CHROM. 9215

IDENTIFICATION OF GASOLINE CONTAMINATION OF GROUND-WATER BY GAS CHROMATOGRAPHY

RENATO DELL'ACQUA*, BRIAN BUSH and JAMES EGAN

Division of Laboratories and Research, New York State Department of Health, Albany, N.Y. 12201 (U.S.A.)

(First received November 3rd, 1975; revised manuscript received March 16th, 1976)

SUMMARY

Individual components that make up different grades of gasoline —or gasolines of the same grade produced by different manufacturers— are resolved and identified by gas chromatography using packed columns and a flame ionization detector. Contaminants at levels as low as 0.5 $\mu l/l$ may be identified by the method if samples of gasoline from the source of contamination can be obtained for comparison. The uniqueness of this method is that it can be applied for routine analysis without the use of sophisticated complements for the gas chromatograph.

INTRODUCTION

Contamination of groundwater by leakage of gasoline from underground storage tanks and by transportation spillage accidents has become common in recent years, as indicated by the frequency with which gasoline-contaminated water samples are submitted to our laboratory for analysis. Frequently not only the level of contamination but also the precise source must be determined. When several possible sources are involved, such as neighboring gas stations or underground tanks, a distinction may be required between gasolines of different grades or between gasolines of the same grade produced by different manufacturers.

Gasoline is a mixture of mostly saturated paraffinic hydrocarbons containing from four to twelve carbon atoms. Identification of its components using capillary columns and SCOT columns has been described in detail[1–9]. The chromatograms obtained show much fine detail, but these methods tend to be rather involved for application to routine analysis. More important, such columns can take only very low loads ($5 \times 10^{-4}/\mu l$ for capillary columns)[2]; and to achieve our required sensitivity, up to 30 μl of an extract must be injected onto the column. Although we cannot take advantage of the high resolution given by the capillary and SCOT columns, our 6-ft. glass-packed column resolves enough fine structure for the chromatogram to be useful for qualitative analysis.

---

* To whom correspondence should be addressed.

In our previously reported method for quantitative determination[10], gasoline is extracted from water by hexane; a portion of this extract is injected on to the gas chromatographic (GC) column; and the signal is obtained from a flame ionization detector (FID). The temperature program allows the discrimination of heptanes, octanes, and higher alkanes from the million-fold excess of hexane in the extract. For qualitative identification, however, the resolution of pentanes, hexanes, benzene, toluene, and xylene is very important, and therefore another solvent is required for extraction of the sample.

In this publication a method of extraction and identification of gasoline is described which may be used to identify a source causing a contamination at a level as low as 0.5 μl/l.

ANALYTICAL PROCEDURE

The sample is collected in a clean all-glass container. During transport —in ice, if possible— the sample should not come into contact with the glass stopper; otherwise gasoline components may be lost by capillary action between the ground-glass surfaces. Extraction, if required, is carried out as soon as possible after collection, preferably in less than 24 h.

In the laboratory, 2 l of the sample are poured into a 3-l separatory funnel with a PTFE stopcock, acidified to pH 1–2 with 50% sulfuric acid, and extracted once with 10 ml of the solvent (for choice, see Discussion) by shaking the funnel for 3–4 min. After the extract has stood for at least 5–6 min, the layers are slowly and carefully separated and the water is discarded. The solvent is collected in a clean 50-ml beaker containing approximately 1 g of granular anhydrous sodium sulfate previously washed with the solvent. The beaker is swirled carefully to complete the drying of the extract, which is then poured into a clean, graduated, 15-ml centrifuge tube.

The extract is now ready for GC analysis as previously described[10], under the following conditions.

Apparatus and operating conditions

A Tracor Model MT 220 gas chromatograph is used. The columns used are: (A) glass, 6 ft. × 1/4 in. O.D., packed with silicone SE-30 on Gas-Chrom Q 80–100 mesh; (B) same but 12 ft. long. Helium H.P. is used as the carrier gas at 40 lb. pressure and at a flow-rate of 110 ml/min. For the FID air H.P. is used at 40 lb. pressure and at a flow-rate of 285 ml/min and hydrogen H.P. at 40 lb. pressure and at a flow-rate of 37 ml/min.

