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# DETERMINATION OF BENZENES AND NAPHTHALENES IN WATER BY PURGE AND TRAP ISOLATION AND CAPILLARY COLUMN CHROMATOGRAPHY

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## SUMMARY

A method for determination of volatile, aromatic hydrocarbons in the range from benzene to $C_2$-naphthalenes has been adapted for monitoring the concentration of these components in water. The hydrocarbons are purged from the water by helium, trapped on an adsorbent, Tenax-GC, desorbed from this by rapid heating, transferred directly to a fused-silica gas chromatography column, which is cooled to $-80°C$ for initial cryotrapping, and finally chromatographed by programmed raising of the temperature of the column. The whole process is automated and takes 40 min, plus 10 min for temperature equilibration for the next experiment. With 5 ml water samples, concentrations of 0.1 $\mu$g/l (ppb) of the individual components were determined. The method was applied to monitoring of a biotest system, and compared to the traditional liquid extraction method.

## INTRODUCTION

Conventional solvent extraction techniques are not well suited for determination of volatile petroleum hydrocarbons, in the range up to approximately $C_{12}$,in water, due to the ease of evaporative loss of the analytes[1]. This will occur during all stages in the procedure, and in particular when the extract is concentrated before the final analysis. The alternative to solvent extraction is to isolate the volatiles from the vapour phase above the water. This can be done in two principally different ways: either by head space sampling, static[2] or dynamic[3], or by extracting the components from the water with an inert gas and trapping them on an adsorbent. This can either be done with a given amount of gas which is pumped continuously through a closed loop with the trap included[4], or by an open-ended system with delivery of gas from a reservoir[5]. This latter method is usually termed purge and trap (P&T), and several devices are commercially available, *e.g.*, from Hewlett-Packard, Chrompack, Chemical Data Systems.

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The possibility of complete automation and short analysis times makes the P&T method attractive. The method was originally developed for use with packed gas chromatography (GC) columns[6]. It is, however, desirable to utilize the high resolution power of the present-day capillary columns in connection with P&T sampling. Interfacing of a P&T sampler with a capillary column has been attempted in several cases[7–9]. In all cases the flow of inert gas through the P&T sampler during the desorption of analytes from the trap was higher than the flow through the capillary column. It was therefore necessary to split the gas flow, allowing only a minor part, *e.g.*, one tenth[9], to enter the column. This results in loss in sensitivity.

Pankow and Rosen[10] have installed a direct interface, without splitting, between a P&T sampler and a fused-silica capillary column. The column terminated at the ion source in the high vacuum of a mass spectrometer. With this low pressure at the end of the column, and a fairly high head pressure of 80 p.s.i., the flow through the trap and chromatography column in the desorption step was approximately 20 ml/min. The head pressure was reduced to 10 p.s.i. during the subsequent chromatography.

In another investigation, Pankow and Kristensen[11] have studied the effect of the flow-rate through a Tenax[12] trap on the desorbability of polycyclic aromatic hydrocarbons. They found that naphthalene was completely desorbed by a 2.8 ml/min flow of helium for 20 min at a trap temperature of 250°C. Lower flow-rates or shorter times were not tested.

When the duration of the desorption is several minutes a trapping of the analytes at the beginning of the column is necessary to obtain proper chromatographic results with sharp peaks. This was accomplished by Trussell *et al.*[7] and Dreisch and Munson[8] by immersing the first loop of the column in liquid nitrogen. According to Pankow and Rosen[10] it is better to cool the whole column, *i.e.*, by letting liquid nitrogen into the GC oven, thereby denoting the method as P&T/WCC, *i.e.*, Purge and Trap with Whole Column Cryotrapping. They used a temperature of −80°C, Pankow and Kristensen[11] used −30°C and Adlard and Davenport[9] cooled the GC oven to −50°C.

A crucial point when the P&T sampler is coupled to a capillary column is obviously the flow-rate during the desorption step relative to the flow-rate during the chromatography step. The first purpose of the present investigation was to see if the flow-rate applied for capillary columns, *i.e.*, of the order of 1 ml/min, could be used during thermal desorption of benzene and naphthalene and their alkylated homologues from Tenax-GC. This was desirable because a commercial P&T sampler, Hewlett-Packard 7675 A, should be directly interfaced, without splitting, to a narrow-bore fused-silica column, and since extra manipulations with head pressures would make automation more difficult.

