RI 8643

Bureau of Mines Report of Investigations/1982

Gravimetric Preparation of Primary Standard Gas Mixtures in the Parts per Trillion Range

By Ernest W. Loya, Charles A. Seitz,
and David E. Emerson

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8643

Gravimetric Preparation of Primary Standard Gas Mixtures in the Parts per Trillion Range

By Ernest W. Loya, Charles A. Seitz,
and David E. Emerson

March 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary

BUREAU OF MINES
Robert C. Horton, Director

This publication has been cataloged as follows:

Loya, Ernest W

Gravimetric preparation of primary standard gas mixtures in the parts per trillion range.

(Report of investigations ; 8643)

Includes bibliographical references.

Supt. of Docs. no.: I 28.23:8643.

1. Helium—Analysis. 2. Chemistry, Analytic—Quantitative. I. Seitz, Charles A. II. Emerson, David E. III. Title. IV. Series: Report of investigations (United States. Bureau of Mines) ; 8643.

TN23.U43 [QD181.H4] 622s [546'.75165] 81-607160 AACR2

CONTENTS

TABLE

GRAVIMETRIC PREPARATION OF PRIMARY STANDARD GAS MIXTURES IN THE PARTS PER TRILLION RANGE

by

Ernest W. Loya,[1] Charles A. Seitz,[1] and David E. Emerson[2]

ABSTRACT

A method for preparing gravimetric primary standards of helium in the parts per trillion range has been developed by the Bureau of Mines. The standards are used to calibrate a specially modified mass spectrometer used in determining the abundance of helium-3 and helium-4 in geochemical samples and of helium-3 in isotopically purified helium-4. The desired gas standards are prepared in 5-kg metal cylinders filled to 1,800 psia. Relative errors of less than 1 pct have been attained in the parts per trillion range using a successive dilution technique.

INTRODUCTION

This report describes an accurate method for preparing primary gas standards in the parts per trillion (ppt) range. A single-pan, high-capacity balance is used to weigh a 5-kg cylinder containing the desired gases. The primary standard mixtures are used to calibrate a CEC-type[3] 21-103 mass spectrometer modified by the Bureau for the analysis of helium in the parts per trillion range.

J. E. Miller, A. J. Carroll, and D. E. Emerson[4] reported a method for preparing gravimetric standards utilizing a double-pan balance with a sensitivity of 0.012 gram. They reported an accuracy of ±0.05 mole-pct or better per component in a mixture in the percent range and ±1 pct in the parts per million (ppm) range.

V. S. Gurvich[5] used a gravimetric method to prepare low concentration

---

[1] Chemist.

[2] Chief, Section of Research and Analytical Services.

All authors are with the Division of Helium Operations, Bureau of Mines, Amarillo, Tex.

[3] Reference to specific equipment is for identification only and does not constitute endorsement by the Bureau of Mines.

[4] Miller, J. E., and A. J. Carroll, and D. E. Emerson. Preparation of Primary Standard Gas Mixtures for Analytical Instruments. BuMines RI 6674, 1965, 10 pp.

[5] Gurvich, V. S. (Preparation of Standard Gaseous Mixtures of Low Concentrations.) Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim, Nauk 1969, No. 2, 165-168; abs. in Chem. Abs., v. 71, October 1969, No. 76979n.

mixtures (0.1- to 1.5-pct argon in carbon dioxide) for mass spectrometer calibration.

H. G. Guillaume[6] reported the preparation of gravimetric standards utilizing a technique sensitive to ±0.1 gram. Standards with accuracies of ±0.001 pct were claimed for mixtures in the percent range.

M. E. Daines[7] prepared gravimetric mixtures with components as low as 20 ppm by the use of a double- or triple-dilution technique. A 200-gram and 1-kg constant-load balance were utilized in obtaining mixtures with accuracies of about ±1 pct.

The method described in this report utilizes a 12-kg single-pan balance with a readability of 0.001-gram and a sensitivity of 0.003 gram. This method reduces the relative error to less than 1 pct when preparing primary standard mixtures containing components with concentrations as low as the parts per trillion level.

APPARATUS

A precise, 12-kg, substitution balance with crossed flexure pivots is utilized to provide a balance of both high sensitivity and ruggedness. The instrument is supplied with a set of weights of Class M construction and Class S tolerance specifications ranging from 1 gram to 1 kg. Weighings below 1 gram are accomplished by the use of a force-balance transducer that restores the weigh beam to a preset null position. Therefore, the force required to null the beam is a measure of the fractional gram needed to complete a weight determination. The absolute inaccuracies of the weights are determined by calibration against National Bureau of Standards certified Class M weights. Corrections for these inaccuracies are applied in the calculation.

The primary standard cylinders weigh about 5 kg, having a volume of approximately 4 liters and a capacity of approximately 490 standard liter-atmospheres at a working pressure of 1,800 psia.

All the cylinders are fitted with forged-body regulating valves with stainless steel stems. To assure that the cylinder tare weight remains constant between weighings, all connections are made with stainless steel fittings, and the cylinder is handled with a lintless cloth.

