

Measurement of Impurities in Helium Using the Dielectric Barrier Discharge Helium Ionization Detector.

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Abstract

Bulk gases are often delivered to local vendors who then re-package the gas in high pressure cylinders for distribution within a local market. This link in the distribution chain can become an entry point for contamination, especially from air. The presence of these impurities is harmful in a number of industries including the analytical chemistry industry. Contaminants, like oxygen, can be detrimental to instruments such as those found in the analytical chemistry industry and can lead to erratic instrument behavior like column bleed, detector poisoning, and noisy baselines. Gas chromatography (GC) can be used to measure these contaminants in high purity gases if the detector used is sufficiently sensitive to detect contamination at less than a part per million level. Advanced Industrial Chemistry Corporation (AIC Corp.) has developed a helium ionization detector based on the dielectric barrier discharge which meets the needs of low-level fixed gas analysis. To demonstrate the capabilities of the detector, a number of commercial helium cylinders from various vendors were analyzed using this detector.

Introduction

The ability to easily measure contaminants at the local vendor level provides quality control oversight of the transfer of gases from a bulk container to individual cylinders. In order to be cost effective and easy to use, it is desirable to have an instrument that needs a minimum amount of care and attention. For analytical laboratories using helium as a carrier gas, helium quality can impact the stability of their instrumentation through a number of pathways including increased column bleed due to oxygen in the carrier, or detector noise through contaminants such as hydrocarbons. The end-users' concern for gas quality must always be balanced with price. For these reasons, it is desirable to measure a number of fixed gases that may be present in commercial helium. The

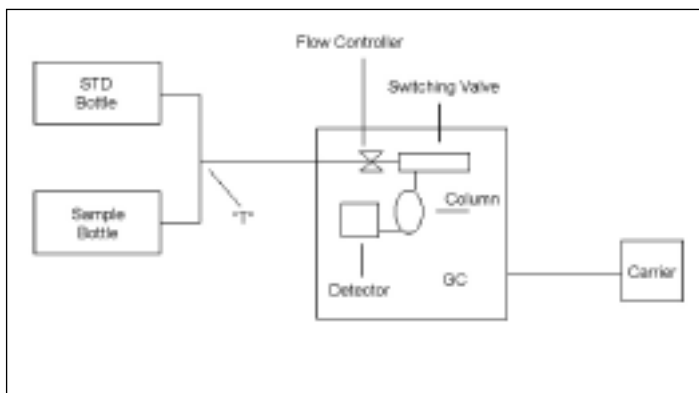


Figure 1: Schematic of helium analysis system.

advent of simple, stable and reliable detectors capable of sub-ppm detection of contaminants makes meeting these objectives within the reach of local vendor and analytical laboratories.

Experiment

Helium samples were measured using a Varian 3400 gas chromatograph with a Restek 2 meter by 1/16 in. mol-sieve micro-packed column. Column head pressure was maintained at 50 P.S.I. using a packed column pressure controller taken from a Varian 3700 G.C. system. Samples were introduced via an automated six-port sampling valve with various loop sizes ranging from 25 microliters to 1000 microliters. The column was operated at 50°C in an isothermal mode while the detector was maintained at 150°C. The detector was an AIC Corp. developed dielectric barrier discharge ionization detector (U.S. Patent 5,892,364) operating in the helium ionization mode using the Varian flame ionization detector electrometer set at a range setting of 12. Due to the high operating background of the detector in helium mode, the zeroing resistor on the electrometer board was replaced with a 100 Mohm resistor.

Figure 1 illustrates the configuration used for the analysis of fixed gases in helium. All gases were supplied

to the system using conventional 1/8 inch copper tubing. Grade 5 helium (BOC, Texas) was supplied to the system using a two-stage high purity regulator held at 80 psi. Helium was passed through a water scrubber system and then conveyed directly to the GC system. No other purifiers were used within the system. Reaction flow helium was taken off of a "T" that supplied helium to the analytical system and controlled using the flow controller already present on the Varian 3400. Reaction flow was held at 85 mL/min.

