

constant potential and has immediately adjacent to it in the solution nearly the same concentration of electroactive species (as 100% *O* or 100% *R*) before and after coulometry. Thus one would expect no appreciable change in the double layer capacitance of this working electrode. From a Q - I plot, the number of coulombs at I -zero (obtained from i_{ss} or R data) can be expected to give Q_{ads} directly without any $Q_{d.i.}$ term: the intercept from the Q - I data should give the amount of species *R* previously adsorbed at the cathode, and the Q - I intercept should give the amount of species *O* previously adsorbed at the anode, assuming that the time required for desorption of these species is short compared to the duration of the individual Q - t curves. At the higher concentrations used in the present studies, the amounts of adsorption of

electroactive species at the anode and at the cathode appear to be 2.0×10^{-9} and 2.6×10^{-9} , respectively. These results would indicate several monolayers of electroactive material. Obviously further studies of this aspect of the system are needed.

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Method and Apparatus for Determining Helium Content of Gas Mixtures

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A method and apparatus are described for determining the helium content of gaseous mixtures. The work was done so that the Bureau of Mines could more accurately and economically analyze helium-containing natural gases, crude helium purchased from private industries, and helium in gases used in research. Activated coconut charcoal is utilized at liquid nitrogen temperature to adsorb components other than helium in the mixture. A transducer is then used to determine the helium pressure. Twenty or more analyses with a standard deviation of $\pm 0.04\%$ can be made in an 8-hour day.

ACTIVATED COCONUT CHARCOAL at liquid nitrogen temperature (77 °K) is used to adsorb all gases except helium and neon, and the neon concentration is usually negligible. This adsorptive property of activated charcoal was discovered by Dewar (1) in 1875. Cady and McFarland (2) utilized activated coconut charcoal at liquid air temperatures to determine the helium content of natural gas. The Bureau of Mines adopted this method with minor modifications as reported by Anderson (3). Frost in 1946 (4) also utilized activated charcoal to analyze concentrations of helium below 10%. Frost, Kirkland, and Emerson (5) described an apparatus and procedure for determining the helium content of gases containing 10% or more helium. However, these methods require corrections for volumes, pressures, and temperatures, and the apparatus must be calibrated with weighed primary standard mixtures (6) to obtain accurate results.

The Bureau of Mines purchases crude helium from private industry and must accurately determine the helium content to

assure proper payment. Approximately 2000 samples per year for the Helium Conservation Program must be analyzed. Because the previous method (5) was time consuming and required frequent calibrations, the present apparatus was developed.

This paper describes the new apparatus and procedure for determining the helium content of gaseous mixtures. This method simplifies the calculations by eliminating the necessity of correcting volume, temperature, and pressure. The pressure of helium in the unknown sample is compared with the pressure of high-purity helium at the same conditions. This results in a primary standard method of determining the helium content of samples that contain from 0.1 to 100% helium.

APPARATUS

The gas flow and the essential elements of the analyzer are shown schematically in Figure 1. Vacuum valve *A* is a pneumatic on-off valve. Sample inject valve *B* is an 8-port pneumatic valve and is shown in the sample flush and sample inject positions in Figure 1. Valves *C*-*F* are 3-port pneumatic valves, and the air-control valves *G*-*K* are 3-port solenoid valves. Metering valves *L*-*N* control the gas flow to flowmeters 4 and 7. The pressure is measured by a 0-1 pound-per-square-inch-differential transducer, 1, with its electrical span set to give 0 to 1.5 volts for the pressure of helium in the sample. The voltage is then converted by a voltage-to-frequency converter and counter. The resulting reading for a 100% helium sample is approximately 150,000 counts on the digital readout, 3, for about 0.2 psid. Flowmeters 4 and 7 are differential pressure gauges that have been calibrated by using a predetermined length of $\frac{1}{16}$ -inch capillary tubing to obtain the pressure range required (7). Charcoal trap, 8, contains 3 grams of 50-60 mesh activated coconut charcoal. The inlet line to the charcoal is as short as possible (6 inches) to minimize the volume of N_2 pusher gas that must be extracted by cryogenic pumping and diffusion. Volume tank, 10 (500