The column temperature is isothermal at 25°, the injection port temperature, 200°, and the detector temperature, 275°.

The recorder is set at 1 mV full-scale.

Reagents

All are at the highest purity available. Hexadecane (b.p. 287°) is purified by distillation in an all-glass apparatus. When hexadecane is used for extraction, it remains in the column, and the column must be cleaned after every four or five gasoline extract runs by a few injections of 5 μl of hexane with the oven temperature at 275°.

DISCUSSION

The grade of a gasoline is represented by its octane rating (octane number), which is defined as the percentage by volume of the octane isomer 2,2,4-trimethylpentane (rating 100) which must be added to *n*-heptane (rating 0) to produce the same knocking characteristics as the fuel under examination in a standard single-cylinder engine operated under specific conditions. 2,2,4-Trimethylpentane is, however, relatively expensive, so alkyllead compounds with great antiknocking power are added. The recent elimination of lead compounds from gasoline for pollution control has led to an increase in the use of branched and cyclic paraffinic hydrocarbons and aromatic compounds.

In this study we found that *n*-pentane, branched paraffins, benzene, toluene, and xylene are used by manufacturers to obtain a product with a high-octane rating. The octane ratings of some of the hydrocarbons which we observed in gasoline components are given in Table I.

TABLE I

OCTANE RATING OF SOME HYDROCARBONS[14]

Hydrocarbon	Octane rating
n-Hexane	26
n-Pentane	63
2-Methylpentane	73
3-Methylpentane	74
Cyclohexane	77
2,2,4-Trimethylpentane	100
o-Xylene	100
Toluene	102
Benzene	115

Chromatograms of high-test and low-test gasolines from the same manufacturer are shown in Fig. 1. The 22 peaks in Fig. 1B are identified in Table II together with their relative retention times (*n*-hexane = 1.00). A chromatogram similar to that of the high-test sample is obtained when the following components are added to the low-test sample: *n*-pentane, 2-methylpentane, 3-methylpentane, benzene, cyclohexane, 2,3-dimethylpentane, 3-methylhexane, 2,2,4-trimethylpentane, *n*-heptane, 2,4-dimethylhexane, 2,5-dimethylhexane, toluene, 3-methylheptane and xylene (three isomers). The retention volumes of the individual peaks vary slightly between chromatograms due to changes in column oven temperature (which is difficult to control so near ambient temperature), but the relative retention times do not vary.

The composition of lots of the same grade of gasoline manufactured at different times varies greatly. Differences in composition introduced by different manufacturers to achieve high antiknock quality also vary widely. Table III illustrates these variations. All the samples were collected from gasoline stations in the summer of 1973.

In our previous work with gasoline, hexane was used to extract the trace of hydrocarbon from water to achieve a sensitivity of 0.25 μl/l. It is clear that another extractant is required if identification of source is to be attempted. The two obvious
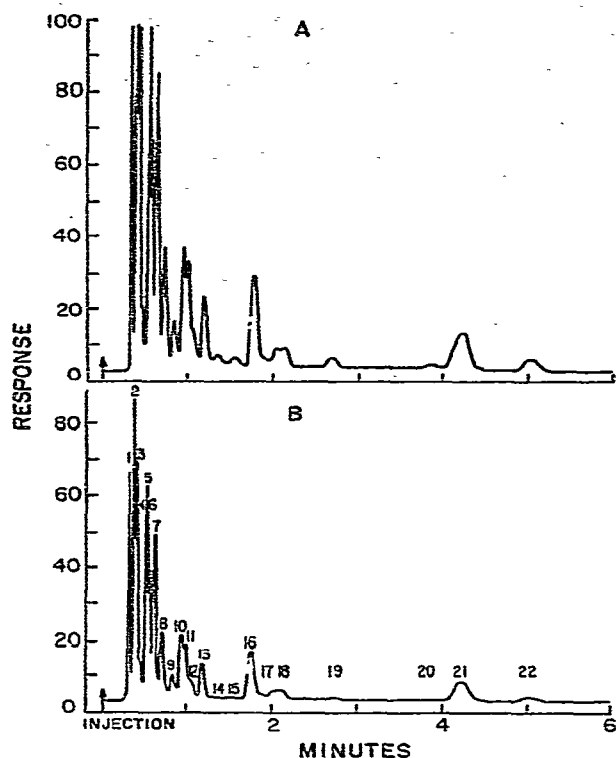
Fig. 1. Chromatograms (column A) obtained from 0.4-μl samples of a single brand of pure gasoline. (A) High-test. (B) Low-test.