The gas standard was a certified mixture (Southwest Airgas) containing 10 ppm each of hydrogen, oxygen, nitrogen, carbon dioxide, and methane in helium. This was connected to the sampling valve using a single-stage regulator which was connected, via 1/8 inch copper tubing, to a variable flow controller held at 35 mL/min. The unknown helium sample cylinders were hooked into the same gas line using a brass three-way Swagelok "T" manually actuated valve.

The dielectric barrier discharge detector is shown schematically in Figure 2. The detector is based on a dielectric barrier discharge plasma used to create a stable ionization source that is then used to ionize (through helium metastables and photoionization) the analytes of interest. The plasma is formed by bringing in pure helium reaction gas at the top of the reactor cell, which is excited by the application of an alternating current voltage to the glass cell via the high voltage electrode. Analytes enter the detector from the base and are ionized by the light source. Electrons generated from the ionization process are driven to a collector by a bias voltage applied to an inner electrode. The electrons are collected at the outer signal electrode as the analytes pass out of the detector.

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The current generated is monitored by the Varian electrometer and converted into a 0-10 volt signal. Data was collected on an SRI Peaksimple data system operating at 2 Hz.

Results and Discussion

An initial chromatogram was generated on the mol-sieve column using a 25:1 injection of Scott Mix 234 which consists of 4-5% fixed gases in a balance of helium. From this chromatogram the retention times for the individual components were established. A four point calibration curve was then generated for each component using various loop sizes ranging from 25:1 to 1000:1. This calibration curve is shown in Figure 3.

Each compound except nitrogen had a correlation coefficient greater than 0.992, while the nitrogen curve had a correlation coefficient of 0.980. It is not known at this time why the nitrogen correlation coefficient was lower than that of the other three components. However, when one looks at the correlation coefficient for the calibration curve excluding the 250 μ L loop volume values, all of the correlation coefficients are greater than 0.999. This would suggest that the problem may be in the loop rather than with the chromatographic system.

A chromatogram of the lowest point in the calibration curve, the 25 μ L injection, is found in Figure 4. Note the absence of CO₂ (which does not elute on a mol-sieve column), and the absence of the CO peak which is not present in the fixed gas calibration standard used. The methane peak has the greatest response due to its lower ionization potential. Hydrogen also has a relatively low ionization potential, but it also has a

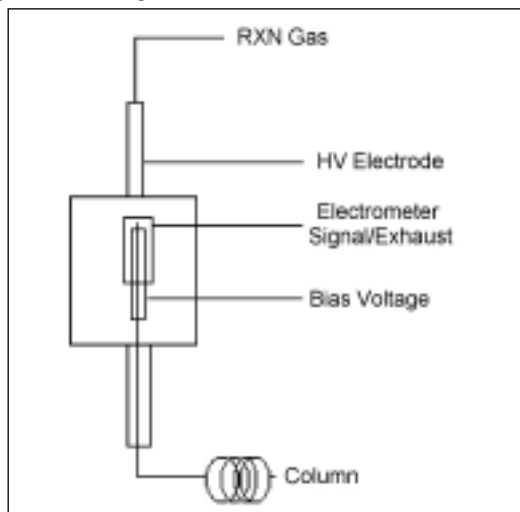


Figure 2: Schematic for DBD detector

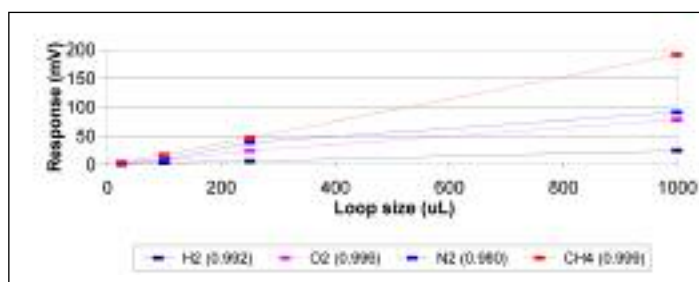


Figure 3: Calibration curve for fixed gases using the DBDHD.

