Journal of Chromatography, 467 (1989) 111–128
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 274

MODIFIED ANALYTICAL TECHNIQUE FOR THE DETERMINATION OF TRACE ORGANICS IN WATER USING DYNAMIC HEADSPACE AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

ALEXANDER BIANCHI*
Exxon Chemical Co., Department of Environmental Affairs, Fawley, Southampton (U.K.)
MARK S. VARNEY
Department of Oceanography, University of Southampton, Southampton (U.K.)
and
JOHN PHILLIPS
Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes (U.K.)
(First received October 3rd, 1988; revised manuscript received January 10th, 1989)

SUMMARY

In this paper we report a modified variant of the purge-and-trap gas chromatographic analysis of volatile organic carbon compounds in water. Samples collected in all-glass 1-l bottles are purged at 60°C for 1 h in an ultrapure helium gas stream using an open-loop arrangement. Volatile eluates are trapped onto selective adsorbents packed inside stainless-steel tubes connected in series. After stripping at a flow-rate of 100 ml min^{-1} for 60 min, the adsorbent tubes are disconnected, fitted with analytical desorption caps and sequentially desorbed for 10 min on a thermal desorber. The desorbed organics are trapped at −30°C on a packed cold trap prior to flash volatilisation of the volatiles across a fused-silica transfer line onto a capillary column.

The method separates over 200 organic compounds within 40 min utilising flame ionisation and ion trap detection and is capable of quantitation down to 5 ng l^{-1} per component. The results of a case study on the Solent estuary in southern England are briefly summarised.

INTRODUCTION

Over the past 10–15 years, concern over the quality of water resources has continued to intensify. The availability of clean water is fundamental to many of the activities of man both in terms of sufficiently pure domestic and unpolluted recreational supplies. Consequently, pressures continue to mount on environmental analysts to detect trace levels of many types of potentially harmful organic pollutants in lakes and estuaries. Many of these compounds arise from the use of surface and ground waters as sinks for industrial effluents and untreated sewage. In addition, a wide range of volatile organic compounds is generated by natural seasonal biogenic[1] processes and chemical reactions between man-made inputs and compounds occurring

0021-9673/89/$03.50

in nature[2]. As the complexity of environmental pollution develops, so the need for systematic and functionally complete analytical methods grows.

Dynamic non-equilibrium headspace analysis represents one of the most scientifically advanced techniques available for the detection of volatile organic micropollutants in water[3]. Recent research has restated the efficiency of the technique under stringent experimental conditions[4]. By performing analysis on a gas phase in thermodynamic equilibrium with the medium under study, it is possible to eliminate many of the disadvantages associated with preconcentration methods at low levels concentrations, *e.g.* ng l^{-1}. Consequently, unlike methods necessitating exensive preliminary procedures, dynamic headspace avoids overloading or contamination of the chromatographic column with water or high-boiling non-volatile compounds[3].

The closed-loop stripping apparatus developed by Grob and co-workers[5–8] represents one of the most powerful techniques developed for the rapid analysis of many types of organic compounds in water. The method has also been widely applied in a variety of reported studies concerning the trace analysis of organics in water samples[9–15]. However, the range of compounds that can be detected using closed-loop stripping is limited. Highly volatile components are lost within the extraction solvent peak, and moderate to highly polar species are inefficiently recovered using the method. The technique has been used to screen large numbers of compounds, but its outstanding concentration factor makes the system useful even when only a small number of compounds is of interest.

We have developed a modification of the open-loop stripping apparatus reported by Borén *et al.*[16]. Although open-loop stripping methods were initially developed by Bellar and Lichtenberg in 1974[17], the basic design continues to represent a practical and realistic alternative to closed-loop stripping. The method of stripping and trapping of analytes both in closed- and in open-loop arrangements have been reported as yielding good analytical results[4]. Whereas in a closed circuit the stripping–trapping process can be accomplished in either a conservation or an equilibration regime, conservation or pseudoequilibration modes are possible when utilising open-loop stripping. Fig. 1 illustrates the basic differences in layout. However, Borén *et al.*[16] reported an improved blank level, the minimisation of contamination by laboratory air and a minimum detection limit at least equal to that achieved by closed-loop stripping methods when using an open-loop arrangement. Drozd *et al.*[4] have stated that when working with an open arrangement, better results are obtained by conservation trapping. This observation has been confirmed by the authors' experience in developing this method.

Several purge-and-trap methods reported rely on the solvent desorption of organics adsorbed onto a charcoal filter bed[5,8,18,19]. However, this method has limitations which must be taken into account where it is applied. Problems include a strong affinity for water, which is frequently found in headspace vapour samples and affects the adsorption properties, an excessive surface activity (activated charcoal) or the presence of large numbers of active sites for polar compounds (graphitized sorbents) which makes their use limited due to irreversible adsorption or decomposition problems. Additional problems include masking of highly volatile compounds by the solvent peak, the increased potential for artefacts generated through impure solvent preparation, and thermal decomposition of unstable organic compounds where high thermal desorption temperatures have to be used. Further

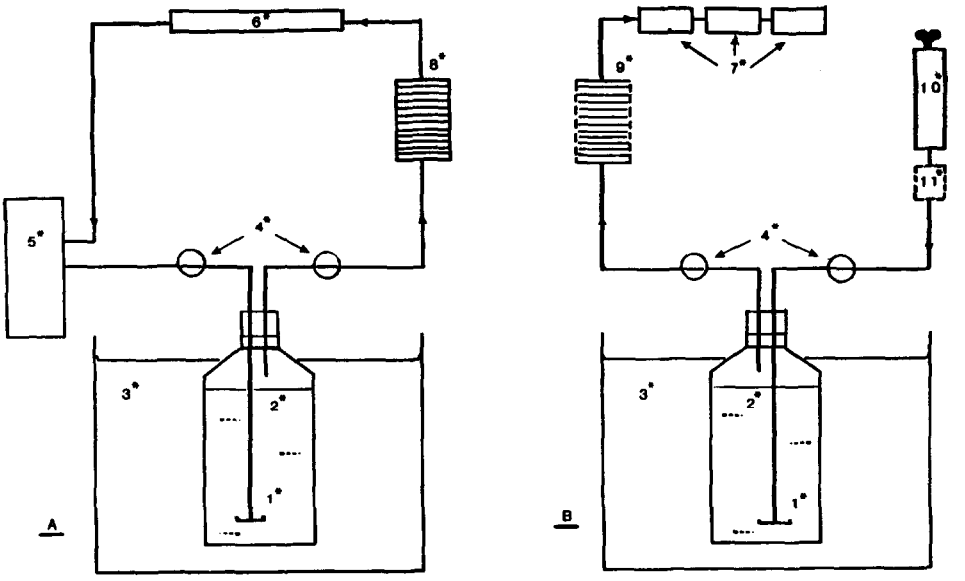

Fig. 1. Diagrammatic representation of (A) closed-loop stripping apparatus and (B) open-loop stripping apparatus. 1 = Gas sparger; 2 = water sample; 3 = thermostatically controlled water bath; 4 = glass–metal union connectors; 5 = pump; 6 = organic vapour adsorbent trap (activated charcoal); 7 = organic vapour adsorbent trap-train; 8 = tube heater unit; 9 = tube heater unit (optional); 10 = purge gas supply (ultrapure); 11 = gas filters (optional).