TABLE II

GASOLINE COMPONENTS IN FIG. 1A IDENTIFIED BY RETENTION TIME RELATIVE TO *n*-HEXANE

Peak No.	Hydrocarbon	Relative retention time
1	Isopentane*	0.50
2	Unknown	0.59
3	*n*-Pentane	0.65
4	2,2-Dimethylbutane	0.73
5	2-Methylpentane	0.84
6	3-Methylpentane	0.90
7	*n*-Hexane	1.00
8	2,4-Dimethylpentane	1.10
9	Benzene	1.34
10	Cyclohexane	1.50
11	2,3-Dimethylpentane	1.59
12	3-Methylhexane	1.68
13	2,2,4-Trimethylpentane	1.90
14	*n*-Heptane	2.12
15	2,5- and 2,4-dimethylhexane	2.43
16	Toluene	2.81
17	3-Methylheptane	3.21
18	Tetramethylcyclopentane*	3.37
19	*n*-Octane	4.25
20	*p*-Xylene	5.68
21	*o*-Xylene	7.34
22	*m*-Xylene	8.03

* Not identified with certainty.

TABLE III

CONCENTRATIONS OF HIGH-OCTANE RATING COMPONENTS IN HIGH- AND LOW-TEST GASOLINES AS INDICATED BY PEAK HEIGHT (mm)

Peak No.	Hydrocarbon	Brand 1		Brand 2		Brand 3		Brand 4	
		High	Low	High	Low	High	Low	High	Low
3	n-Pentane	68	72	76	66	110	59	106	106
5	2-Methylpentane	81	58	21	6	71	42	91	99
6	3-Methylpentane	30	22	22	70	24	13	32	39
7	n-Hexane	31	42	6	39	13	9	52	55
9	Benzene	11	7	25	16	3	4	24	25
10	Cyclohexane	1	7	15	2	6	2	18	21
13	2,2,4-Trimethylpentane	46	11	74	20	2	2	2	4
16	Toluene	50	13	31	13	66	6	64	33
20	p-Xylene	2	1	1	1	5	1	4	2
21	o-Xylene	10	6	12	4	7	1	20	11
22	m-Xylene	1	1	1	1	1	1	6	3

choices were carbon tetrachloride and carbon disulphide, both of which are known to give a low response with the FID while being good solvents for hydrocarbons. Fig. 2 shows the response obtained from injections of 5 μl of these solvents. Carbon tetrachloride is unsuitable. Carbon disulphide is usable for gasoline concentrations above approximately 1 ml/l, but at lower concentrations the response observed —which is
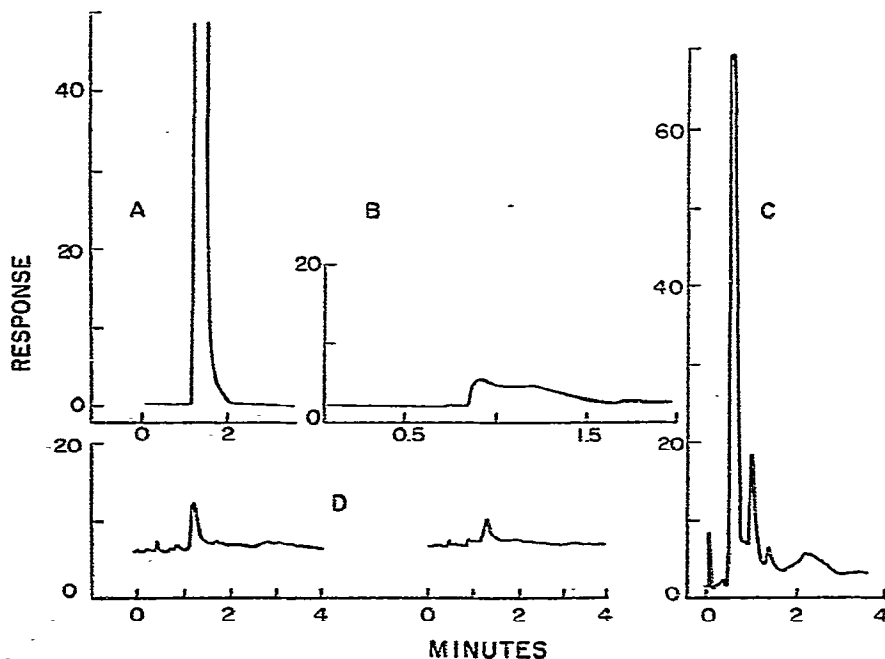

