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AUTOMATED MONITORING OF ORGANIC TRACE COMPONENTS IN WATER

I. CONTINUOUS FLOW EXTRACTION TOGETHER WITH ON-LINE CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

A system for automated monitoring of volatile organic trace compounds in water is described. The water is continuously extracted in a fused-silica capillary tube after flow injection of an immiscible solvent. Separation of the phases is accomplished with a porous PTFE membrane separator. The extract flows through a fused-silica sample loop, connected to a fused-silica capillary column or pre-column. The system operation is controlled by a programmable timer, which allows unattended analysis with regular time intervals. For evaluation of the system, dilute water solutions of aromatic and aliphatic hydrocarbons as well as water samples contaminated with trace amounts of a naphtha fraction were employed. Extraction was performed with *n*-pentane. The results were practically identical to those obtained from batch extractions carried out under comparable conditions. However, a better reproducibility was obtained with the flow extraction procedure. The on-column injection of large sample volumes (150 μl) permitted analyses at the ppt level, as demonstrated with a sample of continuously extracted waste-water from a sewage plant.

Significant adsorption of the trace components can occur on surfaces that are not brought into contact with the extractant. It is suggested that only a short length of fused-silica capillary tubing be used as a connection between the sample and the segmenting device.

INTRODUCTION

There is a growing need for continuous monitoring of the pollution of the world's natural water resources. The aquatic ecological balance has shown to be sensitive to chemical contamination and may eventually be globally affected. In acute situations such as oil spills, a rapid analysis of organic trace compounds in water is required, whereas regular water analyses are necessary for the survey of industrial waste-water effluents and in connection with the off-shore oil industry. Also, potable water is frequently subjected to quality tests, where the determination of organic trace components is of central importance, *e.g.*, in connection with taste and odour.

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Several work-up methods have been described to obtain the trace components in a suitable form for gas chromatography (GC). An enrichment procedure, where the water is first passed through a column containing an adsorbent, *e.g.*, graphitized carbon black[1], XAD resins[2] or C_{18}-bonded phase material[3], followed by elution with a solvent, has frequently been employed. A very powerful technique is the purge-and-trap procedure[4], which allows the analysis of volatile contaminants at the low ppt level. The water is purged with air or an inert gas and the trace components are collected on an adsorbent (charcoal), and then extracted with a suitable solvent. Both closed-loop[5] and open systems[6] have been described. Careful work is required to avoid system contamination, and proper cleaning of the adsorbent is mandatory for reliable operation[7,8].

Direct extraction with an organic solvent is one of the oldest methods and can be very efficient, especially when counter-current techniques are employed. Extraction by shaking with a solvent is the most simple and rapid method. For non-polar compounds this approach is attractive since a near quantitative recovery can be achieved using comparatively high water/solvent ratios. However, when using conventional capillary GC techniques, the extracts obtained are too dilute to detect trace components at the ppt level.

The following strategies can be employed to improve this situation: a reduction of the solvent/water ratio; the use of more sensitive detectors; injections of a larger sample; a pre-concentration of the extract. Reducing the solvent/water ratio will result in a more concentrated extract, but the recovery of the trace components may be considerably reduced. The use of a more sensitive detector such as an electron capture detector is a fruitful approach, and has been used for the determination of halocarbons at very low levels[9,10]. For compounds without electrophores, the most suitable and versatile detector is the flame ionization detector, which has considerably less sensitivity. In isolated cases, multiple ion mass spectrometry may be used, and provide higher sensitivity.

When large sample volumes (100–500 μl) are injected a substantial improvement in detection is obtained, and, combined with electron capture detection, allows the analysis of halocarbons at the low ppt level[11,12]. To detect such levels with a flame ionization detector, it would be necessary to increase the sample volume injected by one or two orders of magnitude.

A preconcentration of the extract prior to GC is an attractive solution. However, this is usually refrained from, at least when volatile trace compounds are the subject of study, due to losses experienced during evaporation of the solvent. In a forthcoming paper, it will be shown how such losses can be avoided when chromatographic evaporation[13] is employed.

