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SIMULTANEOUS DETERMINATION OF C₁- AND C₂-HALOCARBONS AND MONOCYCLIC AROMATIC HYDROCARBONS IN MARINE WATER SAMPLES AT NG/L CONCENTRATION LEVELS

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A Purge & Trap technique for the analysis of volatile organic compounds (VOCs) combined with GC-MS was applied to measure simultaneously concentrations of 13 C₁- and C₂-chlorinated hydrocarbons (CHCs) and monocyclic aromatic hydrocarbons (MAHs) down to the 1 ng/l level. It proved to be impossible to reach this level working with an automated online apparatus because of two reasons. First, the low reproducibility was caused by the water vapour present in the gas stream after purging samples. The second reason was the presence of unpredictable contamination. An off-line purge system, however, combined with thermal desorption by means of the on-line apparatus gave reproducible measurements (standard deviations from 2.6 to 15.7%). Contamination was lower than 0.76 ng/l for all VOCs except for benzene, toluene and chloroform. The signal/noise ratio of three corresponded to concentrations below 0.63 ng/l for all VOCs. In this way limits of detection (LODs) of 0.48 (tetrachloroethylene) to 1.25 ng/l (o-xylene) were obtained, except for chloroform, benzene and toluene. Their LODs were 4.93, 4.79 and 2.68 ng/l because of the contamination. Precision and accuracy were determined. The long term reliability of the method was evaluated using analytical quality control charts. In addition, sample treatment and storage were checked by adding deuterated surrogates. Results of analysis of water samples taken in the North Sea region and the Scheldt estuary illustrate the applicability of the method. Target compounds were detected in concentrations from 0.5 to 100 ng/l.

KEY WORDS: Volatile organic compounds (VOCs), C₁- and C₂-organochlorines, monocyclic aromatic hydrocarbons, purge and trap, marine pollution.

INTRODUCTION

C₁- and C₂-chlorinated hydrocarbons and monocyclic aromatic hydrocarbons are widely spread into the environment. Because of their input from anthropogenic sources, their relative good stability against chemical and microbiological degradation¹ and their toxicity, the CHCs tetrachloromethane, chloroform, trichloroethylene, tetrachloroethylene, 1,2-dichloroethane and trichloroethane were classified at the Third International Conference of Protection of the North Sea (1990) as priority toxic pollutants for the water compartment, while the MAHs benzene, toluene, ethylbenzene and the xylenes were classified in a list of priority pollutants. This list will be taken as basis for further development of national lists of priority pollutants³. In order to obtain

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environmental data of concentration levels and to study the environmental behaviour of this VOCs, appropriate measurement techniques are needed.

For C₁- and C₂-halogenated hydrocarbons the liquid-liquid extraction technique is a well developed and accepted analytical method. The procedure consists of a liquid-liquid extraction, gas chromatographic separation and detection by an electron capture detector (ECD). In the seventies the development of the ECD made trace analysis of CHCs possible^{4,5}. The method was further developed⁶⁻¹¹ and improved by a mechanized system for extractive sample work-up coupled on-line to an on-column injector¹². This analytical technique is sensitive enough to detect CHCs at marine environmental concentration levels. Fogelqvist *et al.*⁷ measured trace concentrations in the Atlantic water current between Greenland and Iceland for tetrachloroethylene of 0.05–0.65, for tetrachloromethane of 0.15–0.65 and for trichloroethane of 0.4–1.7 ng/l. Together with values of other authors they obtained mean concentration levels in the Northern Hemisphere of 0.68 ± 0.23 (n = 32), 0.83 ± 0.17 (n = 20) and 2.5 ± 1.8 ng/l (n = 15) respectively. In a marine coastal site near a petrochemical centre (Stenungsund, Sweden) Abrahamsson *et al.*¹³ detected (all concentrations in ng/l) 5.4 ± 2.0 and 14.8 ± 5.1 for chloroform, 2.4 ± 1.0 and 2.9 ± 0.2 for trichloroethane and 2.0 ± 0.8 and 2.1 ± 0.3 for tetrachloroethene (values on two different sampling days).

The strength of this liquid-liquid extraction technique is all dependent on the very good sensitivity of the ECD, compared to other commonly used detectors as FID (flame ionization detector) or MSD (mass selective detector). The extraction method is not suitable for the analyses of both CHCs and MAHs in one run at marine environmental concentration levels because of the selectivity of the detector.

The most widely applied technique for analysing VOCs in water samples is the purge and trap (P&T) technique. A gas stream is stripping the VOCs out of the water sample¹⁴⁻²¹. The VOCs containing gas stream is subsequently led over a VOCs trap, usually a sorbent trap (in some studies a cryogenic trap is used^{18,21}). Between the purge vessel and the VOCs trap a wet trap can be constructed to remove water vapour^{18,21}. Water vapour can influence the sorption efficiency or can disturb the detection system. Finally VOCs have to be desorbed of the trap and injected on a GC-detection system. Former analyses^{14,15} used solvent desorption of the sorbent trap (activated charcoal). Since this way of desorption limits the detection level and makes determination of compounds eluting in or near the solvent peak impossible, thermal desorption is nowadays commonly used. Out of the several commercially available sorbents, Tenax TA, Tenax GR, silicagel and activated charcoal are the most currently used. More recently trapping materials with high retention volumes and low water affinity, like graphitized carbons, activated coal and carbon molecular sieves, are used in series. The P&T method is well accepted and because of this, commercial P&T analytical instruments are available (from Tekmar, CDS, Chrompack, Dynatherm) to automate analyses.