A further purpose of this investigation was to study the potential of the P&T method for detection of very low levels, *i.e.*, 1 μg/l (ppb) and below, of petroleum hydrocarbons in water. Pankow and Rosen[10] have worked with concentrations of the individual compounds of 10 μg/l. When samples of polluted water are collected close to the pollution source, in time and space, concentrations higher than 10 μg/l are usually detected. However, in studies of the dilution and evaporation of the volatile aromatics a detection limit below 1 μg/l is desirable.

Finally, the goal was to monitor the concentration of the water-soluble light aromatics in a system used for biotesting of the effects of these compounds on eggs and larvae of cod, *Gadus morhua*[13–15]. In this system the supply of the polluted water was

limited, and a P&T method, which, in addition to other advantages, also demands small sample volumes, *i.e.*, 5–10 ml, would be ideal for monitoring of the concentrations. The results from this method should be compared with results from a determination based on liquid extraction.

## EXPERIMENTAL

### *Materials*

Stock solutions in methanol were prepared of the following aromatic hydrocarbons: benzene, toluene, *m*-, *p*- and *o*-xylene, ethylbenzene, *n*-propylbenzene, naphthalene, 1-methylnaphthalene and 1,4-dimethylnaphthalene. Mixtures of all standards were prepared from aliquots of the individual solutions, and test solutions containing 0.1, 1.0 and 10.0 μg/l, respectively, of each component, were prepared by diluting aliquots of the mixtures to 1000 ml in clean sea-water, pumped from a depth of 120 m in Byfjorden, Bergen, Norway.

Immediately after preparation, seven samples were transferred from each solution to purge vessels. Culture tubes, with a total volume of 16 ml, were used as purge vessels. They were completely filled, tightly sealed with screw caps and stored in a refrigerator until analysis. Seven samples of water from a biotest system[15] were collected in similar tubes and treated in the same manner.

Immediately before analysis, approximately 2/3 of the water in the tubes were decanted off, leaving about 5 ml, which were purged as described below. The exact amount of water was determined by weighing after the purging was completed.

### *Instrumentation*

An Hewlett-Packard 7675 A P&T sampler was used. It was supplied with a 100 mm × 4.8 mm I.D. stainless-steel trap containing 1.3 ml Tenax-GC (60–80 mesh). The transfer line supplied with the sampler was replaced by a 30-cm glass-lined metal tubing, GLT, from Scientific Glass Engineering, of 1/16 in. O.D. and 0.4 mm I.D., which was connected directly with a nut and ferrule to the six-port valve of the sampler. With the sampler placed on top of an Hewlett-Packard 5790 gas chromatograph, the tubing ended inside the GC oven. The tubing was passed through a 1/16-in. male fitting, with 1 mm protruding, and silver-soldered to it. An Hewlett-Packard 25 m × 0.2 mm I.D. fused-silica column was led 2 mm into the tubing and connected by way of a graphite ferrule, the flat end being towards the end of the transfer line, and an extended nut. The liner was maintained at 150°C to avoid condensation of components.

The stationary phase of the column was 5% phenyl 95% methyl silicone of thickness 0.33 μm. Helium was used as the carrier gas at a flow-rate of 1 ml/min, led through the P&T sampler.

The purge vessel, containing 5 ml water to be analysed, was securely fastened to the purge unit and purged with helium at a flow-rate of 40 ml/min. Various purge times were tested. The trap was kept at ambient temperature. The GC oven was cooled to −80°C by liquid nitrogen.

For the desorption step, the trap was ballistically heated to 250°C within approximately 1 min, a flow of 1 ml/min helium was led through the trap and further directly through the transfer line to the capillary column in the cooled oven. Various

desorption times were tested. After desorption, the trap was vented for 5 min at 300°C, and thereafter cooled to ambient temperature by compressed air.

The chromatographic step commenced immediately after the desorption step. The oven was heated from −80 to 0°C in 30 s, kept at 0°C for 5 min, then raised at 10°C/min. The eluates from the column were detected by a flame ionization detector at 350°C and with nitrogen, 30 ml/min, as a make-up gas. The peak areas were determined by an Hewlett-Packard 3390 recording integrator.