Continuous automated extraction

Batch extraction with solvents is a fairly rapid procedure. Equilibrium is usually reached after a few minutes of shaking[10,14], and sampling of the extract with a syringe is straightforward when a narrow-necked flask and solvents with a density lower than that of water are employed. However, an automated extraction procedure is highly desirable[15]. In conjunction with automatic injection on capillary columns, an unattended survey of water pollution at remote locations would be possible.

Automated liquid–liquid extraction techniques based on flow injection have

been described, *e.g.*, ref. 16, and it was tempting to use this procedure with capillary GC. Principally, the solvent is injected in small segments in the water sample, which flows through a small diameter tube. Phase separation is conveniently carried out using a semi-permeable PTFE membrane, which has different wetting characteristics for the phases[17]. This technique offers the following distinct advantages over batch extraction: a continuous flow of extract, thus samples can be taken automatically and at any desired interval; a rapid equilibrium is obtained due to the dynamic conditions and the large contact area between the solvent and the sample; the closed system minimizes contamination and losses due to evaporation.

In this paper, a new technique employing continuous flow extraction together with capillary GC is described and some applications are demonstrated.

EXPERIMENTAL

System

The configuration of the system is outlined in Fig. 1. To obtain a continuous flow of the water sample, an high-performance liquid chromatographic (HPLC) pump (Waters, Model M-45), a syringe pump (home-made, equipped with a 10- or 50-ml gas-tight syringe) or a pressurized flask was used. For studies of discrete sample introduction, an eight-port valve (Valco-C8U, electrically actuated), equipped with

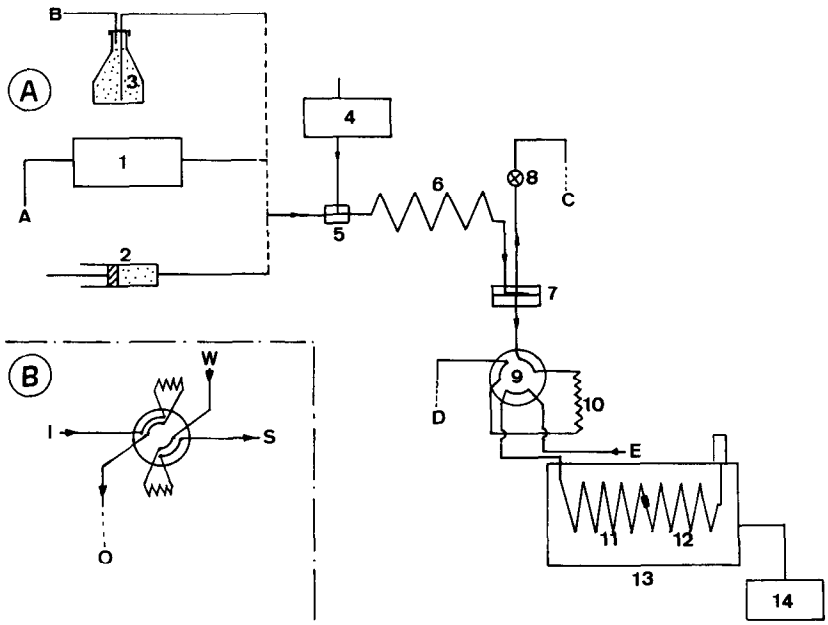

Fig. 1. Schematic set-up of continuous flow extraction with on-line capillary GC. Ⓐ, 1,4 = HPLC pump; 2 = syringe pump; 3 = pressurized flask with water sample; 5 = segmentor; 6 = fused-silica capillary tube; 7 = phase separator; 8 = needle valve; 9 = six-port valve; 10 = sample loop; 11 = empty precolumn; 12 = GC column; 13 = GC oven; 14 = recorder/integrator. A = water sample; B = pressurized nitrogen; C = extracted water; D = extract drain; E = carrier gas. Ⓑ, I = sample inlet; O = sample drain; W = clean water stream; S = segmentor.

