An Improved Method for Determining Helium in Water

By Philip W. Holland
Mission: As the Nation’s principal conservation agency, the Department of the Interior has responsibility for most of our nationally-owned public lands and natural and cultural resources. This includes fostering wise use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also promotes the goals of the Take Pride in America campaign by encouraging stewardship and citizen responsibility for the public lands and promoting citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. Administration.
An Improved Method for Determining Helium in Water

By Philip W. Holland
CONTENTS

Abstract ........................................................................................................... 1
Introduction ....................................................................................................... 2
Acknowledgment ............................................................................................ 2
Apparatus description ..................................................................................... 2
Procedures ........................................................................................................ 3
  Sample collection .......................................................................................... 3
  Gas extraction and addition of diluent gas ..................................................... 5
  Extracted-gas analysis .................................................................................. 5
  Calibration .................................................................................................... 6
Calculations ....................................................................................................... 6
Discussion of results .......................................................................................... 7
  Calibration curve .......................................................................................... 7
  Determination of helium-extraction efficiency ............................................. 7
  Precision of ground-water analysis ............................................................... 8
  Accuracy of ground-water analysis .............................................................. 9
Conclusions ...................................................................................................... 9
References ....................................................................................................... 9

ILLUSTRATIONS

1. Diagram of gas-extraction apparatus and mass spectrometer system .......... 3
2. Cutaway view of water sample container and filling funnel ....................... 4
3. Linear regression plot of calculated helium-in-water contents versus extracted-gas helium contents ... 8

TABLES

1. Time-programmed integrator commands for valve sequencing .................. 5
2. Integration parameters for peak quantification and plotting ....................... 6
3. Composition of gaseous standards used to prepare helium-in-water standard solutions ........................................... 6
4. Calculated helium-in-water contents of calibration solutions and their corresponding "extracted-gas" helium contents ................................................................. 7
5. Determination of helium-extraction efficiency ........................................... 7
6. Precision of helium-in-ground-water analysis ............................................ 9
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>degree Celsius</td>
<td>mm</td>
<td>millimeter</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
<td>mm Hg</td>
<td>millimeter of mercury</td>
</tr>
<tr>
<td>cm³</td>
<td>cubic centimeter</td>
<td>pct</td>
<td>percent</td>
</tr>
<tr>
<td>cm³ (STP)</td>
<td>cubic centimeter at standard temperature and pressure</td>
<td>ppb</td>
<td>part per billion</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
<td>ppm</td>
<td>part per million</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
<td>psig</td>
<td>pound per square inch (gauge)</td>
</tr>
<tr>
<td>in</td>
<td>inch</td>
<td>µV</td>
<td>microvolt</td>
</tr>
<tr>
<td>L</td>
<td>liter</td>
<td>W</td>
<td>watt</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
AN IMPROVED METHOD FOR DETERMINING HELIUM IN WATER

By Philip W. Holland

ABSTRACT

The U.S. Bureau of Mines has developed an improved method for determining dissolved helium in water in the concentration range of $4.0 \times 10^{-8}$ to $270 \times 10^{-8} \text{ cm}^3 \text{ He (STP)/cm}^3 \text{ H}_2\text{O}$. The method is a modification of a previously reported method that was developed for analyzing surface and subsurface waters in geochemical survey work. Water samples are collected in 500-cm$^3$ stainless steel cylinders, and the dissolved gases in a sample are extracted into an evacuated cylinder of equal volume. After addition of 30 psig of nitrogen containing less than 2 ppb helium to the extracted gases, the resulting mixture is analyzed for helium using a helium-tuned mass spectrometer. The helium content of the water sample is determined from an empirical calibration that is established by analyzing standard solutions of helium in water. The accuracy of the method is ±7 pct for helium-in-water concentrations above $10 \times 10^{-8} \text{ cm}^3 \text{ He (STP)/cm}^3 \text{ H}_2\text{O}$. 

