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Note

Effect of helium purity on the helium detector response in the saturation region of the detector field intensity

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In spite of the well recognized high sensitivity of the helium ionization detector, its function has been limited to the analysis of gases utilizing gas-solid chromatography¹⁻⁶. Recently however, it has been shown that the helium ionization detector can be operated in the saturation region of the detector field intensity to provide a reliable and sensitive response⁷. In the saturation region the detector is operated at low applied potential (200 to 2000 V per cm of electrode surface) and the response is independent of the applied potential. It is characterized by high stability, low noise level and high sensitivity. This characterization allows the use of packed and capillary columns utilizing gas-solid and gas-liquid chromatography⁷.

In recent work^{7,8} high purity grade helium, the grade most often used in general chromatography (also called technical helium; minimum purity 99.995%), was used. With this grade of helium the detector response was positive for all gases and compounds tested except for neon for which the response was negative. It is expected that the detector response in the saturation region will also depend on the purity of the helium used as a carrier gas. How the purity of the helium will affect the detector response in this region is the subject of this work.

EXPERIMENTAL

A Varian 1700 gas chromatograph (Varian Aerograph, Palo Alto, CA, U.S.A.) was used in this work. The detector was operated at an applied potential of 150 V (1500 V per cm of electrodes) and maintained at 150°C. A Valco 8-port gas sampling injection valve (Valco Instrument, Houston, TX, U.S.A.) was adapted to the chromatograph. The bucking current circuit of the chromatograph was modified to measure the actual value of the current by installing a Bourns "Knob-Pot" (Bourns, CA, U.S.A.) to replace the old potentiometer. The Knob-potentiometer has a three-digit readout on the front of the knob which indicates the resistance ($0-999 \cdot 10^2 \Omega$) at which the pot is set. The voltage level supplied to this control was then increased

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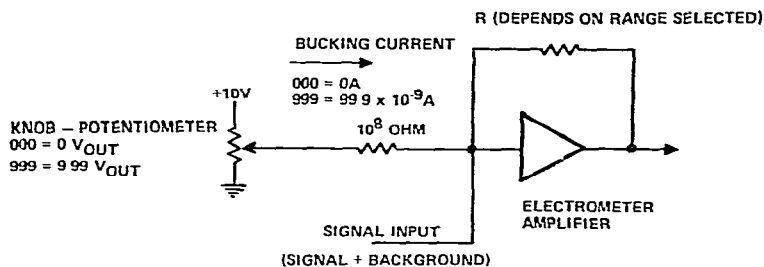


Fig. 1. Modified bucking current circuit.

from 9 to 10 V and was applied as shown in Fig. 1. The three-digit number on the front of the Knob-Pot can be read and then multiplied by 10^{-10} to indicate the magnitude of the bucking current.

The column used in this work was stainless-steel tubing (2 m \times 1.1 mm I.D. \times 1.6 mm O.D.), packed with molecular sieve 13X (60–80 mesh) and conditioned overnight at 150°C with a helium flow-rate of 14 ml/min.

A standard gas sample mixture was used during the course of this work; it consisted of 11 ppm hydrogen, 24 ppm argon, 5 ppm neon, 9 ppm oxygen, 29 ppm nitrogen, 22 ppm methane, and 23 ppm carbon monoxide. The mixture was purchased from Scientific Gas Products (Houston, TX, U.S.A.). For detector calibration a glass exponential dilution flask was used as previously described⁹. Carrier gas used in this work was ultra high purity helium, and was dried over a hydrox purifier (Matheson, La Porte, TX, U.S.A.).

