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# Evaluation of purge-and-trap–high-resolution gas chromatography–mass spectrometry for the determination of 27 volatile organic compounds in marine water at the ng $l^{-1}$ concentration level

Tom Huybrechts, Jo Dewulf, Olivier Moerman, Herman Van Langenhove*

*Department of Organic Chemistry, Faculty of Agricultural and Applied Biological Sciences, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium*

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**Abstract**

Purge-and-trap combined with high-resolution gas chromatography and detection by mass spectrometry was evaluated for the analysis of 27 volatile organic compounds (VOCs) in marine water samples down to ng $l^{-1}$ concentration levels. The target compounds included chlorinated alkanes and alkenes, monocyclic aromatic hydrocarbons and chlorinated monocyclic aromatic hydrocarbons and covered a wide range of VOCs of environmental interest. Limits of detection ranged from 0.15 ng $l^{-1}$ to 6.57 ng $l^{-1}$ for all VOCs, except for dichloromethane (41.07 ng $l^{-1}$), chloroform (19.74 ng $l^{-1}$), benzene (22.05 ng $l^{-1}$) and 1,4-dichlorobenzene (20.43 ng $l^{-1}$). Precision and accuracy were determined at a concentration level of 25.97 to 66.68 ng $l^{-1}$. Besides method validation, emphasis was put on quality control and assessment during routine determination of VOCs in marine water samples. Analytical quality control charts were plotted for all VOCs and a standard addition test was performed, as proposed by the QUASIMEME (Quality Assurance of Information in Marine Environmental Monitoring Programmes in Europe) working group. The analytical charts were incorporated in a working scheme containing guidelines to be applied during routine determinations, ensuring the long time reliability of the analytical method. Results yielded by the QUASIMEME interlaboratory exercise on organohalogen measurements in seawater are presented. The exercise was attended by seven out of eight laboratories who agreed to participate. Samples taken along the Scheldt estuary, from Breskens (The Netherlands) to Temse (Antwerp, Belgium) were analysed according to the developed technique. Concentrations as low as 0.33 ng $l^{-1}$ (1,2-dichloropropane) were detected near the mouth of the river Scheldt, while concentrations up to 326 ng $l^{-1}$ for tetrachloroethene and 461 ng $l^{-1}$ for cyclohexane were found in the vicinity of Antwerp.


*Keywords:* Water analysis; Environmental analysis; Quality assurance; Quality control; Validation; Interlaboratory study; Purge-and-trap methods; Sample handling; Volatile organic compounds

## 1. Introduction

Volatile organic compounds (VOCs) are ubiquitous in the marine environment throughout the world [1–6]. Trace levels of monocyclic aromatic hydro-

*Corresponding author. Tel.: +32-9-2645-953; fax: +32-9-2646-243.

*E-mail address:* herman.vanlangenhove@rug.ac.be (H. Van Langenhove).

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carbons and halocarbons have even been found in Antarctic waters and surface snows [3–5]. Anthropogenic emissions are mainly held responsible for the presence of these compounds in coastal and open seawaters. However, in situ production by macro- and microalgae has been reported to contribute to the local input of VOCs, especially for low-molecular-mass halocarbons [1,7,8].

VOCs have been shown to affect a wide number of biological and environmental systems. They are known to influence various atmospheric processes, some are carcinogens and/or mutagens, while others are persistent and show bioaccumulation effects [9]. In addition many VOCs exhibit toxic effects on aquatic organisms. In the list of 36 priority toxic pollutants established at the Third International Conference on the Protection of the North Sea nine VOCs, all chlorinated $C_1$- and $C_2$-hydrocarbons, were mentioned [10]. Additionally to this priority list it was stated that attention has to be paid to 13 groups of chemicals, out of which four consist of VOCs. Compared to other priority pollutants, e.g., polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) or heavy metals, far less information concerning the presence and input of VOCs in the North Sea is available. In order to investigate the sources, masses and fluxes of these compounds, appropriate measurement techniques are needed.

Because of the low concentration levels found in natural waters (ng $l^{-1}$ to μg $l^{-1}$) a preconcentration step is necessary prior to analysis and detection. A wide number of techniques have been described in the literature for this purpose [11–13]. Liquid–liquid extraction, static headspace techniques and dynamic headspace techniques have for a long time dominated this part of the analytical procedure. Solid-phase microextraction (SPME) and more recently membrane extraction techniques have been introduced as promising and rapid preconcentration tools. Membrane-based methods of analysis such as membrane inlet mass spectrometry (MI-MS) [14–18] or other techniques using a membrane interface [19–21] allow the determination of monocyclic aromatic hydrocarbons and chlorinated $C_1$–$C_2$ hydrocarbons down to the μg $l^{-1}$ concentration level, while detection at pg $l^{-1}$ has been reported at least once [22]. Unless electron-capture detection (ECD) or Hall detection are used, most of these methods fall short on analysis at ultra-trace levels due to lack of concentrating power. Unlike halogenated hydrocarbons, ECD does not allow the measurement of non-halogenated aromatics at concentration levels observed in marine waters. As both halocarbons and monocyclic aromatic compounds are of environmental interest, a sensitive preconcentration tool combined with a less selective detection system is required.