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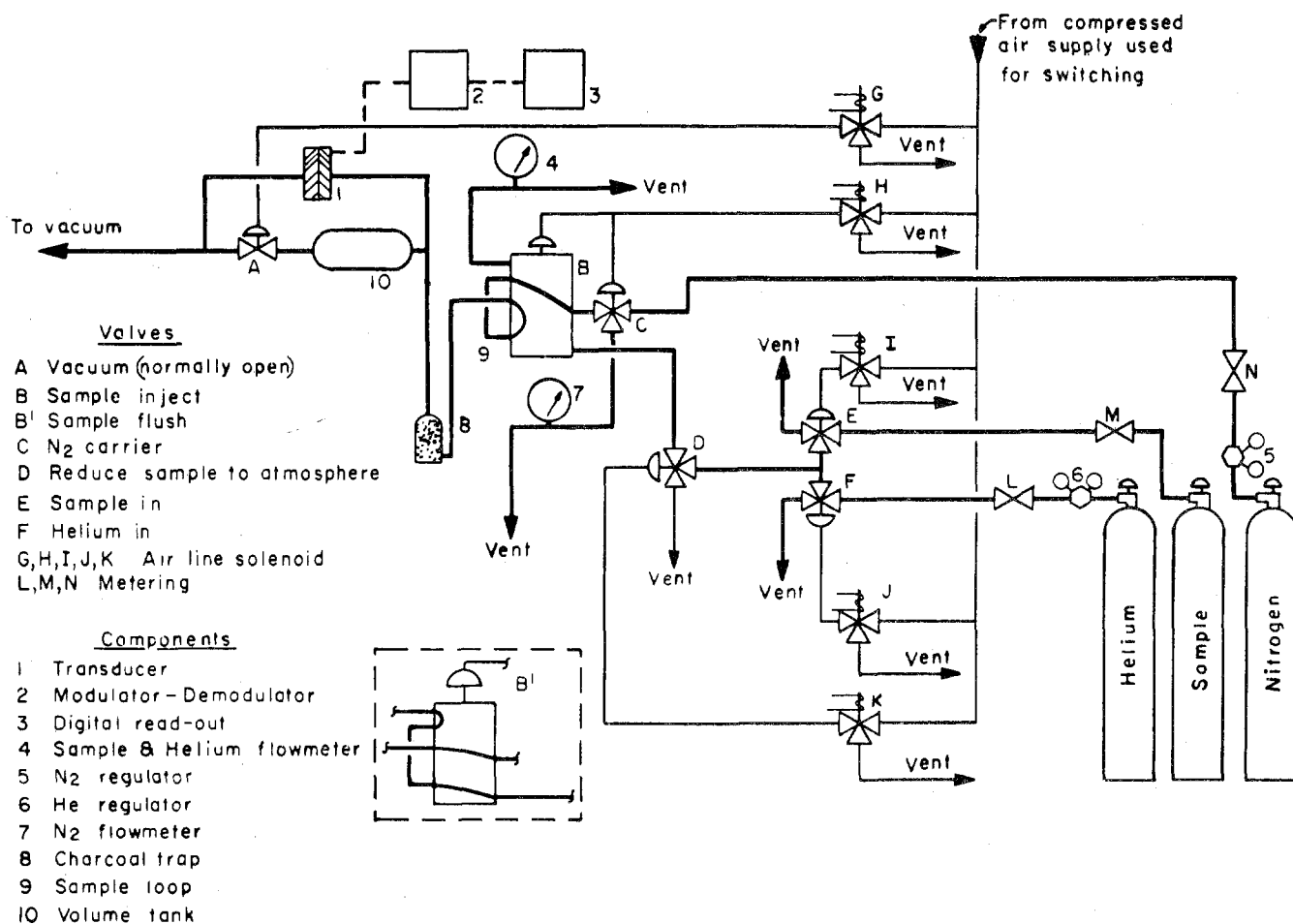


Figure 1. Helium analyzer schematic diagram

cm³), is necessary to assure the movement of almost all the sample through the charcoal, 8.

Size of the sample loop, 9 (7 cm³), is important when considering the resulting pressure in the system and when minimizing possible errors in duplicating the sample volume.

Flow of the gas through the system is controlled by cams which operate on a 500-second cycle. Cam settings control the solenoid operated valves G-K which, in turn, control the pneumatic valves A-F. Control lights are used to show the operator what function is occurring.

THEORY

Activated coconut charcoal at 77 °K is used to adsorb all gases except neon, which is present only in the parts-per-million range, and helium. The neon pressure is neglected, and the resulting helium pressure (P_1) is measured and compared to the pressure (P_2) resulting from the sampling of high-purity helium under the same conditions. The pressure represented by the high-purity helium sample is taken after the unknown sample because adsorption of gases on the charcoal changes the internal volume of the system. Volume and temperature are considered to be constant over the time span required to sample the unknown and the high-purity helium. Helium is treated as an ideal gas because the total pressure in the apparatus does not exceed 1 atmosphere.

Nitrogen is used to force the sample into the volume between valves A and B. The resulting helium pressure is proportional to the partial pressure of helium in the sample loop.