criticisms have been made against the use of activated charcoal, *i.e.* random variability in experimentally derived minimum detection limits and poor recovery performance at ppb[a] concentration levels[20]. However, it has been recognised that activated carbon or graphitized sorbents remain a suitable choice for exceptionally volatile compounds where porous polymers have insufficient sampling capacity and allow such compounds to break through[11], *e.g.* C_2 to C_4 species. The application of organic polymeric sorbents as alternative trapping media for headspace volatiles has increased significantly during the last decade, as they eliminate many of the drawbacks encountered using activated charcoal or graphitized sorbents. They have a low capacity for water and do not display irreversible adsorption or decomposition phenomena in general use[21]. Accordingly, there have been a number of chromatographic reviews assessing the value of polymeric substances[22–27], particularly Tenax-GC [poly(2,6-diphenyl-*p*-phenylene oxide)] and a modified, improved variant, Tenax-TA, which further minimises the generation of low-level artefacts in continuous use[28]. Nevertheless, although good analytical results have been achieved, the use of a single adsorbent has led to compromise in the retention of compounds covering a wide boiling-point range, with highly volatile compounds being poorly retained on some adsorbents, *e.g.* Tenax-TA, resulting in breakthrough and component loss[21] and higher boiling compounds being incompletely recovered from other adsorbents, *e.g.* Chromosorb Century Series. We have experimented with the application of a combination of

[a] Throughout this paper the American billion (10^9) is meant.

adsorbents in the quantitative trapping of volatile organic compounds from water, ranging from C_4 to C_{20} compounds. The modified method avoids component loss and contamination problems associated with extraction solvents and is capable of analysing either for specific groups of compounds, *e.g.* volatile organohalogens, or performing broader analyses of a wide range of volatile and semi-volatile organics found in rivers and estuaries. Used in conjunction with thermal desorption techniques, the method forms part of a high-performance, semi-automated integrated analytical system[29].

EXPERIMENTAL

Chemicals and adsorbents

Standards were prepared using analytical-grade materials (Aldrich, Wimborne, U.K.). Stock standard mixtures encompassing a range of compound classes were blended gravimetrically in all-glass vessels according to certified CONCAWE[30] and U.S. Environmental Protection Agency (EPA)[31] methods. Replicate standards containing organic compounds varying in boiling point from *n*-pentane to eicosane were made up to 1-l volumes in volumetric flasks, inverted and spiked via aluminium-coated poly(tetrafluoroethylene) (PTFE) septa with *n*-butane and 1,3-butadiene gas mixtures (Air Products Specialty Gases, Bracknell, U.K.) using gas-tight syringes.

Blank seawater volumes were prepared by solvent extracting seawater taken from a relatively unpolluted coastal site. Following extraction of solvent-extractable organics into re-distilled dichloromethane [Aldrich, high-performance liquid chromatography (HPLC)-grade, >99.99% purity after re-distillation], seawater aliquots (2 l) were purged overnight with ultrapure nitrogen (grade 5.5) at 500 ml min^{-1} to remove any further organic compounds. Secondary blank seawater was prepared by spiking AnalaR-grade distilled water (BDH, Poole, U.K.) with a heat-treated sea-salt mixture to simulate natural seawater (Instant Ocean, OH, U.S.A.) followed by nitrogen purging. Heat treatment of the sea-salt for 60 min in a clean laboratory oven held at 250°C was utilised to remove any contaminative volatile material present within the sea-salt mixture.

Seawater standards were prepared by chilling 1-l volumes of blank seawater to 4°C, followed by gravimetric addition of stock standard mixtures via hypodermic syringes (SGE, Milton Keynes, U.K.) under zero headspace. The specially made all-glass vessels (Hampshire Glassware, Southampton, U.K.) were then shaken for 10 min on a two-dimensional shaker (Turbula, Geneva, Switzerland), immediately followed by headspace extraction analysis.

The internal standards, 1-chlorohexane, 1-chlorooctane and 1-chlorodecane, were blended gravimetrically into re-distilled isopentane and stored in sealed glass flasks (10-ml volumes) under an ultrapure nitrogen blanket. Internal standards were prepared freshly each day.

Adsorbents

Tenax-TA (60–80 mesh), packed into $\frac{1}{4}$-in. O.D. pre-cleaned stainless-steel tubing was conditioned by heating at 30°C for 10 min in a stream of oxygen-free pre-filtered nitrogen at 15 ml min^{-1}. The packed tubing was then connected via

a Swagelock connection to the packed-column injector inside a gas chromatograph oven. After 10 min, the temperature was raised at 8°C min^{-1} to 350°C, held for 1 h. Maintaining the gas flow, it was cooled to 200°C and conditioned at this temperature overnight prior to packing into adsorbent tubes.

Chromosorb 106 (60–80 mesh), a non-polar resinous hard granular solid, was packed into ¼-in. stainless-steel tubing, and then heated from room temperature to 250°C at 8°C min^{-1} in a 15-ml min^{-1} flow of pre-filtered nitrogen. After 16 h at 250°C, the Chromosorb 106 was cooled and immediately packed into adsorbent tubes[32].

Spherocarb (60–80 mesh), a hard, non-friable molecular sieve, was conditioned according to the protocol for Chromosorb 106.

In Table I a summary is given of individual adsorbent physical properties. All adsorbents were supplied by Perkin-Elmer.

Sampling apparatus

The purge-and-trap stripping apparatus consisted of an all-glass 1-l bottle (nominal capacity, 1150 ml). A modified dreschel-head assembly incorporating a ground glass collar (19/24 mm) was inserted into the ground glass neck of the sample bottle (19/24 mm) and locked using a PTFE cage (Fig. 2).

Ultrapure nitrogen was metered via a metal–glass joint into a 7-mm O.D., 7-cm length of glass tubing fabricated onto the inlet of the purge head assembly. The internal glass tubing of the inlet purge head was fitted with a medium porosity frit (Grade 1) reaching to a depth of 2 cm from the base of the sample vessel. The exit flow glass tubing was lengthened to 12 cm, in order to accommodate a heated-clamp assembly capable of heating a 7-cm length of the glass tubing up to temperatures exceeding 250°C (Bastock Marketing, Oxon, U.K.). This unit, an optional addition to the apparatus, minimises the formation of condensing water droplets on the inner walls of the exit tubing.

Three adsorbent tubes, 90 mm × 5 mm I.D. [automated thermal desorber (ATD)-50 compatible, Perkin-Elmer, Beaconsfield, U.K.] of pre-cleaned stainless-steel fabrication, were packed and connected in series using standard ¼-in.–¼-in. stainless-steel Swagelock connections and ¼-in. PTFE ferrules. The assembled tubes were located via a leaktight PTFE sealing washer into the exit point of the purge head assembly and locked using a PTFE collar. Prior to assembly, the tubes were packed

TABLE I

PHYSICAL PROPERTIES OF ADSORBENTS USED IN THE MODIFIED METHOD FOR PRE-CONCENTRATION OF TRACE VOLATILE ORGANICS

Sorbent	*Composition*	*Specific surface area* (m^2/g)	*Mean pore diameter* (Å)	*Temperature limit* (°C)
Tenax-TA (60–80 mesh)	Poly(2,6-diphenyl-*p*-phenylene oxide)	19–30	720	375
Chromosorb-106 (60–80 mesh)	Polystyrene, non-polar cross-linked resin	600–800	50	250
Spherocarb™ (60–80 mesh)	Molecular sieve, a hard, non-friable carbon	1200	15	300