INTRODUCTION

The U.S. Bureau of Mines has published the results of reconnaissance geochemical helium surveys that were conducted in the vicinity of the Bush Dome helium storage reservoir in the Cliffside Gasfield (1). The surveys revealed that some of the ground waters were anomalously "high" in dissolved helium. The anomalous helium-in-water concentrations averaged about 20 times the air-equilibrated water concentration. The Bureau is investigating the use of soil-gas and ground-water helium measurements as an additional technique for monitoring the Bush Dome reservoir. This report describes an improved mass spectrometric method that is used to determine dissolved helium in water.

Several mass spectrometric methods for the analysis of helium in natural waters are reported in the literature. Dyck (2), Reimer (3), Martin (4), and Butt (5) assembled portable helium mass spectrometers for evaluating measurements of helium in natural waters as an aid in uranium reconnaissance surveying. Pogorsky (6) developed a proprietary mass spectrometer system for analyzing natural waters for helium as a technique for locating uranium and petroleum deposits. Lupton (7) and Craig (8) have described a mass spectrometer method used for determining helium isotopes in seawater as evidence of mantle helium injection at oceanic spreading centers and subduction zones, respectively.

The method described in this report is a modification of a previous Bureau-developed method for determining helium in water (9). This method is an improvement in that (1) the internal standard of pure neon is not required, (2) a semiportable, helium-tuned mass spectrometer having a precision of ±1 ppb is utilized for the helium determinations, and (3) the analysis time per sample is reduced from 1 h to 30 min. Although the method is designed for analysis of helium-in-water concentrations over the range of $4.0 \times 10^8$ to $270 \times 10^8$ cm$^3$ He (STP)/cm$^3$ H$_2$O, the analytical parameters can be adjusted to extend the range.

ACKNOWLEDGMENT

The author expresses his sincere thanks to Dr. Alan A. Roberts for his suggestions and calculations for determining the helium extraction efficiency for the method. Dr. Roberts is the chief geochemist for Comap Exploration Services, Inc., Lakewood, CO.

APPARATUS DESCRIPTION

A diagram of the gas extraction apparatus, inlet system, and mass spectrometer is shown in figure 1. Cylinders N and O are standard 500-cm$^3$ stainless steel gas-sampling cylinders with 1/4-in female pipe openings. Cylinder O, the water sample container, is single-ended and fitted with ball valve 8. Cylinder N, the extracted-gas container, is double-ended and connected to cylinder O through the ball valve. A portion of the dissolved gases extracted from the water sample is admitted from cylinder N to the mass spectrometer inlet system through the moisture-removal trap M. The trap is a 15-cm by 0.5-cm-ID stainless steel tube containing approximately 2 g of anhydrous magnesium perchlorate.

The inlet system of the mass spectrometer consists of calibration standard inert port A, sample inlet port B, stream-switching valve 1, sample valve 2, and air-switching solenoid valves 4 and 5. Valves 1 and 2 are sliding-piston, eight-port chromatograph valves with Fluorel o-ring seals. These valves are actuated by compressed air (30 psig) supplied through valves 4 and 5.

Valve sequencing and switching are accomplished using a Hewlett-Packard model 3390A programmable reporting integrator and model 19400A event-control module. Time-programmed commands from the integrator control the switching of valves 5 and 4, thereby controlling the operation of stream-switching valve 1 and sample valve 2, respectively. The sequencing of the valves' operations creates a standard-sample-standard series of analyses.

The flow of calibration standard or sample through sample valve 2 is controlled using the cylinder metering valves 6 and 7, respectively. The flow rate through the sample loop is maintained at 10 to 25 cm$^3$/min prior to expansion of the sample into the mass spectrometer. Tests have shown that flow rates as high as 35 cm$^3$/min and as low as 5 cm$^3$/min have no detectable effect on the analytical precision.