The on-line P&T instrumentation is provided with a microprocessor controlled switching valve in order to integrate on-line the sorbent trap in the purge line as well as in the desorption line to the GC-detection system. The detection limit of the P&T method, coupled with a GC-FID or GC-MS, is of the $\mu\text{g/l}$ level. This is rather high as compared to the liquid-liquid extraction technique combined with ECD. (P&T-GC-ECD combination can be used²¹ but in this case again the range of detectable VOCs is limited.) The lowest reported limits of detection (LODs) with P&T-GC-FID are from 19 ng/l (benzene) to 43 ng/l (toluene) for benzene, toluene, ethyl benzene and the xylenes²⁰, while Bianchi *et al.*¹⁷ reported their developed P&T system to be able to detect at a 5 ng/l level, although no exact LOD values are given.

In this work an automatic on-line P&T system was evaluated for the analysis of CHCs and MAHs at the environmental marine concentration levels (sub-ppb). Further on, an off-line purge step was combined with desorption in the on-line P&T system. Finally, the developed method was applied to the analysis of VOCs in the marine environment.

EXPERIMENTAL

Materials

The CHCs chloroform, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene (Janssen) and tetrachloromethane (Merck), and the MAHs benzene, toluene (Merck), ethylbenzene and m-, p- and o-xylene (Aldrich) were used as VOCs in the experiments. They were applied without further purification.

Deuterated compounds, chloroform-d and toluene-d8 (> 99.95 atom % D), used as surrogates were obtained from Fluka. Methanol was obtained from Merck (for Chromatography, 99.8%). As internal calibration standard (IS) α,α,α -trifluorotoluene (Aldrich) was used. Tenax TA and Vocab 4000 traps (8.5 cm Carbopack C, 10 cm Carbopack B, 6 cm Carboxen 1000 and 1 cm Carboxen 1001) were used as adsorption traps (1/8" OD).

Apparatus

The microprocessor controlled P&T system, CDS Peakmaster (CDS Analytical Instruments, Oxford, USA) was coupled with a gas chromatograph-mass spectrometer (GC-MS) Carlo Erba QMD 1000 (Carlo Erba Instruments, Milan, Italy) by a heated transferline with a cryogenic focuser at the GC injection port. The P&T system was provided with a 60 ml vessel, a wet trap and a sorbent trap, and a cartridge desorber. All these parts and also the carrier gas and the transferline were connected to an 8-port switching valve. Separation of the VOCs was done on a RTX-502.2 capillary column (length 60 m, ID 0.32 mm, film thickness 1.8 μm , gas helium, inlet pressure 12 psi) (Restek), detection was done using the mass spectrometer in the single ion monitoring (SIM) mode. M- and p-xylene were not separated and were determined together.

The off-line P&T construction consisted of a vessel (internal diameter 3 cm, height 1.2 cm) with a glass frit and an injection septum, connected to a stainless steel 1/4" tube (length 1.5 or 3 m) submerged in a temperature controlled ethylene glycol bath (-10 to -15°C). The end of this wet trap was connected with the sorbent trap. Helium purge gas was led through a liquid nitrogen trap before entering the purge vessel.

Sampling and storage

Samples were taken on board of the Belgian Oceanographic vessel the 'Belgica'. The sampling sites in the Scheldt estuary and on the Belgian Continental Shelf in the North Sea are given in Figure 1.

Samples were taken with a Niskin-Sampling Bottle System (101, General Oceanics Inc., Florida) at a sampling depth of 5 m. The samples were transferred to 0.751 dark flasks (real volume 780 ml), which were completely filled to avoid headspace. Microbial

