

Notes

Determination of traces of water in hydrocarbons by gas-gel chromatography with an electron capture detector

A rapid and precise method for the determination of small quantities of water in hydrocarbons was worked out using the microporous polymer beads "Porapak", as stationary phase in gas chromatography.

This polymeric phase has been shown to be useful for water separation, due to its low retention time for this compound.

HOLLIS and coworkers^{1,2} showed that Porapak, especially the "Q" type, can easily separate water from light hydrocarbons, but is ineffective when the sample contains compounds heavier than hexanes. This difficulty arises from the long retention time and poor peak symmetry due to strong absorption on the polymeric substrate.

We have found that when the Porapak Q is partially inactivated with a small amount of nonpolar liquid phase, such as SE-30 methyl silicone or Apiezon L grease (from 2 to 5% of total weight), hydrocarbons as heavy as octanes and decanes can be eluted in a reasonable time, and their peaks are well resolved and sharp.

Unfortunately, the nonpolar stationary phase causes a loss of sharpness of the water peak, due to tailing. In order to avoid such an effect, a small amount of polar liquid phase was added to the support.

A concentration of about 3% of Carbowax 20 M (the exact concentration depends on the composition of the sample) was found to be effective in reducing the tailing of the water peak.

This combination of stationary phases gives good results, as can be seen from Table I, where the adjusted retention time t_a (relative to air) is reported for water and isooctane; this hydrocarbon was taken as a comparison standard, as its boiling point is so close to that of water. In Table I the sharpness of the peaks is also reported, obtained by dividing the height by the base width.

The sample consists of 10 μ l of isooctane containing 50 p.p.m. of water.

Uncoated Porapak Q gives a good peak shape for water, but shows a long tail for isooctane. On coating the polymer beads, the sharpness of the water peak decreases, but the improvement of the hydrocarbon peak is very good, as can be seen in Fig. 1c.

The sensitivity of the method is very high, due to the high loading capacity of the stationary phase, which permits the injection of large samples without loss of resolving power. For instance, a column 1/8 in. thick, 5 ft. long, can tolerate the injection of 150 μ l of sample, and still give a good separation.

Using a thermal conductivity detector, with helium as the carrier gas, and a filament current of 300 mA, an injection of 150 μ l of sample allows the determination of traces of water as low as 3 p.p.m. The linearity of the peak area *vs.* quantity plot is very good up to 400 p.p.m. of water, and allows the calculation of a correction

TABLE I

RETENTION TIME RELATIVE TO AIR (t_a) AND PEAK SHARPNESS (S) OF WATER AND ISOCTANE ON VARIOUS STATIONARY PHASESColumn length 5 ft., O.D. 1/8 in.; flow 20 ml/min helium; temperature 200°; sample 10 μ l, water concentration 50 p.p.m.

Stationary phase	t_a		S	
	Water	Isooctane	Water	Isooctane
Porapak Q 100/120	1.4	27	10	0.5
Q + 5% SE 30	2.0	18.5	6.23	5.69
Q + 5% SE 30 + 3% Carbowax 20 M	1.8	9.0	7.67	6.70

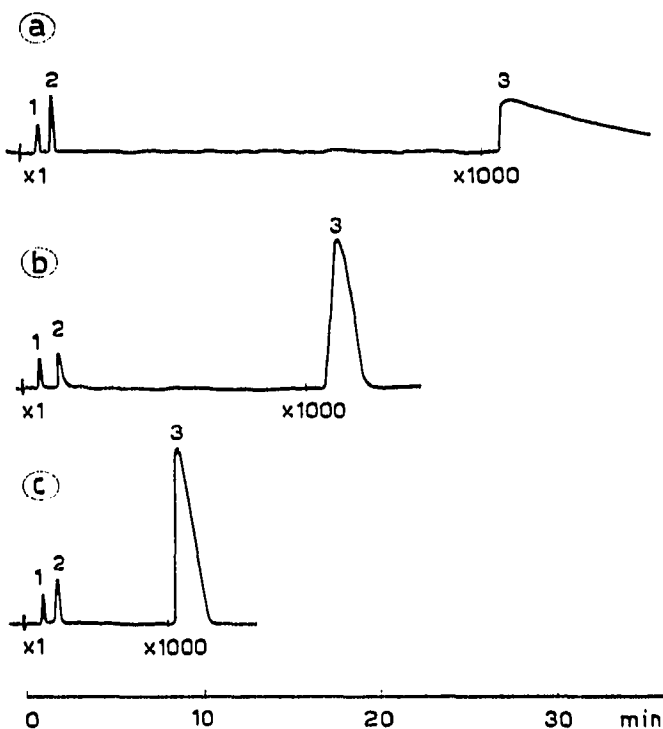


Fig. 1. Analysis of water in isooctane (50 p.p.m.) on 5 ft. \times 1/8 in. stainless steel columns, filled with: (a) uncoated Porapak Q 100/120 mesh; (b) Porapak Q + 5% SE 30; (c) Porapak Q + 5% SE 30 + 3% Carbowax 20 M. Peaks: 1 = air; 2 = water; 3 = isooctane.

factor by injecting known amounts of standard samples and taking into account the thermal conductivities of water and of the hydrocarbons.

Practically no significant error is made using the weight correction factors given in the literature for water (0.848), iso-octane (0.992) and other hydrocarbons³.

An improvement of the sensitivity of the method can be obtained by using an electron capture detector, which is more sensitive to water than to hydrocarbons, and whose sensitivity to water ranges from ten to fifteen times that of the thermal conductivity detector.

We used a detector of the concentric type, containing 250 mC of titanium tritide, manufactured by Varian Aerograph, using pure nitrogen as carrier gas and a cell voltage of 90 V, d.c. The sensitivity was increased by a factor of ten, theoretically

corresponding to a minimum detectable concentration of 0.3 p.p.m., but the poor loading characteristics of such a detector did not allow such large samples as before. In practice the minimum concentration which could be measured, with a standard deviation of about 10 %, ranges from 0.5 to 0.7 p.p.m.

Several difficulties must be taken into account when using the electron capture (EC) detector. As the EC detector is specific for certain types of compounds and does not have the same response to water and to hydrocarbons, it is necessary to prepare a plot of signal amplitude *vs.* water quantity, using known amounts of standards. The difficulty of obtaining samples with known low water contents can be overcome by analyzing a series of samples on the EC detector and on the thermal conductivity (TC) detector, and extrapolating the plot obtained from the TC detector sensitivity range to the range of the EC detector to zero concentration. This procedure is justified by the fact that in this range the detectors' response is linear.

Obviously the EC detector cannot be used when the sample contains excessively large amounts of electron-absorbing compounds (halogens, phosphorus and sulphur compounds, etc.) unless these compounds are removed with scrubber columns.

Furthermore, in order to avoid the temperature limit (225°) of the tritium detector, one could use a nickel EC detector which has a higher temperature limit. But the temperature range extension will not be large since the Porapak itself does not tolerate, at present, temperatures higher than 250°.

Other experiments are in progress in our laboratory to prepare stationary phases of new composition for other and better separations, and to improve the sensitivity of the method described.

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A simple microcell for photometric monitoring of flowing materials

A variety of cuvettes for the continuous photometric monitoring of flowing liquids are commercially available. But, none combines low cost with small sample size and a light path longer than 1 cm. A flow cuvette that combines these features is highly desirable. It could aid in such tasks as monitoring chromatographic effluents and measuring the optical densities of a series of small samples, especially if weakly absorbing solutions were involved.

In considering the desirable features such a cell should possess, we were led to

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