## RESULTS AND DISCUSSION

To find the optimum volume of purge gas, seven replicates, each 5 ml, of sea-water containing 1 μg/l of, respectively, benzene, *o*-xylene, naphtalene and 1,4-dimethylnaphthalene, were purged for 5, 12.5 and 15 min, with a purge flow of 40 ml/min. The resulting areas of the peaks of the four components are given in Fig. 1.

For benzene the recovery is smaller at 500 ml than at 200 ml, showing that the breakthrough volume for benzene lies between these numbers, while the optimum volume for the other three components apparently is 500 ml. This purge volume, *i.e.*, a purge time of 12.5 min at a flow-rate of 40 ml/min, was chosen for the rest of the investigation, even when the recovery of benzene is only 85% of that obtained with 200 ml.

With a desorption temperature of 250°C, which is 50°C below the maximum recommended operating temperature of Tenax-GC, and a flow-rate of 1 ml/min of helium back-flushing the trap, a desorption time of 5 min was tested first. After

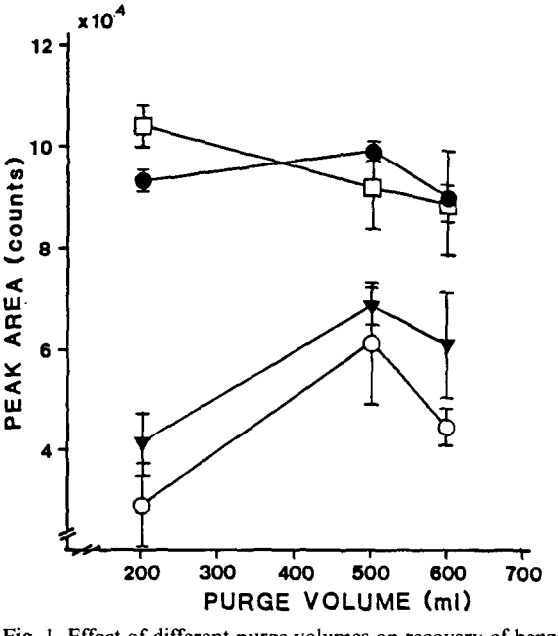


Fig. 1. Effect of different purge volumes on recovery of benzene (□), *o*-xylene (●), naphthalene (▼) and 1,4-dimethylnaphthalene (○) from 5 ml water containing 1 μg/l of each component. The data are given as mean ± standard deviation ($n$ = 5–8).

chromatography of the desorbed material, the trap was re-desorbed for another 5 min. Chromatography showed that the desorption was not complete after the first 5 min. With an initial desorption time of 10 min the desorption was found to be complete for all components from benzene to 1,4-dimethylnaphthalene. In a systematic investigation of the desorbability of different components from Tenax-GC, Pankow and Kristensen[11] obtained complete recovery of naphthalene at a flow-rate of 2.8 ml/min for 20 min at 250°C. Since their investigation covered components with lower desorbability than naphthalene, *i.e.*, larger aromatic hydrocarbons and pesticides, they did not test lower desorption volumes. On the contrary, they needed much higher volumes and higher temperature for the least desorbable components.

Typical chromatograms from analyses of samples of the three different concentrations of test solutions and of a sample of water from the biotest system are