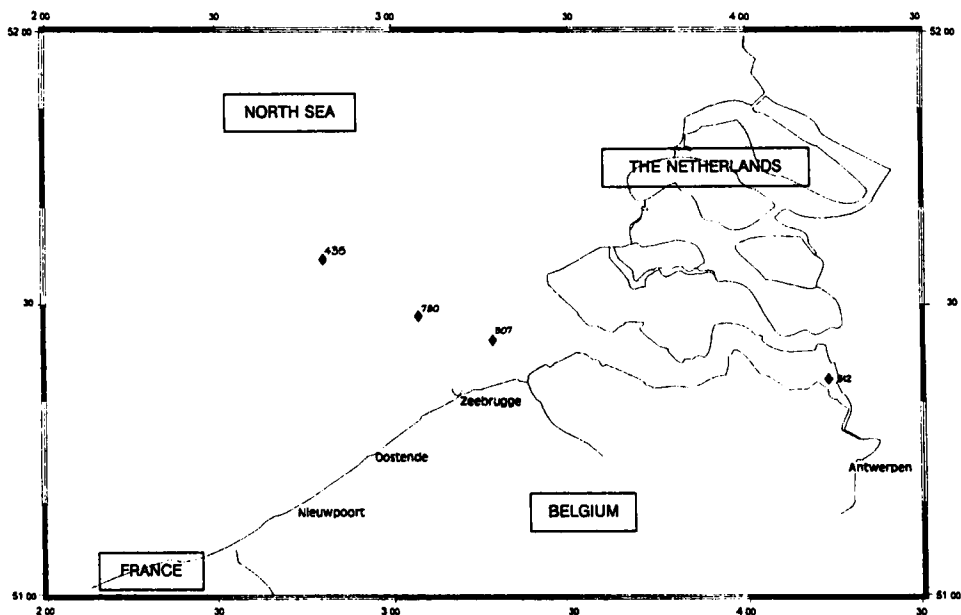


Figure 1 Map of sampling stations on the Belgian Continental Shelf in the North Sea and in the Scheldt estuary.

degradation was prevented by adding 1/1 HCl to obtain a pH level lower than two²². Five μ l of a methanol solution containing 50 μ l chloroform-d and toluene-d8 was injected. Flasks were sealed, kept on board at 4.0°C and stored in the laboratory at the same temperature.

Analytical procedure

Preparation of blanks and reference materials Blanks were prepared by purging sea water for at least 30 minutes at 50 ml He/min. Laboratory reference materials (LRMs) and calibration materials were made by adding 5 μ l methanol stock solution containing the VOCs at the desired concentration.

Preparation and P&T of the sample 60 ml water sample was brought into a 100 ml syringe. Through the Luer opening of the syringe the IS (5 μ l) in 5 μ l methanol was added with a 10 μ l syringe. In both the on-line and the off-line system, samples were purged during 18 min at a rate of 50 ml/min. The trapping temperature for the on-line system was 40°C, while for the off-line system the temperature was room temperature.

Desorption and cryofocussing In the off-line purge system the trap with sorbed VOCs was replaced in the on-line system for desorption. In some cases the desorption was preceded by a dry purge step in which a cold Helium stream was led over the sorbent trap to flush water from the trap in order to prevent it from entering the GC-MS system. Desorption of VOCs in the off-line as well as in the on-line P&T system, was done in the automated P&T system. Tenax TA traps were desorbed at 180°C during 8 minutes,

Vocarb 4000 traps were desorbed during 6 minutes at 250°C. After desorption the trap was conditioned at 200°C for 8 minutes and at 260°C for 4 minutes, for the Tenax and the Vocarb 4000 respectively. The cryofocussing temperature was held at -150°C during the desorption.

Injection, chromatographic separation and detection After the desorption the cryogenic focuser was heated to 260°C (rate 800°C/min) and held at this temperature during 5 minutes. Temperature programming of the GC and data acquisition were started simultaneously. Temperature of the GC oven was held at 50°C during 10 minutes, then increased to 190°C at a rate of 10°C/min. The selected ions, the time windows and the limits of detections expressed as signal/noise (S/N) = 3 for the detector are given in Table 1.

RESULTS AND DISCUSSION

On-line Purge & Trap

Working with the on-line system showed unpredictable amounts of mainly chloroform and benzene (levels up to 800 ng/l) and smaller amounts of 1,1,1-trichloroethane, toluene, ethylbenzene and the xylenes. A series of precautions and measures were taken to eliminate this contamination, or at least, to reduce it to a low constant level. Measures to avoid contamination originating from outside the on-line system, were not effective in controlling the contamination. Further on, several parts of the P&T system were replaced or thoroughly cleaned without improvement of the contamination. In our opinion the 8-port switching valve and the automatic controlled open close valves are the source of contamination at this concentration level. Moreover multiple analysis of a water solution with the internal standard at a 16.7 pl/l concentration, revealed that the reproducibility was low (relative standard deviation on integration areas 37.5% (n = 5)).

Table 1 Selected ion masses, time windows and limits of detection (S/N = 3) for the MS detector in SIM-modus.

<i>Compound</i>	<i>Selected ion masses</i>	<i>Time window (min)</i>	<i>Limits of detection (pg)</i>
Chloroform	83, 85	14.00–15.25	28
Tetrachloromethane	117, 119, 121	15.25–17.50	35
1,1-Dichloroethane	63, 65, 83	12.00–14.00	29
1,2-Dichloroethane	62, 64	15.25–17.50	24
1,1,1-Trichloroethane	61, 97, 99	15.25–17.50	28
Trichloroethylene	95, 130, 132	17.50–20.00	28
Tetrachloroethylene	129, 164, 166	22.00–23.50	18
Benzene	77, 78	15.25–17.50	12
Toluene	65, 91, 92	20.00–22.00	5
Ethylbenzene	91, 105, 106	23.50–27.50	23
m/p-Xylene	91, 105, 106	23.50–27.50	16
o-Xylene	91, 105, 106	23.50–27.50	38
α,α,α,-Trifluorotoluene	127, 145, 146	17.50–20.00	22
Chloroform-d	84, 86	14.00–15.25	21
Toluene-d	70, 98, 100	20.00–22.00	11

