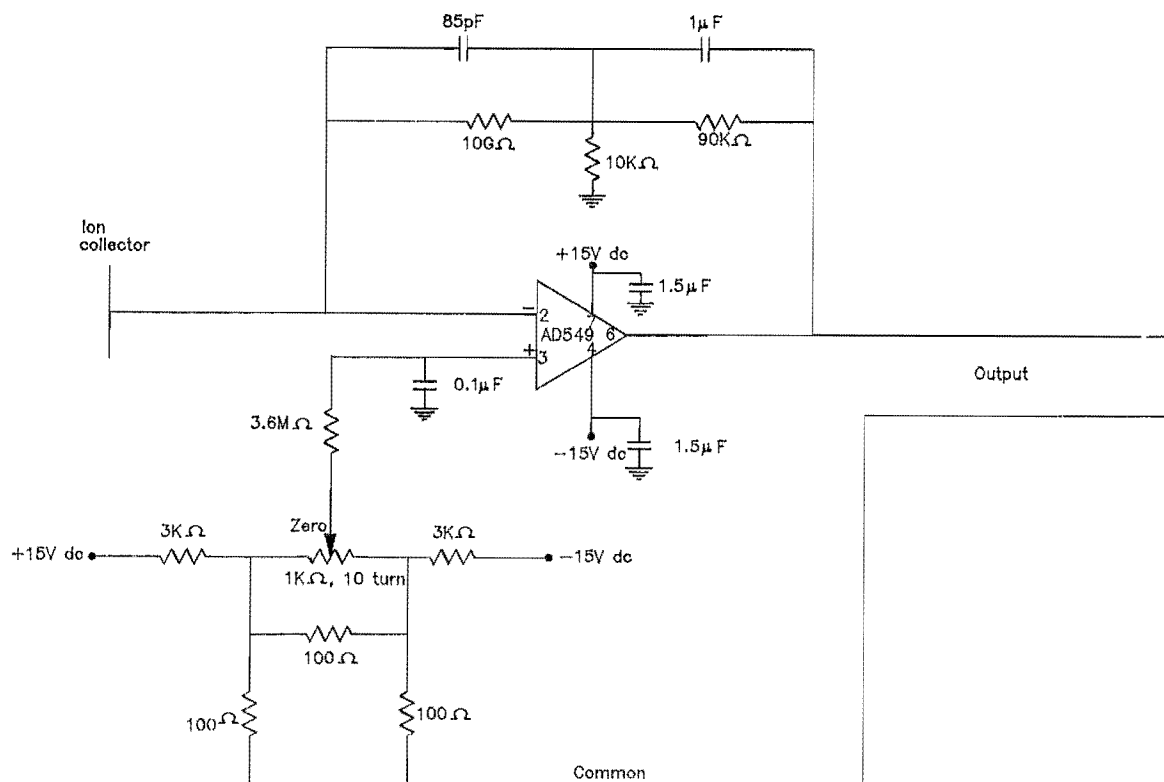


Figure 4.—Schematic of electrometer for modified Du Pont 21-491B mass spectrometer.