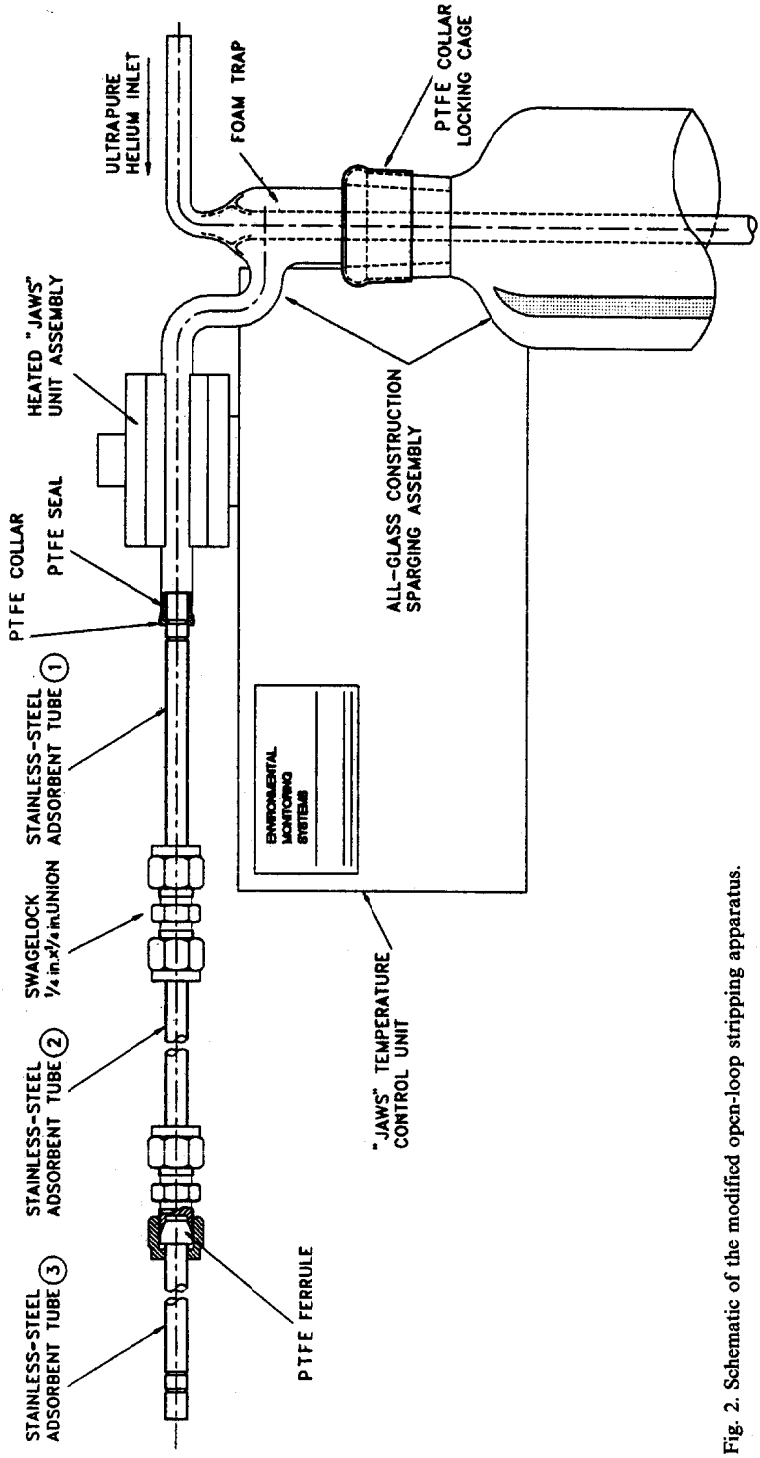

Fig. 2. Schematic of the modified open-loop stripping apparatus.

with 70 ± 5 mg of conditioned Tenax-TA (60–80 mesh), and held in place using stainless-steel gauge frits and silanised glass wool. The glass stripping vessel was then immersed into a thermostatically controlled water bath (Grant Instruments, Cambridge, U.K.) to vessel depth, allowing 15 min for thermostatic equilibrium to be attained.

Instrumentation and capillary column

An ATD-50 was connected to a Model 8310 gas chromatograph (Perkin-Elmer) via a 1-m length of deactivated fused-silica transfer line, 0.22 mm I.D., held at 150°C. The ATD-50 is a multi-functional instrument the principal role of which is for the analysis of organic vapours at very low concentrations (sub-ppm)[33]. A two-stage desorption facility is available whereby organic compounds desorbed from adsorption tubes at 150°C are re-trapped inside an electronically cooled cold trap, packed with a secondary adsorbent at temperatures down to −30°C. Retention of the sample vapours inside the cold trap therefore depends on chromatographic factors rather than condensation[33]. The trap is then heated at a rate exceeding 1000°C min^{-1} to a defined upper limit of 300°C, sending a discrete band of concentrated sample through the fused-silica transfer line to the gas chromatographic (GC) capillary column.

The gas chromatograph was fitted with a cradle-mounted, 50 m × 0.22 mm I.D. BP-1 wall coated open-tubular fused-silica capillary column, 0.5 μm film thickness (SGE). The exit point of the column was connected to a twin-hole split ferrule (Chrompack, London, U.K.) allowing 50% of the column eluent to be routed to a flame ionisation detector. The remaining 50% is swept via a second 1-m length of transfer line at 250°C into an ion trap detector–mass spectrometer[34] (Finnigan MAT, U.K.).

Analytical operating parameters. The final selected GC system conditions instituted were as follows. Carrier gas: ultrapure helium 5.5 grade (Air Products). ATD-50: cold-trap packing, 20 mg Tenax-TA; cold trap low temperature, −30°C; cold trap high temperature, 250°C; split ratio (combined), 200:1; desorption box temperature, 150°C; desorption oven temperature, 250°C; desorption time, 10 min; carrier gas pressure, 25 p.s.i.

Gas chromatograph. Detector temperature, 300°C; carrier gas flow-rate, 1 ml min^{-1}. Temperature conditions: oven temperature, 40°C; isothermal time 1, 10.5 min; ramp rate 1, 5°C min^{-1}; oven temperature 2, 95°C; isothermal time 2, 0.1 min; ramp rate 2, 15°C min^{-1}; oven temperature 3, 235°C; final hold time, 15 min.

Ion trap detector. Ionisation voltage, 70 eV; seconds/scan, 1.0; mass range, 25–250 mass units; transfer temperature, 250°C; ion source temperature, 250°C; multiplier delay, 200 s; mass defect, 100 m.m.u./100 a.m.u.; acquire time, 50 min.

Flame ionisation chromatograms were interpreted by reference to retention indices, and retention times derived from comparison with pure co-injected standard mixtures. Mass spectra were interpreted by comparison with a National Bureau of Standards and General Purpose computerised mass spectral library stored on hard Winchester disk drive (supplied by Finnigan MAT). We also utilised a library of mass spectra kept on laboratory files and co-injected standard reference spectra subsequently stored on a user-defined library within the ion trap detector computer. (Epson PC AX, 40 Mbyte)

Analytical procedure

Known aliquots of multicomponent stock standards were used to prepare fresh seawater standards on a daily basis over a range of concentration from 5 ng l^{-1} per component to 500 $\mu g\ l^{-1}$ per component.