The mass spectrometer is connected to the inlet system through charcoal trap E. The trap is a 0.64-cm-OD (0.10-cm-wall) by 56-cm-long stainless steel U-tube with a 0.95-cm-OD (0.10-cm-wall) by 5-cm "bulb" about 3 cm from the base. The bulb contains approximately 2 g of 40/60-mesh activated charcoal and is submerged in liquid nitrogen. At liquid nitrogen temperature, gases other than helium and neon are adsorbed by the charcoal; thus, use

---

3"Helium" in this report refers to the isotope helium-4.
4Italics numbers in parentheses refer to items in the list of references at the end of this report.
5Atmosphere-equilibrated water at 25° C and 760 mm Hg contains $4.5 \times 10^8$ cm$^3$ He (STP)/cm$^3$ H$_2$O.
6Reference to specific manufacturers or trademarks does not imply endorsement by the U.S. Bureau of Mines.
Figure 1.—Diagram of gas-extraction apparatus and mass spectrometer system.

the trap allows a larger volume of sample to be admitted to the mass spectrometer.

The mass spectrometer is a modified Consolidated Electrodynamic Corp. model 24-120A helium leak detector. Assembly of the mass spectrometer system and subsequent modifications made to improve its performance were described previously (10-11). The mass spectrometer was developed for trace analysis of helium in the range of 0.5 to 20,000 ppb. Performance tests have shown the precision for 10 successive analyses at the 5,000-ppb helium level to be routinely ±1 ppb (10). The instrument was demonstrated to be linear over the range of about 50 to 7,000 ppb helium.

PROCEDURES

SAMPLE COLLECTION

To obtain a water sample, the filling funnel is inserted into the sample container as shown in figure 2. Prior to sampling, the container is placed in a bath of the freshly collected sample water, filled to overflowing with the sample water, then allowed to stand for 5 min. This procedure rinses the interior of the container with the water to be sampled and allows the temperature of the container to approach that of the sample water. The container is then emptied, resubmerged in the water bath, and filled to overflowing with freshly collected sample water. The sample water is poured slowly into the funnel to minimize air-water turbulence. As soon as the container overflows, the funnel is removed, and the ball valve is closed to complete the sampling procedure. The samples are stored at room temperature and analyzed within 48 h from the time of collection.
Figure 2.—Cutaway view of water sample container and filling funnel.
GAS EXTRACTION AND ADDITION OF DILUENT GAS

Since the solubility of gases is temperature dependent, the extraction procedure is performed at 25±2°C. The apparatus is prepared for the extraction procedure as follows: Sample cylinder O is connected to cylinder N as shown in figure 1. With valve 8 closed, the gas extraction apparatus is connected to a mechanical vacuum pump through valve 7, and cylinder N is evacuated to 10⁻⁴ torr. After N is evacuated, valve 7 is closed and the apparatus is disconnected from the vacuum pump.

To perform the extraction, valve 8 (fig. 1) is opened, and the gas extraction apparatus is inverted to allow the water sample in cylinder O to flow to cylinder N. After cylinder O is emptied, the apparatus is re-inverted, allowing the contents of cylinder N to return to cylinder O. Ten inversions are performed to achieve equilibration between the liquid and gaseous phases (9). After the final inversion, the apparatus is left in the vertical position for 5 min to allow residual water in cylinder N to drain into cylinder O. Valve 8 is then closed.

Nitrogen containing less than 2 ppb helium is added to the extracted gases in cylinder N to increase the total pressure to 30.0±0.2 psig. The diluent nitrogen is admitted to N from a high-pressure supply using a dual-stage pressure regulator equipped with a stainless steel diaphragm. The secondary of the regulator is fitted with a 0- to 30-psig gauge having a readability of 0.1 psi and an accuracy ±0.5 pct of span.

Addition of the diluent nitrogen is performed at 25±2°C. Since the same diluent nitrogen is added to the extracted gases of unknown samples and to the extracted gases of the calibration solutions, a correction to account for the helium present in the diluent is not required. After addition of the diluent, the resulting gas mixture in N₂ is analyzed for helium as described below.