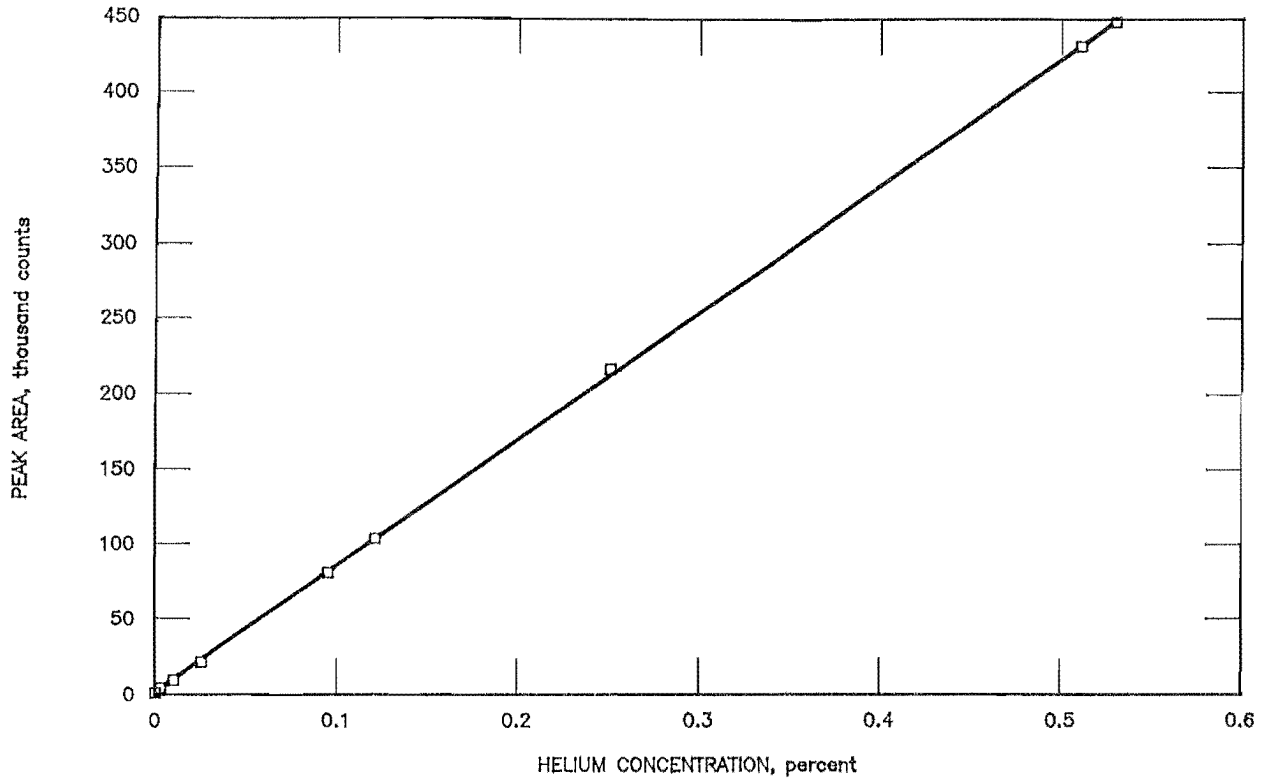


Figure 5.—Linearity of system for He-in-N₂ analyses, 0.001% to 0.53% He, 300-Torr sample inlet pressure.