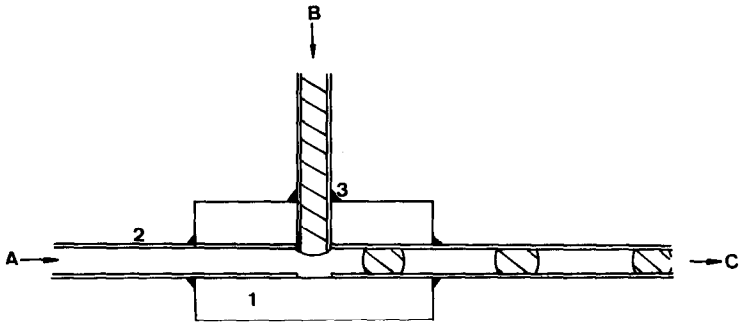

Fig. 2. Schematic view of the segmentor. A = Sample flow; B = solvent flow; C = segmented flow to the extraction capillary; 1 = polyimide cylinder; 2 = fused-silica capillary tube; 3 = polyimide glue.

dual sample loops (stainless steel, 0.8 mm I.D., volume 1 ml), was connected in series as shown in Fig. 1B.

The segmentor (Fig. 2) consisted of a polyimide Tee-piece comprising three fused-silica tubes (0.2 mm I.D.) joined with polyimide glue[18]. The exit tube (length 2 m) served as extraction capillary. The organic phase was delivered from another HPLC pump (LKB, Model 2150) into the side channel of the Tee-piece. Connections to the pumps were made with 1/16-in. fittings and polyimide ferrules (Valco).

Phase separation was accomplished with a membrane separator (Fig. 3), based

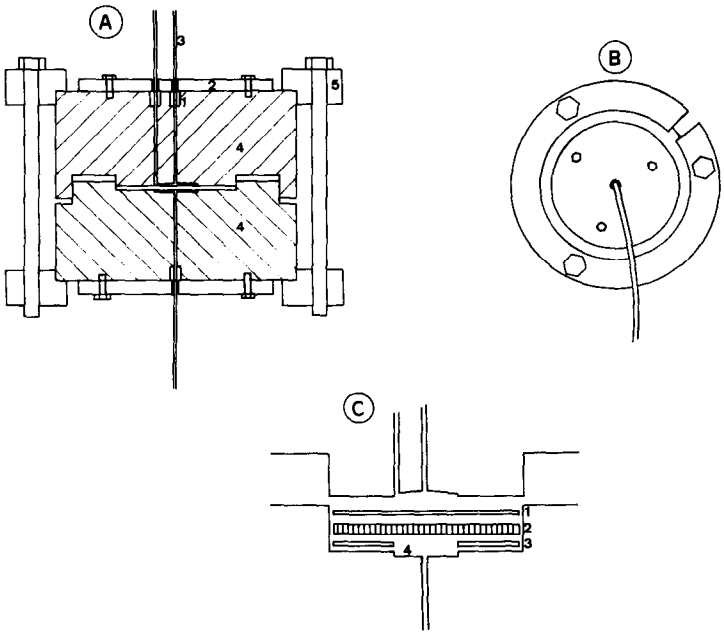

Fig. 3. Schematic of the phase separator. A, 1 = Cavity with silicone rubber O-ring; 2 = stainless-steel compression plate; 3 = fused-silica tubing; 4 = stainless-steel body; 5 = aluminium ring. B, Bottom view of the separator (top view when solvents with a lower density than that of water are employed). C, Enlarged view of the separator cavities. 1 = Fluoropore membrane; 2 = stainless-steel screen; 3 = Fluoropore washer; 4 = cavity for the organic phase (diameter 4 mm depth 0.1 mm).

on a previously described design[19]. However, the following modifications were made: The separator was constructed of stainless steel and the entrance and exit holes were precision-drilled to accommodate fused-silica tubing (0.64 mm O.D., 0.5 mm I.D.). To connect the narrow-bore fused-silica capillary tubing, sleeves (fused silica 0.5 mm I.D., 0.64 mm O.D., length 3 cm) were fixed concentrically with polyimide glue around the end of the tube. The tubing was tightened against the stainless-steel body with small silicone rubber O-rings which fitted in countersunk cavities. The O-rings were compressed with a thin stainless-steel plate, held by three small screws.