EXTRACTED-GAS ANALYSIS

The procedures for preparing the mass spectrometer and liquid-nitrogen-cooled charcoal trap for use were described previously (10). A weighed primary standard (12) having a helium content that approximates that of the extracted gas mixture is selected as a reference gas. The determination of helium in the gas extracted from a water sample is performed as follows: The calibration standard and sample gas supply lines are connected to inlet ports A and B, respectively, as shown in figure 1. Moisture-removal trap M is inserted between the sample gas cylinder and supply line. By keying an "Ext 7" command at the integrator keyboard, valve 1 is switched to allow measurement of the reference gas flow with rotameter C. Using valve 6, the reference gas flow is set at 10 to 25 cm³/min. Using an "Ext -7" command, valve 1 is then switched to allow measurement of the sample gas flow with the rotameter. The sample gas flow is set at 10 to 25 cm³/min by adjusting valve 7.

Alternate analysis of the reference and sample gas is automated using the time-programmed sequence of valve operations shown in table 1. The time-programmed commands and their respective times of execution are entered into the integrator memory via keyboard. The integration parameters are set as shown in table 2. The integrator's "peak-height mode" option is used so that the helium peaks are shown by height counts. The integrator's "automatic runs" option is activated to cause the programmed sequence of valve operations to be repeated after an analysis sequence is completed. The sequence is repeated continuously until manually terminated.

Table 1.-Time-programmed integrator commands for valve sequencing¹

<table>
<thead>
<tr>
<th>Integrator command</th>
<th>Time of execution (from start of run), min</th>
<th>Operation¹</th>
<th>Result of operation¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ext 7</td>
<td>0.01</td>
<td>Air &quot;on&quot; to valve 1.</td>
<td>Purge sample loop with reference gas.</td>
</tr>
<tr>
<td>Ext 5</td>
<td>0.50</td>
<td>Air &quot;on&quot; to valve 2.</td>
<td>Expand reference gas into mass spectrometer.</td>
</tr>
<tr>
<td>Ext -5</td>
<td>2.50</td>
<td>Air &quot;off&quot; to valve 2.</td>
<td>Return valve 2 to purge position.</td>
</tr>
<tr>
<td>Ext -7</td>
<td>2.51</td>
<td>Air &quot;off&quot; to valve 1.</td>
<td>Purge sample loop with sample.</td>
</tr>
<tr>
<td>Ext 5</td>
<td>3.00</td>
<td>Air &quot;on&quot; to valve 2.</td>
<td>Expand sample into mass spectrometer.</td>
</tr>
<tr>
<td>Ext -5</td>
<td>5.00</td>
<td>Air &quot;off&quot; to valve 2.</td>
<td>Return valve 2 to purge position.</td>
</tr>
</tbody>
</table>

¹The time-programmed integrator commands are for a Hewlett-Packard model 3390A integrator.
²References are to valves 1 and 2 as shown in figure 1.
Table 2.—Integration parameters for peak quantification and plotting

<table>
<thead>
<tr>
<th>Integrator parameter key</th>
<th>Description of parameter</th>
<th>Parameter setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK WD</td>
<td>Peak width—time width of peak at half height (min)</td>
<td>0.01</td>
</tr>
<tr>
<td>THRSH</td>
<td>Threshold—discrimination level for eliminating signal changes regarded as noise. (Values entered are integer powers of 2.)</td>
<td>3</td>
</tr>
<tr>
<td>ATT 2</td>
<td>Attenuation—plot height scale. (Values entered are integer powers of 2.)</td>
<td>0-10</td>
</tr>
<tr>
<td>CHT SP</td>
<td>Chart speed—plot width scale (cm/min).</td>
<td>.5</td>
</tr>
</tbody>
</table>

The integration parameters are for a Hewlett-Packard model 3390A integrator.

CALIBRATION

An empirical calibration for the method is established by analyzing a series of six helium-in-water standard solutions. The solutions are prepared by bubbling gaseous standards of helium in air or helium in nitrogen through distilled water at room temperature and atmospheric pressure. The helium contents (with limits of uncertainty) of the gaseous standards used to prepare the solutions are given in table 3. This range of gaseous standards was chosen to result in solutions containing from about $4.0 \times 10^{-8}$ to $270 \times 10^{-8}$ cm$^3$ He (STP)/cm$^3$ H$_2$O. The apparatus and techniques used for preparing the solutions were described by Holland (9). A linear regression plot of the calculated helium-in-water contents of the solutions versus their corresponding "extracted-gas" helium contents establishes the calibration curve for the method.