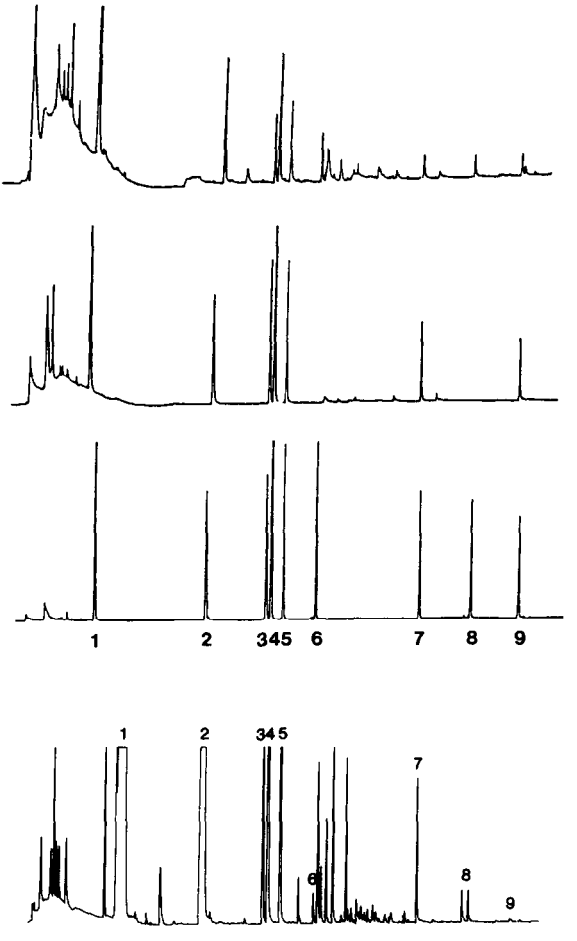


Fig. 2. Chromatograms of standard solutions of aromatic hydrocarbons in water at the following concentrations of each component; from top, 0.1, 1.0 and 10.0 μg/l; and, at the bottom, of water from a biotest system. Peaks: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = *m*- plus *p*-xylene; 5 = *o*-xylene; 6 = *n*-propylbenzene; 7 = naphthalene; 8 = 1-methylnaphthalene; 9 = 1,4-dimethylnaphthalene.

shown in Fig. 2. The elevated baseline at the beginning of the chromatograms, particularly evident at the lowest concentration of the standards, is due to changes in the flow-rate of the carrier gas during the rapid temperature rise from −80 to 0°C. It was necessary to install extra charcoal filters on the helium supply line to obtain stable baselines of the chromatograms.

Even at the lowest concentration, all components give well defined peaks. At this level, peaks representing components naturally present in the water are seen between the aromatics. The signal-to-noise ratio is high, implying that the attenuation might have been decreased. In addition, the volume of water might be increased well above the 5 ml used here. This means that the method has potential for determination of concentrations even lower than 0.1 μg/l of the individual components.

The chromatographic retention time of benzene varies somewhat between the different experiments. A small variation is also seen for toluene, but from ethylbenzene and upwards the retention times are reproducible. The variation for the two most volatile components must be due to the lack of reproducibility of the temperature in the GC oven during the first part of the chromatography from −80°C. This does not, however, pose any problems in the identification of the various peaks, in that the pattern and relative sizes of the peaks are used as guidelines.

The methylnaphthalenes, with the 2-methyl derivative eluted first, are present in equal concentrations in the water. The water had been accommodated by gentle stirring below an oil layer without the formation of a dispersion. The flow-through in the 50-l accommodation tank was 40–60 ml water and 3–4 ml Statfjord crude oil per min[15].

The mean peak areas of the replicate determinations of the ten standards at three different concentrations are given in Table I. The precision in the case of benzene and alkylated benzenes at 1 and 10 μg/l is very acceptable, with a relative standard deviation of between 1 and 6%. Determination of concentrations lower than 1 μg/l obviously has lower precision, especially for the most volatile components.

TABLE I

PEAK AREAS FROM P&T DETERMINATION OF STANDARD SOLUTIONS OF 0.1, 1.0 AND 10.0 μg/l OF EACH OF TEN HYDROCARBONS IN SEA-WATER

The numbers are means and relative standard deviations of seven replicate determinations.

| *Compound* | *0.1 μg/l* | | *1.0 μg/l* | | *10.0 μg/l* | |
|---|---|---|---|---|---|---|
| | *Area* | *% S.D.* | *Area* | *% S.D.* | *Area* | *% S.D.* |
| Benzene | 144 | 45 | 1007 | 5 | 9057 | 3 |
| Toluene | 247 | 28 | 1066 | 3 | 10058 | 2 |
| Ethylbenzene | 124 | 8 | 998 | 1 | 9911 | 3 |
| *m*- and *p*-xylene | 264 | 13 | 1894 | 1 | 18698 | 3 |
| *o*-Xylene | 153 | 5 | 964 | 2 | 9279 | 4 |
| *n*-Propylbenzene | 81 | 5 | [a] | | 8938 | 6 |
| Naphthalene | 43 | 12 | 518 | 11 | 5670 | 10 |
| 1-Methylnaphthalene | 44 | 4 | [a] | | 5751 | 11 |
| 1,4-Dimethylnaphthalene | 36 | 23 | 371 | 25 | 5156 | 17 |

[a] Not present in the 1.0 μg/l solution.