The two separator parts were clamped together by slotted aluminium rings and three screws. The slots facilitate the mounting and removal of the rings, without having to disconnect the fused-silica tubing. The circular design of the parts simplifies alignment and allows the use of standard components used for filtration (13-mm diameter membrane, Fluoropore FGLP, pore size 0.2 μm and a corresponding stainless-steel screen support, Millipore). For a tight seal between the rear of the support and the stainless-steel body, a Fluoropore membrane with a centrally punched hole, having the same diameter as the cavity (5 mm), was placed between these two parts. Alternatively, a PTFE-coated stainless-steel screen support (Millipore) without the Fluoropore washer was used.

The outlet capillary for the aqueous phase (fused-silica tubing, 0.5 mm I.D., length *ca.* 15 cm) was joined to a stainless-steel restrictor in order to obtain sufficient back-pressure for efficient phase separation. The outlet capillary for the organic phase was connected to a six-port micro valve (Valco, Model N6TW electrically actuated) equipped with a fused-silica sample loop (volume 150 μl, 0.32 mm I.D. The valve was also connected to an empty pre-column (deactivated fused silica 0.32 mm I.D., length 50 m). For this purpose, a small hole was pierced in the oven insulation. Thus the connection between the cold valve and the oven could be kept as short as possible. One of the remaining ports of the valve was coupled to the carrier gas stream, while the other port was connected to a length of fused-silica tubing (0.32 mm I.D.) which served as a drain for the organic phase.

The empty pre-column was coupled to a fused-silica capillary column (SE-54, cross-linked, 0.32 mm I.D., d_f = 0.5 μm) using a miniature butt-connector[20]. A gas chromatograph equipped with a flame ionization detector (Varian Model 3700) was used for all experiments. Peak area calculations and quantitations were carried out with a computing integrator (Spectra-Physics, Model SP-4270).

The motor-driven valves were controlled by a programmable multi-timer (resolution 0.1 sec). This microprocessor-based device can also control the start and stop of the pumps, initiate temperature programming of the GC oven and control a number of auxilliary functions. A detailed description of this timer will be reported elsewhere.

Procedure

n-Pentane (Merck, p.a.) was used as a solvent for the water extraction. It was shown to contain unacceptable amounts of impurities. Therefore, a careful distillation was carried out, employing a vacuum-jacketed column (length 50 cm) filled with glass spirals, and operated at a reflux ratio of *ca.* 7:1. Continuous extraction was carried out with *n*-pentane and sample flow-rates of 0.03 and 0.4 ml/min respectively. The GC conditions were as follows: inlet pressure: 1.5 bar; carrier gas, helium; de-

tector temperature 250°C. The sample was injected during a period of 35 sec, then the rotary valve was switched back to the reload postion. The initial oven temperature was kept at 38°C. When the solvent had passed through the column, a temperature program (5°/min) was started. At 220°C the column oven was cooled down to the intitial temperature and the next sample was automatically injected.

RESULTS AND DISCUSSION

Extraction efficiency

In the first study, the extraction efficiency of the continuous flow system was compared with that of a one-step batch extraction. For this evaluation, a solution of decane, undecane, *n*-propylbenzene, isopropylbenzene and naphthalene (2 ppb of each compound in tap-water) was used. A 50-ml volume of the solution was vigorously shaken with 3.75 ml of *n*-pentane for 5 min. The pentane contained 30 ppb of dodecane as an internal standard. A 150-μl volume of the extract was injected on the GC pre-column, using the loop injector.

Fig. 4 shows the results obtained with the two extraction methods. The nearly identical recoveries suggest that a complete equilibrium is obtained with the flow extraction procedure under the conditions described. The relatively low recoveries for the saturated hydrocarbons were surprising. At present, there is no explanation for this result. The reproducibility obtained with flow extraction was significantly better than with batch extraction, as shown in Table I.

