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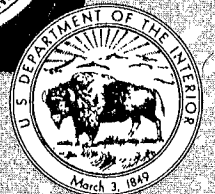
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REPORT OF INVESTIGATIONS/1989

Improved Method for Determination of Helium-4 in Helium-3 by Mass Spectrometry

By Samuel R. M. Burton and David E. Cornelius

BUREAU OF MINES



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 9232

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**UNITED STATES DEPARTMENT OF THE INTERIOR
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere, standard	min	minute
cm ³	cubic centimeter	mm Hg	millimeter of mercury
eV	electron volt	μ Hg	micron of mercury
h	hour	mV	millivolt
K	Kelvin	ppm	part per million
kg	kilogram	ppt	part per trillion
L	liter	s.d.	scale divisions
mA	milliampere	Torr	torr, mm Hg
μA	microampere	V	volt

IMPROVED METHOD FOR DETERMINATION OF HELIUM-4 IN HELIUM-3 BY MASS SPECTROMETRY

By Samuel R. M. Burton¹ and David E. Cornelius²

ABSTRACT

This Bureau of Mines report describes a method for determining parts per million (ppm) of helium-4 (He-4) in helium-3 (He-3) to an accuracy of $\pm 5\%$ by mass spectrometry. Gravimetrically prepared primary standards were used for the calibration of a Dempster 180° magnetic sector mass spectrometer. A comparison between a 2.49% He-4 in hydrogen mixture and a 2.49% He-4 in He-3 mixture shows that He-3 can be replaced with hydrogen as a diluent for standards with comparable mass spectrometry sensitivities for He-4. Using hydrogen as a diluent allows analysis of He-3 samples for He-4 when He-3 for preparation of standards is not available and also conserves the rare He-3 isotope. Standards of He-4 in H₂ were prepared for calibration of the mass spectrometer for quantitative determinations of He-4 in the 2- to 100-ppm range. A minimum detectable limit of 2 ppm He-4 is obtained by this method.

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INTRODUCTION

The Bureau of Mines has a long-term mission to manage, maintain, and operate Federal helium facilities and continues to improve processes for helium purification, separation, and analysis. The purpose of developing a method for determining He-4 in He-3 is to maintain the Bureau's expertise in helium analysis, which includes high-purity He-3 gas analysis. This analytical service has been provided to Government agencies, Government agency contractors, U.S. universities with Federal research grants, private companies, and three private U.S. producers of isotopically pure He-3. The Bureau has provided the He-3 in He-4 isotopic analytical service since 1968 (1)³ and began work on developing the complementary method for analyzing traces of He-4 in He-3 in 1973 (2).

Increased research interest in purified He-3 has resulted in an increased demand for analysis of impurities in the part-per-million range. Previous measurements of the He-4 to He-3 isotopic ratio utilized cyclotrons (3), thermal neutron transmission (4), acoustical analysis (5), and mass spectrometry. Mass spectrometry of helium gaseous isotopes requires only small sample volumes. Six samples can be analyzed per 8-h day using this method, compared to two samples using the previous method by Suttle, Emerson, and Burfield (6).

Alvarez and Cornog (3) proved in 1939 that He-3 existed in nature, and in 1946 Aldrich and Nier (7)

determined that the He-3 to He-4 isotopic ratio varies with the source in natural gas samples.

Other mass spectrometer methods for helium isotopic determinations were developed by Parkinson (8), Schott and Beau (9), Halverson and Herzog (10), Suttle, Emerson, and Burfield (6), Ferguson and Chastagner (11), and Chastagner, Davies, and Hess (12). Ferguson and Chastagner have worked extensively with high-resolution mass spectrometers, greater than 1300X, in the less-than-mass-4 range. These instruments are capable of resolving He-3 and He-4 directly (11). Two Bureau of Mines employees, D. E. Emerson and E. T. Suttle, reported a method for the determination of He-3 in He-4 in the part-per-billion range (13). The Bureau's initial studies (6) were modified to allow pressures greater than 20 Torr and ionizing currents greater than 300 μ A to be used for determining impurities in He-4 (14).

