

Apparatus and Procedure to Reduce Impurities in Helium to Less Than One Part Per Billion

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Abstract

Certain scientific applications require helium of greater purity than that routinely available. This paper describes a laboratory-size apparatus which reduces impurities in helium to less than 1 part per billion. The unit employs easily available, low-cost liquid nitrogen as a refrigerant to cool activated charcoal for the cyclic adsorption of impurities. The essential differences between the new purifier and previous adsorption units are the use of highly purified helium to purge and repressurize the charcoal during and after regeneration, and regeneration of the adsorbent before neon emerges. The unit produces a few hundred cubic centimeters of highly purified helium per minute, the amount depending upon the helium pressure required and the chosen cycle time. Continuous safe operation is achieved with only periodic observation and requires about 20 liters of liquid nitrogen per day.

Commercially available helium has about 20 parts per million (ppm) or more total impurities which are undesirable for certain scientific usages such as the coolant medium in nuclear reactors, inert blanketing gas for crystal growing, and carrier gas for gas chromatographs employing helium ionization detectors. There is therefore an obvious need for improved methods of helium purification.

There is a large volume of literature dealing with the purification of noble gases. Certain phases of helium purification are reviewed below.

One means of helium purification attempts to remove all impurities by permeation of helium through quartz (1). Hydrogen and neon are known to pass through quartz in significant amounts, and the resultant mixture is not necessarily ultrapure helium.

High-purity helium can be obtained by the regassification of filtered liquid helium obtained from beneath the surface of the liquid. The maximum amount of hydrogen and neon which could exist in the vapor in equilibrium with liquid helium has been calculated to be less than that detectable by the current analytical means; i.e., 0.01 ppb of hydrogen and 10^{-6} ppb of neon (2). However, purification of helium by first cooling it to 4.2°K is an expensive method for continuous laboratory application.

Removal of impurities on highly activated adsorbents at low temperature (3,4) is a standard method of purifying helium on a commercial scale. Such purification methods, as practiced, allow the impurity neon to pass through the bed virtually unchanged in concentration. The purification of helium by adsorption can be greatly improved in efficiency (5) by reducing the temperature of the adsorbent from 77°K (boiling point of liquid nitrogen) to about 35°K , by means of a helium refrigerator. At the lower temperature neon and

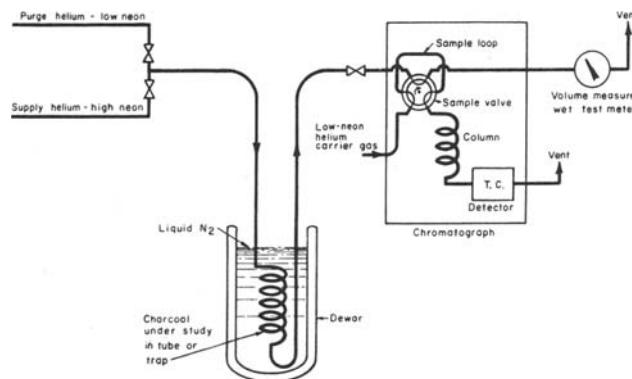


Figure 1. Preliminary experimental apparatus.

all impurities are reduced below detectable limits. The cost is quite high, and equipment for carrying out this type of purification is not available in most laboratories.

The purifier described in this paper is a laboratory-size unit capable of continuously producing a few hundred cubic centimeters per minute of purified helium in which all impurities are below 1 ppb.

The preliminary experimental setup is shown in Figure 1 and was used to establish the order of component elution from activated coconut charcoal at 77°K . A standard GC with a hot-wire, thermal conductivity detector sensitive to about 0.5 ppm each of neon, argon, oxygen, and nitrogen and 10 ppm hydrogen was used to sample and to analyze the effluent gas from the column under study (6). The helium carrier gas and the "low neon" helium sample contained about 1 ppm neon and less than 2 ppm total impurity. (This gas is available in 220-ft³ cylinders from the Bureau of Mines, Amarillo, Texas, upon special request.)

The temperature of the charcoal column was lowered to 77°K and the "high neon" helium used as a supply. Neon was the first component to elute in every case and appeared in less than one-tenth the time required for any other component. Even when the im-

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2. Bourke, P. J., Dawson, R. W., and Denton, W. H., *J. Chromatog.* **14**, 387 (1964).
3. Kohl, A. L., and Riesenfeld, F. C., "Gas Purification," McGraw-Hill Book Co. Inc., New York, 1960, Ch. 12.
4. Nonhebel, G., "Gas Purification Processes," George Newness, Ltd., London 1964, Ch. 9-10.
5. Purer, A., Stroud, L., and Meyer, T. O., *Advan. Cryog. Eng.* **10**, 398 (1965).
6. Purer, A., and Seitz, C. A., *Anal. Chem.* **36**, 1694 (1964).

purities were increased to 5,000 ppm each hydrogen, argon, and nitrogen, the 15 ppm neon was the first to emerge. Neon broke through the adsorbent at the same time whether its concentration was 15 ppm or 150 ppm.