Due to its high sensitivity purge-and-trap still remains the most frequently used preconcentration device for VOC analysis in water samples. In contrast to static headspace techniques an inert gas is bubbled continuously through the aqueous matrix, enhancing the air–water interface and allowing a high preconcentration factor to be achieved. This enables limits of detection to be 10- to 100-times lower as compared to static headspace techniques [14]. The air–water surface area can be further expanded by spraying the liquid in a recipient, accelerating the transfer of chemicals from the liquid to the gas phase [23–26]. Unlike conventional purge-and-trap, the organics constitute a continuous analyte flux of constant concentration, resulting in optimum trapping conditions. Furthermore foaming of samples containing large amounts of surfactants is avoided.

The gas stream enriched with organic compounds is led through a sorbent trap to retain the analytes before injection into the gas chromatograph. The analytes are then desorbed by heating the trap. In order to obtain sharp chromatographic peaks, the volatiles are cryogenically refocused before injection. Cryogenic refocusing can be done on a piece of uncoated fused-silica or directly onto the GC capillary column itself. In some applications the analytes are directly passed through a cryotrap, omitting the use of sorbent materials [27–29].

The advantages of purge-and-trap, besides its sensitivity, include precision and possibility for automation. The major drawbacks are its complexity when compared to SPME or liquid–liquid extraction and the interference of water vapour, generated in the purge stage, during subsequent separation and detection.

The objectives of this work were twofold. First the applicability of purge-and-trap combined with gas chromatography–mass spectrometry (GC–MS) was

investigated towards the analysis of 27 VOCs, e.g., chlorinated alkanes and alkenes, monocyclic aromatic hydrocarbons and chlorinated monocyclic aromatic hydrocarbons, in marine water samples at low ng $l^{-1}$ concentration levels. While previous investigations dealt with the monitoring of 13 VOCs in marine water [34], the volatility range of the target compounds was extended, allowing a much wider set of volatile organic compounds of environmental interest to be measured simultaneously. The organics included ranged from 1,1-dichloroethene (786 kPa; 25°C) to hexachloro-1,3-butadiene (0.2 kPa; 25°C).

Second, besides the development of the analytical method, quality assurance (QA) and quality control (QC) were considered of paramount importance. The use of QA/QC has been recognised to be crucial in environmental analysis [11,30–33]. While analysts tend to measure hazards at increasingly lower concentration levels, the opportunities to obtain erroneous results are more abundant as analytical procedures involve more and more steps. As the results of these determinations are often used as a basis for management operations and guideline policy, inaccurate data may have severe economic and social implications. Although a growing awareness is noticed amongst chemists engaged in marine monitoring programmes [30–33], many data related to VOC measurements are still published without any evidence of quality control and assessment. Therefore, one of the major goals of this study was to establish proper QA/QC measures. All characteristics of the analytical method were rigorously investigated and a quality assurance program for routine analysis was elaborated.

## 2. Experimental

### 2.1. Chemicals

1,1-Dichloroethene, *trans*-1,2-dichloroethene, 1,1,1-trichloroethane, cyclohexane, tetrachloromethane, trichloroethene, 1,2-dichloropropane, 1,1,2-trichloroethane, chlorobenzene, *o*-xylene, hexachloro-1,3-butadiene, 1,2,3-trichlorobenzene (Aldrich, Milwaukee, WI, USA), dichloromethane, benzene, tetrachloroethene (Merck, Darmstadt, Germany), 1,1-dichloroethane, chloroform, 1,2-dichloroethane, toluene, ethylbenzene, *m*-xylene, *p*-xylene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 1,3,5-trichlorobenzene and 1,2,4-trichlorobenzene (Fluka, Milwaukee, WI, USA) were investigated and used without further purification. In all but one case (1,1-dichloroethane, purity ≥96%), quoted purities exceeded 99%. Stock standard solutions were prepared in methanol (purge-and-trap grade, Aldrich). α,α,α-Trifluorotoluene ($I.S._1$) (Aldrich) and *p*-bromofluorobenzene ($I.S._2$) (Fluka) were used as internal calibration standards (I.S.s). [$^2$H]Chloroform (Aldrich), [$^2H_8$]toluene (Fluka) and [$^2H_5$]chlorobenzene (Fluka) were added as surrogates (SGs).

### 2.2. Equipment

Due to contamination problems observed in the past [34] the purge-and-trap stage was conducted in a separate off-line device, while only desorption and subsequent analysis and detection were done in the on-line apparatus.

The off-line construction was made of a purge vessel (3.4 cm I.D., height 20 cm) equipped with a glass frit at the bottom and an injection septum.

Although ultrapure helium (Alphagas 2, Air Liquide, Liège, Belgium) was used, it was passed through a liquid nitrogen trap before it was introduced into the vessel. To avoid water vapour from entering the on-line system, a second condensor was placed between the purge vessel and the sorbent trap. This wet trap was made of two U-shaped glass tubes [1/8 in. I.D. (1 in.=2.54 cm), length 2×42 cm) submerged in a temperature controlled ethylene glycol bath set at −15°C. The end of the condensor was directly connected to a custom-made sorbent trap containing 17 cm Tenax TA, 6 cm Carboxen 1000 and 1 cm Carboxen 1001 (Supelco, Bellefonte, PA, USA). All connections between the different parts of the construction were made of 1/16 in. stainless steel tubing.