The impurity of greatest importance in He-3 samples is He-4. This report describes an improved analytical method for quantitatively determining He-4 in He-3 samples in the part-per-million range using mass spectrometry. This less expensive technique equals or exceeds the accuracy of earlier methods.

ACKNOWLEDGMENTS

We express our sincere thanks and appreciation to Charles A. Seitz for the modification of the mass spectrometer electronic circuitry, to Harold L. Rhodes for the installation of the data acquisition system, to Thomas A. Davidson for conductance studies, and to Nabil A.

Bibawy for the preparation of gravimetric standards. All are chemists in the Section of Technical and Analytical Services, Helium Field Operations, Bureau of Mines, Amarillo, TX.

MASS SPECTROMETER SYSTEM

A schematic of the modified CEC 21-103 C mass spectrometer⁴ used in this study is shown in figure 1. The following modifications were made to the mass spectrometer:

1. The stainless steel inlet system includes a 1-L expansion volume.

2. The electrical circuitry has been upgraded to solid state components. The upgrading resulted in a 50% increase in sensitivity and a 40% decrease in instrument signal noise.

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

⁴Reference to specific products does not imply endorsement by the Bureau of Mines.

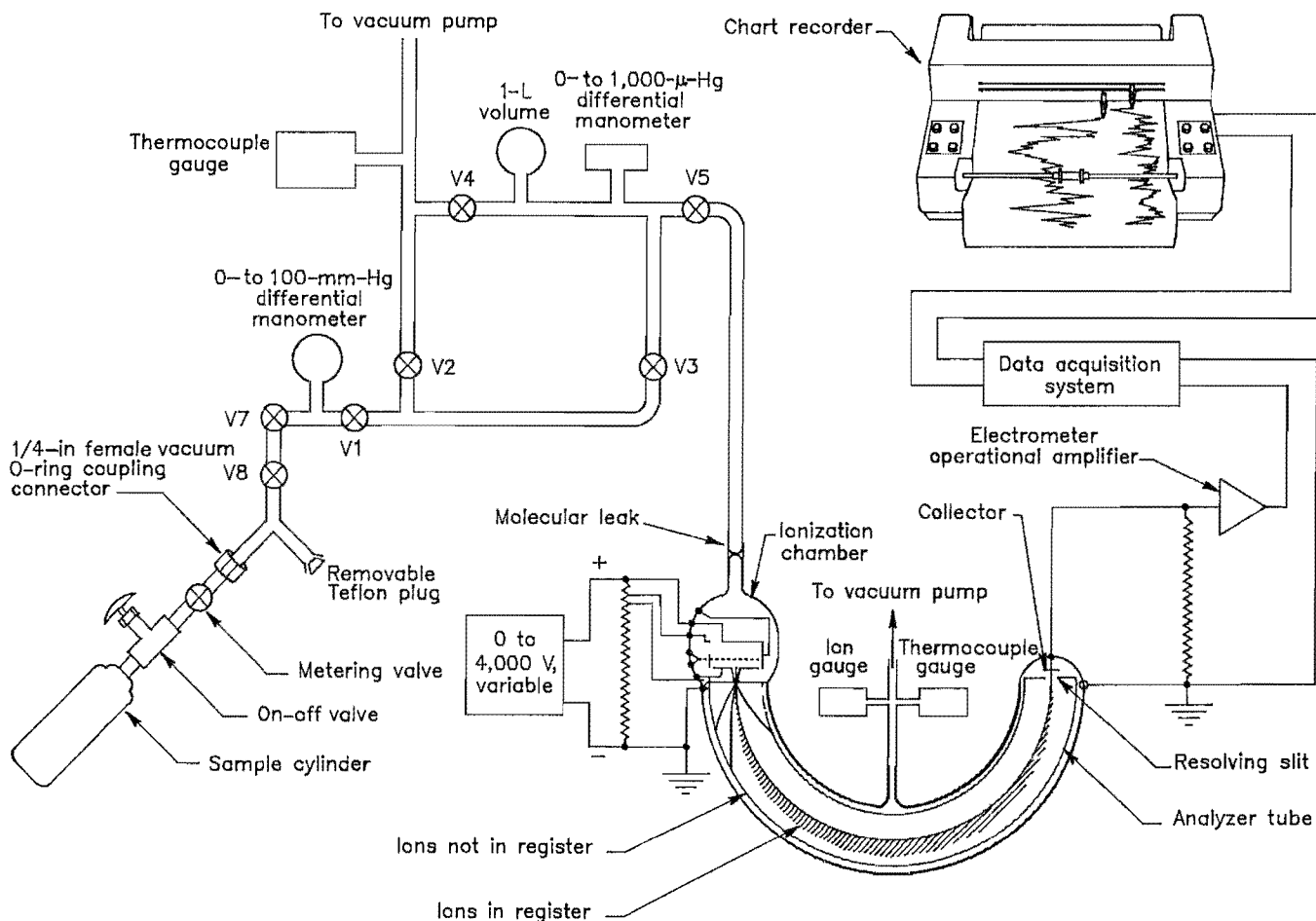


Figure 1.—Schematic of modified CEC-21-103C mass spectrometer.

3. A 1-Torr digital pressure transducer with 5-1/2-digit display is used for inlet pressure measurements.

4. A commercial mass spectrometer data acquisition system is interfaced to a personal computer for data collection and processing.

5. A batch file has been created in the root directory to execute commercial software controlling the digitizer and to manage data files.

6. A high-efficiency three-stage diffusion pump has been installed for the system exhaust vacuum.

INSTRUMENT RESPONSE FOR HELIUM-4 IN HYDROGEN MIXTURES

Standards of He-4 in N₂, CH₄, H₂, and He-3 were prepared to compare the He-4 peak height or instrument response at sample pressures from 2 to 800 μ Hg. Figure 2

shows the instrument response for 2.49% by volume He-4 in N₂, CH₄, H₂, and He-3 mixtures.

