

The gas chromatographic determination of petrol in water*

As a result of accidents subsoil water may be polluted with petroleum products and this may be detrimental to the drinking water supply. The content of petroleum products in water that causes concern is 1 mg/l. Research is now being conducted in our institute concerning the migration of small quantities of petroleum products in the soil. It was necessary for this purpose to have a method whereby hydrocarbons from petrol dissolved in water could be detected.

Direct analysis by gas-liquid chromatography (GLC) of aqueous petrol solutions did not prove successful. An indirect method by which extraction is effected was developed. The solvent selected was nitrobenzene, after it had been found that ether, and to a lesser extent carbon tetrachloride and carbon disulphide, are not suitable for this purpose. With the GLC column used, a fair degree of separation is obtained between the alkanes and aromatics found in petrol as well as between the different aromatics.

Experiments and results

Instrumentation. Gas chromatography was carried out on an Aerograph 1520 with a flame ionization detector, using a 3 m, 0.125 in. O.D. copper column packed with 10% polyethylene glycol 1500 on silanized Chromosorb W (60-80 mesh).

Materials. Nitrobenzene (Noury-Baker, p.a. quality, b.p. 210.9°) was purified by distillation.

An undoped petrol with a boiling range of 42-202° (ASTM D 86) and a specific gravity (20/4°) of 0.76 was used. In order to prevent irregularities due to evaporation of varying quantities of the most volatile components, the fraction with a b.p. < 85° was distilled off. The composition of the modified petrol was determined (Table I; Fig. 1). The calculation was carried out by dividing the respective peak areas (found by triangulation) by their sum. The identification of peaks from the chromatogram was carried out by mixing petrol with a small amount of a compound which was very probably present, and chromatographing the resulting mixture. The unidentified peaks very probably originate from C₉-C₁₁ aromatics. If we assume that the petrol contains only traces of undecanes and dodecanes, it consists of 70% of aromatics (Table I). This was confirmed by U.V. spectrophotometry.

Method. 25 ml of petrol water** was shaken with 0.5 ml of nitrobenzene for 4 min. 2 μl of the extract was analysed. As a rule the following GLC conditions were used: Sensitivity: range 1, attenuation 4-32. The temperature of the column was 68°, of the injector 217°, and of the detector 220°. Flow N₂, H₂: 25 ml/min. Chart speed (c): 80 or 100 × 5/6 in./h. The chromatograms were calculated with the aid of triangulation. For the calculation of the total concentrations of hydrocarbons in water the specific peak area (α) of *p*-xylene was determined in triplicate. The α value found was: 0.62 · 10⁵, 0.63 · 10⁵ and 0.63 · 10⁵ cm²/mg (with range 1, attenuation 8 and c = 100 × 5/6 in./h). We used the value 0.63 · 10⁵. It was assumed that specific peak areas of the other hydrocarbons are equal to that of *p*-xylene.

Nitrobenzene emerges much later than the hydrocarbons of petrol. Ether,

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** Petrol water is the name used for aqueous solutions of petrol.