The on-line apparatus consisted of a microprocessor controlled purge-and-trap system, CDS Peakmaster (CDS Analytical Instruments, Oxford, PA, USA), coupled to a GC–MS system Carlo Erba QMD 1000 (Carlo Erba, Milan, Italy) by means of a transfer line maintained at 275°C. The transfer line was a 0.53 mm I.D. Hydroguard FS (Restek, Belle-

fonte, PA, USA) deactivated fused-silica capillary. A cryogenic focuser was positioned onto the injection port of the gas chromatograph and provided a focusing zone to recollect the trapped organic analytes. Separation was done on a 60 m×0.32 mm I.D. Rtx-502.2 (Restek) fused-silica capillary column with a 1.8 μm film thickness. *m*- and *p*-xylene were not separated and were determined together. The quadrupole mass spectrometer was operating in the selected ion monitoring (SIM) mode to obtain the highest analytical sensitivity. With the exception of [$^2$H]chloroform (*m*/*z* 84 and 86), chloroform (*m*/*z* 83 and 85), benzene (*m*/*z* 77 and 78) and 1,2-dichloroethane (*m*/*z* 62 and 64), all analytes were identified and quantified by means of three selected ions for each compound. The selected ions and time windows, and the I.S. used for quantification are summarised in Table 1. The linearity of the system was tested by preparing and analysing five serial dilutions of a standard stock solution in 60 ml of seawater, purged to blank. This way, analyte masses, from 0.31–0.80 ng to 31–80 ng depending on the analyte, covering three-orders of magnitude were injected into the GC–MS system. The resulting peak areas were plotted against the corresponding masses and analysed with the least-square method. For all target compounds a correlation coefficient ranging from 0.993 to 1.00 was obtained. The linearity was

Table 1
Selected ion masses and time windows for the mass spectrometer operating in the SIM mode, and internal standard (I.S.) used for quantification

| Compound | Selected ion masses (*m*/*z*) | Time window (min) | I.S. |
|---|---|---|---|
| 1,1-Dichloroethene | 61, 96, 98 | 8.55–12.35 | I.S.$_1$ |
| Dichloromethane | 49, 84, 86 | 8.55–12.35 | I.S.$_1$ |
| *trans*-1,2-Dichloroethene | 61, 96, 98 | 8.55–12.35 | I.S.$_1$ |
| 1,1-Dichloroethane | 63, 65, 83 | 12.35–13.50 | I.S.$_1$ |
| [$^2$H]Chloroform | 84, 86 | 14.00–15.45 | I.S.$_1$ |
| Chloroform | 83, 85 | 14.00–15.45 | I.S.$_1$ |
| 1,1,1-Trichloroethane | 61, 97, 99 | 15.45–16.15 | I.S.$_1$ |
| Cyclohexane | 41, 56, 84 | 15.45–16.15 | I.S.$_1$ |
| Tetrachloromethane | 117, 119, 121 | 16.15–17.50 | I.S.$_1$ |
| 1,2-Dichloroethane | 62, 64 | 16.15–17.50 | I.S.$_1$ |
| Benzene | 77, 78 | 16.15–17.50 | I.S.$_1$ |
| Trichloroethene | 95, 130, 132 | 17.50–19.20 | I.S.$_1$ |
| α,α,α-Trifluorotoluene | 127, 145, 146 | 17.50–19.20 | na |
| 1,2-Dichloropropane | 62, 63, 76 | 17.50–19.20 | I.S.$_1$ |
| [$^2$H$_8$]Toluene | 70, 98, 100 | 19.70–21.20 | I.S.$_1$ |
| Toluene | 65, 91, 92 | 19.70–21.20 | I.S.$_1$ |
| Tetrachloroethene | 129, 164, 166 | 21.20–23.00 | I.S.$_1$ |
| 1,1,2-Trichloroethane | 83, 97, 99 | 21.20–23.00 | I.S.$_1$ |
| [$^2$H$_5$]Chlorobenzene | 82, 117, 119 | 23.00–25.50 | I.S.$_2$ |
| Chlorobenzene | 77, 112, 114 | 23.00–25.50 | I.S.$_2$ |
| Ethylbenzene | 91, 105, 106 | 23.00–25.50 | I.S.$_2$ |
| *m*/*p*-Xylene | 91, 105, 106 | 23.00–25.50 | I.S.$_2$ |
| *o*-Xylene | 91, 105, 106 | 23.00–25.50 | I.S.$_2$ |
| *p*-Bromofluorobenzene | 95, 174, 176 | 25.50–27.00 | na |
| 1,3-Dichlorobenzene | 111, 146, 148 | 27.00–30.00 | I.S.$_2$ |
| 1,4-Dichlorobenzene | 111, 146, 148 | 27.00–30.00 | I.S.$_2$ |
| 1,2-Dichlorobenzene | 111, 146, 148 | 27.00–30.00 | I.S.$_2$ |
| 1,3,5-Trichlorobenzene | 180, 182, 184 | 30.50–37.00 | I.S.$_2$ |
| 1,2,4-Trichlorobenzene | 180, 182, 184 | 30.50–37.00 | I.S.$_2$ |
| Hexachloro-1,3-butadiene | 223, 225, 227 | 30.50–37.00 | I.S.$_2$ |
| 1,2,3-Trichlorobenzene | 180, 182, 184 | 30.50–37.00 | I.S.$_2$ |

na = Not applicable.

considered satisfactory according to the analytical goals defined in this study.