Let P = the pressure of helium after expansion into the volume between valves A and B

V = volume of apparatus between valves A and B
 P_{He} = partial pressure of helium in the sample loop
 V_s = volume of the sample loop, approximately 7 cm³
 K = proportionality constant, which is a function of the temperature difference between the sample loop and the volume between valves A and B

and

$$PV = KP_{He}V_s \quad (1)$$

Let P_1 = helium pressure that is proportional to the partial pressure of helium in the sample

$$P_1V = K_1P_{He1}V_s \quad (2)$$

Let P_2 = helium pressure that is proportional to the total of the sample

$$P_2V = K_2P_{He2}V_s \quad (3)$$

The per cent helium is calculated from

$$\% \text{ He} = \frac{P_{He1}}{P_{He2}} (100) \quad (4)$$

and substituting Equations 2 and 3 into Equation 4

$$\% \text{ He} = \frac{P_1V}{K_1V_s} \left(\frac{K_2V_s}{P_2V} \right) 100 \quad (5)$$

and if the temperature ratio of the sample loop and V is constant, $K_1 = K_2$ and Equation 5 reduces to

$$\% \text{ He} = \frac{P_1}{P_2} (100) \quad (6)$$

Table I. Hydrogen Mixtures

Mixture	Hydrogen	Nitrogen	Helium
1	0.99 ^a	40.54 ^a	58.47 ^b
2 ^c	10.297	10.515	79.177

^a Determined by mass spectrometry.^b Helium determined by this study.^c Prepared by weighing method (6).**Table II. Analyses of Hydrogen Mixtures**

Mixture	Number of analyses	Average, %
1	5	58.48 ± 0.05
1	5	58.47 ± 0.05
2	5	79.04 ± 0.20

Table III. Analysis of Natural Gas

Set	Number of analyses	Average, %
1	6	6.01 ± 0.01
2	9	6.03 ± 0.02

Table IV. Sample Analyses

Test	Known He content	Number of runs	Char-coal activations	Average, %
1	0.000	6	1	0.02 ± 0.01
2	11.200	10	1	11.25 ± 0.03
3	60.030	21	3	59.99 ± 0.04
4	79.824	11	1	79.75 ± 0.02
5	97.880	7	1	97.86 ± 0.02

RESULTS AND DISCUSSION

Charcoal Regeneration. Charcoal regeneration requires a bakeout at 205 °C for 5 minutes. After regeneration the charcoal is conditioned by discarding the first analysis. At least nine samples are usually analyzed before the charcoal becomes saturated, except when hydrogen is present. A secondary standard is analyzed after each bakeout to check proper operation of the analyzer.

The adsorptive properties of the charcoal can be destroyed; therefore, the bakeout temperature must be carefully controlled. Overheated charcoal will result in poor precision, which can be readily detected. After the charcoal has been overheated, it must be replaced.

Hydrogen Study. Since hydrogen would be the first gas desorbed after charcoal saturation, two mixtures were prepared and analyzed to determine its effect on the analysis of helium. The analyses of the two mixtures are given in per cent in Table I.

The mixtures were then analyzed using the normal operating procedure. The results in Table II indicate that samples

containing hydrogen can be analyzed accurately. The charcoal was regenerated between the two sets of five runs of mixture 1. The operator can easily detect charcoal saturation because the zero reading increases rapidly between samples. The charcoal requires reconditioning when the vacuum pressure reading increases by as much as 75 counts between samples.

Sample Injection. Helium-free nitrogen is used to sweep the sample into the charcoal area of the apparatus. To determine the amount of nitrogen required, the flow rates were varied from 1 cm³/minute to 40 cm³/minute. The results indicated that the nitrogen could be used at any flow rate within this range. We selected a flow rate of 3 cm³/minute to minimize the saturation effect and volume change of the system.

The sample injection time was varied from 6 seconds to 30 seconds to allow additional nitrogen to flow into the system. The sample was a weighed primary standard containing 60.030% helium and 39.970% nitrogen. The results indicate no effect from the excess nitrogen. We chose an injection time of 6 seconds, which adequately purges the sample into the system.

Natural Gas Analysis. The analysis for helium in natural gas is important in exploration of helium resources and in the helium production plants. A sample of natural gas was analyzed to determine its effect on the charcoal. The results are given in Table III.

Three other samples were also analyzed before set 1, which indicates that at least nine natural gas samples can be analyzed before regeneration of the charcoal is necessary. The charcoal was regenerated between the two sets. This instrument can analyze helium in natural gas to the minimum detectable limit (approximately 0.05%).

PRECISION OF DATA

The performance of the apparatus was tested by analyzing helium-nitrogen samples of known composition. The samples were prepared by an improved procedure based on the weight method described by Miller, Carroll, and Emerson (6). These weighed standards are known to an accuracy of ±0.03, 2σ. The results are shown in Table IV.

This method permits analysis of helium in mixtures from 0 to 100%. Several thousand samples have been analyzed and it has proved to be simple and trouble-free with an accuracy of better than ±0.04%.

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