

Analysis of industrial solvent mixtures in water using a miniature purge-and-trap device with thermal desorption and capillary gas chromatography–mass spectrometry

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ABSTRACT

A dynamic headspace stripping method for the determination of low levels of industrial hydrocarbon solvents in water is reported. Samples taken from industrial aqueous effluents and estuarine waters were sparged at 30 ml min⁻¹ for 30 min at ambient temperature using a miniature all-glass stripping vessel. Solvent vapours were then sorbed on a Tenax-TA trap and subsequently analysed by thermal desorption and gas chromatography–mass spectrometry. Recoveries of five types of common industrial hydrocarbon solvent mixtures at 10, 100, 1000 and 5000 µg l⁻¹ in water were evaluated. Gasoline was included as a solvent as it is frequently used as an industrial cleaning and degreasing medium. The recoveries varied from 83.8 to 103.2% for gasoline and from 87.9 to 99.8% for hydrocarbon solvents such as kerosene and white spirit. Relative standard deviations between 2.8 and 9.6% were obtained for gasoline and between 2.2 and 8.9% for the remaining mixtures. The method has been used to detect traces of solvent mixtures as pollutants in industrial effluent streams and estuarine water, and more recently for investigating solvent contamination of potable water supplies.

INTRODUCTION

Many of the hydrocarbons discharged into effluent waters by chemical, manufacturing and allied industries are present as complex mixtures of compounds, rather than single compounds. Their measurement in water is typically conducted either by performing a crude quantification of total hydrocarbon content as oil-in-water, or by selective analysis of target compounds, based on legislative requirements and/or their relative mutagenicity or toxicity to river or estuarine ecosystems.

However, in some instances it is considerably more useful for the analytical environmental chemist to distinguish the nature and source of low levels of dissolved hydrocarbon mixtures in effluent waters. Strategies based on identification of individual compounds within mixtures may provide less useful information when there are

several sources of contaminated effluents containing identical compounds. Indeed, for pollution control purposes, the chemist is often required to "fingerprint" the identity of the entire hydrocarbon mixture before determining the degree of contamination. Solvent mixtures are widely used in a variety of industries as diluents, fuels, reagents and cleaning agents. Their flexibility of use is a major reason why they represent such a common source of hydrocarbon pollution in effluent waters. Typically, these may vary from kerosenes and fuel oils to aromatized solvents and, in some instances gasolines.

Dynamic "purge-and-trap" headspace analysis represents an expanding methodology available for the analysis of volatile hydrocarbon mixtures in water [1]. However, many analysts are reluctant to use these techniques, believing them to be relatively expensive, complex and time consuming [2]. Many applications of purge-and-trap methods, including those developed by the US Environmental Protection Agency laboratories, are centred on the determination of volatile organohalogenes, volatile aromatics or volatile organosulphide compounds with low water solubilities and boiling points generally below 150°C [3]. There are comparatively few applications of purge-and-trap methods for stripping mixtures of organic substances with boiling point ranges extending above 200°C. One notable exception was demonstrated by Belkin and Esposito [4], who developed an elevated temperature purge-and-trap method for stripping Fuel Oil No. 2 and kerosene from water over three concentration ranges spanning from 10 to 1000 ppb.

In the laboratory, a simple miniature stripping device has been used at ambient temperatures to recover a variety of solvent mixtures from effluent water at low concentrations. The stripped compounds are trapped on Tenax-TA sorbent traps for subsequent analysis by thermal desorption and capillary column gas chromatography (GC) with flame-ionization detection (FID). The resulting chromatograms are then used to identify the nature and identity of the solvent(s) using a combination of "fingerprinting" techniques, comparison with reference mixture chromatograms and mass spectrometry (MS). Used in conjunction with standard infrared methods [5] for determining hydrocarbon oils in water, this technique provides a fast and sensitive means by which to assist in the identification of industrial solvent mixture in water.