Fig. 2. Chromatograms produced by 5 μl of various extracting solvents. (A) Carbon tetrachloride, attenuation $10^2 \times 16$. (B) Carbon disulphide, attenuation $10^2 \times 16$. (C) Carbon disulphide, attenuation 10×8. (D) Distilled hexadecane, attenuation 10×8.

presumably due to carbon disulphide itself and some impurities— would make it un-suitable. Redistilled hexadecane gave an acceptable background and is therefore suit-able for the highest sensitivity work. The small peak observed is not at present ex-plained; it may arise from contamination of the distillate by hydrocarbons in the labo-ratory atmosphere (probably hexane used for pesticide work). Fig. 3 illustrates ex-traction of gasolines from water with this solvent. It is clear that in this brand of gaso-line, branched-chain aliphatics rather than aromatics were used to improve octane rating. In spite of the loss of volatiles during spiking, it is still possible to distinguish between the two gasolines at 0.5 μl/l. After an injection of five hexadecane solutions, the build-up of extractant is removed from the column by heating to 275° for 30 min.
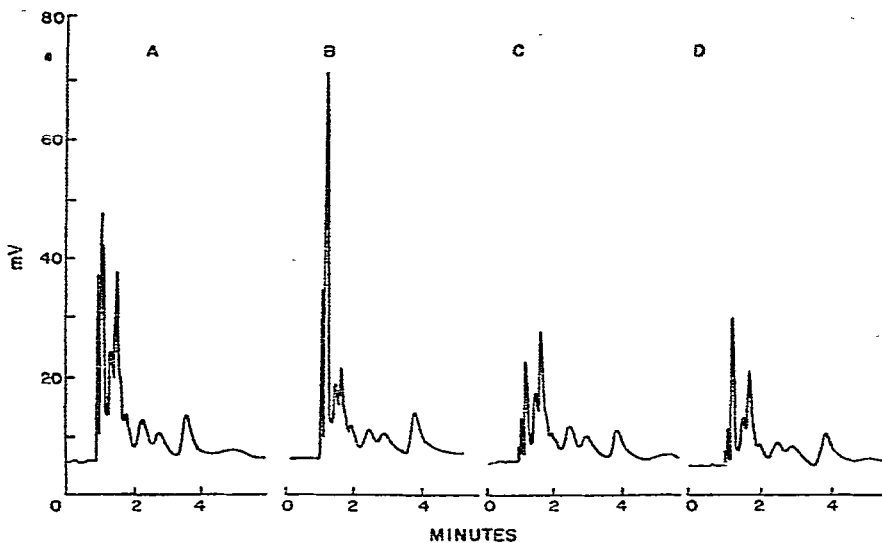

Fig. 3. Brand M gasoline injected in distilled hexadecane solution (5-μl injection, attenuation 10 × 8, column A). (A) Low-test at 200 μl/l. (B) High-test at 200 μl/l. (C) Low-test spiked into water at 0.5 μl/l and recovered with redistilled hexadecane (5-μl injection). (D) High-test spiked into water at 0.5 μl/l and recovered with redistilled hexadecane (5-μl injection).