The lowest concentration of benzene and the alkylated benzenes gives relatively larger peak areas than the two higher concentrations. This indicates contamination of the samples. However, the source of possible contaminations has not been found. Procedural blanks of the sea-water did not show any benzene or alkylated benzenes. Both the lower precision and the unexplained higher peak areas imply that determination of benzenes becomes increasingly ambiguous as the concentrations decrease below 1 μg/l.

Naphthalene and alkyl-substituted naphthalenes behave differently to benzene and alkylated benzenes in two ways: the precision of the determination and the peak areas are both lower. The flame ionization detector on the gas chromatograph is a gram-carbon detector, and theoretically the response of naphthalene should be 1.016 times that of benzene. It is apparent that the recovery of the naphthalenes by this method is much lower than that of the benzenes. The low recovery also gives a lower precision of the method. As mentioned above, no naphthalenes remain in the water sample after 500-ml purging, and no loss occurs in the desorption step. Apart from this, no further tests have been carried out to detect where the naphthalenes are lost. However, quantitation of the naphthalenes is still possible, although with lower precision than for the benzenes, by taking the actual response factors into consideration.

A chromatogram from the P&T determination of a 5-ml sample of water from the exposure tank of a system for biotesting the effects of "water-soluble" petroleum hydrocarbons on marine organisms[15] is shown in Fig. 2. The peaks corresponding to the 9 (10) standards were easily identified. The unidentified peaks between *o*-xylene and naphthalene very likely represent $C_3$- and $C_4$-alkylated benzenes, as is the case in a similar chromatogram of groundwater contaminated with gasoline presented by Pankow and Rosen[10].

The identified components were quantitated in six replicate samples of the biotest water, collected immediately after each other, by the use of response factors obtained from Table I. The results are shown in Table II. The precision of the analyses is good.

A sample of 3 l of the same water, collected immediately after the samples for the P&T analysis, was analysed by Westrheim and Palmork[16], employing liquid extraction with dichloromethane followed by GC. The results, given in Table II, correspond well with the results of the P&T determination. The somewhat lower values for the liquid extraction indicate that an evaporation might have taken place. However, no replicates were obtained here, so that the precision of that method is not known.

The present P&T method has been used successfully in the testing of a new biotest system for studying the long term effect of oil on fish eggs and larvae[17].

In conclusion, the attractive features of the the P&T method for determination of petroleum hydrocarbons in water are as follows: the method allows determination of benzenes and naphthalenes in concentrations down to below 0.1 μg/l. At concentrations of 1 μg/l and above, the precision is high, especially for benzenes. Small sample volumes are needed. This is important in cases where the availability of water is low, *i.e.*, in biotest systems supplying small volumes of water, or in cases when the samples have to be transported from the sampling site to the laboratory. The method is automatic in that the only manipulation of the samples during the determination is limited to attaching the sample tube to the sampler and pressing the start button.

TABLE II

CONCENTRATIONS, IN μg/l OR ppb, OF VARIOUS AROMATIC HYDROCARBONS IN SEA-WATER IN THE EXPOSURE AQUARIUM OF A BIOTEST SYSTEM WITH STATFJORD CRUDE OIL AS THE SOURCE OF THE HYDROCARBONS

The numbers are means and standard deviations of six P&T determinations. The result of one determination based on liquid extraction[a] is also given.

| *Compound* | *P&T* | *Liquid extraction* |
|---|---|---|
| Benzene | 81.0 ± 4.9 | 78 |
| Toluene | 65.9 ± 1.3 | 56 |
| Ethylbenzene | 2.2 ± 0.1 | [b] |
| *m*- and *p*-xylene | 12.6 ± 0.3 | 16 |
| *o*-Xylene | 8.0 ± 0.2 | |
| *n*-Propylbenzene | 1.1 ± 0.1 | |
| Naphthalene | 1.4 ± 0.2 | |
| Methylnaphthalenes | 0.8 ± 0.2 | |

[a] See ref. 16.
[b] Less than 2 μg/l.

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