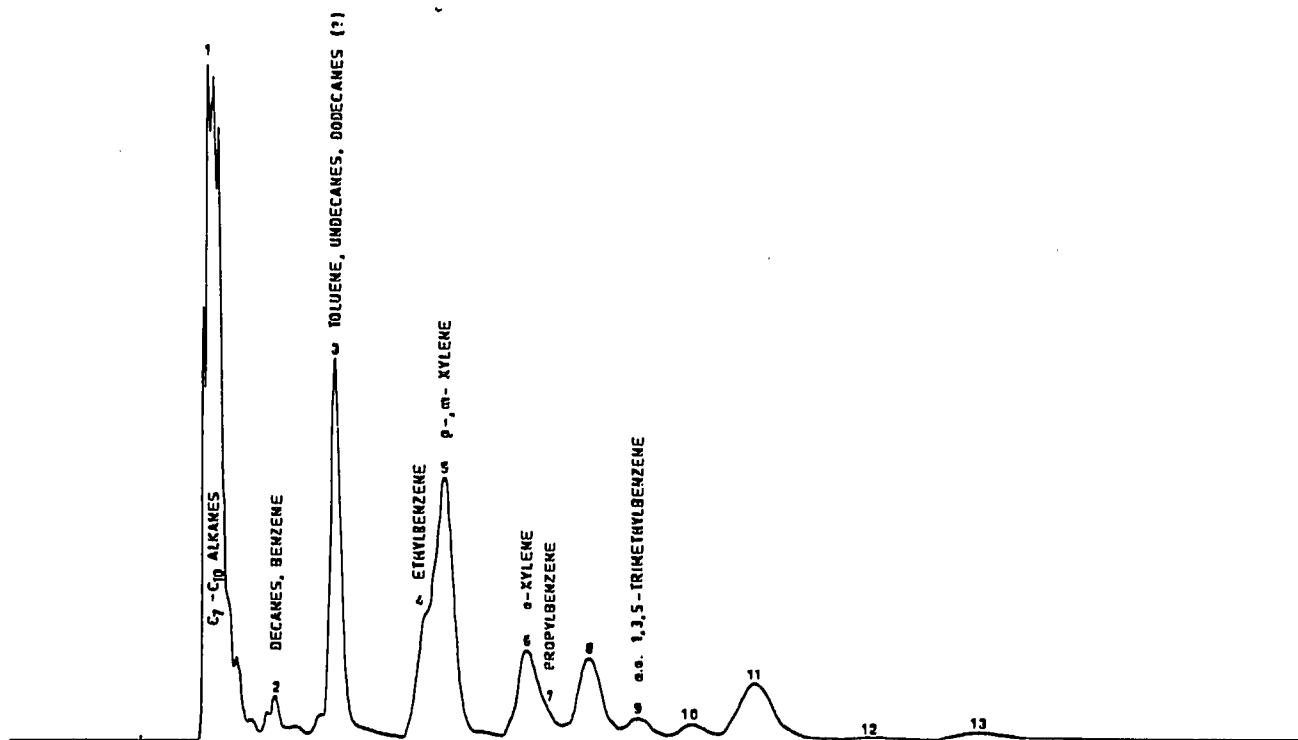


Fig. 1. Chromatogram of the petrol used (boiling range 85–202°). Column: 3 m \times $\frac{1}{8}$ in. O.D., 10% P.E.G. 1500 on silanized chromosorb W (60–80 mesh). Temperature of the column: 68°, of the injector: 217°, of the detector: 220°. Flow carrier gas (N_2): 25 ml/min. Range 10. Attenuation 32. Sample 0.1 μ l.

carbon tetrachloride and carbon disulphide cannot be used for extraction, as they interfere with the analysis.

Direct GLC analysis of a sample of petrol water containing 10 mg/l hydrocarbons was attended by difficulties. Because of the noise accompanying the analysis of small quantities ($< 1 \mu$ l), we attempted to chromatograph less minute quantities, but some unknown interfering peaks were found. They were caused by water, as was demonstrated by injecting pure water under the same conditions. GLC conditions: Range 0.1, 1. Attenuation 1–4. Temperature of the column 55°, of the injector 180°, of the detector 190°. Flow N_2 , H_2 : 25 ml/min.

Verification of method. Standard solutions were analysed by the method described. According to MELPOLDER *et al.*¹ acetic acid was used as a solubilizer in the preparation of standard solutions of hydrocarbons in water. Solutions were prepared by dissolving 1 ml of an acetic acid solution of 1% (v/v) toluene and 1% (v/v) *p*-xylene in 1 l of water. The hydrocarbons in the solution were determined. The whole procedure was repeated three times. Recoveries were respectively 76, 78 and 79% for toluene and 79, 80 and 86% for *p*-xylene. Toluene and *p*-xylene were selected for the standard solutions because they are important constituents of the petrol used and because of their comparatively good solubility in water^{2, 3}.

Application of method. The petrol water used in migration experiments was prepared by shaking 10 l quantities of water with 2 g of petrol. In this procedure a part of the amount of hydrocarbons was lost by evaporation, whilst another part was not dissolved. In Table I the results of the analysis are given for several samples