Table 3.—Composition of gaseous standards used to prepare helium-in-water standard solutions

<table>
<thead>
<tr>
<th>Gaseous standard</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.2204 ± 0.0041 ppm He in air.</td>
</tr>
<tr>
<td>B</td>
<td>56.6 ± 1.0 ppm He in nitrogen.</td>
</tr>
<tr>
<td>C</td>
<td>124 ± 2 ppm He in nitrogen.</td>
</tr>
<tr>
<td>D</td>
<td>158 ± 2 ppm He in nitrogen.</td>
</tr>
<tr>
<td>E</td>
<td>318 ± 4 ppm He in air.</td>
</tr>
<tr>
<td>F</td>
<td>360 ± 4 ppm He in nitrogen.</td>
</tr>
</tbody>
</table>

*Concentration of helium in atmospheric air determined by Holland (13).*

CALCULATIONS

The helium content of the extracted gas mixture obtained from a water sample is calculated using the equation

$$\text{He}_x = \frac{\text{He}_s \cdot D_x}{D_{s<1>} + D_{s<2>}} \quad (1)$$

where $\text{He}_x$ = helium content of the extracted gas mixture, ppb,

$\text{He}_s$ = helium content of the calibration standard, ppb,

$D_{s<1>}$ = helium peak height from first analysis of the calibration standard, $\mu$V,

$D_{s<2>}$ = helium peak height from second analysis of the calibration standard, $\mu$V,

and $D_x$ = helium peak height from analysis of the gas mixture extracted from the water sample, $\mu$V.

The helium concentration in a water sample is determined using the helium content of the extracted gas ($\text{He}_x$) and the linear regression plot of the calibration data as given in the equation

$$C_{\text{He}} = A + B \cdot \text{He}_x \quad (2)$$

where $C_{\text{He}}$ = helium concentration in the unknown water sample, cm$^3$ He (STP)/cm$^3$ H$_2$O,

$A$ = zero-intercept value for linear regression plot of calibration data, cm$^3$ He (STP)/cm$^3$ H$_2$O,

$B$ = slope of linear regression plot of calibration data, cm$^3$ He (STP)/cm$^3$ H$_2$O-ppb,

and $\text{He}_x$ = helium content of the extracted gas mixture obtained from the unknown water sample, ppb.
DISCUSSION OF RESULTS

CALIBRATION CURVE

A series of six standard solutions of helium in water were prepared and used to establish the calibration curve for the method. The solutions were prepared to contain from $4.0 \times 10^{-8}$ to $273 \times 10^{-8} \text{ cm}^3 \text{He (STP)/cm}^3 \text{H}_2\text{O}$ with the accuracies indicated in table 4. Triplicate samples of each solution were collected, and the dissolved gases were extracted, and diluted with nitrogen to a pressure of 30 psig; then determinations of the helium contents were performed. The analyzed "extracted-gas" helium contents of the calibration solutions are also given in table 4.

A linear regression plot of the calculated helium-in-water contents versus the "extracted-gas" helium contents is shown in figure 3. The slope of the curve is $0.302 \times 10^{-8} \text{ cm}^3 \text{He (STP)/cm}^3 \text{H}_2\text{O}$-ppb, and the zero-intercept value is $0.4 \times 10^{-8} \text{ cm}^3 \text{He (STP)/cm}^3 \text{H}_2\text{O}$. The correlation coefficient for the curve is 0.9999. This curve (equation) was used for calculating the helium-in-water contents of ground-water samples that were subsequently analyzed in this study.

