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Use and Calibration of a Gas Chromatograph

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for Gas Analysis at the Project Rover Test Facility*

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by

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ABSTRACT

A gas chromatograph system operated by test site personnel has been used for over a year to monitor the purity of gases used at the Project Rover test facilities at the Nuclear Rocket Development Station. Information has been obtained on the efficiency of gas line purges, total impurities of frozen air in a large liquid hydrogen dewar, and the quality of room inerting systems. Daily monitoring of several block and bleed systems, which prevent hydrogen gas from entering a system through a leaky valve, and periodic monitoring of all gas added to the 8×10^8 standard cubic feet of gas tank farm storage are required for safe facilities operation. In addition the chromatograph has proved useful in special cases for leak detection in vacuum and high pressure systems.

The calibration and operation of the chromatograph system using a column of Linde 5A Molecular Sieve for analysis of H_2 , N_2 , O_2 , will be described. Observations of a thermal conductivity reversal in the binary mixture He- H_2 will be presented and qualitatively described.

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Introduction

Gas chromatography has become an increasingly useful tool in the quality control of manufactured products and as a technique for laboratory analysis. This paper describes a combination of these uses with a gas chromatograph system at The Nuclear Rocket Development Station of the Atomic Energy Commission and the National Aeronautical and Space Administration.

The gas chromatograph system is shown in Figure 1. A Beckman GC-2A gas chromatograph is mounted together with a gas handling system including a diffusion pumped vacuum system. The unit was built to the design of one of us (DHL) by Edgerton, Germeshausen and Grier, Inc. and the flow system is shown in Figure 2. Three of these systems have been made, two for use at the test site in Nevada, and one for the Cryogenic Engineering Section of the Los Alamos Scientific Laboratory. A chromatograph column 8 ft. in length, .201 inches in diameter and filled with Linde 5A molecular sieve, 24-50 mesh, is operated at an upstream pressure of 25 psig and is maintained at a temperature of 100°C to prevent the buildup of water in the column. The thermal conductivity detector is operated at .4 amp and a -.05 to +1.05 millivolt recorder directly measures the bridge imbalance of the thermal conductivity cell and may be attenuated by a factor up to 1000 with 9 intermediate steps.

The chromatograph requires calibration to analyze trace impurities in a gas. The method of equating the sum of the peak heights of the elution curves to 100% and taking individual component peak heights as the corresponding per cent is inadequate with ordinary recorders or integrators, when the second component is present to, say, 0.45%. Sample gases purchased from the Matheson Company having nominally 50 ± 1 ppm, 150 ± 2 ppm, 500 ± 5 ppm and 1000 ± 10 ppm of O_2 , N_2 and H_2 in helium, and supplied with analysis are used to prepare a calibration curve for each column in use. In addition comparison analysis of the above samples with a laboratory mass spectrometer has provided additional confidence in the calibration curves prepared. Pure gas samples of H_2 , N_2 have been introduced at successively lower pressures to extend the calibration curve to the percentage range 0.1 to 100. A typical set of calibration curves for trace impurities is shown in Figure 3 using a column as previously described. Although a calibration based on the integral of the output voltage during elution of one component is theoretically more significant, the observation of the voltage peaks or peak heights is more direct. All calibration is performed using peak heights and as will become apparent, departures from linearity are small and with the prepared calibration curves the sample analysis is both quick and accurate. An accuracy of ± 2 ppm at 25 ppm is held for daily field analysis.

Figure 4 shows the calibration curve for N_2 plotted as log (peak height) versus log (part per million impurities, by volume). A linear relationship between the amount of gas and the voltage output may be seen to hold reasonably well over 3 orders of magnitude. In this log-log graph the errors of measurement are of the size of the plotted points.

Daily check of the chromatograph calibration is made with a standard sample bottle of gas whose analysis is known. On one system the column has been in service for more than 1 1/2 years and some 2000 samples in addition to all calibration samples have been run. Only small changes in the column characteristics have been noted. The column separation is adequate to resolve trace impurities of oxygen in nitrogen gas.

The samples are obtained with a flow through type of collecting bottle. It is important to prevent small air impurities from leaking in. The bottles are prepared by the chromatograph operator by a thorough evacuation--the bottles have been previously helium leak checked--and back filled with pure helium carrier gas to a 5-10 psig over pressure. They are connected to the pressure regulators at the sample ports with a Hansen Company quick disconnect, Series 600, which has been found to be vacuum tight as well as pressure tight. This connection securely holds the bottle during the flow through purge which is customarily 5 minutes at a 5 psig downstream regulator pressure. A flow of one minute duration has been found inadequate to purge the air impurities that occur when sample bottles are connected with unpurged connectors. The five minute purge time is adequate. The inlet connection at the chromatograph gas handling system is a Veeco quick disconnect and the gas handling system is arranged so that one sample bottle may be set up for analysis while another is being analyzed and a third is being purged and back filled with helium gas.