The addition of gaseous additives to the carrier gas was carried out using the permeation tube technique as previously reported⁵. To calibrate the concentration of gaseous additives in helium, two calibrations were made, one in the negative mode and the other in the positive mode. As gaseous additives were added to ultra pure helium carrier gas, the background decreased negatively to a minimum and then increased positively, as shown in Fig. 2. At the minimum, the detector response was positive for all gases except neon and the detector was calibrated in the positive mode. At points below "c", such as point "a" (higher purity helium), the detector response was negative to small concentrations of the selected gases. To measure the concentration of gaseous additive needed to decrease the background current to the minimum (point a to point c), the detector was calibrated in the negative mode as previously reported⁶. The concentration which corresponds to the maximum symmetrical negative peak height is equal to the increase in concentration between points a and c. To measure the amount of gaseous additives added above point c (such as point d), the calibrated positive mode was adopted, and here the concentration which corresponds to the positive peak height is equal to the increase in concentration between points c and d.

RESULTS AND DISCUSSION

To evaluate the effect of carrier gas purity on the detector response, a sample containing a mixture of seven gases in helium was analyzed using different purity grades of helium carrier gas. When ultra high purity helium was used as a carrier gas the detector response was negative for Ne, H₂, Ar + O₂, and N₂, and positive for CH₄ and

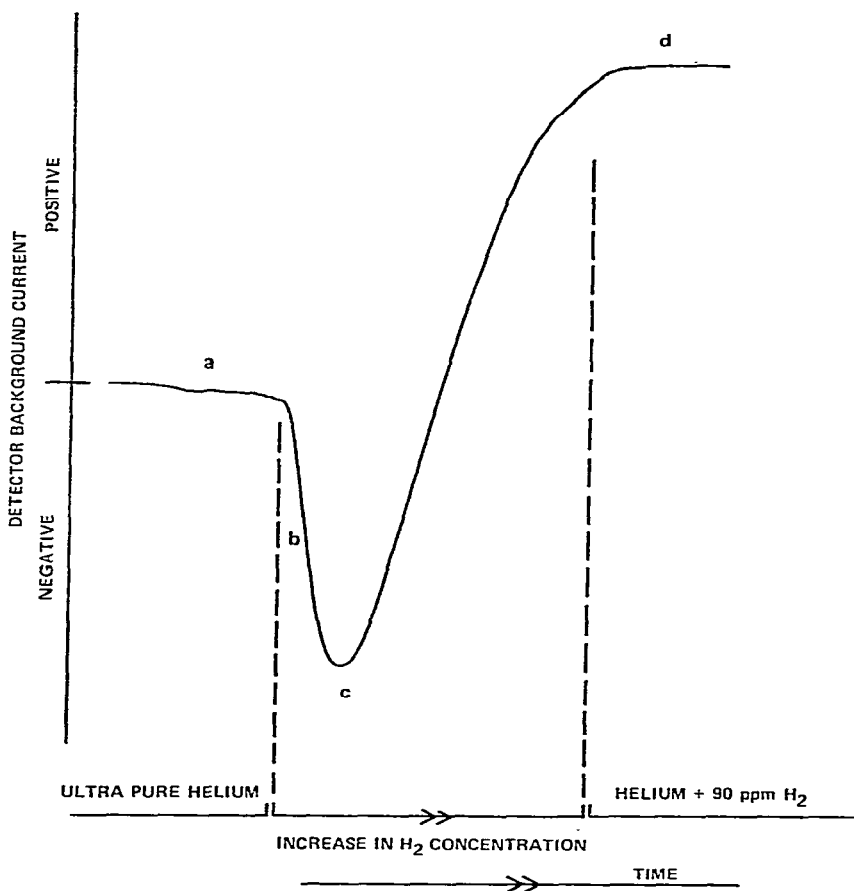


Fig. 2. Profile of adding hydrogen to ultra pure helium carrier gas.

