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# An Improved Method and Apparatus for Analysis of Impurities in Helium

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# An Improved Method and Apparatus for Analysis of Impurities in Helium

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# AN IMPROVED METHOD AND APPARATUS FOR ANALYSIS OF IMPURITIES IN HELIUM

by

David E. Emerson,[1] C. A. Hoffman,[2] and G. W. Weems[3]

## ABSTRACT

An improved method and apparatus for determining the impurities in helium by preconcentration and subsequent analysis by mass spectrometry are described. Preconcentration of the impurities is accomplished by passing a known volume of helium, at slightly above atmospheric pressure, through a metal coil and trap assembly immersed in liquid helium. The concentrated impurities are then analyzed by mass spectrometry. This method can detect impurities in the range of 0.01 to 600 ppm with an accuracy of better than ±0.05 ppm at the 1-ppm level. One operator can analyze 15 samples in an 8-hour day.

## INTRODUCTION

There is a growing demand for ultrapure helium in industry, space, and research applications. As this demand increases, new analytical techniques for accurate identification and quantitative determination of impurities in helium in the parts-per-billion range are required. The purpose of this Bureau of Mines work was to develop a more economical and accurate analytical method for determining impurities in helium, using preconcentration with subsequent analysis by a sensitive mass spectrometer.

Gas chromatography is a popular analytical tool for the analysis of impurities in helium, owing to its simplicity and modest cost. Mosen and Buzzelli (2)[4] determined the impurities in helium by concentrating them on activated charcoal at -196° C and subsequently separating them on a 5 A molecular sieve column and detecting their presence by a thermal conductivity-type detector. Purer and Seitz (5) determined the impurities in helium without prior concentration by chromatography with a 1-mv recorder.

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

Purer (4) developed a procedure for the analysis of impurities in helium by combining the advantages of two existing methods, the preconcentration of impurities (1) followed by analysis with a high-sensitivity gas chromatograph as reported by Purer and Seitz (5). This method yields a procedure with sensitivities for hydrogen, methane, neon, nitrogen, oxygen, argon, krypton, and xenon in the parts-per-billion range.

A chromatograph must be calibrated, as some unknown or unexpected impurity could escape detection by being retained in the column or being eluted simultaneously with another component.

Suttle and others (7) used high-pressure mass spectrometry to analyze impurities in helium. The mass spectrometer was calibrated by use of samples that were analyzed by the Bureau of Mines trace impurity method (1). This method is expensive but useful when only a small volume of the sample is available.

The preconcentration method as described by Kirkland, Brandt, and Deaton (1) has been used by the Bureau of Mines since 1959. With this method, it is necessary to determine the volume of each metal coil and trap assembly and to determine a trap-to-mass spectrometer pressure correction factor. Calculations are based on the total sample pressure and they are time consuming.

The method described in this report has reduced the minimum detectable limit to 0.01 ppm. The calculations are less complex and are less time consuming since this study eliminates the use of the total sample pressure, a pressure correction factor, and the specific volume of the metal coil and trap assembly. The results can be completely calculated in 10 minutes. Only one metal coil and trap assembly connected permanently to the apparatus is required. This eliminates possible air contamination when connecting and disconnecting the metal coil and trap as required by the previous method.

It is also more economical. Fifteen or more analyses can be made in an 8-hour day. The previous method (1) required two men to operate a concentrator and a mass spectrometer to analyze 10 samples a day. Additional time was required to calculate the mass spectrometer data.

## ACKNOWLEDGMENTS

We express our sincere thanks and appreciation to J. R. McVey, electronics technician, for his assistance in designing and constructing the liquid helium dewar position controller and to C. A. Seitz, research chemist, for his advice and assistance.

## APPARATUS AND ANALYTICAL PROCEDURE

### Apparatus Description

The basic analytical instrument of the presently described procedure is a CEC model 21-620A[5] mass spectrometer with a metal batch inlet system and a 1,750-gauss magnet. A CEC model 23-105 micromanometer is used with the mass spectrometer. The apparatus described below is essentially the sample preparation portion of the analytical method.