It was proved that the factor affecting this low reproducibility was the water vapour generated by purging the vessel. A gas mixture of about 5 ng IS, tetrachloroethylene and ethylbenzene in 0.5 ml air was prepared using a closed gas/water system into which an appropriate amount was brought. With the Henry's law constants²³, equilibrium concentrations in air and water can be calculated. By means of a gas-tight syringe 500 μ l of this gas mixture was injected into a gas stream of 50 ml He/min before it entered the Tenax TA trap in an off-line construction. The reproducibility for sorbing this VOCs out of a (dry) gas stream combined with a desorption in the on-line apparatus (unchanged conditions) showed 9.3, 9.3 and 10.2% SD on the absolute area for the IS, tetrachloroethylene and ethylbenzene respectively (n = 4).

The analytical problem was localized in the P&T stage, i.e. purging VOCs out of the water vessel and trapping them out of the water-saturated gas stream. Purging VOCs out of water is not expected to be the cause because it is governed by first order kinetics based on the mass balance $-V.dC_w/dt = Q.C_g$, where V is the purged water volume (l), t time (min) C_w and C_g are the water and gas concentrations (mol/l) and Q is the gas flux rate (l/min)^{24,25}. Assuming the gas-water equilibrium, C_g is $H.C_w$ (H Henry's law constant, dimensionless). So the reproducibility was thought to depend on the sorption (trapping), which could be affected by the water vapour.

Off-line Purge & Trap

The interference of the water vapour with the sorption of the VOCs could be solved by using wet traps which were more effective than the trap in the automatic system, which was only based on adsorption on a metal surface. The existing methods are condensing the water vapour¹⁸ and inserting water adsorbing materials between the sparging vessel and the adsorbent trap²¹.

In a first off-line P&T construction a spiral condenser was installed as wet trap. Ethylene glycol of $-10 \pm 1^\circ\text{C}$ as refrigerant was pumped in the condenser (The contact time for the gas stream was 18s). Using this off-line P&T construction with a Vocab 4000 sorbent trap, combined with thermal desorption in the automatic P&T system, gave a relative area reproducibility against the internal standard for all 13 VOCs between 2.4 (tetrachloroethylene) and 11.9% SD (ethylbenzene) (n = 4).

Although the reproducibility of the quantitation was under control, the peaks at the chromatographic time window of chloroform till benzene were broad and split. When ion 17 and 18 were monitored it was clear that a large amount of water entered the MS-detector at the same time window. The water peak was broad and asymmetric. The fronting peak started at time 14 min. and lasted till 18.5 min. with a peak maximum at 18 min. The peak shapes of the VOCs were getting worse during consecutive analyses on the same day.

It became clear that water accumulated in the CDS Peakmaster system, or at least that the evacuation of water was insufficient. When a desorbed trap was desorbed for a second time, a similar amount of water was detected. The accumulated amount of water could be removed by using the 'auto empty' option of the automated P&T system and by removing the on-line sparging vessel. When using the 'auto empty' option a cleaning gas stream is passing via the 8-port switching valve through the wet trap and finally through the on-line vessel entering at its top to remove the analysed water. This is done while the sorbent trap is thermally desorbed. On the other hand the on-line vessel was never completely dry. Since the gas stream for conditioning the sorbent trap passes first through the on-line vessel (and the wet trap) via the 8-port switching valve, it was removed.

To conclude, the method developed consisted of an off-line P&T step with a purging time of 18 minutes at a purge rate of 50 ml/min and using a wet trap consisting of a 3 m empty 1/4" stainless steel tube at $-11 \pm 1^\circ\text{C}$ and a Vocarb 4000 sorbent trap. Next, the Vocarb 4000 trap was desorbed at $250^\circ\text{C}/6$ min in the automated P&T system and the VOCs were cryofocussed at -150°C . Finally, they were injected by heating the cryogenic focuser up to 260°C during 5 minutes.

Limits of detection (LODs)

The limits of detection (LODs) (ng/l) of the P&T technique are proportional to the limits of detection of the detector and are inversely proportional with the sample volume V (1) for a given compound. Increasing the volume V lowers the LODs but requires a longer purging time. Using FID-detection, a sample of 870 ml and a purge rate of 100 ml/min during 30 min Plass *et al.* (1991)¹⁸ analysed C_2 – C_4 hydrocarbons with LODs of 0.030 to 0.120 ng/l. Even these parameters would be insufficient to purge out MAHs and CHCs because their Henry's constant is considerably lower than the Henry's constant of the C_2 – C_4 hydrocarbons ($H \leq 1$ versus $H = 20.0, 29.0$ and 39.0 for ethane, propane and butane respectively²³).