DETERMINATION OF HELIUM-EXTRACTION EFFICIENCY

The extraction efficiency for removing dissolved helium from the water samples is shown in table 5. The determination was accomplished using the results obtained from analysis of the calibration solutions. The extraction efficiency was calculated using the equation

$$X_{\text{Eff}} = \frac{C_{\text{He(g)}}}{C_{\text{He(s)}} \cdot V(s)} \cdot 100,$$

where $X_{\text{Eff}}$ is the extraction efficiency, pct,

$C_{\text{He(g)}}$ is the analyzed helium content of the diluted extracted gases minus the helium present in the diluent nitrogen, ppb (column E, table 5),

$C_{\text{He(s)}}$ is the theoretical dissolved helium content of the calibration solution, cm$^3$ He (STP)/cm$^3$ H$_2$O (column A, table 5),

$V(s)$ is the internal volume of the water-sampling container, 500 cm$^3$, and

$V(g)$ is the volume that 30 psig of an ideal gas in the gas-extraction container would occupy at STP, 1,520 cm$^3$.

Table 4.-Calculated helium-in-water contents of calibration solutions and their corresponding "extracted-gas" helium contents

<table>
<thead>
<tr>
<th>Calibration solution</th>
<th>Calculated helium-in-water content, $10^{-8}$ cm$^3$ He (STP)/cm$^3$ H$_2$O</th>
<th>Accuracy, pct</th>
<th>&quot;Extracted-gas&quot; mean helium content and precision, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ...................</td>
<td>4.0±0.003</td>
<td>±0.1</td>
<td>16.5±0.5</td>
</tr>
<tr>
<td>B ...................</td>
<td>42.0±0.7</td>
<td>±1.7</td>
<td>135±3</td>
</tr>
<tr>
<td>C .............</td>
<td>84.0±1.5</td>
<td>±1.8</td>
<td>274±4</td>
</tr>
<tr>
<td>D .............</td>
<td>119±2</td>
<td>±1.7</td>
<td>391±6</td>
</tr>
<tr>
<td>E .............</td>
<td>242±3</td>
<td>±1.2</td>
<td>809±9</td>
</tr>
<tr>
<td>F .............</td>
<td>273±3</td>
<td>±1.1</td>
<td>898±7</td>
</tr>
</tbody>
</table>

Table 5.-Determination of helium-extraction efficiency

<table>
<thead>
<tr>
<th>Dissolved helium content of calibration solution, $10^{-8}$ cm$^3$ He (STP)/cm$^3$ H$_2$O</th>
<th>Volume of helium in 500-cm$^3$ aliquot of calibration solution, cm$^3$ (STP)</th>
<th>Calculated concentration of helium in &quot;diluted&quot; extracted gas, ppb</th>
<th>Analyzed concentration of helium in &quot;diluted&quot; extracted gas, ppb</th>
<th>Corrected analyzed concentration of helium in &quot;diluted&quot; extracted gas, ppb</th>
<th>Extraction efficiency, pct</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>2.0 x $10^{-5}$</td>
<td>13</td>
<td>16.5</td>
<td>14.5</td>
<td>110</td>
</tr>
<tr>
<td>42.0</td>
<td>2.10 x $10^{-5}$</td>
<td>138</td>
<td>135</td>
<td>133</td>
<td>96.4</td>
</tr>
<tr>
<td>84.0</td>
<td>4.20 x $10^{-5}$</td>
<td>276</td>
<td>274</td>
<td>272</td>
<td>98.6</td>
</tr>
<tr>
<td>119</td>
<td>5.95 x $10^{-5}$</td>
<td>391</td>
<td>391</td>
<td>399</td>
<td>99.5</td>
</tr>
<tr>
<td>242</td>
<td>1.21 x $10^{-5}$</td>
<td>796</td>
<td>809</td>
<td>807</td>
<td>101</td>
</tr>
<tr>
<td>273</td>
<td>1.37 x $10^{-5}$</td>
<td>898</td>
<td>898</td>
<td>896</td>
<td>99.8</td>
</tr>
</tbody>
</table>
Figure 3.-Linear regression plot of calculated helium-in-water contents versus extracted-gas helium contents.