The ion source temperature of the mass spectrometer was held at 200°C. The emission electron energy was set to 70 eV and the trap current to 150 μA. Data acquisition was controlled by Masslab v1.3 data system (Fisons Instruments, UK).

### 2.3. Sampling and storage

Samples were taken along the River Scheldt, from Breskens (The Netherlands) to Temse (Antwerp, Belgium), during a 2-day cruise (2–3 November 1999) on board of the research vessel *Luctor* from the Nederlands Instituut voor Oecologisch Onderzoek (NIOO), Yerseke, The Netherlands. Fourteen sampling sites were monitored as shown in Fig. 1. All water sampling was performed with a 10-l Niskin bottle (General Oceanics, Miami, FL, USA) equipped with a CTD (conductivity, temperature, depth) probe (Sea-Bird Electronics, Bellevue, WA, USA) for continuous monitoring of temperature, salinity and depth. Water was immediately transferred to dark green bottles (volume 780 ml) by means of a silicone tube. Two flasks were filled at each station. Each bottle was filled to capacity to avoid any headspace. Thirty-seven drops of 1/1 HCl had been added prior to sampling to obtain a final pH lower than 2, avoiding microbial degradation [34]. Before sealing the recipients with PTFE tape, 5 μl of a surrogate solution in methanol containing 50 pl of [$^2$H]chloroform, [$^2H_8$]toluene and [$^2H_5$]chlorobenzene was injected. All samples were stored at 4°C.

### 2.4. Analytical procedure

#### 2.4.1. Preparation of standard stock solutions

All analytical stock solutions were prepared by two serial dilution steps in methanol. With the exception of 1,4-dichlorobenzene (m.p. 52–54°C), 1,3,5-trichlorobenzene (m.p. 62–64°C) and 1,2,3-trichlorobenzene (m.p. 53–55°C) standards were prepared by volume and calculated to mass by density. The stock solutions were kept at −20°C in a solvent-free compartment. Because of the high volatility of

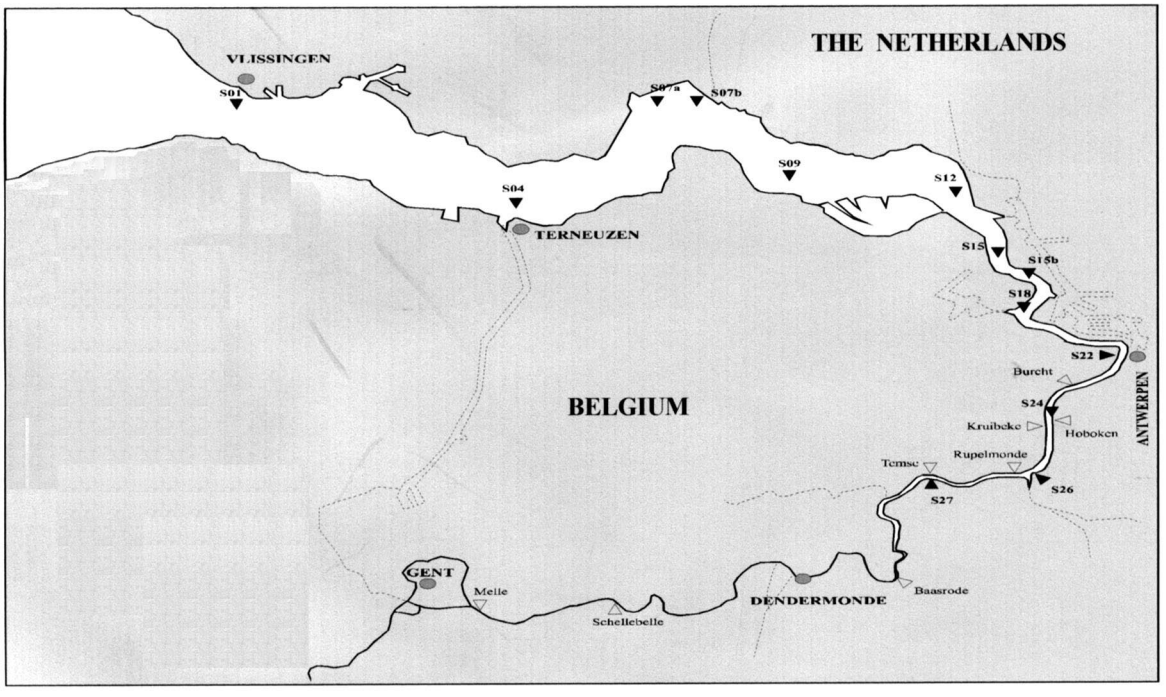


Fig. 1. Sampling sites along the Scheldt estuary, from Breskens to Temse (Antwerp).

the analytes new standards were prepared at the start of each new batch of samples. Stock solutions were renewed after 2 weeks of use.

#### 2.4.2. Preparation of blanks and reference materials

Blank water was prepared by purging 60 ml of natural seawater for at least 1 h at 45°C and a He flow-rate of 50 ml $min^{-1}$. System blanks, laboratory reference materials (LRMs) and calibration materials (CMs) were prepared by injecting 5 μl of the appropriate analytical stock solution in water, purged to blank. Concentration levels of 25.97 to 66.68 ng $l^{-1}$ for LRMs and 64.92 to 166.70 ng $l^{-1}$ for CMs were obtained this way. With the exception of LRMs, system blanks and calibration materials were analysed daily.