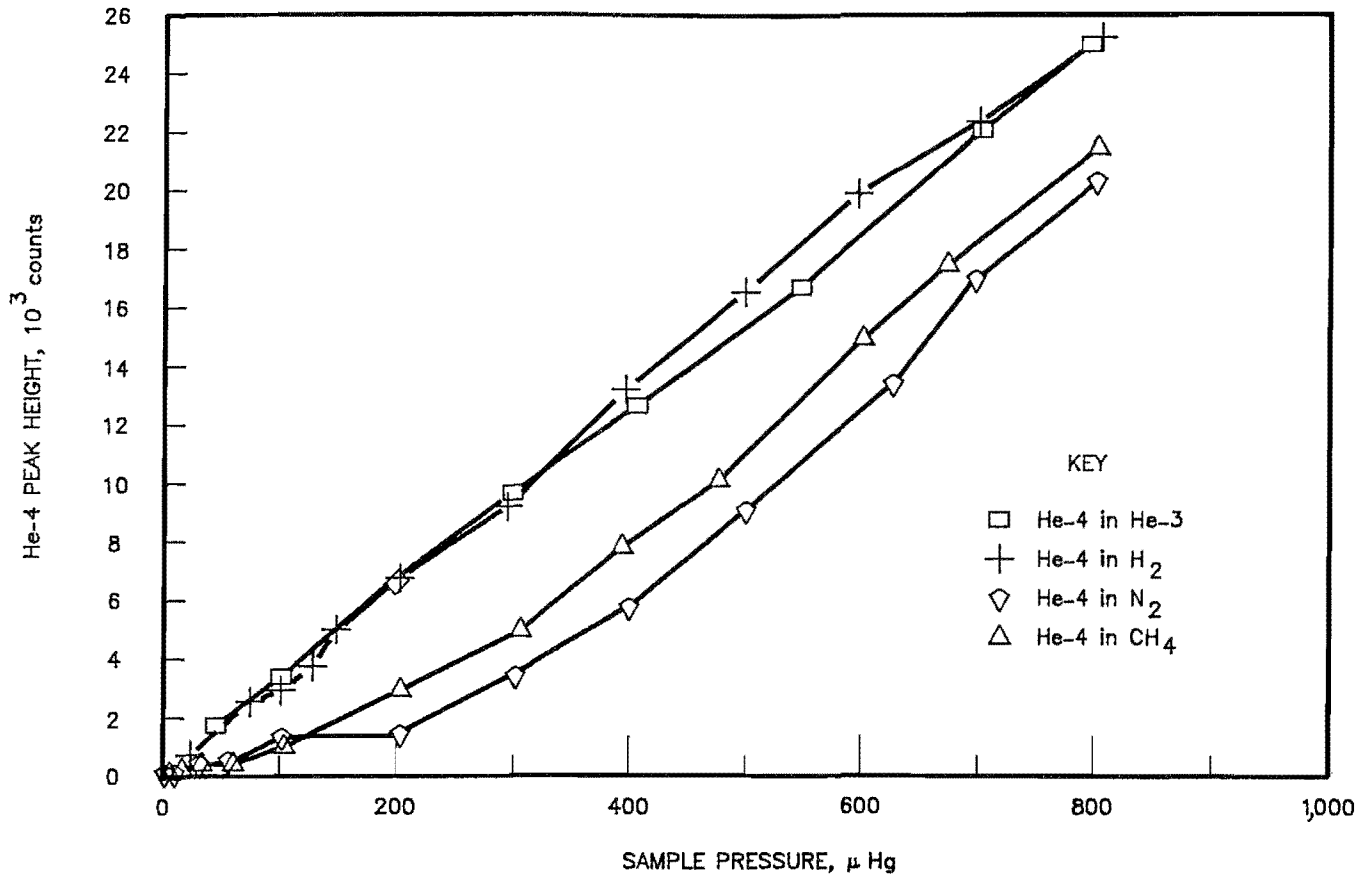


Figure 2.—Instrument response to 2.49% He-4 mixtures.

The data show agreement between the mixtures of He-4 in He-3 and He-4 in H₂. The variation in the least-square correlation at 300 μ Hg between H₂ and He-3 diluent is +1.46%, compared with -36% for CH₄ and -46% for N₂.

Based on these results, hydrogen is used as the diluent in the standards required, and 300 μ Hg was selected as the optimum sample pressure.

LINEARITY

Bureau gravimetric gas mixtures (15-16) are used to provide maximum accuracy. Three gravimetric standards containing 5.71 ± 0.02 , 37.4 ± 0.4 , and 98.1 ± 1.2 ppm He-4 in H₂ were prepared and analyzed to check the linearity of

the method. The three standards were run six times each, and the average response for each mixture is shown in figure 3. The data show a linear fit between 5.71 and 98.1 ppm He-4.