An additional comparison between the continuous flow extraction procedure and batch extraction is shown in Fig. 5, where a water sample, containing a total of 200 ppb of a naphtha fraction, was extracted. Nearly identical results were obtained. A repeated (batch) extraction of the extracted water samples showed that practically

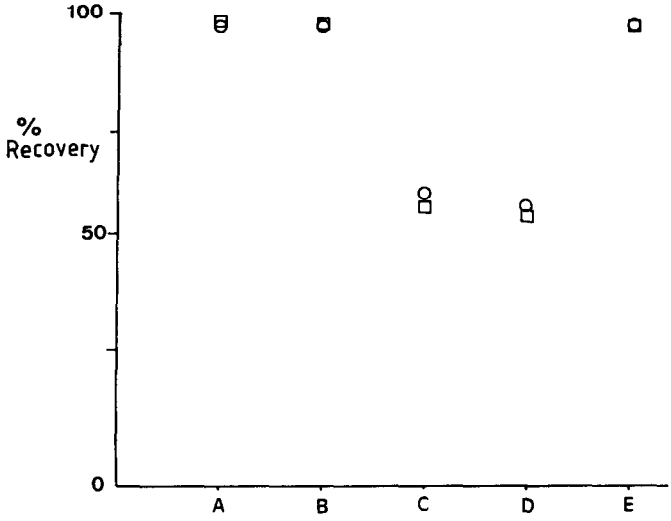

Fig. 4. Recovery for some model hydrocarbons (2 ppb of each compound in water), using continuous flow or batch extraction. □ = Continuous flow extraction; ○ = batch extraction. A = Isopropylbenzene; B = *n*-propylbenzene; C = decane; D = undecane; E = naphthalene.

TABLE I

REPRODUCIBILITY OF EXTRACTION WITH *n*-PENTANE FOR SOME HYDROCARBONS

2 ppb of each compound in water. The figures represent the relative standard deviation (%) calculated from five measurements.

Compound	*Flow extraction*	*Batch extraction*
Isopropylbenzene	2.6	8
n-Propylbenzene	0.8	7
Decane	1.5	12
Undecane	1.8	12
Naphthalene	1.5	3

all of the naphtha had been removed by the first extraction. However, the flow-extracted water consistently contained a higher concentration of remaining naphtha. This is understandable, since the phase separation process is not 100% complete, and small amounts of the petane extract are transported along with the water phase. This effect was quantified in the following way. Pure water was saturated with *n*-pentane and 2 μl of the water were injected on the capillary column (split 1:30, pre-column removed). The same analysis was carried out with the water phase that had passed

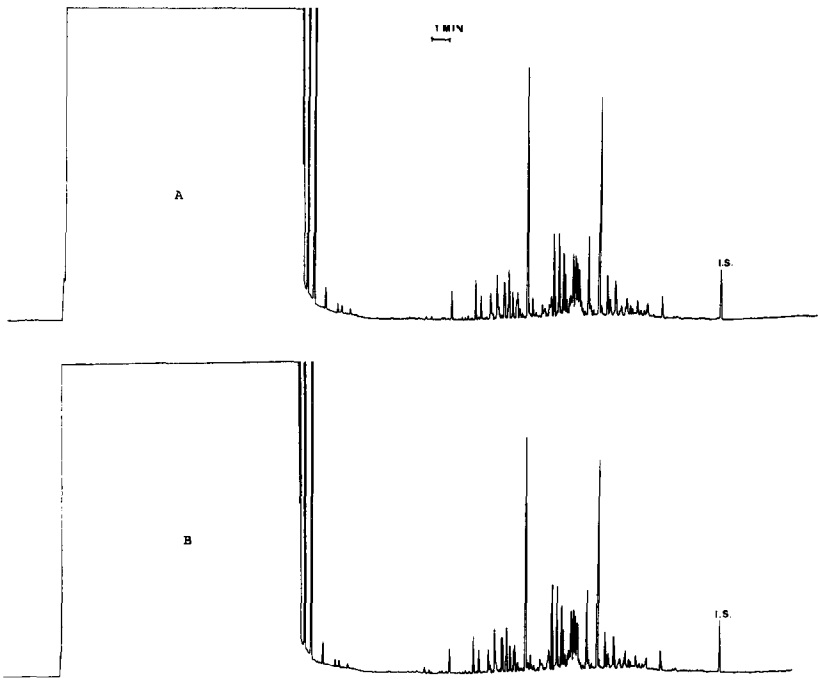

Fig. 5. Pentane extract of a water sample containing a total of 200 ppb of a naphtha fraction. A, Sample extracted with the continuous flow system. A pressurized bottle was used as a sample-delivery system. B, Batch-extracted sample. Attenuation: $\times 32$. For the chromatographic conditions, see Experimental. I.S. = Internal standard (30 ppb of dodecane added to the pentane prior to extraction).

through the separator. This showed that the last sample contained about five times more pentane than the batch-saturated sample.