EXPERIMENTAL

Standards

Standards were prepared by using commercial-grade solvent mixtures supplied by Esso Petroleum (Esso Research Centre, Abingdon, Oxford, UK) and Shell Oil (Thornton, Cheshire, UK) research laboratories. The usefulness of the method was assessed using five important industrial solvents *viz.*, (i) kerosene, (ii) white spirit, (iii) regular leaded gasoline and (iv) solvent 100 and (v) solvent 150, the last two being common aromatic solvent mixtures. Some common properties of these materials are summarized in Table I.

Industrial fresh water supplied by Southern Water Authority (SWA, Otterbourne, Winchester, UK) was purged under purified nitrogen overnight at 100 ml min⁻¹. Water blanks were analysed to ensure that interfering compounds had been removed. The solvent reference mixtures were gravimetrically added to 1-l volumes of stripped industrial fresh water. Serial dilutions were made in order to obtain standards at various concentration ranges.

TABLE I
COMMON PROPERTIES OF TYPICAL INDUSTRIAL HYDROCARBON SOLVENT MIXTURES

Solvent	Density (g cm ⁻³)	Molecular weight (mean)	Boiling range (°C)
Kerosene	0.75	200	150–325
White spirit	0.78	141	165–210
Gasoline	0.70	114	–0.5–216
Solvent 100	0.87	120	165–179
Solvent 150	0.89	138	190–210

Standard mixtures containing reference components present in the solvent mixtures were prepared according to certified ConCAWE methods [6], added to stripped water and used to assess recoverability and method response. These standard mixes were used as a secondary calibration check.

Adsorbents

Tenax-TA (60–80 mesh) (400 ± 10 mg) (Phase Separations, Clwyd, UK) was packed into 0.25-in. O.D. precleaned stainless-steel (ATD-50) thermal desorption tubes (Perkin-Elmer, Beaconsfield, Bucks, UK). These were conditioned by heating at 30°C for 10 min in a stream of oxygen-free prefiltered nitrogen at 15 ml min⁻¹. The temperature was then raised at 5°C min⁻¹ to 350°C, held there for 1 h and allowed to cool. These tubes were analysed by thermal desorption and capillary GC in order to ensure the absence of background signals from contaminant peaks.

Sampling apparatus

The purge-and-trap device is shown in Fig. 1. The device, a miniature sparger, was developed from an original Bellar and Lichtenberg design intended for the determination of volatile priority pollutants in water [7]. The modified variant was developed and tested in the environmental laboratory [8] as a component part of a research programme investigating the occurrence and behaviour of volatile organic compounds in estuarine water [9].

Sample water was injected into the device using a 10-ml glass syringe (SGE, Milton Keynes, UK) with a Luer-Lok fitting according to Environmental Protection Agency recommended procedures. After removal of the all-glass stopper, the syringe needle and hub was inserted in the ground-glass neck of the vessel and located in place. The Luer-Lok was then opened and 7 ml of sample gently introduced to minimize the formation of pressure bubbles. The needle was then removed and the stopper replaced. The stopper was secured using two springs, as shown in Fig. 1, to ensure a leak-tight connection once stripping gas was introduced.

Ultrapure helium, used as the stripping gas, was metered via a metal-glass joint into the inlet arm of the stripping device. The gas passed through a 15- μ m frit to produce a finely divided stream of gas bubbles. The effluent gas then passed through a bubble trap at the uppermost section of the device before flowing into the exit arm. A ground-glass insert connected the exit arm to a 0.125–0.25-in. Drallim reducing union. The stainless-steel tube containing the Tenax-TA sorbent was connected in turn to the 0.25-in. Drallim union. The design is leak-tight and permits a smooth