The gas flow diagram of the impurity concentration portion of the analyzer is shown schematically in figure 1. There are eight manually actuated valves, A, B, C, D, E, F, H, and J, a solenoid sample valve, G, a sample valve timer, 5, which is detailed in figure 2, a 1/3-psig back pressure valve, 9, a differential pressure gage, 10, which is used as a flow indicator (3), and a wet test meter, 4. A metal coil and trap assembly (fig. 3) is mounted to an aluminum panel which is secured to a mass spectrometer. The pressure purge and safety pressure relief system shown in figure 4 prevents back diffusion of impurities into the system while purging. It consists of a 15-micron filter, 1, a 1/3-psig relief valve, 2, a helium reservoir, 4, and a 50-psig relief valve, 3. During purging, both pop-off valves allow gas to escape at high velocity, thus reducing back diffusion. They close instantaneously when the flow is stopped. The filter protects both pop-off valves from collecting solids under the seats. The reservoir of the pressure purge system contains helium; therefore, if the 1/3-psi back pressure valve (which acts only as a check valve) should leak, only helium, and not air, would leak into the system. It is necessary in an analyzer of this sensitivity to employ materials and seals that reduce outgassing and leakage to virtually zero. Threaded fittings were coated with Glyptal. Stainless steel was used throughout the system and bellows valves were used whenever possible.

### Liquid Helium Level Controller

A laboratory jack whose height is automatically controlled is used to maintain the liquid helium level at the desired position around the coil and trap assembly. The level of the liquid helium must remain essentially constant to maintain the heat balance of the sample. Too much cooling will liquefy the sample since it is above atmospheric pressure, and too little cooling will not freeze out low-boiling impurities such as neon and hydrogen. The electrical schematic diagram for the automatically controlled laboratory jack is shown in figure 5. A 1/10-watt carbon resistor is used as the sensing device and is attached to the trap. As the liquid helium level drops, the resistance of the carbon changes, causing a change in the signal that is sent to a high-gain operational amplifier which energizes the "up" relay and activates a 1/150-hp DC reversible motor with a 200-to-1 gear reduction ratio. It raises the laboratory jack and the dewar flask of helium so that the sensing resistor remains at the liquid helium level. The jack may be operated either automatically or manually on the "up" travel, but manually only on the "down" travel. Limit switches prevent overloading the motor.