Phase separation

As reported previously[19], the principal feature of the separator design is the incorporation of a rigid support for the semi-permeable membrane, which allows the cavity to be pressurized to a few bar without damaging the membrane. Thus, almost complete phase separation is achieved. The present construction was made of stainless steel instead of plastic, in order to minimize possible adsorption. For demanding applications, the use of other materials may be required. The direct connection of the fused-silica inlet and outlet tubing to the separator cavities avoids possible dead-volume from joints, and should be particularly attractive for analytical flow injection systems, where discontinuities in the flow path, such as sharp edges in a connector, are specially undesirable.

The internal hold-up volume of the separator is only a few microlitres, which is acceptable when compared with the volumes of the connecting tubes and the volumetric flow of sample and extractant. However, the design of the flow path in the cylindrical cavity of the separator is not optimal. A direct conduit between the entrance and exit tubes, such as a rectangular channel, would be preferable, especially when reduced solvent-to-sample volume ratios are employed. An improved design is presently under construction.

Initially, the outlet capillary of the aqueous phase was connected to a piece of stainless-steel tubing, which was squeezed in order to provide some back-pressure, and thus a satisfactory phase separation. This moment is critical. If the back-pressure becomes too high, part of the water phase will be forced through the membrane. Although the GC capillary column is not damaged by water injections, the following deleterious effects are obtained: an uncontrolled amount of water in the sample results in poorer reproducibility of the chromatography; water droplets in the pentane cause a fluctuation of the back-pressure in the sample loop, which upsets the pressure balance between the two separator cavities, and can eventually lead to a rupture of the membrane. The effect is particularly critical when gas bubbles are present in the sample loop. It is therefore recommended to employ a variable restrictor (needle valve) in the outlet of the aqueous phase, preferably together with a pressure monitor.

GC injection system

In order to be able to detect trace components in the ppt range, it is necessary to inject a large sample volume (100 μl or more). On-column injection is the only realistic method for this purpose. The use of a rotary valve with a sample loop is ideal for applications where a continuous flow of sample is available, and the technique is very simple to automate. In the present study, a direct sampling method as reported by Steele and Vassilaros[21] was used with slight modifications. Instead of a six-port valve with an internal sample loop, a six-port valve with an external loop was employed. The heated injector body interface was omitted, while keeping the distance between the oven and the exit port of the valve as short as possible.

However, during the course of this study it became evident that this injection method is still imperfect. Remaining traces of compound and particularly solvent in the unheated valve seem to cause memory effects, which resulted in an elevated and

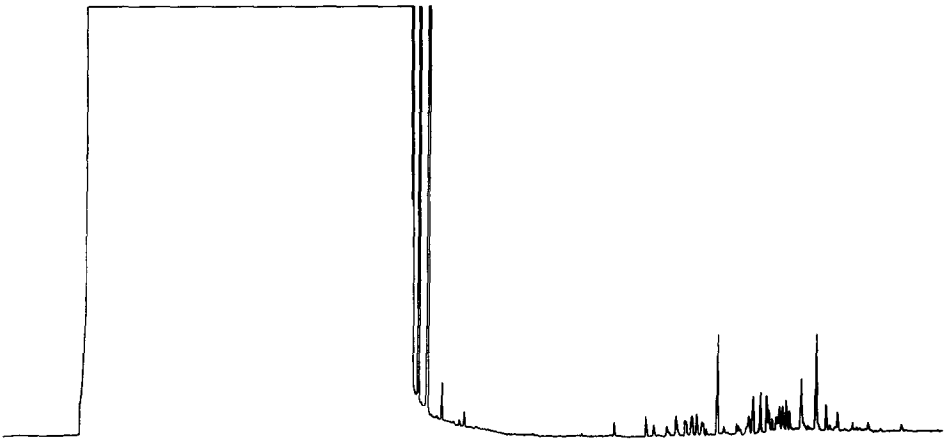

Fig. 6. Pentane extract of an identical water sample to that in Fig. 5. The sample was dispensed by a gas-tight syringe with a PTFE plunger and a PTFE-tipped Luer lock connection. (GC conditions as in Fig. 5).

unstable baseline. When an electron capture detector is employed the solvent traces do not interfere, since these are not detected, but the effect is pronounced when using a flame ionization detector at high sensitivity settings. Thus, it is desirable to back-flush the unheated parts with pure solvent, and/or with carrier gas as described by Grob *et al.*[22]. Preliminary modifications have given improved results.