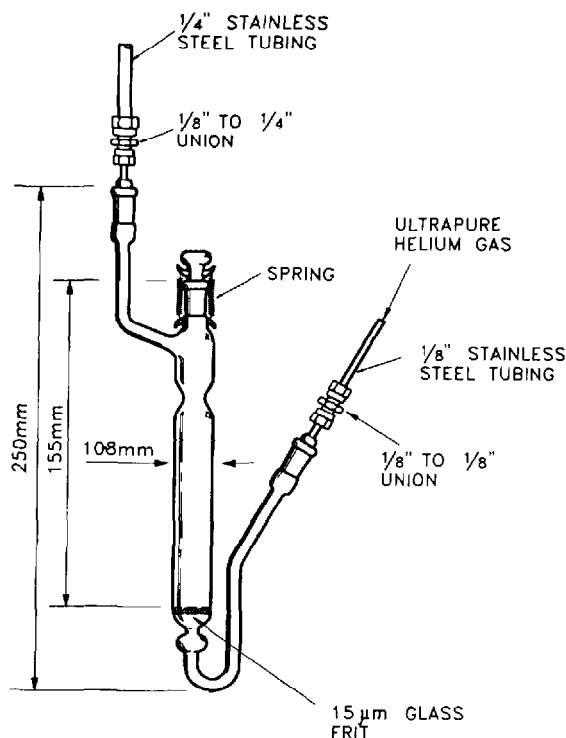


Fig. 1. Schematic diagram of the Bianchi miniature stripping vessel.

laminar flow of gas through the device. The flow-rate through the device can also be measured and adjusted by connecting a bubble flow-meter to the end of the Tenax-TA sorbent tube and altering the inlet flow accordingly. At the end of the stripping cycle, the gas is switched off and the Tenax-TA tube disconnected for thermal desorption-GC analysis.

Instrumentation and capillary column

An ATD-50 automated thermal desorber was connected to a Model 8700 gas chromatograph (Perkin-Elmer) via a 1-m length of fused-silica transfer line. This device was used for all thermal desorption analysis. A brief discussion of the principle of operation of the thermal desorber has been given in a previous paper [9].

The gas chromatograph was fitted with a cradle-mounted, 50 m \times 0.22 mm I.D. OV-1701 wall-coated open-tubular fused-silica capillary column, 0.5- μ m film thickness (SGE). The column effluent was connected to a twin-hole ferrule, allowing 50% of the column eluent to be routed to a flame-ionization detector. The remaining 50% was routed to an ion-trap detector-mass spectrometer (Finnigan MAT, Beaconsfield, UK).

Analytical operating parameters. The GC system conditions were as follows: carrier gas, ultrapure helium, 5.5 grade (Air Products, Basingstoke, UK); ATD-50, cold-trap packing, 20 mg of Tenax-TA; cold-trap low temperature, -30°C ; cold-trap

high temperature, 280°C; splitting ratio, 300:1; desorption box temperature, 150°C; desorption oven temperature, 250°C; desorption time, 10 min; carrier gas pressure, 25 p.s.i.

Gas chromatograph. The detector temperature was 300°C, carrier gas flow-rate 1 ml min⁻¹, oven temperature isothermal at 50°C for 7 min then increased at 15°C min⁻¹ to 250°C, final hold time 1 min.

Ion-trap detector. The ionization voltage was 70 eV, scan rate 0.5 s per scan, mass range 25–250 μ , transfer temperature 250°C, ion-source temperature 250°C, multiplier delay 200 s, mass defect 100 mu per 100 u and acquire time 30 min.

Chromatograms obtained by GC-FID and GC-MS were compared directly with a reference library of industrial solvent standards. The ion trap detector was used to identify and confirm major peaks in the chromatographic profiles and the presence of additional substances of environmental concern co-eluting with the solvent mixtures, e.g., organohalogen compounds.

Analytical procedure

Wastewater samples were taken in precleaned 1-l amber-glass bottles capped with aluminium foil-lined inserts. A 10-ml glass syringe fitted with a removable plunger and Luer-Lok was used to transfer sub-samples to the stripping device. The syringe plunger was removed and the barrel filled with the water sample. The plunger was replaced and the sample flushed through the syringe needle to waste. The syringe barrel and needle were then flushed with ultrapure helium to remove any remaining sample. The Luer-Lok was closed and the filling procedure repeated. A 7-ml volume of water sample was then injected into the device as described previously. Water samples were stripped at flow-rates between 10 and 100 ml min⁻¹ at 10 ml min⁻¹ intervals. To complement these experiments, blank laboratory water was spiked with an ethoxyethanol solution (BDH, Poole, UK) of all five mixtures at concentration levels equivalent to 10, 100, 1000 and 5000 $\mu\text{g l}^{-1}$. Five replicates of each sample were purged and analysed to determine the accuracy and precision of the method. Quantification of recoveries was accomplished by summing the areas under all the integrated chromatographic peaks desorbed from the adsorbent tubes. The total peak area was then compared with the mass of solvent mixture added to the water standard. As no single component in the solvent mixtures can be considered as truly representative of the concentrations of the other solvent components in wastewater, summing the total peak area provides a more reliable measure of total solvent concentration.