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

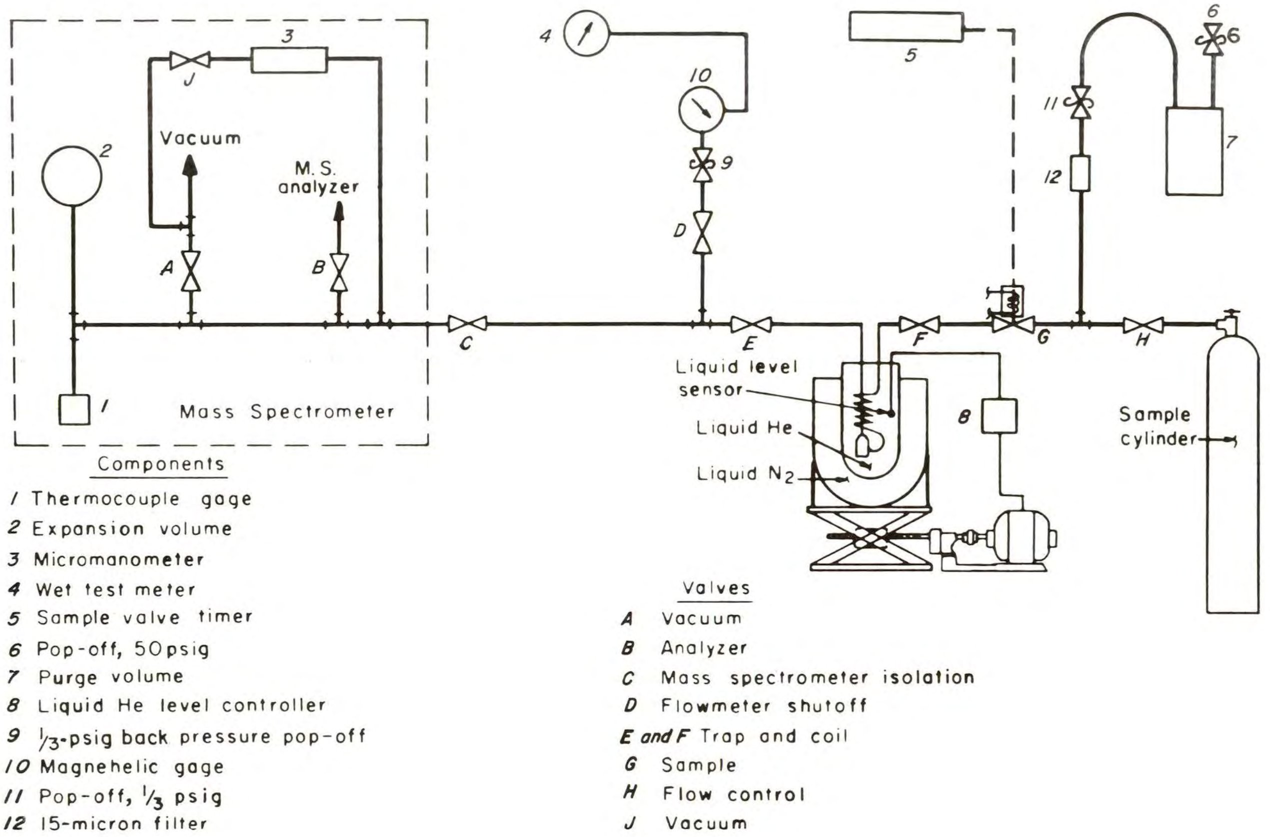

FIGURE 1. - Gas Flow Schematic Diagram.

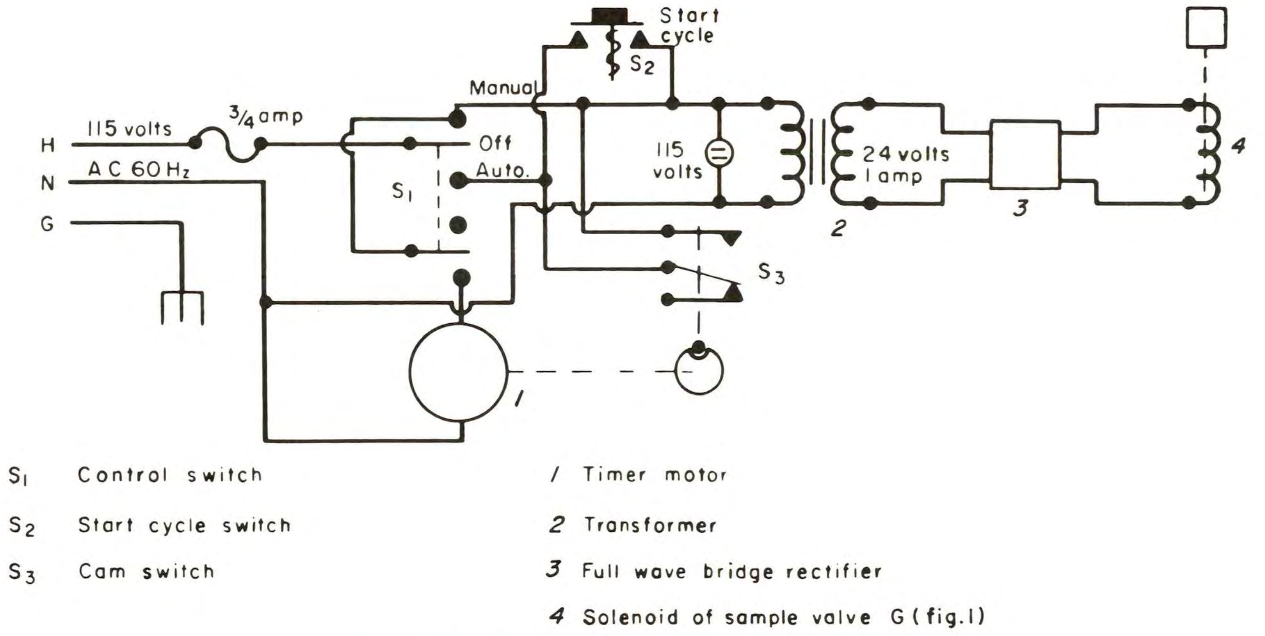

FIGURE 2. - Sample Valve Timer Schematic Diagram.