At liquid nitrogen temperature a given amount of charcoal will adsorb a *fixed amount* of a strongly adsorbed gas, such as nitrogen, regardless of the concentration of the nitrogen in the supply gas. Apparent at this point of the study, the passage of neon through the charcoal was found to continue to be retarded only with reference to the helium from the supply gas, and the *time of breakthrough seemed to be essentially independent of the concentration of neon in the supply gas*. As in an analytical chromatograph the elution of the neon is essentially "velocity based" and its frontal appearance at the detector is predictable, based on the velocity of the carrier gas and *not* on the concentration or total amount of the neon. Therefore, the presently described purifier may be thought of as a preparative-scale chromatographic separator, in which none of the contaminating components are allowed to emerge with the carrier gas. These facts led us to the conclusion that neon retention was time- or velocity-based at this temperature whereas the elution time of other components was capacity-based or concentration dependent.

Commercial adsorption purifiers take advantage of the capacity-based adsorption of nitrogen and other contaminants and disregard the chromatographic action of neon at this temperature. By contrast, the presently-described purifier is limited by the time of neon breakthrough and cannot, therefore, take advantage of the much higher capacity of charcoal for N_2 and other components which are strongly adsorbed. It is known that at a lower temperature, 35°K (5), the retention of neon is enhanced many fold over that obtained at 77°K and may be capacity-based at that temperature.

The preliminary design was next expanded to allow one such column to be used to supply purge gas to a second identical column during its activation, cooling, and repressurization.

After successful operation of the preliminary two-column system, a prototype, two-column automated system was built. The charcoal was initially activated by heating it to 200°C for 6 hours while purging with normal Grade A helium. Typical purifications obtained are shown in Table I for the analysis of the purified gas at the beginning and end of each column use during startup. The operating pressure for this series of cycles was 34 atm. The supply gas was normal Grade A helium, approximately 25 ppm total impurity including 15 ppm neon. The analysis was made in place by a special analyzer to be described. Notice each column use lowers the neon content by a factor of approximately 3 and at the end of the sixth column use (3 cycles) the neon content is less than 1 ppb.

The two-column system was arranged as shown in Figure 2 for a convenient and automatic operating system. Each column contains 200 grams of 20/60 coconut charcoal. All joints below liquid nitrogen were silver brazed and all threaded joints were coated with lead before being screwed together, forming a leak-proof system.

During regeneration of column No. 1, liquid nitrogen is removed from around the charcoal by closing

Table I. Neon Analysis During Startup at 34 atm

Number column uses	Cycles	Neon concentration, ppb Beginning	End of Use
1			1,300
2	1	1,000	390
3		330	110
4	2	80	11
5		11	4.5
6	3	3.5	<1

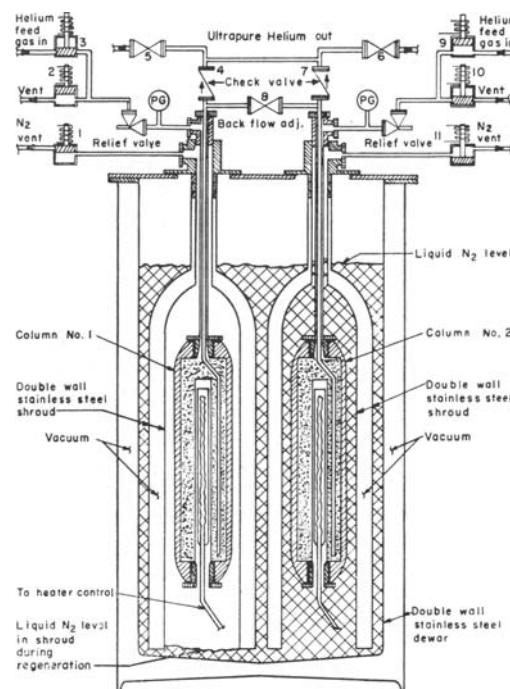


Figure 2. Purifier showing gas flow paths.

valve No. 1 and preventing the escape of gaseous nitrogen from the top of the shroud. The column is slowly heated to near room temperature (about 1 hour, requiring approximately 80 watts). At the same time, column No. 2 is purifying helium and part of the gas is used to backpurge column No. 1 through valve No. 8. Vent valve No. 2 is open during regeneration, thus depressuring column No. 1 and is closed at the end of the heating portion of the cycle, thereby allowing the column to be repressured to about 90% of its operating pressure before it is put into use. When power is removed from the heater, shroud vent valve No. 1 is opened, and nitrogen vent valve No. 2 is closed. Liquid nitrogen is automatically added from a pressurized 160-liter dewar and the LN_2 level is thereafter automatically controlled.

Column No. 2 is activated in the same manner as No. 1 with the corresponding valve and heater changes.

A list of significant components of the purifier, along with the names of the suppliers, can be obtained by contacting the authors.