Upon receipt of a sample in the laboratory, the decision as to whether to ex-tract —and, if so, with which solvent— is made by visual examination. If contami-nation is gross and visible, as an oily layer thick enough to be sampled directly with a microsyringe, extraction is not required. If contamination is visible but slight, carbon disulphide extraction is necessary. If contamination can be detected only by odor, extraction with redistilled hexadecane must be resorted to. When the approximate level of contamination has been found, reference samples of gasoline from possible sources are diluted to the required level with the chosen extractant.

The procedure has been applied to resolve several seepage problems. Two of the more complex are described.

Example 1 (June 1973)

In Albany County, N.Y., downslope from a highway intersection with four gasoline stations, is a home with an adjacent workshop, which has a sump to collect

excess drain water. For some time the owner noticed a persistent odor of gasoline in the workshop but gave it no serious consideration. One day, when lighting a match, he ignited the gasoline vapors which had accumulated in the workshop at that time. A few days later, samples were collected from the sump and from the four gasoline stations (a total of 11 tanks). Chromatographic comparison indicated that one specific tank was responsible for the seepage. Fig. 4 shows the two chromatograms (A and C) which most resembled the chromatogram of the oily layer from the sump (B). Peaks lying in the region 1.5–5 min are low relative to the group around 1 min in chromatograms A and B; they are relatively high in chromatogram C. Pressure testing of the suspect tank confirmed that it was leaking.
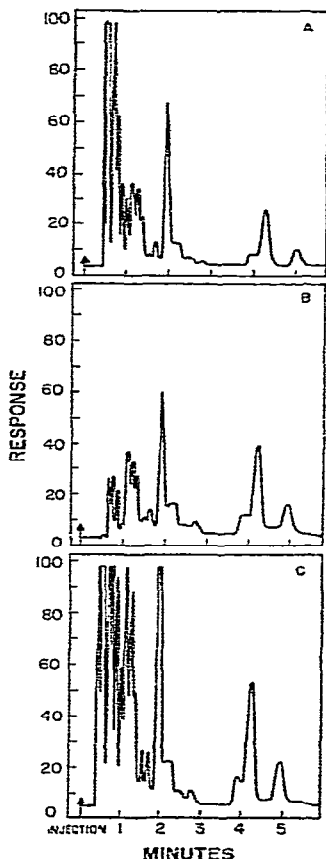

Fig. 4. Seepage problem in Albany County, N.Y. Chromatograms were made on column A. (B) Oily layer of contaminated sump water. (A, C) Samples from two nearby gasoline station storage tanks.

Example 2 (August 1974)

In Yates County, N.Y., a strong odor of gasoline was noticed in an underground drainage system, which probably presented an explosion hazard. Four gasoline stations located at a nearby intersection have a total of nine underground tanks contain-