#### 2.4.3. Analysis of samples, system blanks and reference materials

A sample aliquot of 60 ml was brought into the purge vessel off-line, kept in a water bath set at 45°C. A 5-μl volume of the I.S. solution was added with a 10-μl Hamilton precision syringe (Supelco). The sample was allowed to thermally equilibrate for 7 min before purging for 20 min at a rate of 50 ml He $min^{-1}$. The compounds of interest were trapped at room temperature onto the multibed sorbent. Breakthrough was not observed for any of the analytes investigated. The trap was manually transferred from the off-line device into the on-line purge-and-trap apparatus. The sorbent trap was thermally desorbed at 275°C during 15 min. In the meantime the cryofocusing temperature was held at −150°C. After desorption, the cryofocusing device was heated at a rate of 800°C $min^{-1}$ to 260°C and kept at that temperature for 6 min. Temperature programming of the GC and data acquisition were started simultaneously. The temperature of the GC oven was held at 40°C for 10 min, then increased to 150°C at a rate of 10°C $min^{-1}$ and finally heated to 220°C at 8°C $min^{-1}$. Temperature was kept at 220°C for 10 min. System blanks, calibration materials and laboratory reference materials were analysed as described above.

## 3. Results and discussion

### 3.1. Limits of detection

Based on statistical considerations, limits of detection (LODs) are defined as three-times the standard deviation of the blank level, hereby assuming that the mean blank level is equal to zero [35]. In most cases, the blank standard deviation is estimated by the noise magnitude and LODs are calculated as the amount of analyte corresponding to a signal-to-noise ratio of three ($S/N$ 3) [36]. In the absence of significant background levels, LODs were estimated on the basis of the signal-to-noise ratio. The masses corresponding to $S/N$ 3 were determined by analysing a LRM containing all 27 VOCs at 25.97 to 66.68 ng $l^{-1}$.

For most target compounds background concentrations larger than the amount corresponding to a signal-to-noise ratio of three seemed unavoidable. Hence LODs should be calculated as the sum of the mean blank level and the amount of analyte corresponding to $S/N$ 3. However, this way of calculating LODs disregards the variability of blank levels. As large day-to-day variabilities were often noticed, two different methods were used to determine the LOD. If a significant background level was observed and if the daily variability of the blank level remained below 30% RSD, the LOD was determined as the sum of the mean blank level and the amount of analyte corresponding to $S/N$ 3. If the day-to-day variability of the blank level exceeded 30% RSD, the LOD was set at two times the mean blank value. Similar approaches have been reported in the literature [37,38].

LODs ranging from 0.15 ng $l^{-1}$ (1,1,1-trichloroethane) to 6.57 ng $l^{-1}$ (trichloroethene) were found, except for dichloromethane (41.07 ng $l^{-1}$), chloroform (19.74 ng $l^{-1}$), benzene (22.05 ng $l^{-1}$) and 1,4-dichlorobenzene (20.43 ng $l^{-1}$). LODs for all VOCs and surrogates are listed in Table 2. High blank levels were observed for a number of compounds such as dichloromethane (20.53 ng $l^{-1}$), chloroform (9.87 ng $l^{-1}$), benzene (21.99 ng $l^{-1}$) and 1,4-dichlorobenzene (10.22 ng $l^{-1}$). The presence of these compounds in method blanks can be

Table 2
Signal-to-noise ratio ($S/N$ 3), mean blank values (Blank), day-to-day variability of blank values (RSD) and limits of detection (LODs) ($n=10$)

| Compound | $S/N$ 3 (ng $l^{-1}$) | Blank (ng $l^{-1}$) | RSD (%) | LOD (ng $l^{-1}$) |
|---|---|---|---|---|
| 1,1-Dichloroethene | 0.29 | 0.30 | 75.0 | 0.60[a] |
| Dichloromethane | 0.09 | 20.53 | 65.9 | 41.07[a] |
| *trans*-1,2-Dichloroethene | 0.17 | 0.22 | 134.1 | 0.45[a] |
| 1,1-Dichloroethane | 0.30 | 0.46 | 54.1 | 0.92[a] |
| [$^2$H]Chloroform | 0.22 | 0.40 | 74.7 | 0.80[a] |
| Chloroform | 0.17 | 9.87 | 54.3 | 19.74[a] |
| 1,1,1-Trichloroethane | 0.15 | <0.15 | – | 0.15[b] |
| Cyclohexane | 0.11 | 0.63 | 71.4 | 1.25[a] |
| Tetrachloromethane | 0.41 | <0.41 | – | 0.41[b] |
| 1,2-Dichloroethane | 0.48 | 2.52 | 54.0 | 5.04[a] |
| Benzene | 0.06 | 21.99 | 13.9 | 22.05[c] |
| Trichloroethene | 0.09 | 3.28 | 45.0 | 6.57[a] |
| 1,2-Dichloropropane | 0.19 | 0.22 | 39.1 | 0.44[a] |
| [$^2H_8$]Toluene | 0.11 | 0.13 | 28.9 | 0.24[c] |
| Toluene | 0.09 | 4.90 | 12.9 | 4.99[c] |
| 1,1,2-Trichloroethane | 0.23 | 0.32 | 60.6 | 0.65[a] |
| Tetrachloroethene | 0.16 | 0.56 | 67.1 | 1.13[a] |
| [$^2H_5$]Chlorobenzene | 0.24 | <0.24 | – | 0.24[b] |
| Chlorobenzene | 0.21 | 2.67 | 16.8 | 2.88[c] |
| Ethylbenzene | 0.20 | 1.16 | 31.8 | 2.31[a] |
| *m*/*p*-Xylene | 0.20 | 2.63 | 23.9 | 2.83[c] |
| *o*-Xylene | 0.24 | 0.96 | 33.8 | 1.92[a] |
| 1,3-Dichlorobenzene | 0.04 | 0.91 | 111.1 | 1.82[a] |
| 1,4-Dichlorobenzene | 0.03 | 10.22 | 63.9 | 20.43[a] |
| 1,2-Dichlorobenzene | 0.04 | 1.36 | 165.4 | 2.72[a] |
| 1,3,5-Trichlorobenzene | 0.07 | 0.38 | 40.1 | 0.76[a] |
| 1,2,4-Trichlorobenzene | 0.10 | 2.87 | 19.5 | 2.97[c] |
| Hexachloro-1,3-butadiene | 0.12 | 0.62 | 58.3 | 1.24[a] |
| 1,2,3-Trichlorobenzene | 0.23 | 1.80 | 82.6 | 3.59[a] |

