Standardization of Helium Carrier Gas for Helium Detector Applications

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Carrier gas purity is a significant problem in all sensitive detectors, but for the helium ionization detector (HID) the purity of the helium carrier gas is essential for the operation of the detector. The presence of impurities in the carrier gas will influence the detector's background current, noise level, signal polarity, magnitude of response, and overall detector stability. The introduction of the helium ionization detector led to an efficient method to achieve an ultra-high-purity grade of helium (minimum purity of 99.9995%). In such grades of helium, impurities are in the range of a few parts per billion (*1*, *2*). Using this grade of helium in a leak-free chromatographic system, the detector will characteristically respond negatively to a small concentration of selected gases (Ne, H_2, Ar, O_2, and N_2) and positively to other gases (*3–5*). Addition of a small concentration of gaseous additive will provide a positive response to all gases and compounds tested (*3–5*). Recently the HID was operated in the saturation region of the detector field intensity to provide a sensitive and reliable response (*6*, *7*). In this work the detector was operated with a high-purity grade of helium (minimum purity of 99.995%) and the detector response was positive for all gases and compounds tested except neon. The use of the high-purity grade of helium, however, does not imply that the purity of the helium carrier gas used is not a significant factor. We have noticed that the detector response will vary with the carrier gas cylinder used due to a slight difference in purity level from one cylinder to another. In this work we evaluated the detector response when high-purity and ultra-high-purity grades of helium were used as carrier gases. A method to achieve a high-precision analysis using different cylinders of helium as a carrier gas was also investigated.

EXPERIMENTAL SECTION

A Varian 1700 gas chromatograph (Varian Aerograph, CA) was used in this work. The detector was operated at an applied potential of 150 V (1500 V/cm of electrodes) and maintained at 150 °C. A Valco eight-port gas sampling injection valve (Valco Instrument, Houston, TX) was adapted to the chromatograph with 100-μL sample loops. A Spectra-Physics SP-4000 was used to integrate peak areas.

The column used in this work was stainless steel tubing (2 m × 1.1 mm i.d. × 1.6 mm o.d.), packed with molecular sieve 13 × (60–80 mesh), and conditioned overnight at 150 °C with a helium flow of 14 mL/min.

A standard gas sample mixture was used during the course of this work; it consisted of 11 ppm H_2, 24 ppm argon, 5 ppm neon, 9 ppm O_2, 29 ppm N_2, 22 ppm CH_4, and 23 ppm CO (Scientific Gas Products, Houston, TX). Carrier gas used in this work was ultra-high-purity and high-purity grades of helium (Scientific Gas Products).

During the course of this work, a number of helium cylinders were used as carrier gas. Normally, opening the system to the atmosphere to exchange a cylinder will allow air and moisture into the system and purging this air and moisture completely requires several hours. In order to avoid this problem, we used a four-way valve (Whity, Cleveland, OH). This allows helium cylinders to be exchanged without opening the system to atmosphere.

Table I. Table of Responses to Various Gases[a]

gas tested	response for ultra-high-purity helium						response for high-purity helium					
	1	2	3	4	5	6	7	8	9	10	11	12
Ne	−	−	−	−	−	−	+	+	−	−	−	−
H_2	−	−	−	−	−	−	+	−	+	−	−	−
Ar + O_2	−	−	−	−	−	−	17	12	20	13	9	4
N_2	−	−	−	−	−	−	20	8	14	10	9	4
CH_4	61	65	61	69	51	49	20	35	34	37	40	34
CO	91	102	91	106	78	72	36	55	57	57	62	53

[a] Peak area in counts $\times 10^{-3}$. Signs indicate signal polarity.

RESULTS AND DISCUSSIONS

To evaluate the detector response when different grades and different cylinders of helium are used, we analyzed the sample mixture using six different cylinders each of ultra-high-purity and high-purity grades. The results obtained from these analyses are summarized in Table I. The detector response to Ne, H_2, Ar + O_2, and N_2 was negative when the ultra-high-purity helium was used as a carrier gas but the response to Ar + O_2 and N_2 became positive when high-purity helium was used. The response to Ne and H_2 was either positive or negative depending on the cylinder used. A positive response to Ne is due to a higher concentration of Ne in the carrier gas than in the sample analyzed. The negative response to H_2 in four cylinders of high-purity helium indicates that these cylinders have purity levels that are higher than that which produces the minimum background current, because at the minimum background current the detector response to H_2 is positive (*8*). The magnitude of the detector response to CH_4 and CO was higher when using the ultra-high-purity grade than when using the high-purity grade of helium as a carrier gas. It appears from Table I that the high-purity helium would be adequate for most chromatographic applications. The ultra-high-purity grade will improve the detector response, but this grade of helium is also more expensive. Table I also shows variation in the detector response within the two groups of helium grades. This variation may not be significant for some applications, but if high precision is required, the carrier gas purity should be standardized to a point in which this variation between cylinders is minimized.