ing gasoline and one tank containing kerosene. Samples from all the tanks were collected, and because one of the three samples of contaminated water had a thick oily layer, the tank samples were injected undiluted. Fig. 5 shows eight chromatograms from this series, chosen to illustrate the typical variations between grades of gasoline from the same manufacturer and between the same grades from different manufacturers. (Note the chart recorder speed change early in each chromatogram.) The main distinction between high and low octane in these samples appears to be the ratio of the aromatics toluene (T) and xylene (X) to the rest of the aliphatic hydrocarbons.
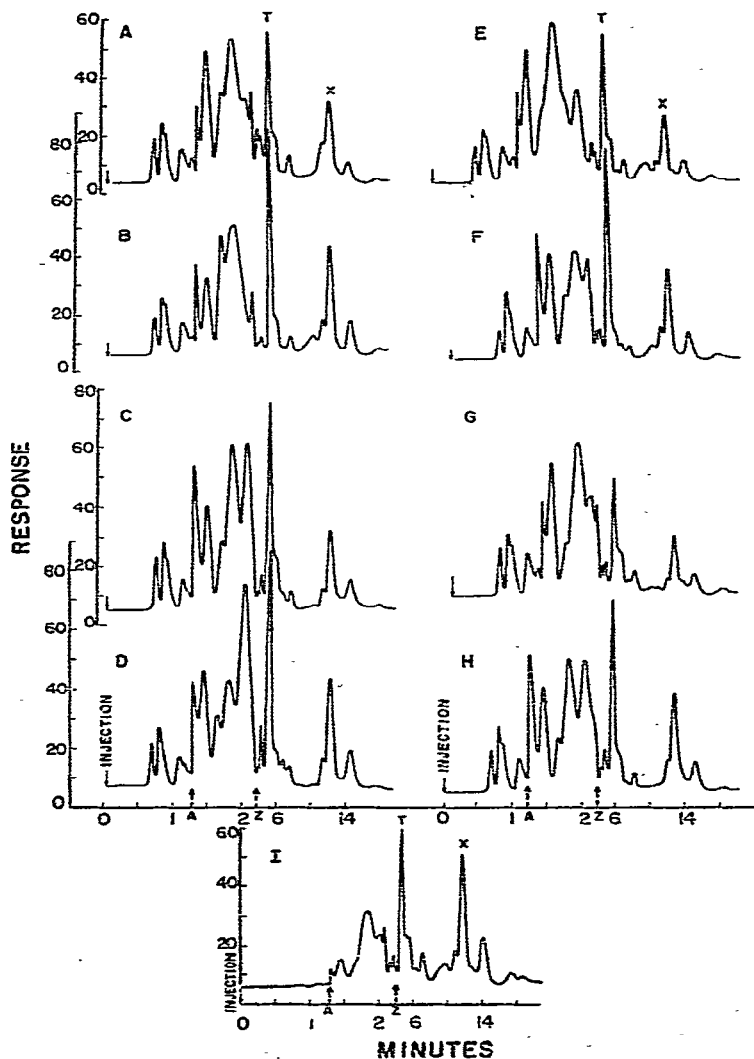

Fig. 5. Chromatograms made on column B of gasoline samples collected in Yates County, N.Y.; 0.2 μl, attenuation $10^2 \times 256$ until point A, thereafter $10^2 \times 32$. At point Z, the chart speed was changed from 2 to 0.5 in./min. (A) Mi low-test. (B) Mi low-lead. (C) Mi high-test. (D) S high-test. (E) T low-test. (F) T high-test. (G) G low-test. (H) G high-test. (I) Oily layer from water sample.

Differentiation between manufacturers is clearest in the region of the chromatograms around 2 min.

The ninth chromatogram (Fig. 5I) is the oily layer from the water below a manhole of the drainage system. It is clearly weathered: the light fractions have been lost
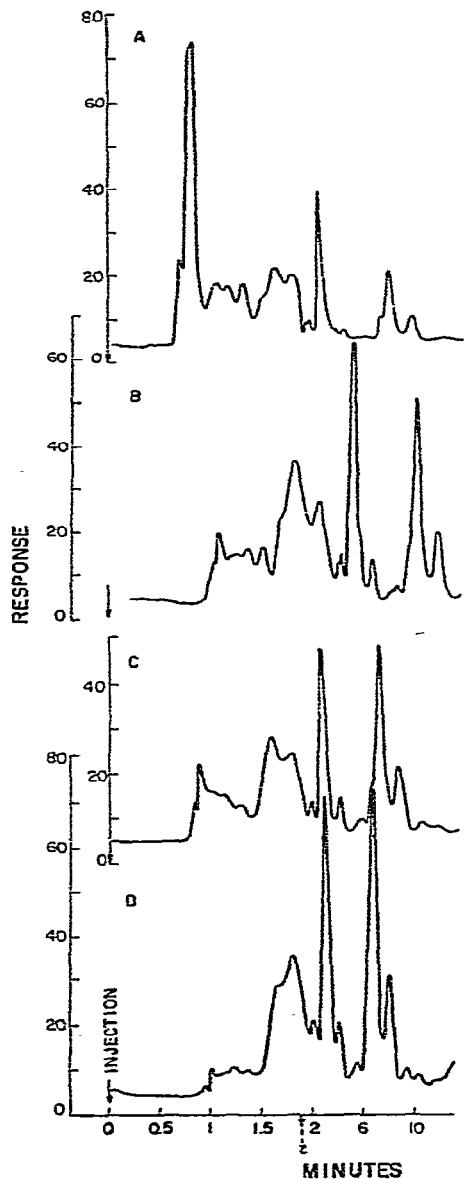

