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N. GETOFF

Institut für Radiumforschung und Kernphysik
der Österreichischen Akademie der Wissenschaften,
Vienna.

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Analysis of the Major Constituents of Fuel Gases by Gas Chromatography

RECENTLY, Hollis¹ has reported retention data for the separation of methane, carbon dioxide, and polar materials on porous polymer beads. In these laboratories a polymeric bead column packing commercially available in the United Kingdom² has been investigated, and has been found to have considerable advantages over conventional adsorption columns for the analysis of fuel gases which contain hydrogen, carbon monoxide, methane, carbon dioxide, and the C₂-hydrocarbons as major constituents.

Hitherto the gas chromatographic analysis of fuel gas has necessitated the use of two adsorption columns. Usually a type 5A or 13X molecular sieve column is preferred for the separation of methane and carbon monoxide, but because this material strongly absorbs carbon dioxide, which eventually poisons it, a second column of silica gel must be used to separate this gas and the C₂-hydrocarbons³. It has now been found possible using a single column to analyse a fuel gas for these components including carbon dioxide.

Fig. 1. Chromatogram of seven-component gas on ethylvinylbenzene polymer at 30° C. (1) Hydrogen; (2) air; (3) carbon monoxide; (4) methane; (5) carbon dioxide; (6) ethylene and acetylene; (7) ethane

The chromatogram in Fig. 1 was produced using a Perkin-Elmer model 451 gas chromatograph. A methane-rich gas containing 3 per cent carbon monoxide was analysed at 30° C using a column 10 ft. long and 3/16 in. internal diameter, packed with 80-100 mesh beads of an ethylvinylbenzene polymer. This was conditioned before use by heating to 230° C for 1 h as recommended by the manufacturer. Helium was used as carrier gas at an inlet pressure of 15 lb./in.² gauge and a flow rate of 40 ml./min, and the components were detected using a thermistor

katharometer. On this column carbon monoxide and methane were well separated, and carbon dioxide eluted within 5 min of injection. The column separated unsaturated C₂-hydrocarbons from ethane under the same conditions.

When ethylvinylbenzene polymer was used as column packing, rapid analyses were obtained with good separation and without the 'tailing' peaks associated with other adsorption columns. In this laboratory it has enabled a gas to be analysed for seven components in 30 min with a single injection on one column, the sample size being adjusted according to the recommendations of Pauschmann⁴ so as to obtain a nearly linear response for hydrogen using helium as carrier gas.

R. A. CROSS

The Gas Council,
Midlands Research Station,
Solihull,
Warwickshire.

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Sensitivity to Oxygen of an Ionization Detector with Helium and Neon as the Carrier Gases

WE are interested in the analysis by chromatography of trace (v.p.m.) mixtures of oxygen in gases, and the Lovelock radioactive ionization detector¹ was selected as the most appropriate for the purpose. This detector, originally developed for sensitive detection of organic compounds in a carrier stream of argon, is not very sensitive to permanent gases in argon because the metastable energy of argon (11.6 eV) is slightly less than the ionization potentials, 12-16 eV, of most of the permanent gases. Berry² suggested that helium which has a metastable energy of 19.8 eV would be a suitable carrier gas. We have carried out tests first with helium³ and later with neon, the metastable energy of which is 16.5 eV.

In these tests we determined the sensitivity of a Lovelock strontium-90 detector (made by W. G. Pye, Ltd., Cambridge) to helium and neon containing constant (v.p.m.) amounts of added oxygen, for different voltages applied to the detector. In each case, the flow was maintained at 85 cm³ (N.T.P.)/min and the original carrier gas was purified to less than 0.1 v.p.m. oxygen. The sensitivity was found to increase with detector voltage up to 1,300 V for helium and 850 V for neon, above which voltages spark discharge occurred.

Table 1

Carrier gas	Detector voltage (V)	Standing current (amp)	Sensitivity amp/v.p.m. oxygen	Noise-level (amp)
Helium	1,300	5×10^{-9}	3×10^{-9}	5×10^{-11}
Neon	850	5×10^{-9}	5×10^{-9}	5×10^{-11}

Using these voltages, we determined the standing current and the noise-level for this current with carrier gas containing no added oxygen, and the change in current with added oxygen. The variation in current with added oxygen is linear up to at least 1.0 v.p.m.

The results are given in Table 1, from which it can be seen that the minimum detectable addition of oxygen, defined as that producing a change in detector current of twice the noise level, is 0.03 v.p.m. oxygen for helium and 0.02 v.p.m. oxygen for neon.

In practice, neon with its much higher cost would scarcely be chosen in preference to helium unless there were some special reason, for example if the gases to be detected were already mixed with neon, or if a recirculation system were used, the gases being recirculated through the purifier which is needed in any event when