[a] Calculated as twice the mean blank value.
[b] Calculated as the amount of VOC corresponding to $S/N$ 3.
[c] Calculated as the sum of the mean blank value and the amount of VOC corresponding to $S/N$ 3.

assigned to several effects, e.g., carry-over, artefact formation, contamination from laboratory air. Carry-over was not observed for any analyte. As far as artefact formation is considered, benzene is known to be formed when using Tenax TA as a sorbent material [39]. Benzene was indeed found when thermally desorbing the multibed sorbent in the on-line apparatus, suggesting artefact formation to be a source of contamination. Dewulf and Van Langenhove [34] observed a mean blank level for benzene of only 4.58 ng $l^{-1}$ during their investigation. Tenax TA was however not included as a sorbent material. Sampling laboratory air, followed by GC–MS analysis, revealed the presence of chloroform and dichloromethane, while 1,4-dichlorobenzene was not found.

The lowest LOD found in literature using purge-and-trap were achieved in combination with GC–ECD analysis. Limits of detection for chlorinated $C_1$- and $C_2$-hydrocarbons from 0.01 to 5 ng $l^{-1}$ have been reported several times [40–42]. Due to the selectivity of ECD towards halocarbons, only a limited number of compounds can be detected at the concentration levels given. MS allows one to monitor a wider range of organics. Using a mass spectrometer Lee et al. [25] found LODs ranging from 3 to 10 ng $l^{-1}$ for low-molecular-mass chlorinated hydrocarbons. Borelli et al. [27] observed a detection limit of 0.5 ng $l^{-1}$ for 1,2,4-trichlorobenzene with a purge-and-cryotrap system coupled to a GC–MS operating in the single ion monitoring mode while a LOD of 2 ng $l^{-1}$ was found using ECD. Recently a purge-and-trap injection system coupled to a gas chromatograph–ion trap mass spectrometer, developed by Miermans et al. [43], was introduced, allowing the simultaneous determination of halocarbons, monocyclic aromatic hydrocarbons and chlorinated monocyclic aromatic hydrocarbons down to 2–40 ng $l^{-1}$ in Dutch surface waters. Although cryotrapping was applied, a limit of detection of 40 ng $l^{-1}$ was observed for benzene. Dichloromethane, cyclohexane and hexachloro-1,3-butadiene were not investigated and no detection limit is given for 1,4-dichlorobenzene. Information regarding accuracy, precision or any form of quality assurance were not mentioned.

### 3.2. Precision and accuracy

Precision and accuracy were assessed by analysing LRMs 10 times in a 20-day period [44]. Results are shown in Table 3. At a concentration level of 25.97 to 66.68 ng VOCs $l^{-1}$, precision, measured as the relative standard deviation, was better than 12.9% for all analytes and surrogates except for dichloromethane (103.1%) and benzene (26.0%).

The accuracy ranged from 82.9% to 103.9% for 28 VOCs and surrogates, except for dichloromethane (54.4%) and benzene (66.9%).

Table 3
Precision and accuracy, determined as the relative standard deviation and mean recovery of a laboratory reference material (LRM), at the given concentration level ($n=10$)