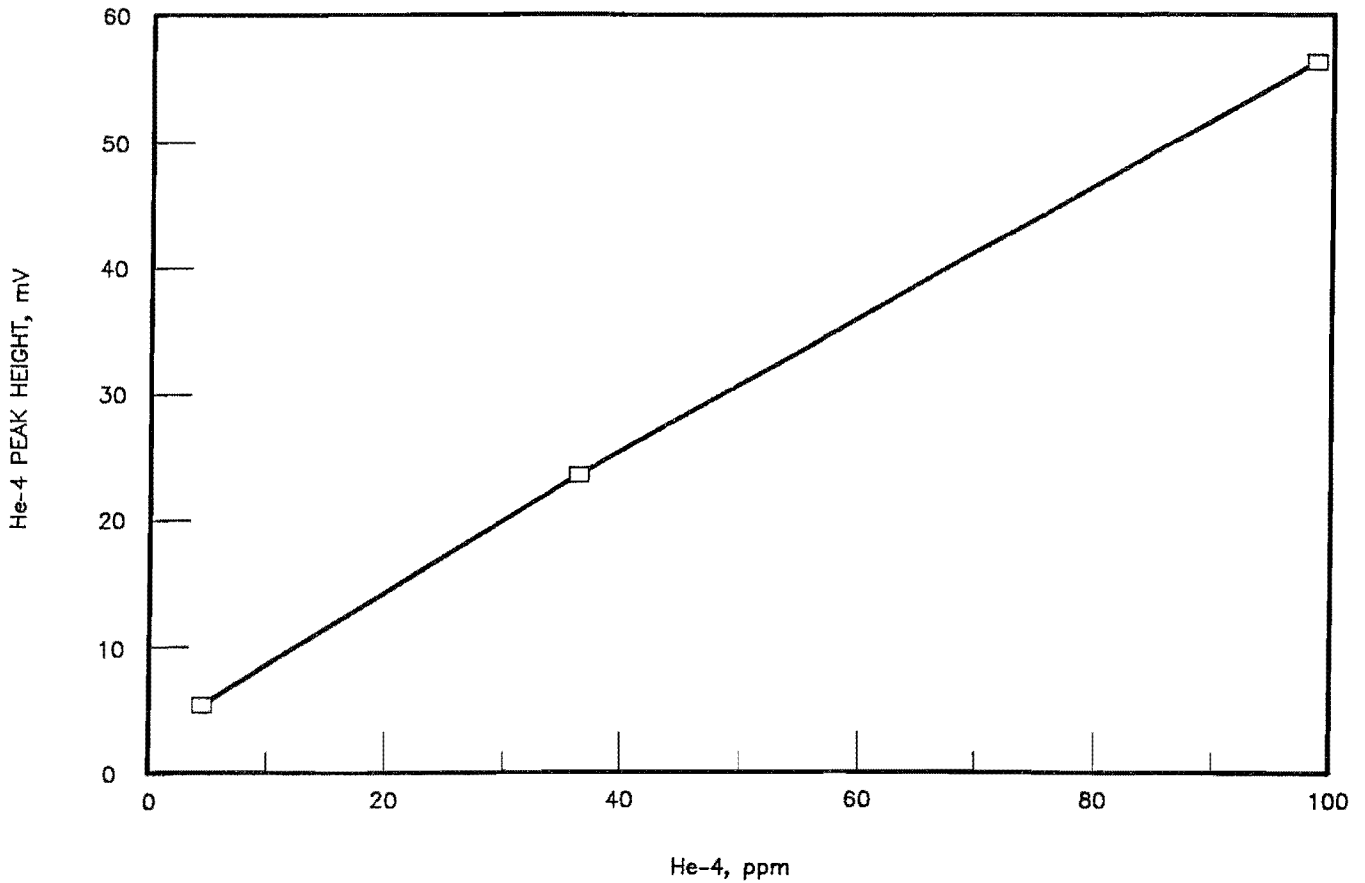


Figure 3.—Linearity of He-4 in H₂ mixtures.

MINIMUM DETECTABLE LIMITS

The minimum detectable limits for the most common impurities in He-3 are shown in table 1.

Table 1.—Minimum detectable limits for impurities in He-3

<u>Component</u>	<u>Minimum detectable limits, ppm</u>	<u>Component</u>	<u>Minimum detectable limits, ppm</u>
Neon	2	Nitrogen	10
Hydrogen	3	Argon	10
Carbon dioxide	5	He-4	2
Oxygen	6		

ANALYTICAL PROCEDURE

The following instrument parameters are used for this study. The magnet current is set at 108.2 mA; the scan voltage range is from 4,318 V to 150 V. A complete scan requires 7 min. A scan for He-4 requires 1 min. Samples and standards are analyzed at a sample pressure of 300 μ Hg.