The effect of several key analytical variables on the analytical system were examined experimentally. A standard containing approximately 5–15 $\mu g\ l^{-1}$ of each component was prepared, and the selective influence of stripping temperature, stripping time and flow-rate investigated.

Temperature: Standards were initially stripped at a flow-rate of 100 ml min^{-1} at 30°C over several time periods. At a strip time of 60 min (which preliminary analyses had indicated as the optimum for many low-boiling compounds), we logged recovery percentages at 10°C temperature increments up to 90°C.

Time: Standards were stripped at 7.5-, 15-, 30-, 60- and 120-min intervals at a flow-rate of 100 ml min^{-1} and 60°C.

Flow-rate: Flow-rates between 50 ml min^{-1} and 500 ml min^{-1} were experimented with in order to determine the effect of flow-rate on recovery.

The trapping efficiency of the adsorbent train was investigated by preparing three Tenax-TA tubes in series according to Bertsch *et al.*[21] and purging standards at optimised experimental parameters, *i.e.* 100 ml min^{-1}, and 60°C for 1 h. Each tube was disconnected after purging and individually thermally desorbed and analysed. The recovery (%) of each component on each tube was quantitated and logged. Repeat experiments using a fourth Tenax-TA tube in series was used in order to detect breakthrough of volatile components.

We decided to evaluate different adsorbents using the model standards in order to achieve improved selective trapping of volatile organics and minimise breakthrough[3]. We repeated the experiments using more powerful adsorbents by substituting Chromosorb 106 into the second tube, Spherocarb into the third tube and retaining Tenax-TA in the first tube. A fourth tube was double-packed containing a mixture of Tenax-TA and Chromosorb 106 (50:50) in order to detect breakthrough.

RESULTS AND DISCUSSION

The results of these basic experiments showed that temperature, stripping time and purge flow-rates all influence the recovery of organic compounds.

Although recoveries in excess of 50% were achievable for many compounds at 30°C, total recoveries increased over a broad range of compounds including alcohols and ketones as strip temperature was increased. Recoveries for a wide range of compounds, *e.g.* volatile aromatics, organochlorines and low-molecular-weight alkanes reached a maximum at 60°C. These data are presented in Table II.

The effect of varying the stripping time (at 60°C and 100 ml min^{-1} flow-rate) of a standard containing seven key compounds found in contaminated coastal seawater samples is shown in Fig. 3, and exemplifies the variation in recovery percentages we obtained as a function of time.

Flow-rates above 250 ml min^{-1} were found to generate excessive back pressure inside the purging assembly due to resistance from the purge frit, sample and adsorbent train. It was noted that differences of $< 1\%$ recovery were obtained when flow-rates between 50 and 200 ml min^{-1} were used. At 100 ml min^{-1} the vigorous dispersion of

TABLE II

RECOVERIES OF MODEL ORGANIC COMPOUNDS FROM WATER AT 30 AND 60°C

Conditions: Nitrogen flow-rate, 100 ml min^{-1}; sampling time, 60 min; water volume, 1 l.

Compound	*Molecular mass*	*Boiling point (°C)*	*Recovery (%)*	
			30°C	*60°C*
n-Pentane	72.1	35	88	103
n-Hexane	86.2	69	86	102
n-Heptane	100.2	98	86	101
n-Octane	114.2	125–127	85	101
n-Nonane	128.2	151	83	99
n-Decane	142.3	174	83	99
n-Undecane	156.3	196	82	98
n-Dodecane	170.3	216	81	97
n-Tridecane	184.4	234	80	95
n-Tetradecane	198.4	254	77	92
n-Pentadecane	212.4	270	73	89
n-Hexadecane	226.5	287	70	87
n-Heptadecane	240.48	302	66	85
3-Methyl-1,3-butadiene	68.1	34	77	95
2,2-Dimethylbutane	86.2	49.7	52	84
2,3-Dimethylbutane	86.2	57.9	50	85
2-Methylpentane	86.2	62	65	93
3-Methylpentane	86.2	64	65	93
Cyclopentane	70.1	50	73	95
2,2,4-Trimethylpentane	114.2	98	70	90
2,4,4-Trimethylpentene-2	112.2	102	77	96
2,4,4-Trimethylpentene-1	112.2	104	77	96
Benzene	84	79	93	102
Methylbenzene	92.1	111	87	101
1,3-Dimethylbenzene	106.2	139	87	100
1,2-Dimethylbenzene	106.2	144	88	99
Ethylbenzene	116.2	135	89	114
Isopropylbenzene	120.2	153	85	100
n-Propylbenzene	120.2	159	84	99
1,2,3-Trimethylbenzene	120.2	176	84	99
1,2,4-Trimethylbenzene	120.2	168	83	92
1,3,5-Trimethylbenzene	120.2	163	80	92
1,2,3,4-Tetramethylbenzene	134.2	205	79	89
1-Methyl-2-ethylbenzene	120.2		65	79
1,2-Dichlorobenzene	147	179	90	104
Dichloromethane	86.95	40	92	106
Chloroform	120.39	61	94	99.5
1,1,1-Trichloroethane	133.4	75	95	110
Trichloroethylene	131.4	86.9	95	107
Bromodichloromethane	163.8	87	93	101
Trichlorofluoromethane	137.37	23.7	100	107
Chloroethane	64.52	12.5	98	105
1,1,2-Trichlorotrifluoroethane	187.4	47	98	106

(Continued on p. 120)

TABLE II *(continued)*

Compound	*Molecular mass*	*Boiling point (°C)*	*Recovery (%)*	
			30°C	*60°C*
Dimethylsulphide	62	38	79	99
Dimethyldisulphide	94.2	109	80	97
2-Methylthiophene	98.2	113	80	96
Ethanol	46	78	59	87
Propanol-2	60	82	59	87
tert.-Butanol	75	118	58	84
n-Butanol	75	118	58	84
2-Butanol	74	98	59	85
Propanal	58	46–50	79	91
Pentanal	86.1	103	78	90
Heptanal	114.2	153	75	90
Benzaldehyde	106	179	70	91
2-Butanone	72.1	80	48	89
2-Pentanone	86.1	101	48	88
2-Heptanone	114.2	150	46	85
2-Decanone	156	211	65	72
Methyl isobutyl ketone	100	118	57	90
Naphthalene	128.2	217	60	97
Indene	116.6	182	71	100
1,3-Dimethylnaphthalene	156.2	263	57	94
1,2-Dimethylnaphthalene	156.2	266–267	58	94
2-Methylfuran	82.1	63–66	81	94
2,5-Dimethylfuran	96.1	92–94	74	93
1-Chloroheptane	134.7	159–161	92	101
1-Chlorodecane	176.7	183	93	101
1-Chlorooctane	148.68	223	94	104
2-Methylbutane	72.2	30	95	102
1,3-Butadiene	54.09	−4.5	100	103
cis-Butene-2	56.11	3.7	100	101
trans-Butene-2	56.11	1	97	101
1-Butene	56.11	−6.3	99	102

gas bubbles through the sample was achieved allowing maximum gas–sample contact without generating excessive internal pressure which could precipitate leaks.

Where Tenax-TA tubes were used in series according to the protocol of Bertsch *et al.*[21], the recovery percentages are shown in Table III. The resulting improvements in recoveries obtained by substituting the second Tenax-TA tube with Chromosorb 106 and the third Tenax-TA tube with Spherocarb are shown in Table IV.