The injection of very large amounts of extract gives rise to an excessive elution time for the solvent, and the use of the long pre-column prohibits fast temperature programming. Thus, there is a need for development of pre-column techniques other than the conventional retention gap[23].

Adsorption losses

Initially, the sample was delivered by an HPLC pump. This appeared to be an

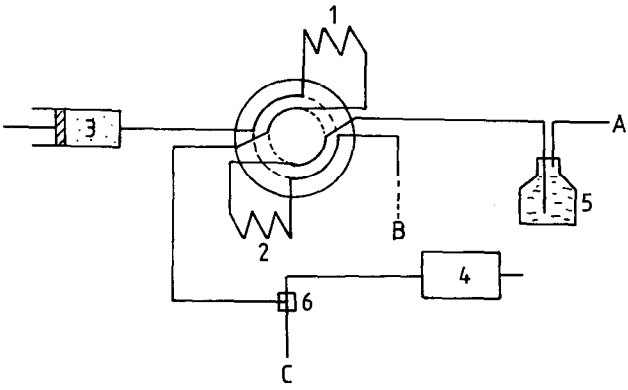

Fig. 7. Loop injection of a water sample in a continuous stream of pentane prior to segmentation. 1,2 = Sample loops (stainless steel, 1 ml); 3 = pentane dispenser (home-made syringe pump); 4 = HPLC pump delivering pentane; 5 = pressurized bottle with water sample; 6 = segmentor. A = nitrogen (*ca.* 2 bar); B = drain; C = extraction capillary.

attractive way to obtain a continuous and uninterrupted sample flow. It showed, however, that the hydrocarbon traces were tenaciously retained by the inner surface of the pump and the aspiration (PTFE) tube. Thus, the concept had to be abandoned. Additional experiments revealed that a considerable adsorption of the trace components occurs even when relatively small PTFE parts, such as valves and small pieces of connection tubing are present. This implies that gas-tight syringes with PTFE plungers cannot be used for sample dispensing. The effect of the use of such a syringe is shown in Fig. 6.

It was also noticed that adsorption occurred on the surface of the stainless-steel tubing, which was used as a sample loop for discrete injections. This could be due to the formation of a monomolecular film of (high molecular weight?) hydrophobic material during the continuous flushing with sample. The effect remains to be investigated under more controlled conditions.

The injection of a discrete sample into a flow of pentane was also evaluated. The sampling set-up is shown in Fig. 7. The water-sampling valve and the GC injection valve were actuated with a time difference, corresponding to the exact time necessary for the whole extract to enter the sample loop of the GC valve. The resulting chromatogram showed that only minor amounts of the expected extract were present. When the experiment was repeated with an increased switching delay between the valves, the major part of the previously expected chromatogram appeared. However, based on the flow-rates of the fluids and the total hold-up volume of the system, the extract should have passed the loop. This anomaly was found to have the following explanation (verified by additional off-line experiments). The sample loop and the flow path of the valve are initially wetted by pentane, before a water sample is injected. However, the water does not entirely displace all the pentane. Small amounts of solvent remain adhered and accomplish an efficient extraction of the water. The extract is retained on the surface until it is displaced by the interrupted pentane flow.

Adsorption in the short fused-silica connection tube to the segmentor was shown to be negligible. When the sample was dispensed from a pressurized bottle, directly coupled to the fused-silica tube, reproducible chromatograms were rapidly obtained. Changing to a bottle with clean water almost immediately gave a blank level similar to that of the clean solvent.