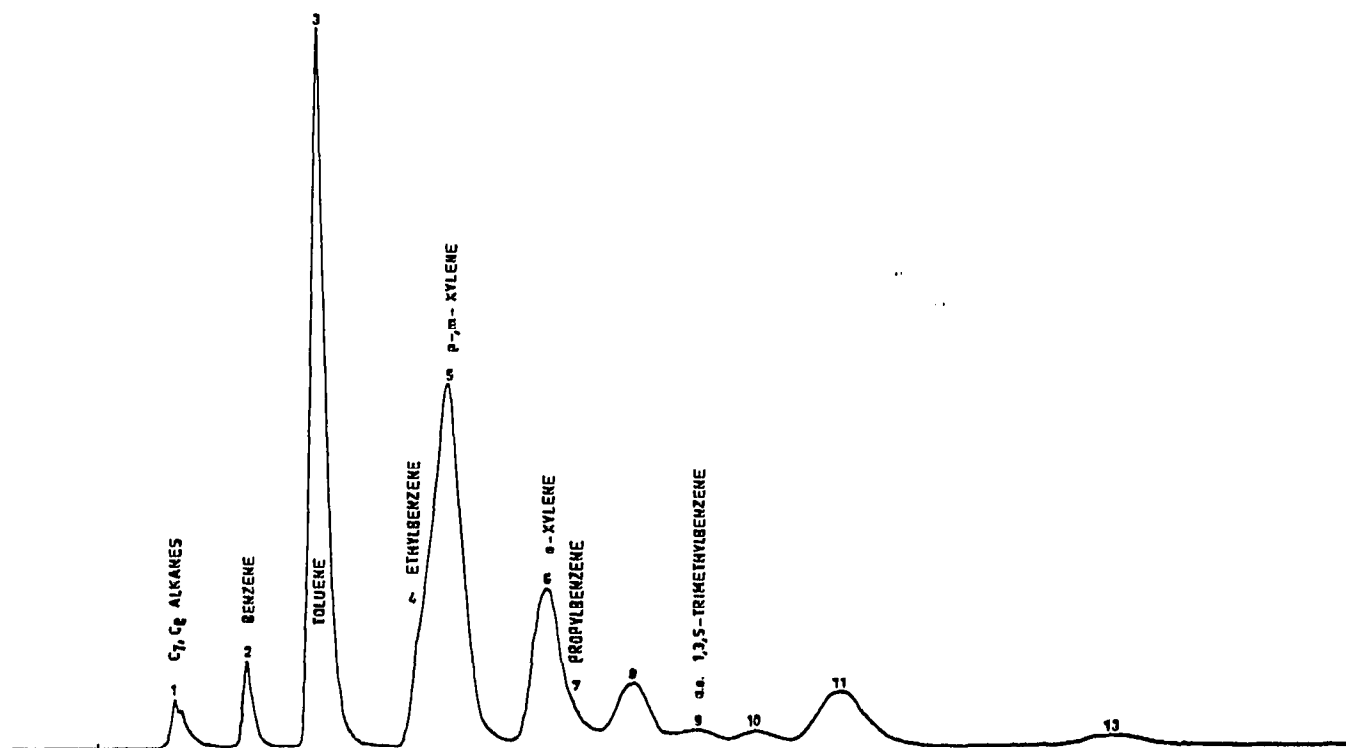


Fig. 2. Chromatogram of an extract of a sample of petrol water (sample 3, inlet, from Table I). Column, temperatures and flow as in Fig. 1. Range 1, attenuation 32. Sample 2.2 μ l.

taken during the migration experiments. Fig. 2 is the chromatogram of sample 3 (inlet).

Discussion

Far more attention was paid to the aromatics in the petrol than to the alkanes because of the better solubility in water of the former. The higher normal alkanes with n (= number of carbon atoms) > 8 are practically insoluble^{2,3}. We therefore assume that the branched alkanes with $n > 8$ are also insoluble. The term "insoluble"^{2,3} should most probably be understood to mean a solubility < 1 mg/l at 20°. The lower decanes ($n = 7$ or 8) dissolve slightly but easily evaporate from aqueous solutions.

With the method used we can determine as low a content as 0.1 mg/l of hydrocarbons from petrol in water, with a precision of 0.1 mg/l. For concentrations of hydrocarbons > 0.5 mg/l the precision of the method is estimated at 5% for the major components and 10% for the others.

We have stated that for standard solutions of toluene and *p*-xylene the recoveries were about 80%. The losses may be attributed to: evaporation of the hydrocarbons (even during preparation of the solutions), incomplete extraction and an error in the determined specific peak area (α) of a hydrocarbon (furthermore α may vary because of fluctuations in the flow of hydrogen and air to the detector).

The inlet samples (Table I) are from different batches of petrol water. The differences between the concentrations in these batches are caused by slight differences during preparation. The differences between the inlet and the corresponding exhaust

TABLE I
RESULTS OF THE ANALYSIS OF PETROL AND PETROL WATER

Peak fraction	Petrol (wt. %)	Samples of petrol water ^a					
		1		2		3	
		Inlet (wt. %)	Ex- haust (wt. %)	Inlet (wt. %)	Ex- haust (wt. %)	Inlet (wt. %)	Ex- haust (wt. %)
1 Heptanes, octanes, nonanes ^b , decanes ^b	28.7	1	1	2	2	2	3
2 Decanes ^b , benzene	1.7	3	3	3	3	3	3
- ^c Undecanes	1.4						
3 Toluene, undecanes ^b , dodecanes ^b (?)	12.6	27	28	29	29	30	30
- ^c (?)	0.6						
4, 5 Ethylbenzene, <i>m</i> -, <i>p</i> -xylene	21.3	30	33	33	30	32	31
6, 7 <i>o</i> -Xylene, propylbenzene	8.7	12	13	13	13	13	12
8 (?)	7.6	8	7	6	8	6	7
9 1,3,5-Trimethylbenzene (among others)	2.9	3	2	2	3	2	2
10 (?)	2.1	2	2	2	3	2	2
11 (?)	7.7	9	8	8	8	7	8
12 (?)	0.7						
13 (?)	1.8	3	3	2	2	2	2
14 (?)	1.2						
15 (?)	0.6						
Concn. (total), mg/l	—	26.4	19.5	16.6	18.7	26.6	22.0

^a Inlet and exhaust samples from petrol water fed into a column packed with a bed of sand impregnated with water.

^b Not found in petrol water.

^c Not numbered.

samples are due to analytical and sampling errors, and to errors in the migration experiments.

It is concluded that when an unknown sample of water is analysed by the method described and results in a chromatogram like the one in Fig. 2, it is highly probable that the water is polluted with petrol.

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