We investigated the possibility of standardizing different cylinders of helium. A practical way to achieve this is to use helium carrier gas at the minimum background current. The addition of small concentrations of gaseous additives to the ultra-high-purity helium carrier gas will decrease the background current to a minimum point. After this point is reached, further increase in the concentration of the gaseous additives will increase the background positively (*8*). At the minimum background current all cylinders will contain a constant total impurity level, and consequently they should provide a constant response. This minimum background current can easily be achieved by adding a gaseous additive

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Table II. Detector Response at the Minimum Background Current[a]

gas tested	response for ultra-high-purity helium						response for high-purity-helium					
	1	2	3	4	5	6	7	8	9	10	11	12
$Ar + O_2$	21	19	20	19	18	16	18	12	17	21	20	18
N_2	18	17	14	16	14	12	12	13	13	19	16	14
CH_4	32	31	33	31	31	28	29	26	31	34	31	30
CO	53	50	53	50	50	46	47	47	52	56	52	49

[a] Peak area in counts $\times 10^{-3}$.

to the ultra-high-purity helium. However, the high-purity helium grade may contain a concentration of impurities greater than that at minimum background current. A typical analysis for impurities in high-purity grade helium as provided by the producers is 1 ppm of each of CH_4, O_2, Ar, and CO_2 and 10 ppm H_2, 14 ppm N_2, 14 ppm Ne, and 12 ppm H_2O. To purify the helium carrier gas, we used a hydrox purifier (Matheson, LaPort, TX) which contains a zirconium, titanium, and nickel alloy. This alloy when heated is effective in retaining some of these impurities, but others such as H_2, Ne, Ar, and N_2 just pass through. The H_2O content in helium is reduced to H_2 increasing the content of H_2 to twice that of H_2O. To further purify this helium grade, we inserted a well-conditioned molecular sieve trap upstream from the hydrox purifier. The molecular sieve trap will effectively retain most of the H_2O and CO_2. With this arrangement all the high-purity helium cylinders produced a partial negative response to H_2, Ar + O_2, and N_2. After a partial negative response to H_2, Ar + O_2, and N_2 was achieved, gaseous additive was added to the helium to achieve the minimum background current. The addition of gaseous additives was carried out via the permeation tube technique (9). H_2, Ar, O_2, or N_2 could be used as gaseous additives (3–5); however, we used H_2 in the work described here. Table II shows the magnitude of the detector response at the minimum background current using the two grades of helium. The variation in the detector response, when different cylinders of helium are used, is now minimized.

It appears from Table I that for most applications the high-purity grade of helium is adequate and provides a positive response for almost all gases and compounds tested. Ultra-high-purity helium shows an improved response, but it provides a negative response to some selected gases. The variation in the detector response with different cylinders of helium could be minimized by adjusting the total impurities to that which produces the minimum background current.

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Cooling System for High-Power Ion Lasers

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Most commercial ion lasers are equipped with water cooling systems which require flow rates of 3–8 gal/min. In principle, ordinary tap water can be used in these systems. However, the use of poor quality water can lead to several detrimental effects. Particulate matter in the water can block water passages in the laser power supply and plasma tube and thus increase the system's flow impedance. This problem can be reduced but not eliminated by using filtered tap water. Water having an appreciable ion content is also undesirable as a cooling medium. Magnesium and calcium ions, for example, can precipitate out to form scale on the walls of the laser water passages thereby decreasing the efficiency of the cooling system.

The Spectra-Physics line of ion lasers, in particular, should be cooled with water which is sufficiently purified so that water in a 10 ft length of 0.5 in. diameter hose has at least 100 kΩ resistance when measured under flowing conditions (1). This requirement follows from the plasma tube design employed by Spectra-Physics in which the plasma tube anode passes through the water cooling jacket. Thus, the cooling water is in direct contact with the anode and can be considered to be at that potential. High conductivity water in the cooling system, therefore, provides an alternate path to ground. In extreme cases, this could lead to unstable laser output power or premature plasma tube failure.

This paper describes a simple recirculating loop cooling system designed to eliminate the above potential problems. The system employs off-the-shelf plumbing components where possible to minimize cost without sacrificing performance. The system is most appropriate for small industrial or university laboratories where the cost of commercial cooling systems of similar design may be prohibitive.

DESCRIPTION OF COOLING SYSTEM

The major components of the cooling system are shown schematically in Figure 1. The pump, laser, heat exchanger, and reservoir form a recirculating cooling loop which employs deionized water. The water purity is maintained by a deionizer located in a parallel line between the pump and the reservoir inlet.

The pump is a Burkes Model 3CT6M close coupled turbine pump (Burkes Pumps, Decatur, IL) of all bronze construction which provides a water flow rate of 4.3 gal/min at a pressure of 70 psi.

The water from the laser is cooled with an American-Standard Model BCF-06-036-001 shell and tube type heat exchanger (American Standard, Buffalo, NY). This particular model is a single pass unit having a diameter of 6 in. and a length of 36 in. The heat exchanger is used in a counterflow configuration as shown in Figure 1 in which water in the

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