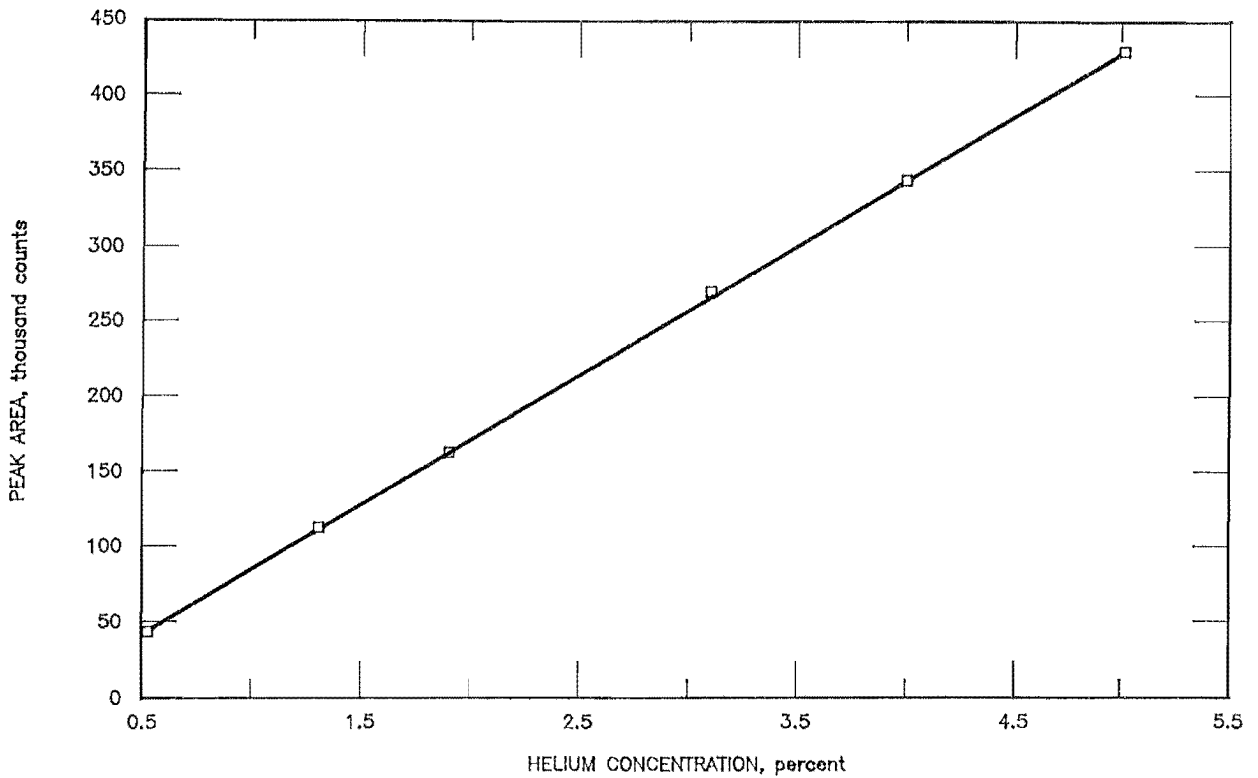


Figure 6.—Linearity of system for He-in-N₂ analyses, 0.53% to 5.05% He, 30-Torr sample inlet pressure.

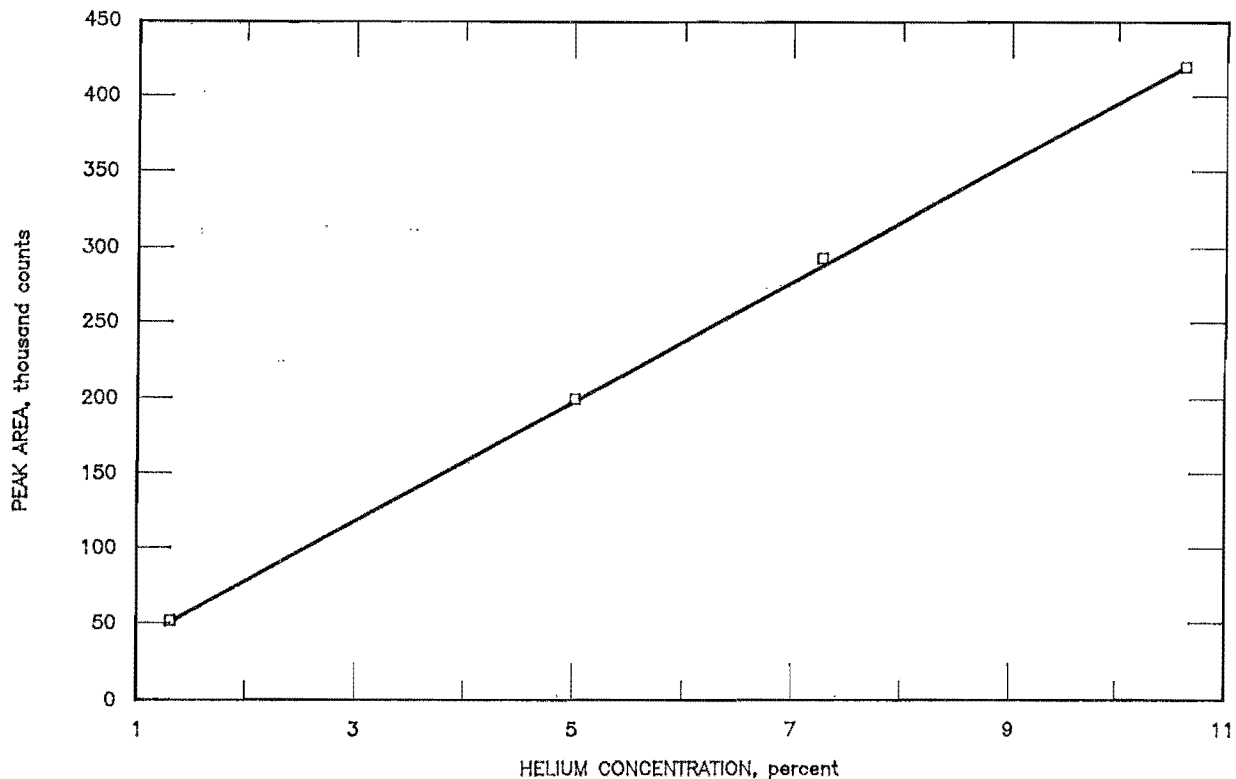


Figure 7.—Linearity of system for He-in-N₂ analyses, 1.34% to 10.66% He, 15-Torr sample inlet pressure.