CO as shown in Fig. 3a. To obtain a positive response to H₂, Ar+O₂, and N₂, gaseous additives have to be added to the helium carrier gas. The effect of adding H₂ to the helium carrier gas is illustrated in Figs. 3 and 4. In order to fully understand the response it is important to correlate Figs. 2, 3, and 4 together. At a purity level such as that at point a (Fig. 2), the detector response is the highest for all compounds except H₂, Ar+O₂, and N₂ where the detector response is negative. Fig. 3a shows a typical chromatogram obtained at level a (Fig. 2). At intermediate level between a and b (Fig. 2), the detector response to Ar+O₂ and N₂ is fully positive but the response to H₂ remains negative and decreases (Fig. 3b). At point c (Fig. 2) the minimum background current is achieved, and the detector response is positive for all gases except Ne as seen in the chromatogram in Fig. 3c. At point c the response to H₂ almost vanishes; however, increasing the concentration of H₂ in the sample produces a positive response to H₂. As the H₂ concentration in the helium carrier gas increases to level d in Fig. 2, the background current increases positively, the response to H₂ is negative, and the response to Ar+O₂ and to N₂ is optimized, as seen in Fig. 3d. A further increase in H₂ concentration above that which established level d causes a

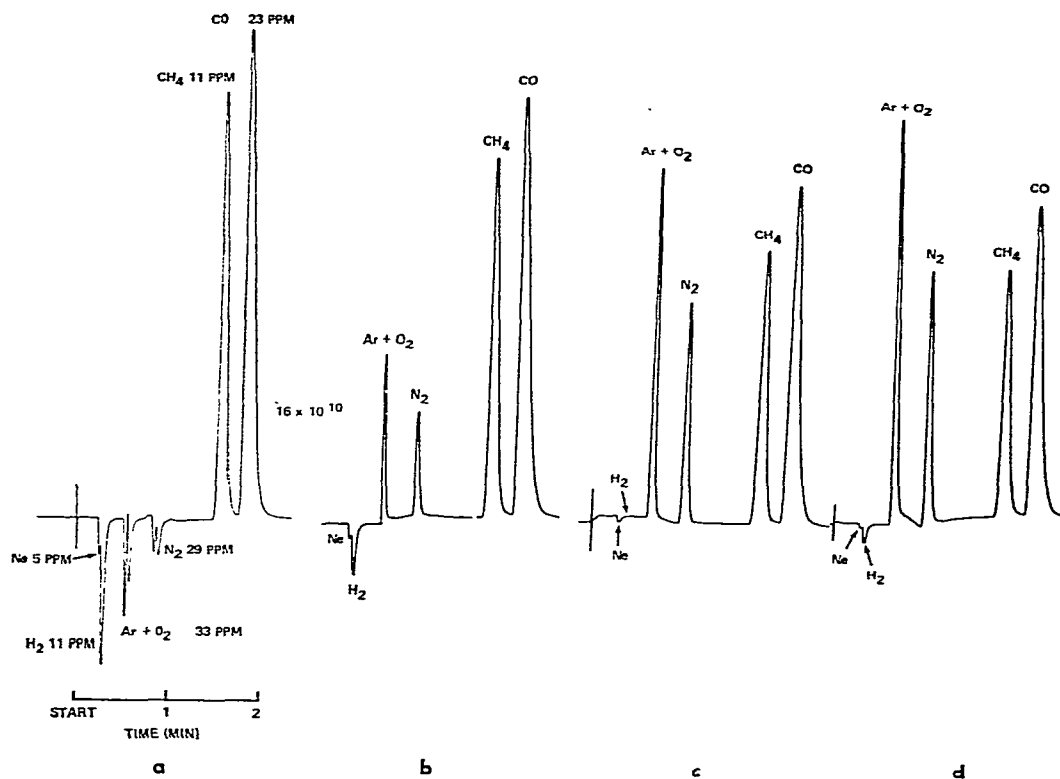


Fig. 3. Effect of adding hydrogen on the detector's response. Sample size 100 μ l.