At the Nuclear Rocket Development Station in Nevada, quantities of the order of eight million standard cubic feet of He, H₂, and N₂ are stored in tank farms and some 156,000 gallons of liquid hydrogen can presently be stored in dewars. It is essential to maintain a high purity in the hydrogen tank farm gas used for dewar pressurization and a high purity in the helium and nitrogen kept in storage.

Since the size of the cryogenic system required the use of 8-inch diameter liquid hydrogen shut-off valves and these valves tend to leak at room temperatures, a helium block system is monitored daily for hydrogen or air contamination. Figure 5 shows a typical test cell piping layout suitably simplified and the gas sampling points detailed. The helium block is a section of line between the dewars with an additional valve installed. This section of line is maintained at a helium pressure greater than the dewar storage pressure. The tank farm is shown, with a sample port on each storage bottle. There are additional gas headers in the system for low impedance supply which have sample ports to monitor the effectiveness of line purges.

In order that the buildup of air impurities in the hydrogen storage dewars be kept small, the impurity of the pressurizing gas from the tank farm must be kept less than 25 ppm, by volume.

On a day when the facility will be used in the test program, the completeness of the purge given all hydrogen lines is monitored

by samples taken for gas chromatograph analysis and upon the acceptance of results hydrogen is introduced in these lines. The shut down purge of all hydrogen lines is monitored and repeated until the line is accepted as purged. Using this technique some conservation of gases such as helium is effected. Since 100,000 standard cubic feet of helium may be used during an operation, a significant savings can result.

Gas filling operations are monitored routinely, and it has turned out that several gas trailers have either contained the wrong gas entirely or have had larger impurity content than could be accepted. The savings effected in terms of man hours, test data fulfillment, and gas quantities saved from contamination is obvious.

The use of inerted rooms to house liquid hydrogen pumps has been found of value to prevent fires that often accompany liquid hydrogen spills. The adequacy of the inerting system was checked by taking samples of gas in previously evacuated bottles and performing an analysis on the gas chromatograph. Some 20 samples were taken from different parts of each room and at two different heights. Results indicated uniform displacement by the nitrogen gas which was introduced at floor level. These measurements were in addition to the permanent oxygen monitor installed.

After the dewars had been in use as storage and run tanks for a period of six months, a dewar warmup was made and the contents of the warming gas were monitored for oxygen and nitrogen impurities. Periodic samples were taken for chromatographic analysis. The results indicated a measurable impurity of oxygen and nitrogen of $\sim 1/10$ gram of material collected in a 55,000 gallon dewar over the six-month

period. Such quantities are not considered dangerous but point out the need for using high purity pressurization gas and for periodic warming of large liquid hydrogen dewars.

Use of the chromatograph with gas samples at an absolute pressure of 1 mm Hg has been possible. This has allowed in some special cases the detection of leaks in a system that could not be evacuated to a better pressure than this. The manway between the inner and outer shells of one of the dewars had such a leak. Since the inner shell was filled with nitrogen at the time and the outer flange would leak air, a sample analysis readily provided information that an inner flange leak obtained.

Returning to the question of calibration, a brief discussion will be given of the calibration curve for hydrogen with helium as a carrier gas. More detailed results will be reported elsewhere. The general character of the peak heights versus increasing hydrogen concentration is shown in Figure 6. Similar observations by others have been reported.¹ Since the total pressure in the detector is constant with time, the profile observed represents the difference in thermal conductivity of the H_2 -He mixture and pure He as a varying function of the partial pressure of hydrogen. Although the thermal conductivity of pure H_2 is greater at 100°C than that of pure He, the mixture H_2 -He has a thermal conductivity which is for some mixtures less than that of pure helium. This departure from elementary ideas of simple additivity can be treated with the aid of the thermal conductivity equation of a polyatomic binary mixture

based on the work of Chapman-Enskog and using the Lennard-Jones intermolecular potential.² Qualitative agreement with the observations is shown in Figure 7. The complications of the time varying thermal conductivity caused by the varying concentration of the eluting hydrogen in the helium carrier gas makes quantitative discussion difficult. However, the qualitative agreement of the thermal conductivity of the H₂-He mixture extends the generality of the theory.

References

1. J. Madison, Analytical Chemistry 30, p. 1859-1862, 1958.
2. J. Hirschfelder, C. Curtiss and R. Bird, Molecular Theory of Gases and Liquids, Wiley and Sons, New York, 1954, p. 536.

Fig. 1 The Gas Chromatograph.

Fig. 2 The Gas Chromatograph Flow Diagram.

PEAK HEIGHT (MILLIVOLTS IMBALANCE)
 O_2, N_2

PEAK HEIGHT (M. V.) H_2

Fig. 5 Test Cell Schematic showing gas sample points (S) for gas storage, helium block, and gas transfer lines as described in the text.

Fig. 6 The character of the hydrogen elution peak when helium is the carrier gas.
Shown as a function of hydrogen impurity.

**DIFFERENCE IN THERMAL CONDUCTIVITY
(He)-(H₂, He) ARBITRARY UNITS**

Fig. 7 The difference in the thermal conductivity of the mixture (H₂, He) and pure He demonstrating the qualitative agreement between predictions of the Chapman-Enskog theory and chromatograph observations.