Considering the limits of detection of the detector (in ng or pg, Table 1), the H -values of the VOCs²³, the analysis time and the desired LODs, a sample volume of 60 ml was used. In this way LODs for the 13 VOCs, the 2 deuterated surrogates and the IS were calculated by determining the blank results and the signal/noise ratio of 3. The blanks were much better under control in the off-line system than in the on-line work. Blanks were measured daily for correction. They were for all VOCs under 0.76 ng/l, except for chloroform (4.46 ± 2.14 (48.0% SD)), for benzene (4.58 ± 1.33 (29.1% SD)) and for toluene (2.59 ± 0.90 (34.7% SD)) (Table 2).

The amounts of VOCs corresponding to a signal/noise ratio of 3 were determined by analysing a 83.3 pl/l solution of all VOCs, surrogates en the IS (Table 2). In this way mean LODs (mean blank + signal/noise 3) from 0.48 (tetrachloroethylene) to 1.25 ng/l (o-xylene) were obtained, except for chloroform (4.93), benzene (4.79) and toluene (2.68) (Table 2).

Table 2 Signal/noise 3 ratio's (S/N 3), mean blank values (Blank) (n = 9) and limits of detection (LODs) for all VOCs, surrogates and the IS (ng/l).

Compound	S/N 3	Blank	LOD
Chloroform	0.47	4.46	4.93
Tetrachloromethane	0.58	0.19	0.77
1,1-dichloroethane	0.49	0.65	1.14
1,2-dichloroethane	0.40	0.70	1.10
1,1,1-trichloroethane	0.47	0.12	0.59
Trichloroethylene	0.47	0.04	0.51
Tetrachloroethylene	0.30	0.18	0.48
Benzene	0.21	4.58	4.79
Toluene	0.09	2.59	2.68
Ethylbenzene	0.38	0.73	1.11
m/p-Xylene	0.27	0.76	1.03
o-Xylene	0.63	0.62	1.25
Trifluorotoluene	0.36	0.00	0.36
Chloroform-d	0.36	0.00	0.36
Toluene-d	0.19	0.00	0.19

Precision and accuracy

The precision of the developed method was checked by analysing 10 times (over a two-week period) a laboratory reference material (LRM). This LRM was made by adding all VOCs and surrogates at a 41.67 pl/l concentration to a matrix being a 30 minutes purged sample. Results shown in Table 3 demonstrate a precision with a standard deviation better than 10% for all VOCs and surrogates except for benzene (11.3%) and 1,2-dichloroethane (15.7%).

The accuracy was assessed by evaluating mean concentrations (X) and the expected concentration X_{exp} (Table 3). The mean X/X_{exp} for all VOCs and surrogates was 109.3 ± 10.4 (9.5% SD, $n = 14$). This slight overestimation is due to the MAHs with X/X_{exp} 117.4 ± 10.7 (9.5% SD, $n = 6$) as compared with 103.2 ± 4.2 (4.1% SD, $n = 8$) for the CHCs.

Analytical quality assurance

International organizations dealing with marine sciences as the OSPARCOM (Oslo and Paris Commissions)²⁶ and the QUASIMEME working group (Quality Assurance of Information in Marine Environmental Monitoring Programmes in Europe)²⁷ propose general procedures to ensure data quality. According to the QUASIMEME guidelines the analytical quality assurance consists of measuring recovery by a standard addition test, a system of quality control and assessment, the use of an appropriate analytical procedure and an evaluation of bias.

In order to guarantee the analytical results a standard addition test was done on an environmental sample. The sample of the S12 sampling station (Figure 1) was fortified with 16.7 pl/l of each VOC and surrogate (laboratory fortified matrix, LFM). For all 13 VOCs and the 2 surrogates a mean recovery of $105.8 \pm 11.1\%$ ($n = 14$) for the LFM was found as compared to the concentration expected from the sum of the measured sample results and the added amount (Table 4). So the recovery of stripping VOCs out of a

Table 3 Measured concentrations (X) and % standard deviation (%SD) of a laboratory reference material and comparison with the expected concentration (X_{exp}) (ng/l).

Compound	X	%SD	X_{exp}	X/X_{exp} (%)
Chloroform	61.02	5.7	62.08	98.3
Tetrachloromethane	64.75	9.3	66.38	97.6
1,1-dichloroethane	51.65	7.3	48.92	105.6
1,2-dichloroethane	54.74	15.7	52.21	104.9
1,1,1-trichloroethane	54.77	3.9	54.58	100.3
Trichloroethylene	64.81	3.5	61.00	106.3
Tetrachloroethylene	69.52	2.6	67.58	102.9
Benzene	44.87	11.3	36.63	122.5
Toluene	45.69	9.3	36.13	126.5
Ethylbenzene	43.38	9.1	36.13	120.1
m/p-Xylene	38.34	8.4	35.96	106.6
o-Xylene	46.69	8.8	36.71	127.2
Trifluorotoluene	99.17	0.0	49.58	100.0
Chloroform-d	68.47	8.3	62.50	109.6
Toluene-d	40.03	6.7	39.33	101.8

Table 4 Standard addition test with analysis of a laboratory fortified matrix (LFM) in comparison with the analysis of the original matrix (sample) and the added amount (ng/).