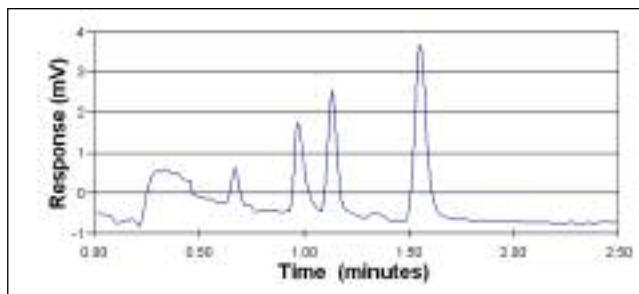


Figure 4: Chromatogram of a 25 microliter injection of a 10 ppm fixed gas standard mix

much lower cross section and does not ionize as efficiently as the other components in this mixture. This would indicate that the ionization process is due, at least in some part, to metastable helium interactions as well as photoionization. The section of the chromatogram where hydrogen comes out was magnified in order to show the signal to noise ratio for the hydrogen peak (Figure 5.) The noise level is about 0.02 mV

while the hydrogen peak is over 0.8 mV in height, yielding a signal-to-noise ratio of greater than 40:1 at this level.

Following the establishment of a calibration curve, the system was evaluated for long term stability. Forty runs of the fixed gas mixture were made over a period of two days with a 100 μ L loop. These data are shown in Figure 6. Oxygen, nitrogen, and methane had percent rela-

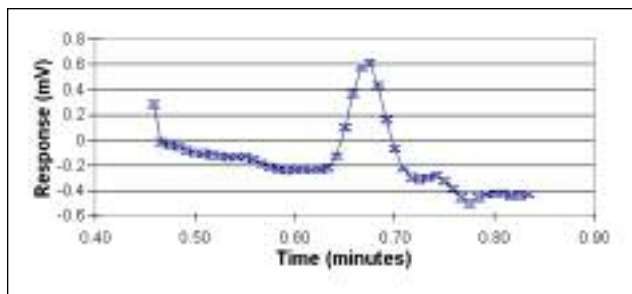


Figure 5: Expanded view of hydrogen peak from 25 u(Mu)L injection

tive standard deviations (%RSD) near or below the 2% level while hydrogen had the highest % RSD at 7.8%. It is apparent from Figure 6 that methane had more variability than the hydrogen, but the higher response for the methane peak (relative to the hydrogen) offset the variability leading to the lower %RSD. Hydrogen, with the lowest response factor and eluting nearest to the valve switching injection, was expect-

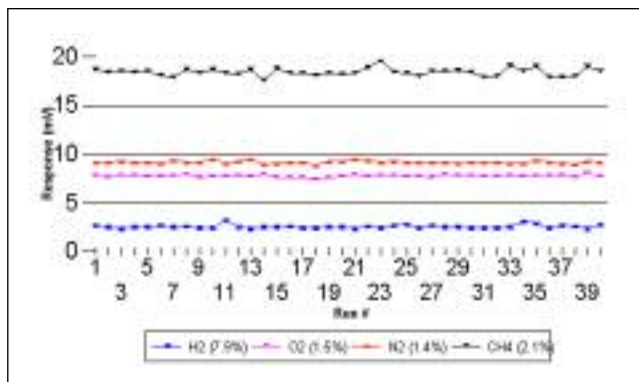


Figure 6: Reproducibility data: 40 injections of 100 μ L of 10 ppm fixed gas mixture.

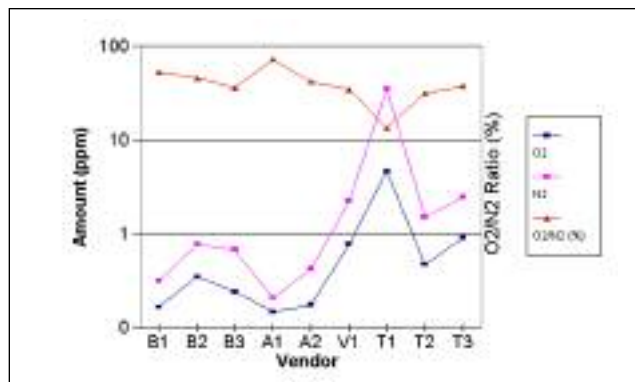


Figure 7: Fixed gas impurities in commercial helium cylinders.

ed to have the highest %RSD of any of the components measured.