Zero breakthrough of the standard compounds was observed from analysis of the third tube up to individual concentrations of 500 $\mu g\ l^{-1}$ per component. It was found that by utilising such progressively stronger adsorbents, with an increasing

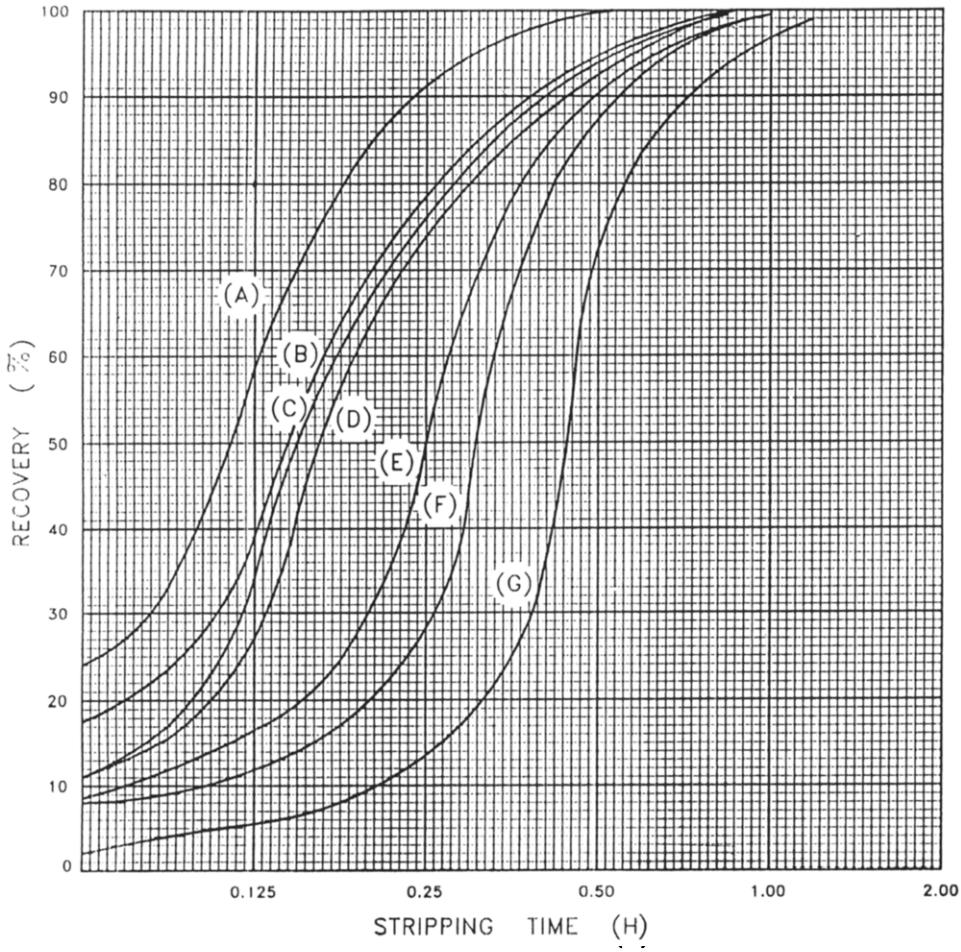

Fig. 3. Experimental effects of stripping time on the recovery of seven different compounds at 60°C and a flow-rate of 100 ml min^{-1}. (A) 1,2-Dichlorobenzene; (B) benzene; (C) methylbenzene; (D) 1,3-dimethylbenzene; (E) trichloromethane; (F) *n*-nonane; (G) naphthalene.

retention volume capacity for volatile compounds, extremely volatile compounds such as light hydrocarbons (which break through porous polymer sorbents) were efficiently retained *i.e.* on Spherocarb. Further, the comparitively poor trapping of alcohols, ketones and lighter substituted alkanes, *e.g.* 2,2-dimethylbutane, on Tenax-TA was overcome by employing Chromosorb 106, as predicted by Murray[32]. Components of higher molecular weight and boiling point were found to be efficiently retained by Tenax-TA.

The relative differences in the volatility and physicochemical properties of many organic compounds found in surface waters complex the analytical task. The results achieved by the application of a multi-sorbent trapping apparatus have yielded complete recovery of compounds varying in volatility from *n*-butane to eicosane. The combination of sorbents minimises overloading which may be encountered when

TABLE III

BREAKTHROUGH CAPACITIES OF TENAX ADSORBENT TUBES FOR VARIOUS COMPOUNDS

Conditions: Nitrogen flow-rate, 100 ml min^{-1}; sampling time, 60 min; air temperature, 20°C; tube dimensions, 90 × 5 mm I.D.; 60–80 mesh; strip temperature, 60°C.

Compound	*Recovery (%)*			
	Tenax, tube 1	*Tenax, tube 2*	*Tenax, tube 3*	*Breakthrough loss*
n-Butane	5.3	10.0	15.9	68.8
1,3-Butadiene	17.2	28.7	18.5	35.6
n-Pentane	57.8	32.9	6.6	2.7
3-Methyl-1,3-butadiene	23.9	54.5	12.7	8.9
Dichloromethane	19.1	28.3	47.6	5.0
Dimethylsulphide	84.2	12.7	2.2	0.9
tert.-Butanol	29.0	33.7	33.4	3.9
2,2-Dimethylbutane	33.7	38.5	26.1	1.7
3-Methylpentane	40.1	49.3	10.4	0.2
Trichloromethane	81.5	8.3	6.1	4.1
2-Butanone	29.3	50.8	13.6	6.3
2-Methyl-pentane-1	42.2	53.2	3.7	0.1
Benzene	85.7	10.5	3.7	0.1
Pentanal	63.2	27.5	7.5	1.8
n-Heptane	90.0	8.3	1.3	0.4
Methylbenzene	89.9	7.8	2.2	0.1
n-Octane	79.1	15.6	5.2	0.1
Chlorobenzene	68.3	24.9	6.8	–
Ethylbenzene	85.6	13.5	0.9	–
1,2-Dimethylbenzene	88.8	10.7	0.3	0.2
n-Nonane	82.5	17.3	0.2	–
n-Propylbenzene	92.7	6.9	0.4	–
Benzaldehyde	75.3	20.1	4.6	–
1,2,3-Trimethylbenzene	96.0	3.3	0.7	–
1,2,3,4-Tetramethylbenzene	96.9	3.1	–	–
Naphthalene	96.3	3.7	–	–

employing a single tube, with organic eluates, and potential interferences which may occur between the sorbates on a single tube. Indeed, if there are great differences in the sorbabilities of the trapped components, and some of the components are sorbed so strongly as to precipitate displacement of the less strongly sorbed components, the latter will be subjected to displacement rather than frontal chromatography. Components that form displacement zones during the trapping process will be pushed out of the trapping column and consequently only small amounts of such components will be recovered from the trap tube in the state of final equilibration. With conservation trapping such effects are not as significant as compared to equilibration trapping, where the components are lost for analysis. Nevertheless, with multi-sorbent trapping, any displaced components are re-trapped on the subsequent tube and therefore retained for desorption analysis. A specimen purge standard chromatogram (Tenax-TA tube) is shown in Fig. 4.