Flow-rates were measured at the exit point of the Tenax-TA sorbent tube. All samples were stripped at room temperature. A second Tenax-TA sorbent tube was connected in series in order to investigate whether breakthrough of solvent mixture components occurred during the stripping step. On completion of stripping, the purge gas was gently closed off and the sorbent tube disconnected for immediate thermal desorption and GC-MS analysis.

RESULTS AND DISCUSSION

The results of the basic experiments show that the purge rate reaches an optimum value at 30 ml min⁻¹ (see Table II). At flow-rates above 40 ml min⁻¹ it was observed that the formation of the finely dispersed gas bubbles, which effect the

TABLE II

EFFECT OF STRIPPING FLOW-RATE ON RECOVERY USING THE MINIATURE STRIPPING VESSEL

Conditions: ultrapure helium gas; standard concentration, $10 \mu\text{g l}^{-1}$; stripping time, 30 min.

Solvent	Purge flow-rate (ml min^{-1})	Recovery (%)	Breakthrough onto back-up trap (%)
Kerosene	10	80.1	0
	20	85.5	0
	30	95.7	0
	40	95.6	0
	50	95.5	0
	60	95.6	0
White spirit	10	82.4	0
	20	88.7	0
	30	96.5	0
	40	96.7	0
	50	96.2	0
	60	96.5	0
Gasoline	10	90.1	0
	20	93.5	6.1
	30	96.3	6.9
	40	96.1	7.1
	50	95.7	7.5
	60	95.5	7.7
Solvent 100	10	83.3	0
	20	89.5	0
	30	99.7	0
	40	99.4	0
	50	99.6	0
	60	99.3	0
Solvent 150	10	79.3	0
	20	85.8	0
	30	99.8	0
	40	99.3	0
	50	99.4	0
	60	99.4	0

TABLE III

VOLATILE COMPONENTS IDENTIFIED ON THE TENAX BACK-UP TUBE FOLLOWING GASOLINE PURGING ANALYSIS

<i>n</i> -Butane	2,3-Dimethylbutane
<i>trans</i> - + <i>cis</i> -2-Butene	2-Methylpentane
Isopentane	3-Methylpentane
<i>n</i> -Pentane	Cyclopentane
<i>trans</i> -2-Pentene	<i>n</i> -Hexane
2-Methyl-2-butene	Methylcyclopentane
2,2-Dimethylbutane	

stripping action, was disturbed by the formation of turbulence inside the vessel chamber. At flow-rates higher than this, channelling of the stripping gas was noted, leading to a single flow path of large gas bubbles. These are less effective at stripping than a stream of slower moving, evenly dispersed bubbles.

Except for gasoline, no breakthrough of any component from the solvent mixtures was found on the back-up adsorbent tube during these experiments. With gasoline, the amount of breakthrough is related directly to the purge rate. However, once the maximum recovery had been attained, further stripping did not yield higher overall recoveries. Only the most volatile components of gasoline broke through onto the back-up Tenax-TA adsorbent tube. These components, which were identified by retention time and ion-trap detection, are listed in Table III. Tenax has a low retention volume for very volatile compounds [10]. Accordingly, the loss of volatiles from Tenax adsorbents is theoretically predictable, based on several comprehensive and detailed studies of the retention volume characteristics of Tenax [11-14].

In general, recoveries increased with decreasing standard concentrations (see Table IV). Prolonged stripping for 60 and 90 min (*i.e.*, in excess of 30 min) afforded no improvements in recovery at any of the standard concentration levels. Recoveries for all five solvent mixtures varied from 83.8 to 103.2%. Gasoline exhibited the widest variation in recovery, *i.e.*, from 83.8 to 103.2%. This is due to the broad range of volatile components which constitute gasolines.