The values given in column A \((C_{He(s)})\) of table 5 are the theoretical concentrations of dissolved helium in the calibration solutions as shown in table 4.

Calibration of the internal volumes of the water-sampling containers and gas-extraction containers showed the volumes to vary no more than \(\pm 1\) pct from the manufacturer's stated volume of 500 cm\(^3\). Values in column B \((C_{He(s)} \cdot V(s))\) are the calculated volumes of helium, expressed as cm\(^3\) He at standard temperature and pressure (STP), theoretically present in 500-cm\(^3\) aliquots of each calibration solution.

The values in column C \((C_{He(g)} \cdot V(g)/V(g))\) are the calculated theoretical concentrations of helium in the "diluted" extracted gases. The constant, \(V(g)\), is 1,520 cm\(^3\) and is the volume that 30 psig of an ideal gas in a 500-cm\(^3\) container would occupy at STP.

The experimentally determined "extracted-gas" helium contents (obtained from table 4) are given in column D. The nitrogen used in diluting the gases extracted from the calibration solution aliquots was analyzed to contain 2.0±0.4 ppb helium. The values in column E \((C_{He(g)})\) were determined by subtracting 2 ppb from the values in column D.

Dividing the corrected analyzed extracted-gas helium values (column E) by the calculated extracted-gas helium values (column C) results in a theoretical determination of the extraction efficiency \((X_{Eff})\), which is given in column F. Thus, it is concluded that within the experimental error, essentially 100 pct of the dissolved helium is removed from solution by the extraction technique used in this method.

**PRECISION OF GROUND-WATER ANALYSIS**

The precision of helium-in-ground-water analysis was determined by obtaining samples from four windmill-pumped water wells located in the Cliffside Gasfield. The results are given in table 6. The five samples obtained from each well were collected within a 45-min period. All samples were analyzed within 48 h of collection. The standard deviation for the average helium content of the five samples obtained from each well was within \(\pm 5\) pct.
Table 6.-Precision of helium-in-ground-water analysis,
10^{-8} \text{cm}^3 \text{He (STP)/cm}^3 \text{H}_2\text{O}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Well 1</th>
<th>Well 2</th>
<th>Well 3</th>
<th>Well 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>160</td>
<td>126</td>
<td>44.3</td>
<td>14.1</td>
</tr>
<tr>
<td>2</td>
<td>164</td>
<td>118</td>
<td>45.1</td>
<td>13.5</td>
</tr>
<tr>
<td>3</td>
<td>171</td>
<td>126</td>
<td>40.7</td>
<td>13.6</td>
</tr>
<tr>
<td>4</td>
<td>151</td>
<td>113</td>
<td>42.6</td>
<td>12.4</td>
</tr>
<tr>
<td>5</td>
<td>158</td>
<td>115</td>
<td>44.2</td>
<td>13.3</td>
</tr>
<tr>
<td>Average</td>
<td>161</td>
<td>120</td>
<td>43.4</td>
<td>13.4</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>±7</td>
<td>±6</td>
<td>±1.8</td>
<td>±6</td>
</tr>
</tbody>
</table>

ACCURACY OF GROUND-WATER ANALYSIS

The accuracy of the method is dependent on the precision of the method and the accuracy of the standard solutions used to establish the calibration curve. Since the standard solutions used for calibration were accurate to within ±2 pct (table 4), the uncertainty in a single determination is estimated to be within ±7 pct.

CONCLUSIONS

The procedure described in this report provides a precise and reliable method for determining dissolved helium in natural waters. The method was shown to be linear over the investigated range of 4.0 \times 10^{-8} to 273 \times 10^{-8} \text{cm}^3 \text{He (STP)/cm}^3 \text{H}_2\text{O}. The accuracy of the method is ±7 pct for helium-in-water concentrations above 10 \times 10^{-8} \text{cm}^3 \text{He (STP)/cm}^3 \text{H}_2\text{O}. Within the experimental error, essentially 100 pct of the dissolved helium is removed from the water sample by the vacuum extraction technique employed in this method.

REFERENCES