Strict adherence to method parameters was found to be essential for precise

TABLE IV

BREAKTHROUGH CAPACITIES OF TENAX, CHROMOSORB-106, AND SPHEROCARB ADSORBENT TUBES FOR VARIOUS COMPOUNDS

Conditions: Nitrogen flow-rate, 100 ml min^{-1}; sampling time, 60 min; air temperature, 20°C; tube dimensions, 90 × 5 mm I.D.; 60–80 mesh, each tube; strip temperature, 60°C.

Compound	*Recovery (%)*		
	Tenax, tube 1	*Chromosorb 106, tube 2*	*Spherocarb, tube 3*
n-Butane	6.9	39.7	53.4
1,3-Butadiene	17.7	43.3	39.0
n-Pentane	56.1	40.4	3.5
3-Methyl-1,3-butadiene	22.4	75.5	2.1
Dichloromethane	18.5	80.7	0.8
Dimethylsulphide	84.5	15.5	–
tert.-Butanol	27.4	70.7	1.9
2,2-Dimethylbutane	33.0	64.4	2.6
3-Methylpentane	40.7	58.5	0.8
Trichloromethane	80.1	19.8	0.1
2-Butanone	29.7	68.3	2.0
2-Methylpentene-1	42.0	57.8	0.2
Benzene	85.7	14.3	–
Pentanal	62.9	36.4	0.7
n-Heptane	90.4	9.6	–
Methylbenzene	90.1	9.8	0.1
n-Octane	79.5	20.5	–
Chlorobenzene	68.7	31.3	–
Ethylbenzene	85.7	14.3	–
1,2-Dimethylbenzene	88.0	12.0	–
n-Nonane	82.9	17.1	–
n-Propylbenzene	91.5	8.5	–
Benzaldehyde	75.2	24.8	0.2
1,2,3-Trimethylbenzene	96.7	3.3	–
1,2,3,4-Tetramethylbenzene	96.7	3.3	–
Naphthalene	96.1	3.9	–

operation of the method, *i.e.* temperature and strip time. The repeatability of the system method (expressed as the coefficient of variation, %) was within 2% for all components, except *n*-butane (5.8%) and 1,3-butadiene (4.9%). The optimum recovery of many environmentally important components, *e.g.* benzene, methylbenzene (toluene) and ethylbenzene (EPA-listed priority pollutants)[35] approached maximum at 60 min stripping time and 60°C strip temperature. Alcohols and ketones were less efficiently recovered, being more hydrophilic and polar. For the more volatile ketones, however, *e.g.* 2-butanone, recoveries greater than 80% were achieved.

Further increases in high-performance capillary column separation of light hydrocarbons, *i.e.* C_2, C_3 and C_4 gases, can be achieved by subjecting the Spherocarb tube (upon which the majority of light hydrocarbons are retained) to a modified sub-ambient method devised by Bianchi and Cook[36] using identical desorption parameters and chromatographic capillary column but operating the column isothermally at −35°C.

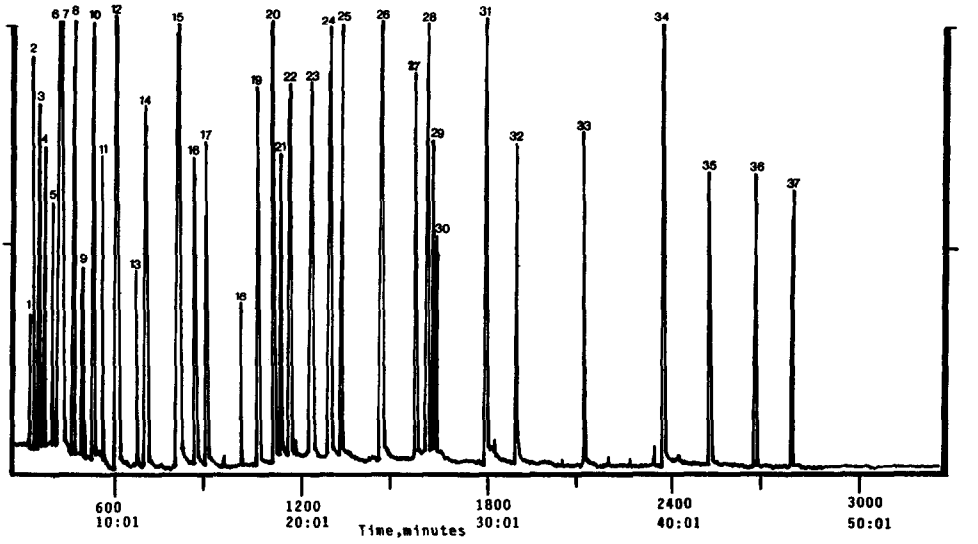

Fig. 4. Specimen purge seawater standard chromatogram obtained from Tenax-TA tube. Peaks: 1 = *n*-Pentane; 2 = 3-methyl-1,3-butadiene; 3 = dimethyldisulphide; 4 = 1,1,2-trichloro-1,2,2-trifluoroethane; 5 = 2,2-dimethylbutane; 6 = methyl *tert.*-butyl ether; 7 = 2-methylpentane; 8 = methylcyclopentane; 9 = 1,2-dichloroethane; 10 = benzene; 11 = thiofuran; 12 = *n*-heptane; 13 = 2,4,4-trimethylpentane; 14 = 1,1,2-trichloroethane; 15 = methylbenzene; 16 = hexanal; 17 = 1,2-dibromoethane; 18 = tetrachloroethylene; 19 = chlorobenzene; 20 = 1-chlorohexane; 21 = ethylbenzene; 22 = 1,3-dimethylbenzene; 23 = 1,2-dimethylbenzene; 24 = *n*-nonane; 25 = isopropylbenzene; 26 = 1,3,5-trimethylbenzene; 27 = 2-phenylbutane; 28 = 1,2,3-trimethylbenzene; 29 = indene; 30 = (+)-limonene (optically active); 31 = *n*-undecane; 32 = 1,2,3,4-tetramethylbenzene; 33 = 1-chlorodecane; 34 = *n*-tetradecane; 35 = 1,4-dimethylnaphthalene; 36 = *n*-hexadecane; 37 = *n*-heptadecane.

The modified stripping method is now routinely used in two industrial environmental laboratories and a university laboratory. It has proved reliable in use, having been applied to the analysis of several hundred wastewater, riverine and estuarial water samples and recently for domestic water quality studies.

The Solent estuary —a case study

The Solent estuary forms a body of water separating the Isle of Wight from the submerged channel of Southampton Water on the coastline of central southern England. The sub-estuary of Southampton Water, a semi-industrialised water stretch accomodating an extensive range of activities including petrochemical processing, large-scale electric power generation and intense boating and marine operations, has become a major sink for many of the waste products associated with such activities. In addition the estuary receives wastes from water treatment plants and agricultural run-off which have recently been the topic of a separate study programme[37]. Analysing the total volatile organic content of the estuarine water presents difficulties as individual component numbers frequently in excess of 200 separate compounds have been recovered from a single sample. A specimen chromatogram from the head of the estuary is shown in Fig. 5a. (The respective purge blank chromatogram is also shown, in Fig. 5b.) Organic classes identified include alkanes, alcohols, ketones,