| Compound | Concentration (ng $l^{-1}$) | Precision (%) | Accuracy (%) |
|---|---|---|---|
| 1,1-Dichloroethene | 40.43 | 6.8 | 97.9 |
| Dichloromethane | 44.17 | 103.1 | 54.4 |
| *trans*-1,2-Dichloroethene | 41.73 | 7.0 | 96.5 |
| 1,1-Dichloroethane | 39.13 | 5.2 | 97.6 |
| [$^2$H]Chloroform | 50.00 | 4.4 | 99.8 |
| Chloroform | 49.63 | 9.7 | 91.6 |
| 1,1,1-Trichloroethane | 43.67 | 5.4 | 91.6 |
| Cyclohexane | 25.97 | 9.7 | 100.3 |
| Tetrachloromethane | 53.10 | 5.2 | 96.0 |
| 1,2-Dichloroethane | 41.77 | 4.1 | 97.1 |
| Benzene | 29.30 | 26.0 | 66.9 |
| Trichloroethene | 48.80 | 4.7 | 94.8 |
| 1,2-Dichloropropane | 38.60 | 7.5 | 103.9 |
| [$^2H_8$]Toluene | 31.47 | 7.2 | 102.4 |
| Toluene | 28.90 | 9.2 | 89.0 |
| 1,1,2-Trichloroethane | 47.83 | 8.2 | 98.6 |
| Tetrachloroethene | 54.07 | 4.2 | 96.1 |
| [$^2H_5$]Chlorobenzene | 38.57 | 4.7 | 99.5 |
| Chlorobenzene | 36.87 | 5.5 | 95.9 |
| Ethylbenzene | 28.90 | 6.8 | 98.1 |
| *m*/*p*-Xylene | 57.53 | 5.9 | 93.5 |
| *o*-Xylene | 29.37 | 4.6 | 95.7 |
| 1,3-Dichlorobenzene | 42.93 | 4.3 | 93.4 |
| 1,4-Dichlorobenzene | 66.68 | 11.2 | 82.9 |
| 1,2-Dichlorobenzene | 43.50 | 5.9 | 93.5 |
| 1,3,5-Trichlorobenzene | 66.68 | 12.2 | 95.5 |
| 1,2,4-Trichlorobenzene | 48.50 | 10.0 | 93.4 |
| Hexachloro-1,3-butadiene | 56.03 | 12.9 | 99.6 |
| 1,2,3-Trichlorobenzene | 66.68 | 11.4 | 103.2 |

The poor results observed for dichloromethane and benzene can be caused by the relatively high background levels found in method blanks, compared to the concentrations present in LRMs, and the daily variability of blank levels. As the actual concentration present in the LRM ($C_{LRM}$) is calculated by subtracting the concentration of analyte present in the method blank ($C_B$) from the concentration measured during the analysis of the LRM ($C_m$), an estimation of the expected RSD on $C_{LRM}$ can be made by the following equation:

$$\mathrm{RSD}(C_{LRM}) = \frac{\sqrt{[\mathrm{RSD}(C_m)]^2 \cdot C_m^2 + [\mathrm{RSD}(C_B)]^2 \cdot C_B^2}}{C_{LRM}}$$

From this equation it becomes clear that a large $C_B/C_{LRM}$ ratio will result in a large RSD on $C_{LRM}$, even if the variability on the mean blank concentration $C_B$ and measured concentration $C_m$ are small. The expected RSD becomes even larger if the RSD on the mean blank value is large. The agreement between the predicted RSD on $C_{LRM}$ and the observed value is given in Fig. 2 for chloroform, dichloromethane, benzene and 1,4-dichlorobenzene. Blank levels for dichloromethane varied from 11.45 ng $l^{-1}$ to 20.23 ng $l^{-1}$ during the experiment, while a blank of 58.28 ng $l^{-1}$ was noticed once, resulting in a mean concentration of 20.53 ng $l^{-1}$. This amount represents almost 50% of the amount of dichloromethane present in LRM (44.17 ng $l^{-1}$). In the case of benzene, background levels remained rather constant (13.6% RSD). However, blanks (21.99 ng $l^{-1}$) were almost as high as the amount of benzene present in

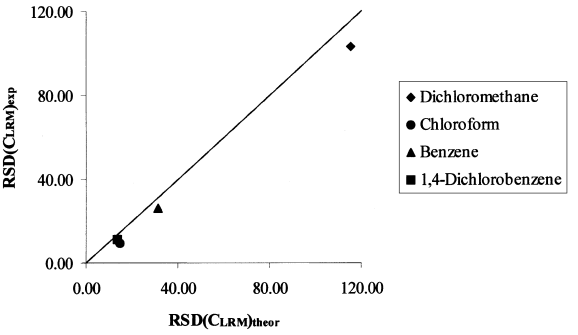


Fig. 2. Observed relative standard deviation RSD$(C_{LRM})_{exp}$ on the concentration recovered from LRM versus the predicted value RSD$(C_{LRM})_{theor}$ for chloroform, dichloromethane, benzene and 1,4-dichlorobenzene.

LRM (29.30 ng $l^{-1}$). At a higher concentration level (10 μg $l^{-1}$) Yan et al. [45] observed a RSD of 2.5% for dichloromethane using purge-and-trap and GC–MS analysis, while an absolute recovery of 83.4% and a method recovery of 97.1% were found.

### *3.3. Analytical quality assurance*

The growing need for QC and QA in environmental monitoring has been underlined by many authors in recent years [11,30–33]. Both QA/QC are essential for the proper functioning of an analytical laboratory and the integrity of the data it produces. Therefore, a system of quality control and assessment proposed by the QUASIMEME (Quality Assurance of Information in Marine Environmental Monitoring Programmes in Europe) working group [44] was applied to all stages of field and laboratory work.