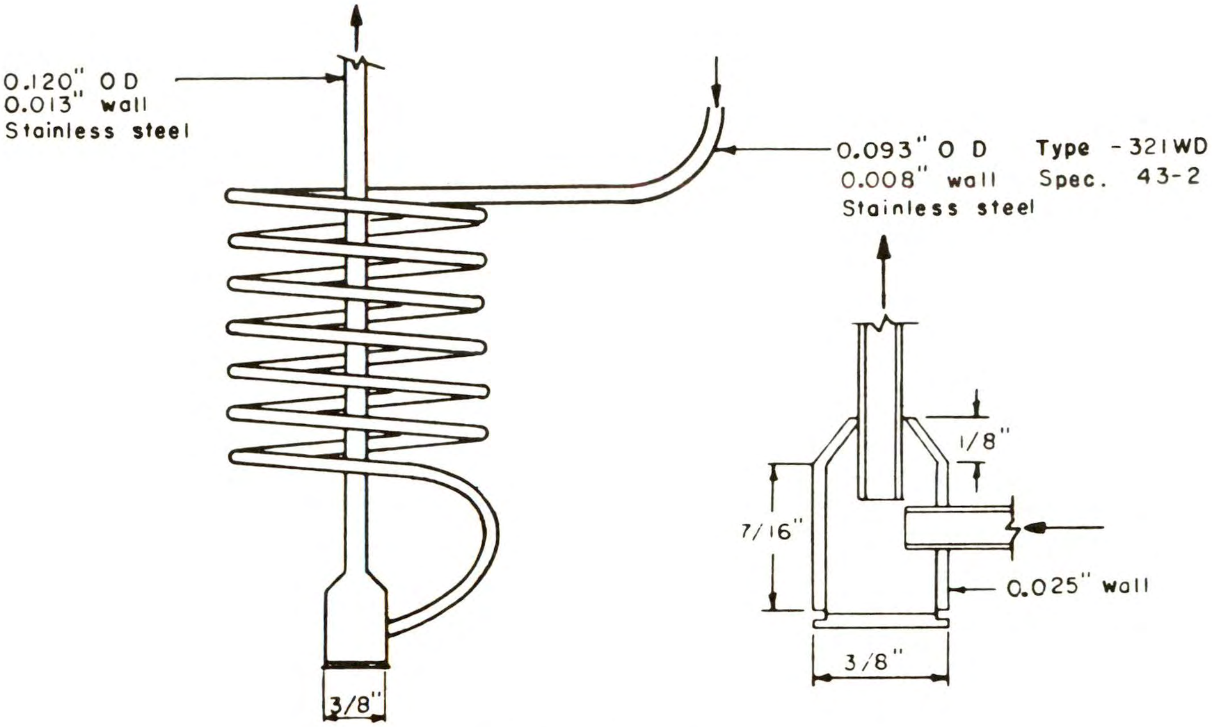

FIGURE 3. - Trap and Coil Assembly.