The sample is scanned for He-4 and compared to the gravimetric standards. An ionizing current of 90 μ A at 70-eV ionizing voltage provides adequate sensitivity. The analog output of the electrometer is displayed graphically on a chart recorder and is simultaneously digitized and stored through the data acquisition system. The chart record is used to calculate He-4 content below 100 ppm; the data acquisition system is used above 100 ppm. Comparing peak heights of the unknowns directly to those of standards provides the concentration of He-4 in the unknowns.

Standard gas mixtures and samples are attached to a metal-bellows-sealed metering valve to introduce the sample into the inlet system. Each analysis is performed according to the sequence shown in table 2. This sequence is used to minimize the possibility of cross-contamination and provide better evaluation of data.

The first two runs are vacuum backgrounds to assure that there are no traces of residual gases from previous

Table 2.—Analytical sequence of standards and samples

Analyte	Number of runs
Vacuum background	2
Standard 1	3
Standard 2	3
Unknown sample	3
Standard 1 or standard 2	3
Unknown sample	3
Standard 1 or standard 2	3

analyses. Fifteen-minute evacuation of the inlet sample reservoir is required between sample runs to remove residual helium. Standards 1 and 2 are run three times each. These standards are selected on the basis of the expected range of He-4 in the sample.

The unknown is run three times, followed by three runs of standard 1 or 2 that bracket the unknown. The unknown is run again three times, followed by the final three runs of the selected standard. The He-4 values for the standard runs before and after the unknown should be within 5% relative error. If the relative error exceeds 5%, the sample analysis must be repeated.

CALCULATIONS

The concentration of He-4 in an unknown is calculated according to the following equation:

$$X = \frac{Q P_s (H - H_b)}{P (H_s - H_b)}, \quad (1)$$

where X = quantity of He-4 in the unknown (ppm),

Q = quantity of He-4 in the standard (ppm),

P_s = pressure of the standard (run at 300 μ Hg),

P = pressure of the unknown (μ Hg),

H_s = He-4 peak height of the standard (s.d.),

H = He-4 peak height of the unknown (s.d.),

and H_b = He-4 peak height of the background (s.d.).

A standard gas mixture containing 98.1 ppm He-4 (Q) in H_2 was used to determine the He-4 content of a weighed standard containing 37.4 ppm He-4 as an unknown. The standards and samples were run at the same ionizing current and at a sample pressure of 300 μ Hg. The data are shown in table 3.

Table 3.—Sample data for standard containing 98.1 ppm He-4

	P	H	P_s	H_s	H_b
Run 1	317.54	23.0	321.31	56.8	0.5
Run 2	318.75	23.0	319.91	57.0	.5
Run 3	319.37	23.2	318.95	57.2	.5
Run 4	310.19	23.2	317.80	57.0	.5
Run 5	315.39	22.8	323.79	58.7	.5
Run 6	319.55	23.2	303.61	53.0	.5
Mean	316.80	23.0	317.56	56.62	.5
Standard deviation ..	3.58	.18	7.13	1.90	NAp
Relative error	1.13	.78	2.25	3.40	NAp

NAp Not applicable.

Using equation 1, the He-4 concentration in the unknown is calculated as follows:

$$X = \frac{(98.1 \text{ ppm}) (318 \mu \text{ Hg}) (23.0 - 0.5 \text{ s.d.})}{(317 \mu \text{ Hg}) (57.0 - 0.5 \text{ s.d.})}$$

$$X = 38.8 \text{ ppm}$$

The value determined by this method differed from the weighed standard value of 98.1 ppm by 1.4 ppm, which is a relative error of 3.7%.

CONCLUSIONS

An accurate method for determining the content of He-4 in He-3 in the 2- to 100-ppm range was developed. A mixture of He-4 in H₂ provides an accurate and economical method of determining the He-4 content in

He-3. This method was found to be valid below 800- μ -Hg sample inlet pressure. This improved mass spectrometer procedure provides a method that is accurate to $\pm 5\%$.

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