Gravimetric standards and samples are attached to the inlet system using an O-ring-sealed vacuum coupling (fig. 1). Water vapor is removed from the sample by passing it through a drying tube containing anhydrous magnesium perchlorate (anhydron). The sample is metered into the sample loop of the gas-sampling valve to an absolute pressure of 300, 30, or 15 Torr, depending on the expected range of helium in the sample. The gas sample is admitted to the liquid-nitrogen-precooled charcoal trap and analyzer section of the mass spectrometer 10 s after initiating the acquisition mode of the data system. The analog output of the electrometer is displayed graphically on the monitor of the personal computer. The digitized helium peak areas are stored on the fixed disk of the computer through the data acquisition system software. A BASIC language computer program compares the helium peak area of the unknown sample directly to those of the calibration standard and calculates the concentration of helium in the unknown sample.

Each analysis is performed according to the sequence of events shown in table 1. The gas-sampling valve is returned to the "evacuate" position 0.5 min after admitting a sample of gas to the mass spectrometer; therefore, the acquisition and sample loop pumpout events run and expire concurrently. To minimize the effects of cross-contamination, a calibration standard is selected so that its helium content is within an order of magnitude of the expected helium content of the unknown sample. This procedure also allows comparison of the standard and unknown sample under matching parameters.

Table 1.—Analytical sequence of samples and standards

Event	Duration of event, min
Acquire sample peak with mass spectrometer . . .	3.0
Pump out sample loop	2.5
Acquire standard peak with mass spectrometer . .	3.0
Pump out sample loop	2.5

ACCURACY AND MINIMUM DETECTABLE CONCENTRATION

To evaluate the accuracy of the method, a series of helium-in-nitrogen certified and/or gravimetric standards were treated as "unknowns" and compared to gravimetric standards used as calibration standards. The accuracies of the calibration standards were verified previously by comparing the series of standards to each other using the gas chromatography method described in the introduction of this report. The hypothetical unknowns were analyzed five times in succession. Each sample run was followed by a run of a calibration standard, and the "unknown" sample helium content was calculated. The results of the comparisons are given in table 2. The reported accuracy is the root-mean-square addition of the precision (standard deviation) for five analyses plus the standard error in the helium content of the calibration standard. Since the standard error in each calibration standard is insignificant compared to the precision for five analyses of each "unknown," the accuracy is essentially equal to the analytical precision. The accuracy over the concentration range of 0.0115% to 10.66% helium is within $\pm 1\%$. The minimum detectable concentration, which is considered to be a peak with a height of twice the width of the baseline noise, is calculated to be 5 ppm, or 0.0005%.

Table 2.—Comparison of helium-in-nitrogen standards to determine accuracy of method, percent

Helium in nitrogen		Mean helium content for 5 analyses of Unknown	Precision for 5 analyses	Accuracy at 68% confidence
Standard	Unknown			
0.01154 $\pm .00001$	0.001006 $\pm .000001$	0.0009	± 0.0001	± 10
0.01154 $\pm .00001$	0.0057 $\pm .0001$.0057	$\pm .0001$	± 2
0.09534 $\pm .00004$	0.01154 $\pm .00001$.0116	$\pm .0001$	$\pm .9$
0.09534 $\pm .00004$	0.256 $\pm .003$.2551	$\pm .0008$	$\pm .3$
1.9407 $\pm .0001$	0.530 $\pm .005$.5287	$\pm .0034$	$\pm .6$
5.0463 $\pm .0001$	1.9407 $\pm .0001$	1.9331	$\pm .0187$	± 1
9.1069 $\pm .0002$	10.6569 $\pm .0002$	10.6886	$\pm .1100$	± 1

CONCLUSIONS

The method described is reliable for determining helium in the parts-per-million to 10% range. The accuracy over the concentration range of 0.0115% to 10.66% helium is within $\pm 1\%$ when performing

five successive analyses and employing gravimetric standards for calibration of the mass spectrometer. The minimum detectable helium concentration is calculated to be 5 ppm.

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