The experimental data on the accuracy and repeatability of the method are

TABLE IV
RECOVERY DATA FOR FIVE HYDROCARBON SOLVENT MIXTURES IN WATER AT DIFFERENT CONCENTRATION LEVELS

Mixture	Concentration level ^a ($\mu\text{g l}^{-1}$)	Recovery (%)
Kerosene	5000	89.7
	1000	91.9
	100	93.5
	10	95.7
White spirit	5000	90.8
	1000	94.8
	100	87.9
	10	96.5
Gasoline	5000	83.8
	1000	89.4
	100	97.8
	10	103.2
Solvent 100	5000	96.8
	1000	97.9
	100	98.3
	10	99.7
Solvent 150	5000	95.2
	1000	97.4
	100	99.2
	10	99.8

^a Five samples at each concentration level.

TABLE V

ACCURACY AND REPEATABILITY DATA FOR THE STRIPPING METHOD FOR EACH SOLVENT MIXTURE OVER FOUR CONCENTRATION LEVELS

Mixture	Reference concentration ^a ($\mu\text{g l}^{-1}$)	Sample mean ($\mu\text{g l}^{-1}$)	Bias ($\mu\text{g l}^{-1}$)	Relative standard deviation (%)
Kerosene	4485	4499	14	8.9
	919	915	-4	5.8
	94	87	-7	5.1
	10	10	0	4.9
White spirit	4540	4558	18	6.3
	948	943	-5	8.3
	88	91	3	5.9
	10	9	-1	3.9
Gasoline	4190	4168	-22	9.6
	894	901	7	6.2
	98	100	2	7.0
	10	10	0	2.8
Solvent 100	4840	4851	11	4.9
	979	983	4	4.8
	98	96	-2	3.1
	10	10	0	2.8
Solvent 150	4760	4751	-9	7.2
	974	953	-21	6.4
	99	105	6	3.2
	10	10	0	2.2

^a Five samples at each concentration level.

listed in Table V. Again, these data were based on the total summed peak area rather than on individual components. Accuracy and repeatability are expressed over four concentration ranges for each solvent mixture. Accuracy has been expressed as bias (bias = average value - reference value) for five replicates. Bias is a directional value which shows how much the sample results deviate from the known "true" value. The repeatability is expressed as the relative standard deviation (R.S.D., %).

Inspection of Table V shows that gasoline exhibits the greatest bias ($-22 \mu\text{g l}^{-1}$). However, the bias values for all solvent mixtures at four concentration levels fall within 1% of the sample mean. All R.S.D.s were below 10%, with the lowest concentration standards yielding the smallest values.

Most of the individual compounds which constitute common solvent mixtures are non-polar and hydrophobic. Hence, despite the relatively high boiling point ranges of the mixtures, they can be purged from water at ambient temperature. Using this technique, it was possible to recover all five mixtures within the concentration range $10\text{--}5000 \mu\text{g l}^{-1}$. Specimen gas chromatograms obtained with FID for kerosene and solvent 100 are shown in Fig. 2. Each of the chromatograms was obtained by stripping $10 \mu\text{g l}^{-1}$ concentrations of each of the mixtures in water. A list of the principal components of these solvent mixtures is provided with each chromatogram.

CONCLUSIONS

The method described represents a novel application for an existing analytical protocol. Hydrocarbon solvent mixtures were recovered from both industrial effluent and estuarine water at trace concentrations by purging at ambient temperature. The method is also comparatively rapid, with each purging cycle taking only 30 min to complete. Small sample sizes (7 ml) are used, although the sample size can be readily increased. In some instances it would be acceptable to scale up the sparger in order to accommodate larger sample volumes. No solvents are required in the protocol, which eliminates the cost and laboratory effort required to use them for trace organic analy-

