

Anomalous response of a helium ionization detector

It is generally accepted that the correct functioning of a helium ionization detector, as used in gas chromatography, is dependent upon a reduction of the impurity content of the helium carrier gas to a very low figure^{1,2} and furthermore, that a criterion of optimum performance is the lowest attainable standing current when the detector shows an increase in conductivity in the presence of a trace of an impurity.

Recently, a gas chromatograph, with a helium ionization detector and using purified helium as the carrier gas, was used for the analysis of samples of high purity helium and it was noted that instead of obtaining positive peaks, corresponding to an increase in cell conductivity, for hydrogen, oxygen plus argon, and nitrogen, peaks were obtained which were either wholly or partly negative. Methane, carbon monoxide and nitrous oxide always gave positive peaks. Previously this gas chromatograph had only been used for the determination of carbon monoxide and nitrous oxide in hydrogen when in each case normal, positive peaks were obtained.

The gas chromatograph analysis system comprises a cylinder of helium which feeds a recirculation system containing an activated charcoal purifier (77°K), a simple gas sampling system, a column (1 m × 5 mm I.D. stainless steel tube packed with 30–60 mesh molecular sieve type 5A and activated *in situ*), a helium ionization detector³ and a diaphragm pump. During analysis the column–detector outlet is not connected in the recirculation system to avoid pressure effects associated with the diaphragm pump. Neither renewal of part or all of the system nor extended reactivation of the molecular sieve material, resulted in the formation of positive peaks although it was often found that immediately after a change had been made that the peaks were positive for a short time and then became increasingly negative. It was also found that if the helium cylinder was connected to the sample system, *via* a gas regulator only, positive peaks were always observed.

A series of tests was therefore carried out in which impurities were continuously introduced into the purified carrier gas stream, the molecular sieve material having been previously reactivated at 300°C for 24 h with a continuous helium purge of 20 ml/min. Operation of the column at ambient temperature with a flowrate of 100 ml/min of purified helium containing from 0–20 v.p.m., in turn, of each of hydrogen, argon, nitrogen and methane showed that:

1. With the addition of each of the impurities to the carrier gas the standing current fell initially with increasing impurity content and then rose with further increase in the impurity content, except in the case of methane where a continuous rise was observed, Fig. 1.

2. As the concentration of each of the added impurities in the carrier gas was increased the height of the negative peaks from an injected sample, decreased, and in some cases, finally became positive. An example of this change, where nitrogen is added in increasing amounts to a helium carrier gas containing 4.5 v.p.m. Ne, is shown in Fig. 2.

It is interesting to note that of the gases tested only those having an ionization potential greater than about 15 eV show this phenomenon of inversion.

The purified helium used in these experiments was analysed mass spectrometrically and compared with a corresponding analysis of 'Specpure' helium, Table I.

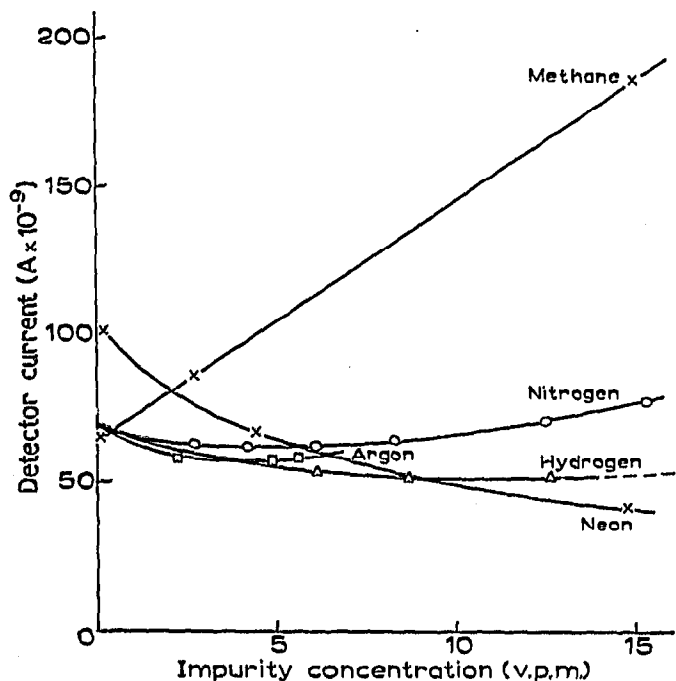


Fig. 1. Effect of carrier gas purity on the detector standing current.