<i>Compound</i>	<i>LFM</i>	<i>Sample</i>	<i>Added amount</i>	<i>Sample + added amount</i>	<i>Recovery (%) (LFM/sample + added)</i>
Chloroform	64.12	42.60	24.83	67.43	95.1
Tetrachloromethane	32.63	3.04	26.55	29.59	110.3
1,1-dichloroethane	25.82	6.93	19.57	26.50	97.4
1,2-dichloroethane	70.56	47.97	20.88	68.85	102.5
1,1,1-trichloroethane	136.84	101.55	21.83	123.38	110.9
Trichloroethylene	83.46	54.65	24.40	79.05	105.6
Tetrachloroethylene	86.51	52.87	27.03	79.90	108.3
Benzene	39.89	21.02	14.65	35.67	111.8
Toluene	67.06	46.36	14.45	60.81	110.3
Ethylbenzene	59.13	36.92	14.45	51.37	115.1
m/p-Xylene	44.98	22.95	14.38	37.33	120.5
o-Xylene	43.67	21.00	14.68	35.68	122.4
Trifluorotoluene	99.17	99.17	0.00	99.17	100.0
Chloroform-d	130.2	105.21	25.00	130.21	100.0
Toluene-d	83.43	59.11	15.73	74.84	111.5

(marine) water matrix is complete. In fact, the recovery is mainly dependent on the possibility of the compounds to be purged out of the matrix. Their high Henry's law constants are even enhanced by the salinity, while the presence of dissolved organic matter is of no importance with respect to the air-water partitioning of these VOCs²⁸.

The system of quality control and assessment proposed by QUASIMEME is to plot the analytical data for reference materials on an analytical quality control chart (AQCC). Guidelines to assess these charts are given. According to the authors²⁶, this is a better approach than just analyse once a reference material as a check on the quality of analytical data. Laboratory reference material (LRM) was analysed 10 times spread at random over a two week period to construct an AQCC with \bar{X} the mean measured concentration, with $\bar{X} \pm 2s$ the upper and lower warning limits (WL), and with $\bar{X} \pm 3s$ the upper and lower control limits (CL) for each VOC and surrogate, as illustrated in Figure 2 for the CHC tetrachloroethylene and for the MAH toluene. Of the 140 obtained data 135 values fell within the warning limits (96.4%) while 95.0% is statistically expected. Four points, one of tetrachloroethylene, benzene, ethylbenzene and chloroform-d, all in different analyses, fell between the warning and control limits so that 99.3% of the data fell within the control limits (99.7% statistically expected). One point fell out of the upper control limit. This was due to the use of a matrix for making the LRM which was insufficiently blank even after 30 minutes purging because the matrix was of a sampling point containing > 10000 ng/l chloroform. To conclude, these results are of an acceptable quality according to the QUASIMEME guidelines.

Marine sample analysis

The results of the samples taken on the sampling stations S12 (N 51°21.90, E 4°13.50), B07 (N 51°25.80, E 3°17.80), 780 (N 51°28.27, E 3°03.48) and 435 (N 51°34.84, E 2°47.42) in the Scheldt estuary and in the North Sea region (Figure 1) in may 1993 are shown in Table 5. The measured values for all the VOCs are in the 0.5 to 100 ng/l