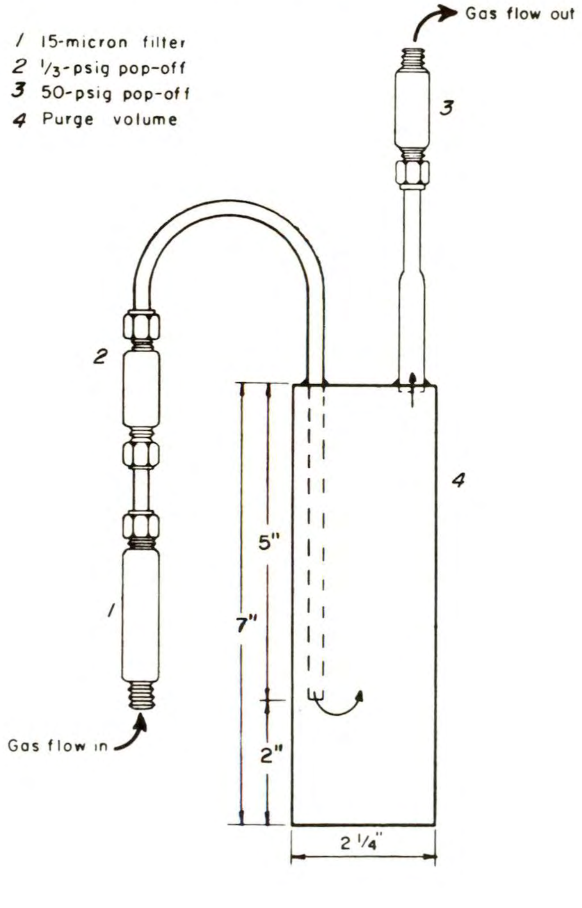

FIGURE 4. - Purge System.