The only significant difference between the two sets of figures is the level of neon. When the cylinder of commercial helium which supplied the purifier, was replaced by 'neon free' helium a much higher standing current was obtained which fell as the neon impurity content was increased, Fig. 1. Insufficient neon could be added, however, to explore fully the change in standing current with neon concentration, and therefore to determine if neon had the same effect as the other impurities. Preliminary experiments indicate that, for hydrogen at least, the use of high purity helium giving negative peaks offers an improvement in sensitivity by a factor of at least 10, although it is probable that a method for the determination of hydrogen

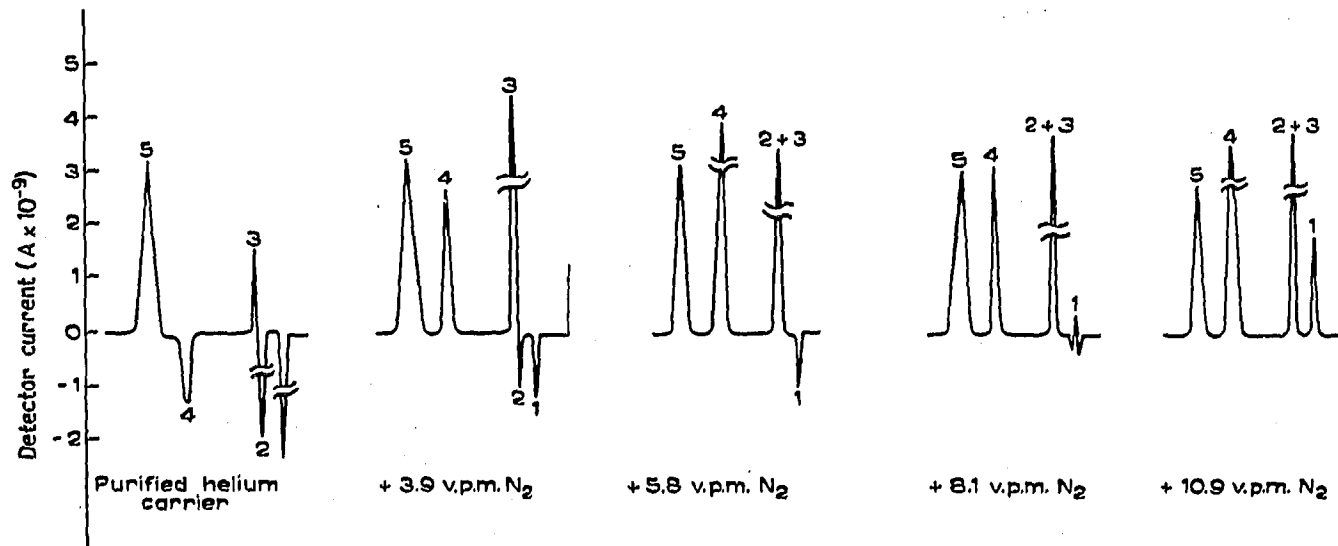


Fig. 2. The effect of the nitrogen concentration in the carrier gas on the sample impurity peak shape. 1 = Hydrogen; 2 = argon; 3 = oxygen; 4 = nitrogen; 5 = methane.

TABLE I
IMPURITY CONCENTRATION IN HELIUM (v.p.m.)

	H ₂	N ₂	O ₂	A	CO ₂	Ne
Purified	< 0.5	0.3	0.1	0.1	< 0.1	4
Specpure	0.8	0.3	0.1	< 0.1	0.2	0.5

based upon this effect will cover a very limited range. Experiments are being carried out in which it is hoped to develop methods for each of the gases capable of giving negative peaks.

We would like to acknowledge the cooperation of Mr. J. A. J. WALKER (U.K.A. E.A. Culcheth), who was able to confirm that negative peaks could be obtained using his gas chromatograph and our purifier.

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Säulenchromatographie von polycyclischen aromatischen Kohlenwasserstoffen an lipophilem Sephadex LH-20*

Hydrophobisierte Adsorbentien eignen sich gut zur Trennung polycyclischer Aromaten (1-4). Vor Kurzem hatten wir auf anderem Weg festgestellt, dass Sephadex (G-10 und LH-20) ein starkes Adsorptionsvermögen für Kohlenwasserstoffe höherer Ringzahlen besitzt⁵. Es war daher interessant zu prüfen, in welchem Mass sich die Adsorption bei der Säulenchromatographie bemerkbar macht. Zu diesem Zweck wurden an einer Säule von in Isopropanol gequollenem Sephadex ein Gemisch mehrerer Kohlenwasserstoffe chromatographiert. Das Ergebnis (Fig. 1) war eine mit steigendem Molekulargewicht abnehmende Eluierbarkeit und stand somit im Gegensatz zur normalen Sephadex-Chromatographie. Wie der Fig. 1 zu entnehmen ist, lassen sich sehr gute Trennungen durchführen, z.B. von 1,2-Benzofluoren-Chrysen, Chrysen-Benzpyrene etc. Ja selbst die isomeren 1,2- und 3,4-Benzpyrene sind hinreichend gut trennbar. Die Reproduzierbarkeit der Versuche ist ausgezeichnet.

* Vgl. Firmenschrift: *Sephadex LH-20 zur Gelfiltration in organischen Lösungsmitteln*, Pharmacia Fine Chemicals, Uppsala, Schweden.