---

[6] Guillaume, H. G. Very Accurately Defined Gas Mixtures for Use as Primary Standards. Pres. at Pittsburgh Conf. Anal. Chem. and Appl. Spectrosc., Pittsburgh, Pa., Mar. 2-6, 1964, 7 pp.; copies available from the Bureau of Mines Division of Helium Operations, Amarillo, Tex.

[7] Daines, M. E. Methods, Apparatus: New Product Research, Process Development and Design. The Preparation of Standard Gas Mixtures By a Gravimetric Technique. Chem. & Ind. (London), No. 31, Aug. 2, 1969, pp. 1047-1053.

BLENDING TECHNIQUE

The initial primary standard mixture in a series of dilutions is prepared from high-purity gases. It is essential that the gases used form homogeneous mixtures and do not react chemically with each other or with the cylinder. The following procedure is used in the preparation of each mixture. The cylinder is evacuated and weighed. Each required gas is added to the cylinder to a predetermined partial pressure. After the addition of each gas, the cylinder is allowed to equilibrate to the balance temperature; then it is weighed three or more times. The following parameters are measured and recorded during each weighing so that buoyancy corrections can be determined and applied: mass of the weights used, volume of the cylinder, barometric pressure, temperature of balance upper chamber (chamber housing pan and cylinder), temperature of balance lower chamber (chamber housing balance weights), relative humidity of upper chamber, and relative humidity of lower chamber.

Parts per trillion mixtures are prepared by diluting the initial primary standard mixture with a pure gas. The same diluent gas is used throughout a series of dilutions, if possible. Thus the diluent serves as a "zero" or "background" gas that can be compared with the final primary standard in calibrating the analytical instrument.

The mass of each gas is calculated by difference, and the number of moles and mole fraction are determined for each component.

DISCUSSION AND RESULTS

When a primary standard mixture is prepared, a particular sequence of dilutions is selected to minimize the error of the final mixture. The factors to be considered when making the sequence selections are (1) availability of gases, (2) availability of containers, (3) volume of containers, (4) density of gases, and (5) pressure rating of cylinders.

The results shown in table 1 are from a set of dilution sequences from each of two primary standard mixtures of parts per trillion of helium-3 in nitrogen. The helium-3 content of the diluent gas used in mixture 1 was determined by mass spectrometry to be less than the minimum detectable limit of 0.2 ppt. The accumulated error in the four-step dilution was calculated to be 0.85 pct; however, this increased to 1.18 pct when the maximum uncertainty of the helium-3 content of the diluent gas was considered. In mixture 2, the helium-3 content of the diluent gas was determined by mass spectrometry to be less than the minimum detectable limit of 0.6 ppt. When the maximum uncertainty was applied, the accumulated helium-3 concentration was 16.27±0.61 pct with an accumulated relative error of 3.75 pct.

TABLE 1. - Dilution sequences for two primary standard mixtures of parts per trillion of helium-3 in nitrogen[1]

	Helium-3 concentration	Relative error, pct
MIXTURE 1		
Dilution:		
1...............	2.0875±0.0051 pct	0.24
2...............	22.29 ± .12 ppm	.54
3...............	21.47 ± .15 ppb	.70
4...............	23.44 ± .20 ppt	.85
Cumulative[2]..	23.64 ± .28 ppt	1.18
MIXTURE 2		
Dilution:		
1...............	2.0875±0.0051 pct	0.24
2...............	18.132 ± .087 ppm	.48
3...............	16.43 ± .11 ppb	.67
4...............	15.67 ± .12 ppt	.77
Cumulative[2]..	16.27 ± .61 ppt	3.75

[1] Dilutions 1 through 4 of mixture 1 and dilution 1 of mixture 2 were prepared with helium-3 and nitrogen determined to be 99.946±0.022 pct and 99.957±0.033 pct pure, respectively; dilutions 2 through 4 of mixture 2 were prepared with nitrogen determined to be 99.977±0.018 pct pure.

[2] With maximum uncertainty applied.

These results are typical for the preparation of multidilution primary standard mixtures in the parts per trillion range. The accuracy of the procedure is limited primarily by the sensitivity of the balance and the purity of the gases used. Changes in buoyancy of the cylinder are determined by calculating the air density, volume of the cylinder, and volume of the weights used in each weighing. In the preparation of 60 mixtures, the change in buoyancy was as high as 0.0968 gram, with an average of 0.0269 gram.

CONCLUSIONS

The Bureau of Mines has developed a method for preparing gravimetric primary standard mixtures in the parts per trillion range. The use of this multidilution technique has not only facilitated the preparation of low-level primary standard gas mixtures but has also reduced the relative error to less than 1 pct. The method is limited only by the purity of gases and the sensitivity and precision of the balance used.

☆U.S. GOVERNMENT PRINTING OFFICE: 1982 - 505 - 002/22

INT.-BU.OF MINES,PGH.,PA. 25959