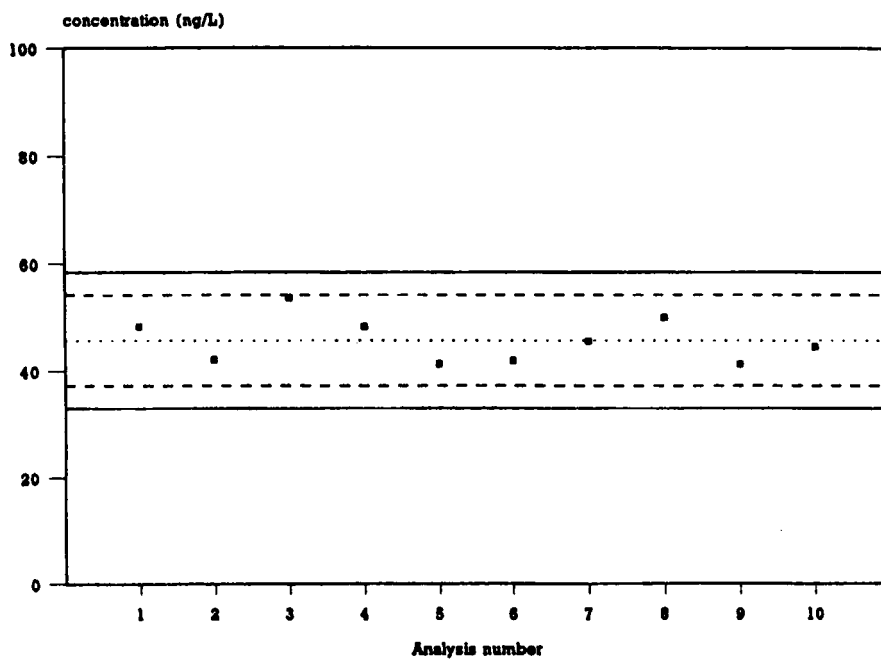
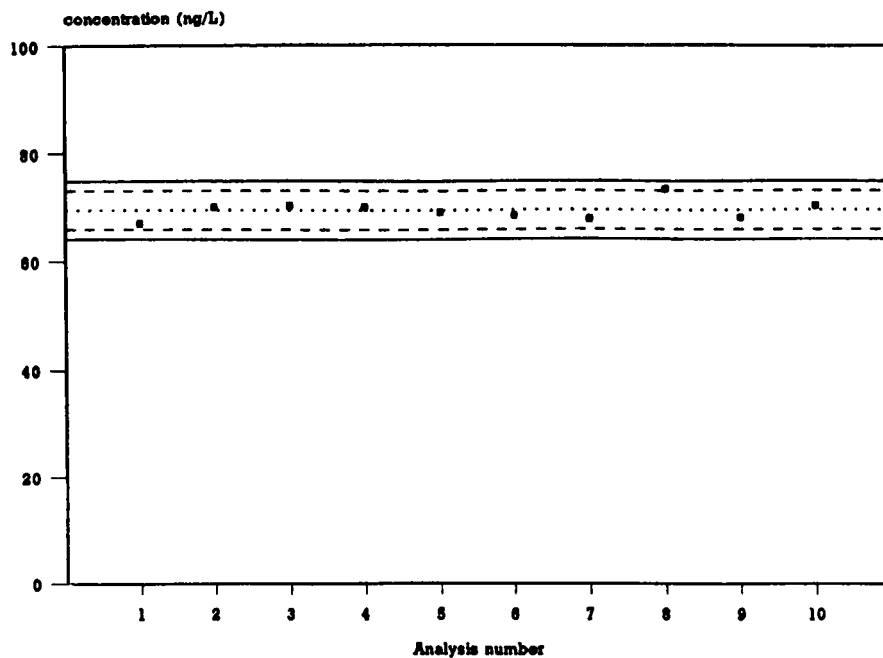


Figure 2 Analytical quality control chart (AQCC) of tetrachloroethylene and toluene:
 ■ : measured concentration (x) ··· : mean measured concentration (X)
 --- : warning limits (WL) — : control limits (CL)

Table 5 Analysis of environmental marine samples from the North Sea and the Scheldt estuary (ng/l).

Compound	435	780	B07	S12
Chloroform	12.8	11.3	17.4	42.6
Tetrachloromethane	1.4	0.6	2.4	3.0
1,1-dichloroethane	0.3	0.5	0.07	6.9
1,2-dichloroethane	9.8	4.9	8.7	48.0
1,1,1-trichloroethane	3.1	2.1	3.6	101.6
Trichloroethylene	6.0	4.9	7.3	54.7
Tetrachloroethylene	1.0	1.5	1.4	52.9
Benzene	26.8	26.5	34.7	21.0
Toluene	49.7	35.2	52.0	46.4
Ethylbenzene	11.4	9.4	18.7	36.9
m/p-Xylene	12.8	11.0	15.1	23.0
o-Xylene	10.9	9.8	11.9	21.0
Trifluorotoluene	99.2	99.2	99.2	99.2
Chloroform-d	117.2	75.8	118.3	105.2
Toluene-d	77.6	42.2	68.7	59.1

concentration range. Only the values of 0.07 and 0.29 ng/l of 1,1-dichloroethane at the sampling stations B07 and 435 are lower than the signal/noise ratio 3.

The recovery of the surrogates was $108.3 \pm 20.6\%$ (19.0% SD) for chloroform-d (96.2 ng/l added) and $102.3 \pm 25.1\%$ (24.5% SD) for toluene-d8 (60.5 ng/l added) (n = 4). This result showed that the chosen sample treatment and storage had avoided losses by diffusion, chemical degradation and microbiological breakdown.

The range of concentrations in the three North Sea samples (B07, 780 and 435) is rather narrow for the CHCs as well as for the MAHs: for all the VOCs the % SD varies from 10.0 (ortho-xylene) to 36.9% (ethylbenzene). Two remarkable exceptions were found: tetrachloromethane and 1,1-dichloroethane, although their concentration levels are very low. The measured values for the CHCs show a significant difference between the sampling point S12 in the Scheldt estuary and the North Sea sampling points, especially for tetrachloroethylene, 1,1,1-trichloroethane and trichloroethylene. Their concentration ratio's calculated as S12 concentration over the average concentration of B07, 780 and 435 are 40.2, 34.7 and 9.1 respectively. This might indicate a possible contamination contribution of the Scheldt river to the North Sea region for these compounds.

On the contrary the data for the MAHs concentrations in the Scheldt estuary are more comparable to those of the three North Sea measurements. Their concentration ratio varies between 0.72 for benzene to 2.8 for ethylbenzene.