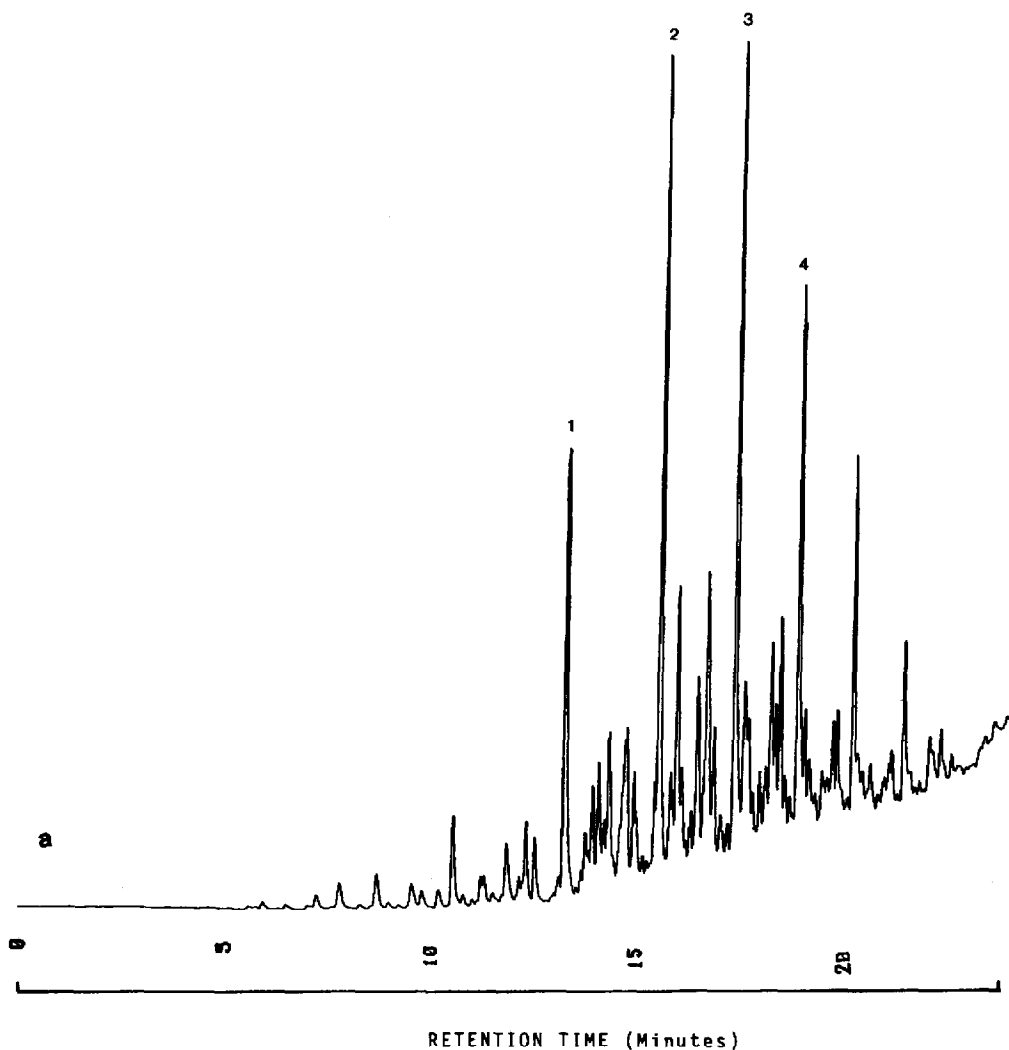


Fig. 2.