Two complete two-column purifiers were constructed. One was used to supply carrier gas to a special chromatograph employing a laboratory-built helium ionization detector system. This purifier was op-

erated in such a way that the neon front was never allowed to break through the charcoal (about 30% of the time required for a ppm neon breakthrough). The minimum detectable limit of the special chromatograph was shown to be less than 1 ppb neon by the use of an exponential dilution system equipped with a chromatograph sample valve for the introduction of known amounts of impurities. This system established the detector sensitivity and its zero was determined by using gaseous helium which came from beneath the surface of filtered liquid helium. No peaks were observed for this analysis, indicating the neon content from the liquid helium and the purified carrier gas to be the same. The expected total impurities in helium at the temperature of liquid helium (4.2°K) are less than 0.01 ppb (2) as calculated from the Clausius-Clapeyron equation. The sensitivity of the analyzer for other contaminants at the time of the above comparison was 2 ppb hydrogen, 0.2 ppb argon, and 5 ppb nitrogen.

The second purifier was used to determine the volume of pure helium which can be delivered from one column to the 1-ppb breakthrough. This quantity was found to be a function of the pressure and linear velocity as shown in Figure 3.

The cluster of three points near the 30 cm/hr and 67 atm isobar was used to represent the repeatability of a point. All other points and isobars are presented as a constant set and are satisfactory from an operational standpoint.

Operational purifier cycle times were calculated from the data in Figure 3, allowing for the quantity of helium used for supply, purge of activating column, and repressuring of activated column. The "normal engineering factor" should be used to ensure that neon does not break through during each column use. We suggest that each column be used to about 70-80% of the breakthrough volume shown in Figure 3. This will result in an overall helium use efficiency of about 30%. The purifier is most efficient at the lowest pressure for the particular use condition.

This purified gas is expected to provide a carrier gas of constant composition to a chromatograph, making possible a constant background for helium ionization detectors which will require less frequent calibration.

One anomaly observed while using this purified gas as carrier to the special ionization chromatograph was over-activation of the molecular sieve column for oxygen. Samples of helium containing small amounts of air showed the normal peak for nitrogen, but oxygen appeared to be chemisorbed and elutes without distinct peaks over a long period of time.

The use of this gas in spectra work should prove to be very interesting.

Three unique features which distinguish this purifier from others utilizing charcoal at liquid-nitrogen temperatures are emphasized below.

1. A portion (approximately 9 liters, STP) of the helium which has been purified from one column is utilized to purge impurities from the column being regenerated and to pressurize it for the next usage. Previous purifiers have utilized the unpurified feed gas for this purge and pressurization operation. It is essential that the highly purified helium be used for purge and pressurization to have all impurities swept out of the system when the regenerated column is put back into service.

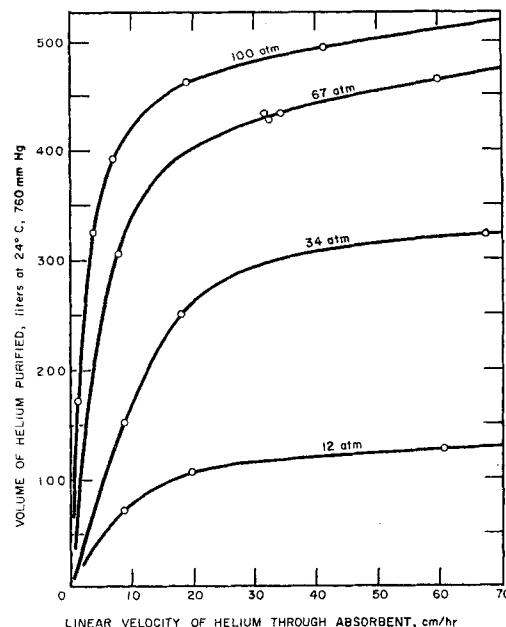


Figure 3. Effect of velocity on the volume of helium purified.

2. Production of purified helium is stopped and the adsorbent is regenerated well in advance of the appearance of the first contaminant (neon) to break through the column. Breakthrough times for neon were determined in advance by continuous analysis of the helium emerging from the purifier. Only 80% or less of this neon breakthrough time is utilized to assure that neon is not allowed to elute from the purifying column.

3. With the insulated shrouds surrounding the charcoal column, it is possible to heat one column in excess of 250°C, if needed, while liquid nitrogen remains in the outer dewar and simultaneously cools the other column producing ultrapure helium without undue loss of liquid. This is accomplished merely by closing the vent at the top of the shroud. The heat required for regeneration vaporizes some of the liquid nitrogen within the shroud and forces the remaining liquid nitrogen out the open end. In this way, only a small amount of metal and charcoal need be heated during the regeneration cycle, and liquid nitrogen is automatically removed from contact with the heated surfaces. This third feature improves nitrogen usage efficiency and allows for automatic operation.

The above innovations, which distinguish the present purifier from conventional adsorption units, are the bases of an invention report and possible patent application.

This purifier has been shown to produce helium with less than 1 ppb impurity.

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