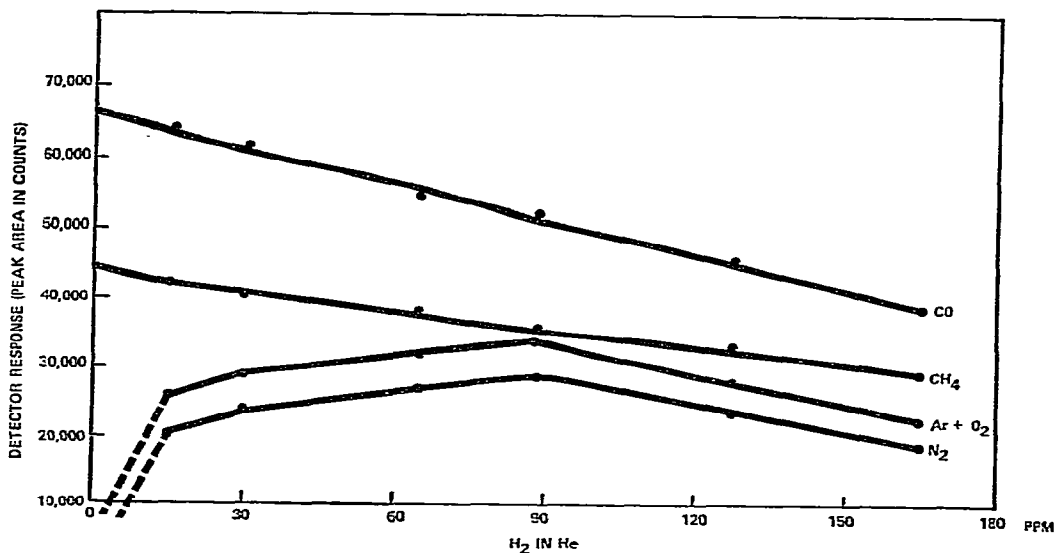


Fig. 4. Effect of adding hydrogen on the detector's response. Dotted line indicates change in polarity.

further increase in the background current, increase in the negative response to H_2 , and decrease in the detector response to $Ar+O_2$ and N_2 . The response to CH_4 and CO is optimized when ultra high purity helium is used (Fig. 2 at point a and Fig. 3a) and any increase in the impurity level causes a decrease in the response to CH_4 and CO . Fig. 4 shows that the detector can be operated with a relatively high content of gaseous impurities without drastically decreasing the detector response. The addition of about 165 ppm H_2 to the helium carrier gas decreases the detector response to CH_4 and CO to approximately one-half the response seen with the ultra high purity helium.

To examine the effect of carrier gas purity on the lower detection limit the detector response was calibrated for CH_4 using helium carrier gas of different purity levels. At points a, c and d (Fig. 2) the detection limits of methane were found to be 0.4, 1.0, and 4.0 ppb*, respectively. Any impurities in the carrier gas increase the lower detection limits.

The purity of the helium reaching the detector is a significant factor that influences the detector performance. It can be evaluated from the signal polarity of the detector response to small concentrations of H_2 , Ar , O_2 and N_2 . The negative response to some of these gases is a good indication of high purity level. This method is particularly important since the purity of the helium in the cylinder is not necessarily identical to that of the helium reaching the detector due to contamination by atmospheric leakage or by a poorly conditioned chromatographic system.

With respect to the purity of helium, the detector response is optimized differently for two classes of compounds. For the class of compounds that characteristically produces a positive response, the detector response is optimized by using maximally pure helium. On the other hand, for the class that characteristically produces a negative response, the detector response is optimized using ultra pure helium + 90 ppm H_2 .

The difference between the detector response to gaseous additives in the saturation and in the multiplication regions is due to the function of secondary electrons in the multiplication region. At high applied potential (> 350 V) the secondary electrons have sufficient energy to take part in the ionization process. While impurities in this region will consume some of the metastable helium, in return they will produce secondary electrons that are capable of taking part in the ionization process. In the multiplication region, impurities will increase the background current and the response⁵. In the saturation region, on the other hand, the secondary electrons produced by the presence of impurities will not have sufficient energy to take part in further ionization process. The presence of any impurity in the saturation region will decrease the detector response for all compounds except the gases that characteristically produce a negative response, in which case gaseous additives are needed in small concentrations to produce an optimum positive response.

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* The American billion (10^9) is meant here.

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