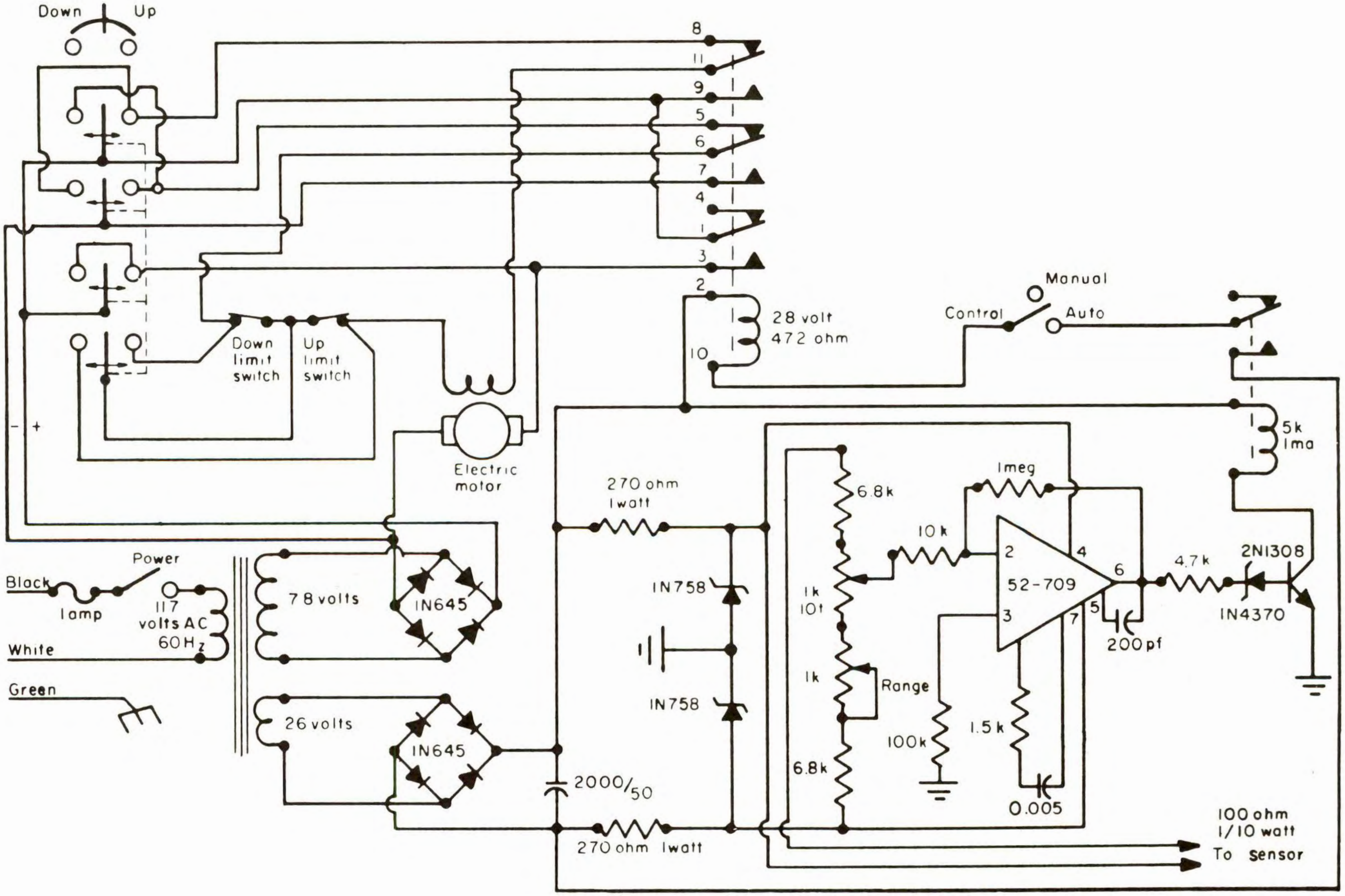

FIGURE 5. - Liquid Helium Level Controller.

## CALCULATIONS

The internal volume of the mass spectrometer inlet system and the apparatus was determined by comparison with a previously calibrated known volume (6). The volume is 2.888 liters.

Mass spectrometer sensitivities were determined by the analysis of pure gases. The ionizing current was set at 20 microamperes, and the resulting sensitivities are given in table 1.

TABLE 1. - Mass spectrometer sensitivities

| Component | Sensitivity[1] |
|---|---|
| Hydrogen | 400.3 |
| Methane | 216.0 |
| Neon | 73.0 |
| Nitrogen | 199.9 |
| Carbon monoxide | 209.1 |
| Ethane | 56.2 |
| Oxygen | 150.6 |
| Argon | 210.6 |
| Carbon dioxide | 159.0 |

[1] $\frac{\text{Peak height, divisions}}{\text{Sample pressure, microns}}$.

These sensitivities vary slightly each day. To correct for these slight variations, a neon calibration gas is analyzed on each operating day and is used as a base to adjust the other sensitivities for that day.

The partial pressure of each impurity is determined by dividing the peak height of the component by its sensitivity as shown in equation 1:

$$\text{partial pressure (mm)} = \frac{\text{peak height (divisions)}}{\text{sensitivity}\left(\frac{\text{divisions}}{\text{micron}}\right)} \times 10^3 \qquad (1)$$

When analyzing a sample by mass spectrometry, the partial pressure of a component in a gas mixture is independent of the total pressure as long as the system is at low pressure and the flow of gas molecules through the gold leak is molecular. Therefore, the impurities in the sample were calculated as follows:

$$\frac{P_2V_2}{P_1V_1} \times 10^6 = \text{ppm of component in sample,} \qquad (2)$$

where $P_1$ = barometric pressure, mm Hg,
$V_1$ = volume of gas passed through apparatus, liters,
$P_2$ = partial pressure of component, mm Hg,
and $V_2$ = calibrated internal volume, 2.888 liters.

For any one analysis, $P_1$, $V_1$, and $V_2$ are constant and may be grouped together for convenience into one factor which will be designated as the factor K.

$$\frac{V_2}{P_1 V_1} \times 10^6 = K \qquad (3)$$

When this factor and the value of $P_2$ are substituted into equation 2, the result is equation 4:

$$\left(\frac{\text{peak height}}{\text{sensitivity}}\right) K = \text{ppm of component in sample.} \qquad (4)$$

The sum of the partial pressures obtained from each component in the sample should equal the total sample pressure obtained with the mass spectrometer micromanometer. This is a normal mass spectrometer procedure to check instrument accuracy.

The reproducibility of this method for each component was checked by analyzing a sample of high-purity helium 12 times. The results are listed in table 2.

TABLE 2. - Precision evaluation

| Analysis | Impurities, ppm | | | | |
|---|---|---|---|---|---|
| | $H_2$ | Ne | $N_2$ | $O_2$ | $CO_2$ |
| 1.................... | 0.054 | 15.69 | 0.263 | 0.059 | 0.024 |
| 2.................... | .054 | 15.92 | .249 | .057 | .024 |
| 3.................... | .056 | 15.91 | .232 | .045 | .025 |
| 4.................... | .058 | 15.76 | .241 | .055 | .022 |
| 5.................... | .057 | 15.90 | .234 | .053 | .021 |
| 6.................... | .055 | 15.98 | .222 | .047 | .022 |
| 7.................... | .055 | 15.86 | .248 | .059 | .020 |
| 8.................... | .056 | 15.86 | .235 | .054 | .023 |
| 9.................... | .055 | 15.82 | .230 | .042 | .022 |
| 10.................... | .054 | 15.69 | .262 | .066 | .022 |
| 11.................... | .055 | 15.81 | .241 | .052 | .021 |
| 12.................... | .054 | 15.93 | .235 | .054 | .024 |
| Mean............. | .055 | 15.84 | .241 | .054 | .022 |
| Standard deviation[1].... | .001 | .09 | .013 | .009 | .002 |