Determination of trace components

In order to estimate the practical detection limits for the present automated on-line procedure, a waste-water sample from a municipal sewage plant in Stockholm was extracted and analysed under the described conditions. Dodecane was added to the pentane as an internal standard. Fig. 8 shows a chromatogram of the extract, from which it is seen that individual components can be quantified roughly down to 50 ppt. With a reduced solvent/water ratio and an improved pre-column technique, it ought to be possible to increase the sensitivity by about two orders of magnitude, which would make the method suitable for monitoring organic trace components in drinking water. When used with an electron capture detector, *e.g.*, for monitoring halocarbons or pesticides, the detection limit can be further improved by some orders of magnitude, provided that the solvent impurities and adsorption can be kept to an acceptable level.

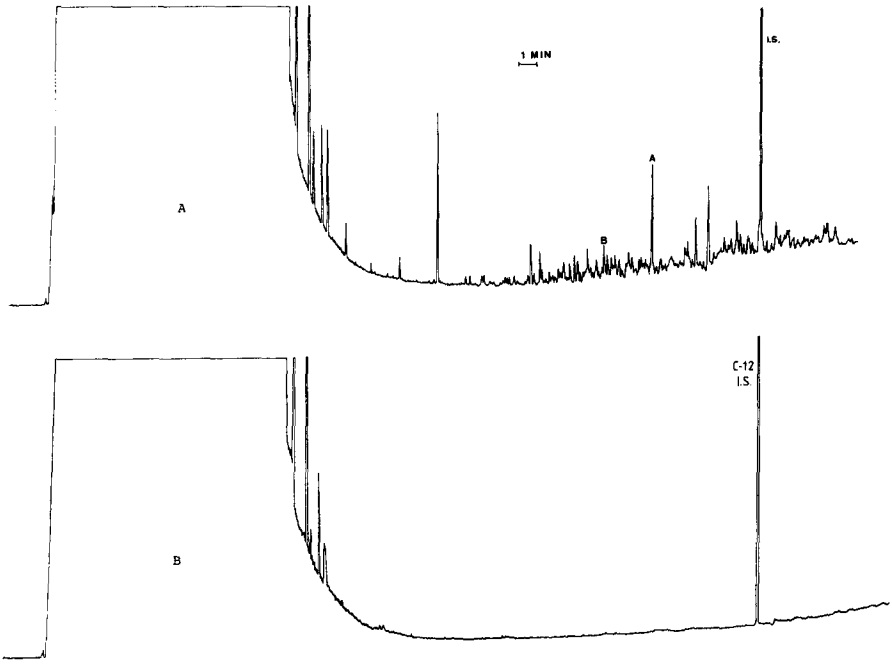

Fig. 8. A, Chromatogram of a concentrate from Stockholm municipal sewage waste-water, obtained by continuous flow extraction and capillary GC. B, Chromatogram of the solvent blank (*n*-pentane with 30 ppb of dodecane as internal standard). Conditions: attenuation: ×4; column temperature, 38°C during the elution of the solvent, subsequent temperature program rate: 4°C/min. Peaks A and B represent a level of *ca.* 200 and 50 ppt respectively, as calculated from their peak areas (100% extraction efficiency has been assumed).

There should be many other applications for the combination of on-line flow extraction and capillary GC, and it is anticipated that the technique may become a versatile tool in clinical and pharmaceutical laboratories, as well as in other fields where development is directed towards automation.

CONCLUSIONS

It has been demonstrated that an automatic monitoring of volatile organic trace components in water down to the ppt level can be realized when a combination of continuous flow extraction and capillary gas chromatography is employed. A rapid equilibrium is established and a higher reproducibility than with batch extraction is obtained.

Prior to solvent extraction, particular attention should be paid to adsorption effects, which can distort both the qualitative and the quantitative results. The water should not be transported through a long (capillary) tube, particularly if plastic (PTFE) parts are included. The segmentor should preferably be placed directly at the water source, where a pressurizing device with a large flow/surface area can be employed, from which the sample is directed into a short fused-silica inlet capillary.

The flow extraction process has not yet been subjected to a more detailed

study. This will be necessary when designing an optimum system for reduced solvent/water ratios. Also, the ability to handle turbid samples should be investigated. Such studies are presently in progress.

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