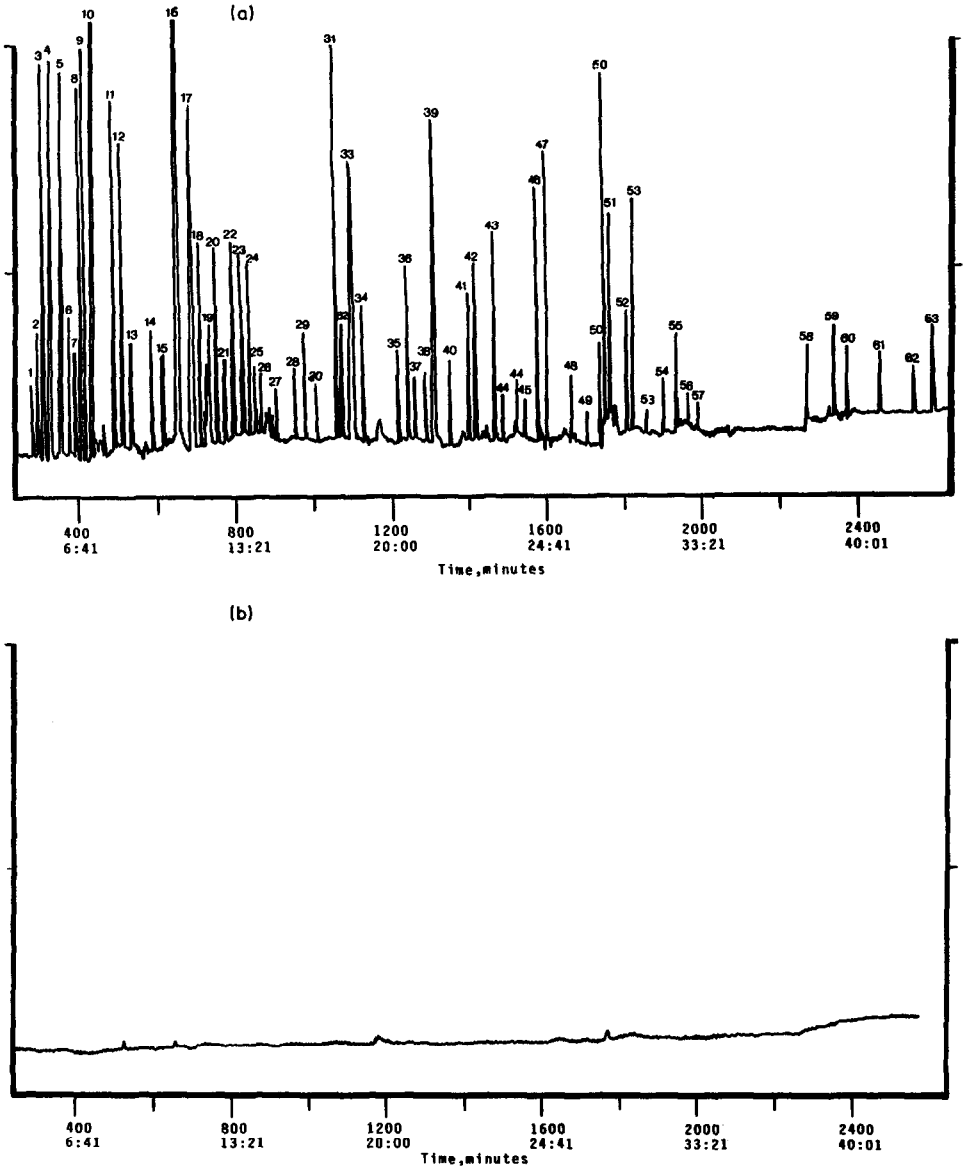

Fig. 5. (a) Specimen chromatogram of seawater sample taken at the head of the Southampton Water estuary, and (b) respective purge blank chromatogram. Peaks: 1 = *n*-Butane; 2 = propanal; 3 = *n*-pentane; 4 = 3-methyl-1,3-butadiene; 5 = dichloromethane; 6 = dimethylsulphide; 7 = 1,1,2-trichloro-1,2,2-trifluoroethane; 8 = 2,2-dimethylbutane; 9 = *n*-hexane; 10 = 2-methylpentene-1; 11 = 3-methylbutanal; 12 = benzene; 13 = cyclohexane; 14 = 2,4,4-trimethylpentane; 15 = 2,5-dimethylfuran; 16 = *n*-heptane; 17 = 2,4,4-trimethylpentene-1; 18 = 2,4,4-trimethylpentene-2; 19 = dimethyldisulphide; 20 = 2,3-dimethylpentene-1; 21 = 3-methyl-2-butenal; 22 = methylbenzene; 23 = 3,4,4-trimethylpentene-2; 24 = 3-methylthiophene; 25 = hexanal; 26 = 2,2,5-trimethylhexane; 27 = 1,2-dibromoethane; 28 = tetrachloroethylene; 29 = *n*-octane; 30 = chlorobenzene; 31 = unknown ?; 32 = 2,3,5-trimethylhexane; 33 = 2,2,3-trimethylhexane; 34 = 1-chlorohexane; 35 = ethylbenzene; 36 = 1,3-dimethylbenzene; 37 = 1,2-dimethylbenzene; 38 = *n*-nonane; 39 = isopropylbenzene; 40 = (α)-pinene; 41 = benzaldehyde; 42 = aldehyde?; 43 = 1,3,5-trimethylbenzene; 44 = 1,2,4-trimethylbenzene; 45 = *n*-decane; 46 = 1,2,3-trimethylbenzene; 47 = 3,3,5-trimethylpentane ?; 48 = 2,3-dihydroindene; 49 = (+)-limonene; 50 = indene; 51 = nonanal; 52 = *n*-undecane; 53 = 1,2,3,5-tetramethylbenzene; 54 = naphthalene; 55 = *n*-tridecane; 56 = 1-methylnaphthalene; 57 = branched alkene ?; 58 = biphenyl; 59 = dodecanal; 60 = *n*-tetradecane; 61 = 1,3-dimethylnaphthalene; 62 = 1,4-dimethylnaphthalene; 63 = aldehyde structure ?.

TABLE V

IDENTIFIED ORGANIC COMPONENTS FOUND IN DOMESTIC TAP WATER DRINKING SUPPLIES

Samples: (1) City of Southampton; (2) Marchwood (a semi-rural village, 10 km S.W. of Southampton City); (3) Dibden Purlieu (a village 17 km S.W. of Southampton City).

Substance	*Concentration ($\mu g\ l^{-1}$)*		
	Sample 1	*Sample 2*	*Sample 3*
Trichloromethane	20.01	29.73	35.07
Tetrachloromethane	0.01	0.13	0.01
Dichlorobromomethane	15.73	19.17	23.65
Chlorodibromomethane	7.94	10.00	14.72
Dichlorodibromomethane	1.11	2.56	4.69
Tribromomethane	2.45	2.99	4.00
1,1,1-Trichloroethane	0.01	0.71	1.01
Benzene	0.29	0.53	1.02
1,2,-Dichloroethane	0.05	0.42	0.04
Methylbenzene	0.57	0.99	1.73

aldehydes, furans, aromatic and alkylaromatics, organosulphides and organohalogens.

Seasonal differences are marked within the estuary, with simple aromatic compounds reaching a maximum in winter months (benzene concentrations exceeding 350 $\mu g\ l^{-1}$ during December) and a secondary short-term maximum in summer months. These are largely due to increases in the use of fossil fuels by the inhabitants of Southampton and its urban conurbations in winter and major increases in pleasure boating in the summer, respectively. There are other causes which contribute to the dynamic nature of such inputs including random pollution events and a progressively developing contribution from motor vehicles.