CONCLUSIONS

This study elaborated the P&T technique to the ng/l level for VOCs with a GC-MS detection system. This means that a wide range of compounds are detectable at this concentration level. The major problems occurring in the application of the on-line automated P&T equipment at this concentration level (reproducibility and contamination) were overcome by an off-line P&T stage. In the off-line device the use of a simple constructed wet trap inserted between sparging vessel and adsorbent trap eliminated reproducibility problems. The contamination problem in the application of

the on-line equipment turned out to be originating in the automated P&T apparatus itself during the P&T stage, since it was under control in the off-line P&T work.

The accuracy, precision, limits of detection and the analytical quality on the basis of constructing analytical quality control charts were considered. These checks confirmed the reliability of the method.

The technique was successfully applied in the analysis of VOCs, as well as CHCs and MAHs, in environmental marine samples at a concentration range of 0.5 to 100 ng/l. Knowledge of marine concentrations of the latter group is scarce because of shortage of suitable analytical methods applicable in a routine way.

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References

1. P. H. Howard, R. S. Boethling, W. S. Jarvis, W. M. Meyland and E. M. Michalenko, *Handbook of Environmental Degradation Rates* (Lewis Publishers, Chelsea (USA) 1991), 725pp.
2. M. Sittig, *Priority Toxic Pollutants* (Noyes Data Corporation, New Jersey (USA) 1980), 370pp.
3. *Ministerial Declaration of the Third International Conference on the Protection of the North Sea* (Den Hague, 1990), 48pp.
4. J. E. Lovelock, R. J. Maggs and E. R. Adlard, *Anal. Chem.*, **43**, 1962–1965 (1971).
5. J. E. Lovelock, R. J. Maggs and R. J. Wade, *Nature*, **241**, 194–196 (1973).
6. G. Eklund, B. Josefsson and C. Roos, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, **1**, 34–40 (1978).
7. E. Fogelqvist, B. Josefsson and C. Roos, *Environ. Sci. Technol.*, **16**, 479–482 (1982).
8. E. Fogelqvist, *J. Geophys. Res.*, **90**, 9181–9193 (1985).
9. S. Klick, *Limnol. Oceanogr.*, **37**, 1579–1585 (1992).
10. D. W. R. Wallace, P. Schlosser, M. Krysell and F. Bönisch, *Deep-Sea Research*, **39**, S435–S458 (1992).
11. K. Abrahamsson and A. Ekdahl, *J. Chromatogr.*, **643**, 239–248 (1993).
12. E. Fogelqvist, M. Krysell and L.-G. Danielsson, *Anal. Chem.*, **58**, 1516–1520 (1986).
13. K. Abrahamsson, D. Dyrssen, G. Jøgebrant and M. Krysell, *Vatten*, **45**, 3–8 (1989).
14. K. Grob and F. Zürcher, *J. Chromatogr.*, **117**, 285–294 (1976).
15. K. Grob, *J. Chromatogr.*, **84**, 255–273 (1973).
16. J. Drozd, Z. Vodáková and J. Novák, *J. Chromatogr.*, **354**, 47–57 (1986).
17. A. Bianchi, M. S. Varney and J. Phillips, *J. Chromatogr.*, **467**, 111–128 (1989).
18. C. Plass, R. Koppmann and J. Rudolph, *Fresenius J. Anal. Chem.*, **339**, 746–749 (1991).
19. T. Yamasaki, N. Oki and T. Okuno, *Wat. Sci. Tech.*, **25**, 33–39 (1992).
20. R. P. Eganhouse, T. F. Dorsey, C. S. Phinney and A. M. Westcott, *J. Chromatogr.*, **628**, 81–92 (1993).
21. M. Krysell and P. D. Nightingale, *Continental Shelf Res.*, **14**, 1311–1329 (1994).
22. R. W. Slater jr. and J. S. Ho, *Methods for the determination of organic compounds in drinking water* (US Environmental Protection Agency, Cincinnati 1989), 31–62.
23. R. P. Schwarzenbach, P. M. Gschwend and D. M. Imboden, *Environmental Organic Chemistry* (Wiley & Sons, New York 1993), 617–625.
24. D. Mackay, W. Y. Shiu and R. P. Sutherland, *Environ. Sci. Technol.*, **13**, 333–337 (1979).
25. D. P. Lin, C. Falkenberg, D. A. Payne, J. Thakkar, C. Tang and C. Elly, *Anal. Chem.*, **65**, 999–1002 (1993).
26. G. Topping, D. E. Wells and B. Griepink, *Quality Assurance of Information in Marine Environmental Monitoring Programmes in Europe (QUASIMEME), Guidelines on Quality Assurance for Marine Measurements* (Quasimeme Project office, Aberdeen 1993).
27. Oslo and Paris Commissions, *Oslo and Paris Commissions: Principles and Guidelines of the Joint Monitoring Program* (Oslo and Paris Commissions, London 1990).
28. J. Dewulf, D. Drijvers and H. Van Langenhove (1994), accepted for publication in *Atmos. Environ.*