[1] Standard deviation = $\sqrt{\frac{\Sigma(\text{deviations})^2}{n-1}}$.

Ten cylinders of helium were analyzed to compare this method with the Bureau of Mines trace impurity method. The results are listed in table 3.

TABLE 3. - Comparison of analyses with the Bureau of Mines trace impurity method

| Cylinder | This work | Trace imp. method | Δ | This work | Trace imp. method | Δ | This work | Trace imp. method | Δ |
|---|---|---|---|---|---|---|---|---|---|
| | Hydrogen, ppm | | | Neon, ppm | | | Nitrogen, ppm | | |
| H-1137094 | 0.02 | 0.0 | 0.02 | 23.1 | 21.0 | 2.1 | 0.08 | 0.2 | -0.12 |
| J-221186 | .04 | .0 | .04 | 22.7 | 22.1 | .6 | .15 | .3 | -.15 |
| H-175060 | .00 | .0 | .00 | 16.0 | 15.1 | .9 | .14 | .3 | -.16 |
| AF-163041 | .02 | .0 | .02 | 19.1 | 17.1 | 2.0 | .07 | .3 | -.23 |
| H-159076 | .18 | .0 | .18 | .70 | .6 | .10 | .10 | .1 | .00 |
| H-107945 | .05 | .0 | .05 | .27 | .3 | -.03 | .06 | .2 | -.14 |
| H-123499 | .20 | .1 | .10 | .40 | .4 | .00 | .32 | .3 | .02 |
| AEC100536 | .12 | .0 | .12 | .32 | .2 | .12 | .08 | .1 | -.02 |
| H-1098803 | .03 | .0 | .03 | .23 | .3 | -.07 | .20 | .2 | .00 |
| H-1091434 | .06 | .0 | .06 | .21 | .3 | -.09 | .10 | .2 | -.10 |
| | Oxygen, ppm | | | Carbon dioxide, ppm | | | Total impurities, ppm | | |
| H-1137094 | 0.05 | 0.2 | -0.15 | 0.00 | 0.1 | -0.1 | 23.3 | 21.5 | 1.8 |
| J-221186 | .04 | .2 | -.16 | .00 | .0 | .0 | 22.9 | 22.6 | .3 |
| H-175060 | .06 | .2 | -.14 | .00 | .0 | .0 | 16.2 | 15.6 | .6 |
| AF-163041 | .03 | .2 | -.17 | .00 | .0 | .0 | 19.2 | 17.6 | 1.6 |
| H-159076 | .05 | .0 | .05 | .07 | .1 | -.03 | 1.1 | .8 | .3 |
| H-107945 | .03 | .0 | .03 | .02 | .0 | .02 | .43 | .5 | -.07 |
| H-123499 | .04 | .1 | -.06 | .05 | .1 | -.05 | 1.01 | 1.0 | .01 |
| AEC100536 | .04 | .0 | .04 | .02 | .0 | .02 | .58 | .3 | .28 |
| H-1098803 | .05 | .1 | -.05 | .02 | .0 | .02 | .53 | .6 | -.07 |
| H-1091434 | .05 | .1 | -.05 | .02 | .0 | .02 | .44 | .6 | -.16 |

This study shows less air contamination and a much higher sensitivity for components in the parts-per-billion range. The moisture peak, m/e 18, cannot be used owing to the dry internal surface of the mass spectrometer. An electrolytic moisture analyzer is used independently to determine this component.

## CONCLUSIONS

An improved method has been developed for the analysis of impurities in helium. Its advantages are greater sensitivity, a lower detectable limit, better reproducibility, and less possibility of air contamination; also calculations are less complex, and it is more economical.

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