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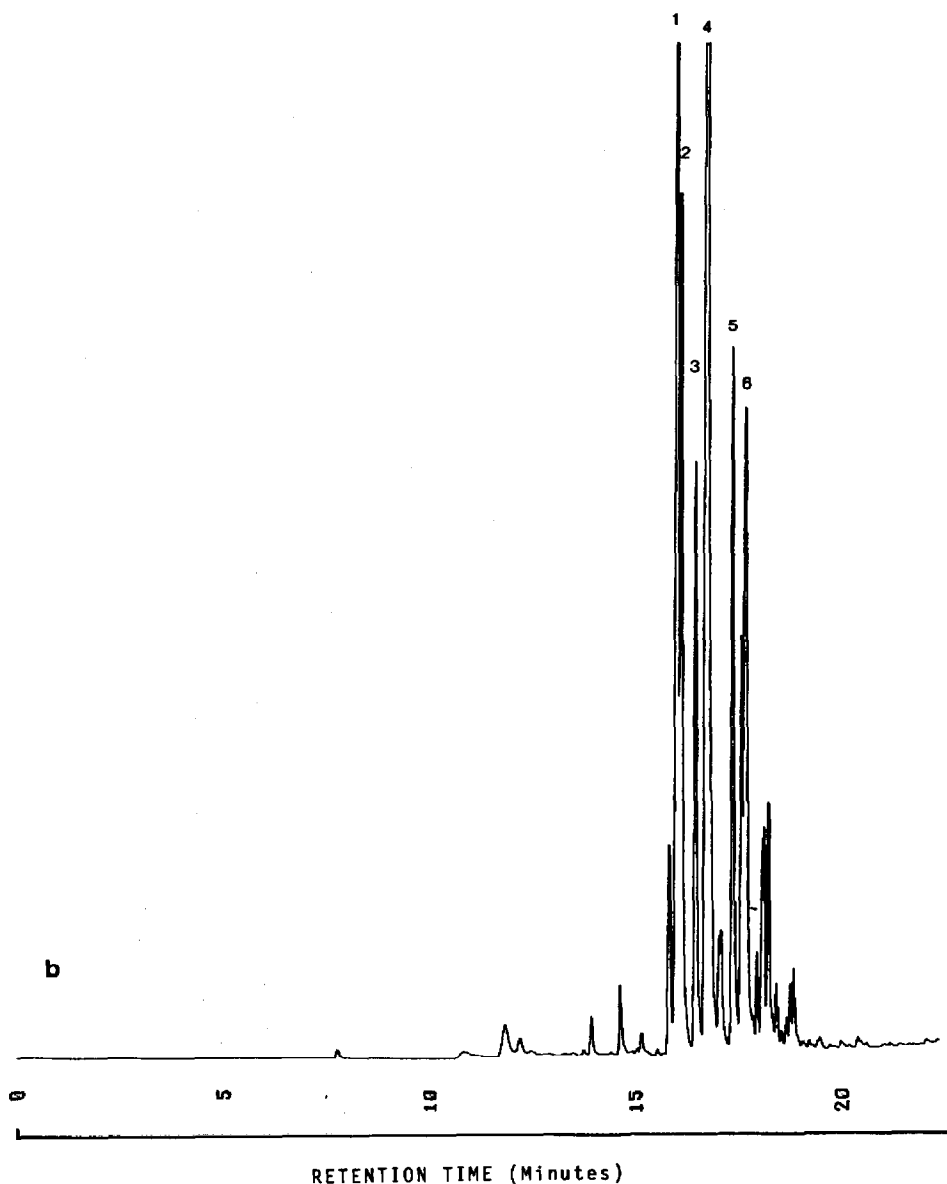


Fig. 2. Specimen purge chromatograms of each of the five standard hydrocarbon solvent mixtures in water ($10 \mu\text{g l}^{-1}$ of each). (a) Kerosene: 1 = *n*-nonane; 2 = *n*-decane; 3 = *n*-undecane; 4 = *n*-dodecane. (b) Solvent 100: 1 = 1-methyl-3-ethylbenzene; 2 = 1-methyl-4-ethylbenzene; 3 = 1,3,5-trimethylbenzene; 4 = 1,2,4-trimethylbenzene; 5 = 1,2,3-trimethylbenzene; 6 = 1-methyl-3-*n*-propylbenzene + 1-methyl-4-*n*-propylbenzene.

sis. The flexibility of the technique means that it can also be used to analyse for trace solvent mixture contamination in potable and fresh water supplies. The low cost and flexibility of the technique may also be useful for developing environmental lab-

oratories operating within Eastern Bloc countries, where rapid, reliable and cost-effective techniques are required to assist in pollution assessment and control measures within the aquatic environment.

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