Fig. 6. Chromatograms made on column B of gasoline seepages, extracted with CS_2, and of a sample from the faulty tank. (A) T high-test 100 μl/10 ml CS_2. (B) Drainage manhole, collected 21 August 1974. (C) Drainage manhole, collected 27 August 1974. (D) Hole dug near station with faulty tank, collected 27 August 1974.

and the heavier components concentrated. It is certainly not a kerosene[11]. The pattern at 2 min resembles brand G low-test, but the high content of aromatics would indicate a high-test gasoline, probably brand T. The aromatic content could have increased during the weathering process, and so fresher samples were requested from the engineer at the site.

Meanwhile, the other two original samples were extracted with carbon disulphide and examined. Only one had a detectable contamination. Its chromatogram is shown in Fig. 6B, along with those of two samples taken later and the chromatogram of brand T high-test dissolved in carbon disulphide for comparison (A). The sample from the manhole is the closest match to brand T high-test, but the samples from the hole dug specifically for this investigation (D) also resemble it closely enough to have made this tank the prime suspect. Excavation around the tank confirmed the seepage.

There has been much speculation about possible changes in composition which are thought to occur during passage through soil by differential volatilization and bacterial action[12]. However, Matis[13] observes that little such deterioration occurs, and this is in agreement with our experience reported here. Probable reasons for this are the relative scarcity of bacteria in subsoil, the improbability of evaporation, and the attainment of a steady state in which the hydrocarbon seeps continuously along the top of the water table. Modifications which might be observable during initial seepage due to a chromatographic type of separation will have disappeared with the attainment of a steady state. Of course, the light fractions tend to be reduced before the sample is received at the laboratory due to evaporation in the well and during sampling, but the chromatograms still allow different sources to be distinguished. Although such evidence, based on visual pattern recognition, may be difficult to sustain in a legal proceeding, it is valuable to the public health engineer concerned about terminating a loss of valuable fuel and eliminating acute risks of fire and explosion.

REFERENCES

1 J. V. Brunnock and L. A. Luke, *Anal. Chem.*, 40 (1968) 2158.
2 L. R. Durrett, L. M. Taylor, C. F. Wantland and I. Dvoretzky, *Anal. Chem.*, 35 (1963) 637.
3 S. I. Krichmar and V. E. Stepanenco, *Gaz. Khromatogr.*, 14 (1970) 62.
4 A. G. Polgar, J. J. Holst and S. Groenning, *Anal. Chem.*, 34 (1962) 1226.
5 W. N. Sanders and J. B. Maynard, *Anal. Chem.*, 40 (1968) 527.
6 K. Grob, *J. Chromatogr.*, 84 (1973) 255.
7 K. Grob and G. Grob, *J. Chromatogr.*, 90 (1974) 303.
8 K. Grob, *Chromatographia*, 8 (1975) 423.
9 W. May, *J. Chromatogr. Sci.*, 13 (1975) 535.
10 R. Dell'Acqua and B. Bush, *Int. J. Environ. Anal. Chem.*, 3 (1973) 141.
11 R. Dell'Acqua, J. A. Egan and B. Bush, *Environ. Sci. Technol.*, 9 (1975) 38.
12 A. L. Bridie, J. Bos and S. Herzberg, *J. Inst. Petrol.*, 59 (1973) 263.
13 J. Matis, *Ground Water*, 9 (1971) 57.
14 American Society for Testing and Materials, *Physical Constants of Hydrocarbons C_1 to C_{10}*, No. DS 4A, Philadelphia, Pa., 1971.