Halogenated hydrocarbons, *e.g.* Freons, are recovered all year round resulting from a myriad diversity of anthropogenic activities. Disturbingly, following recent concern over the effects of Freons in depletion of the ozone layer, we have found Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane) consistently at concentrations rarely below 10 $\mu g\ l^{-1}$ in both water and sediment samples. We have not yet been able to pinpoint a significant single key source and investigative work is continuing in this area.

Confirmation of the identity of many volatile Freons has been conducted by independant consulting laboratories who have also confirmed the presence of yet further higher-molecular-weight Freon species in estuarine samples.

Organic sulphur compounds, particularly dimethylsulphide, are ubiquitous in the estuary due to anaerobic decomposition of organic matter in saltmarsh muds. The dumping of untreated sewage is a second major source of organic sulphur compounds and a wide range of organosulphur species have also been found in marine sediments throughout the estuary.

However, compounds of non-anthropogenic source have been identified, including terpenoid materials. Found in midsummer and late autumn at concentra-

tions up to 100 $\mu g\ l^{-1}$, they are associated with fresh water runoff into the estuary. Isoprene (3-methyl-1,3-butadiene), a biogenically derived plant breakdown product, reaches an absolute maximum by mid-November whereas a structurally similar compound, (+)-limonene, is found in higher concentrations in midsummer, mainly produced by peak phytoplanktonic activity.

Such detailed studies have illustrated a range of natural, seasonal and pollution-related processes occurring within the water column and yield significant information on complex interactions and inter-relationships between organic compounds. The modified stripping method has also been applied to a detailed examination of potable-water supplies piped into domestic households. A number of organohalogens have been recovered from tap water samples taken from Southampton City supplies, and from villages in the semi-rural districts outside of the city which have regularly shown higher concentrations of contaminant compounds (see Table V). We believe the results show a constant bias as a result of inefficient chlorination of the water by the Water Authority or alternatively a yet unquantified function of the relationship between the piped supply network (which is known to be subject to irregular pressure distribution), and an adsorption–desorption phenomenon inside the walls of the supply pipework. As the village sampling points are in area of increased pressure, it is feasible that organochlorines are being pressure concentrated in zones immediately prior to entering dwelling houses. Research is continuing in this area and a more comprehensive report is planned for 1990.

CONCLUSION

The modified purge-and-trap thermal desorption method, developed for comparitive simplicity in use combined with low-level accuracy at sub-ppb levels should be worthy of serious consideration by the environmental chemist. A low-cost laboratory computer system has been added to the analysis to perform simultaneous integration and data handling operated in conjunction with the ion trap detector, Available to most laboratories, modern simple benchtop personal computers can be programmed to identify and integrate assignable and non-assignable compounds from each of the three chromatograms produced from one sample. We believe that with the advent of new research projects examining the occurrence, source and fate of organic micropollutants in areas such as the North Sea and developing interests in coastal pollution, these methods have a role to play in facilitating such analytically complex tasks.

REFERENCES

1 F. Jüttner and J. J. Henatsch, *Nature (London)*, 323 (1986) 797.
2 R. Pizzie, *Ph.D. Thesis*, University of Southampton, Southampton, 1984.
3 A. J. Núñez, L. F. González and J. Janák, *J. Chromatogr.*, 300 (1984) 127.
4 J. Drozd, Z. Vodáková and J. Novák, *J. Chromatogr.*, 354 (1986) 47.
5 K. Grob, *J. Chromatogr.*, 84 (1973) 255.
6 K. Grob and G. Grob, *J. Chromatogr.*, 90 (1974) 303.
7 K. Grob, K. Grob, Jr. and G. Grob, *J. Chromatogr.*, 106 (1975) 299.
8 K. Grob and F. Zürcher, *J. Chromatogr.*, 117 (1976) 285.
9 M. M. Thomason and W. Bertsch, *J. Chromatogr.*, 279 (1983) 383.
10 J. Curvers, Th. Noy, C. Cramers and J. A. Rijks, *J. Chromatogr.*, 289 (1984) 171.

11 A. J. Núñez and H. Maarse, *Chromatographia*, 21 (1986) 44.
12 B. Brown, Senior Analytical Chemist, Wessex Water Authority, Bristol, personal communication.
13 P. M. Gschwend, O. C. Zafiriou, R. F. C. Mantoura, R. P. Schwarzenbach and R. B. Gagosian, *Environ. Sci. Technol.*, 16 (1982) 31.
14 S. G. Wakeham, J. T. Goodwin and A. C. Davies, *Can. J. Fish. Aquat. Sci.*, 40 (1983) 304.
15 R. P. Schwarzenbach, R. H. Bromund, P. M. Gschwend and O. C. Zafirioù, *Org. Geochem.*, 1 (1978) 93.
16 H. Borén, A. Grimvall and R. Sävenhed, *J. Chromatogr.*, 252 (1982) 139.
17 T. A. Bellar and J. J. Lichtenberg, *J. Am. Water Works Assoc.*, 66 (1974) 739.
18 R. D. Kleopfer and B. J. Fairless, *Environ. Sci. Technol.*, 6 (1972) 1036.
19 J. W. Swinnerton and V. J. Linnenbom, *J. Gas Chromatogr.*, 5 (1967) 570.
20 B. A. Colenutt and S. Thorburn, *Int. J. Environ. Anal. Chem.*, 7 (1975) 701.
21 W. Bertsch, E. Anderson and G. Holzer, *J. Chromatogr.*, 112 (1975) 701.
22 K. Kawata, T. Uemura, I. Kifune, Y. Tomikaga and K. Oikawa, *Bunseki Kagaku*, 8 (1982) 453.
23 K. J. Krost, E. D. Pellizzari, S. G. Walburn and S. A. Hubbard, *Anal. Chem.*, 54 (1982) 810.
24 N. R. Rakshieva, S. Wičar, J. Novák and J. Janák, *J. Chromatogr.*, 91 (1974) 59.
25 R. F. Simpson, *Chromatographia*, 12 (1979) 733.
26 R. D. Barnes, L. M. Law and A. J. MacLeod, *Analyst (London)*, 106 (1981) 412.
27 A. G. Vitenberg, B. V. Ioffe and V. N. Borisov, *Chromatographia*, 7 (1974) 610.
28 G. MacLeod and J. M. Ames, *J. Chromatogr.*, 355 (1980) 393.
29 A. Bianchi, *Int. Environ. Saf.*, 6 (3) (1988) 8.
30 *Oil Companies International Study Group for the Conservation of Clean Air and Water (ConCAWe), Report No. 8/86*, ConCAWe, The Hague, 1986.
31 *Method 624-Purgeables*, U.S. Environmental Protect. Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, July 1982.
32 K. E. Murray, *J. Chromatogr.*, 135 (1977) 49.
33 R. A. Hurrel, *Int. Environ. Safety*, June (1981) 18.
34 P. Bishop, *Proc. Anal. Div. Soc. Chem.*, 24 (1987) 368.
35 R. L. Grob (Editor), *Modern Practice of Gas Chromatography*, Wiley, 2nd ed., 1985, Ch. 10, p. 495.
36 A. Bianchi and H. A. Cook, *J. Chromatogr.*, 449 (1988) 175.
37 A. Bianchi and M. S. Varney, *Water Waste Treat*, 31, No. 9 (1988) 14.