Commercial helium cylinders from a variety of vendors were then evaluated. Each cylinder was connected to a brass, single-stage regulator and connected through a Swagelok "T" to the six-port sampling valve. Each cylinder evaluated

was allowed to purge for a minimum of six hours before being analyzed. Each cylinder evaluated was run a minimum of three times and the average of these results are shown here. Four vendors were evaluated using nine different sample cylinders. Cylinders B1 through B3 were filled in Texas as were cylinders A1

and A2. Cylinders T1 through T3 were filled by a local air separation facility off of a tube trailer, and cylinder V1 was filled by a local vendor off of a tube trailer. Results for the analysis of these cylinders appears below in Figure 7. Note the Y-axis in Figure 7 is in log scale.

None of the cylinders evaluated

were found to have hydrogen, methane or carbon monoxide levels above the detection limit for the system. Cylinder T1 is an AIC Corp. owned cylinder that was filled by a

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local air separation plant off of a tube trailer and then returned to AIC Corp. It is apparent from the significant level of contamination that this cylinder was probably filled without purging the equipment, which led to the incursion of air into the cylinder. However, it is also interesting to note that the oxygen/nitrogen ratio for this cylinder is less than what would be expected from an air incursion. It is possible that this cylinder was used for nitrogen prior to being used for helium and was not sufficiently purged to remove the residual nitrogen. All of the cylinders evaluated in this study, other than T1, were labeled as either five 9's helium or UHP helium. All the cylinders evaluated would meet the five 9's criteria (including T1) since all of the cylinders had less than 100 ppm total contamination. All of the cylinders except T1 would meet six 9's criteria based on the total contamination found in this analysis. All of the cylinders except A1 and T1 (as noted above) had oxygen/nitrogen ratios between 31 and 53 percent indicating the incursion of air in the sys-

tem, possibly during the fill process. The lowest values for contaminants were found in the cylinders filled in the Texas facilities (B1 through B3, A1 and A2.) Those filled from tube trailers locally had levels of oxygen and nitrogen higher than those filled at the Texas facilities.

A concern was raised about the possible infusion of air into the system leading to spurious results in the evaluation of the commercial helium cylinders. The data do not indicate that this is the case. If one examines the response of the oxygen and nitrogen peaks from the 25 microliter chromatogram above (Figure 4), it is apparent that no leak is present in the system between the six-port sampling valve and the brass “T” used for cylinder selection. If there were a leak of any significance, the oxygen and nitrogen peaks in the standard chromatogram would be greater than the methane peak which is not the case. Furthermore, if there were a leak in this segment of the chromatographic system, the oxygen and nitrogen peak would have a response ratio approaching one to three. Instead, the standard chromatograms have response ratios for oxygen to nitrogen on the order of 0.7:1.

It is possible that there was a leak between the sample bottle and the sample selection “T”. However, the low responses for oxygen and nitrogen for all the samples except T1 do not indicate that this is the case. Furthermore, the fluctuation in the oxygen/nitrogen ratio for the samples (from 34% to 72%) does not suggest an air leak of any significance.

Finally, it is necessary to ask if the analytical data presented here meet the objective of low level impurity measurements in commercial helium. If a significant leak were present in the analytical system, one

would expect higher reported values for oxygen and nitrogen contamination. If the contamination reported here were due to a small air leak, it would suggest that the commercial helium cylinders were actually less contaminated than reported, since at least a portion of the reported value would be due to the leak. Considering that all of the cylinders meet the criteria for five 9's helium, the analytical system clearly demonstrates the ability to monitor the purity levels of ultra high purity grade commercial helium.

Conclusion

The sensitivity of the dielectric barrier discharge detector in helium ionization mode enables the user to evaluate high-purity gas cylinders supplied from various vendors. Using a simple configuration, without additional hardware such as getters and purge valves, it is still possible to measure sub ppm levels of impurities in commercial cylinders using standard gas chromatographic configurations. A number of commercial cylinders were evaluated and found to meet the specifications for requirements of Grade 5 quality gases, and most of the cylinders met the requirements for Grade 6 gas quality. One cylinder was found to be significantly more contaminated than all of the other cylinders evaluated, which is believed to be due to poor fill procedures. Local implementation of a quality assurance program using this detector would have identified the higher contamination of this cylinder compared to the balance of cylinders analyzed.

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