#### *3.3.1. Analytical quality control charts*

According to QUASIMEME guidelines the analytical data for reference material were plotted on an analytical quality control chart (AQCC) or Shewart chart [44]. Control charts are an inherent part of the method validation protocol. Furthermore, the charts form the basis for continuous evaluation of the analytical method, ensuring the long term accuracy and precision. LRM was analysed 10 times ad random in a period of time corresponding to 20 days. Results were used to construct an AQCC, with $X$ the mean value of measured concentrations, SD the standard deviation, $X \pm 2$SD the upper and lower warning limits (WLs) and $X \pm 3$SD the upper and lower control limits (CLs). The bias was evaluated using QUASIMEME guidelines. Ninety-five percent of the analytical data should fall within the upper and lower warning limits. Similarly 99.7% of the results should fall between the upper and lower control limit. Both conditions were satisfied. A total of 290 values were obtained out of which 287 fell within warning limits (98.9%) while all data fell within control limits (100%). All results falling outside the warning limits originated from different compounds. The warning limit was never exceeded in two consecutive analyses. The analytical quality control charts were considered satisfactory according to QUASIMEME guidelines, except for benzene and dichloromethane. Successive measurements of these analytes were not randomly distributed around the mean value.

As an example analytical quality control charts are shown for 1,3,5-trichlorobenzene in Fig. 3. The upper graph shows that the analytical process was out of control when the AQCC chart was first constructed. While replacing a defective heating element, a slight change in the position and distance of the ion source to the entrance hole of the quadrupole filter had been observed. When evaluated before this finding, the analytical technique gave erroneous results for a number of compounds including 1,3,5-trichlorobenzene [46]. Only 57.2% of the initial amount of 1,3,5-trichlorobenzene was recovered (57.9% RSD). As a consequence, measurements of 1,3,5-trichlorobenzene, along with other analytes, were considered as non-reliable. The use of record books allowed to identify and solve the problem, and new charts were constructed. This time a mean recovery of 95.5% (12.2% RSD) was found. This incident once more demonstrates the need and usefulness of quality control and assessment tools such as AQCC when evaluating analytical techniques or performing routine analysis, and underlines the importance of log books to record any change or deviation in or from the analytical method.

#### *3.3.2. Standard addition test*

Besides analytical quality control charts, bias was also evaluated by means of a standard addition test [44]. The test consisted of adding a known amount

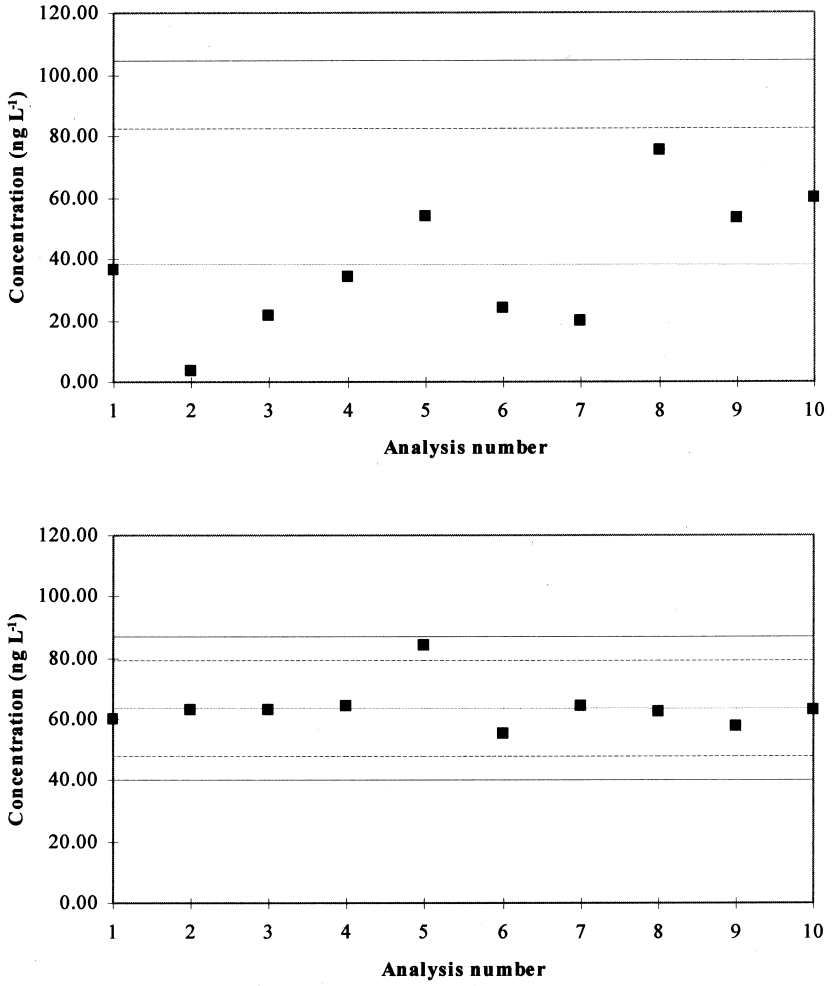


Fig. 3. Analytical quality control charts (AQCCs) of 1,3,5-trichlorobenzene: the analytical process is out of control (upper graph); the analytical process is under control (lower graph); ■ = measured concentration; --- = mean measured concentration ($X$); - - - = warning limits (WLs); — = control limits (CLs).

of LRM to a sample with known concentrations. The sample taken at station S15 was fortified with concentrations of target VOCs and surrogates ranging from 11.69 ng $l^{-1}$ to 30.01 ng $l^{-1}$. The experimental results were then compared with the expected concentrations. Results of the standard addition test are shown in Table 4. Recoveries were within 80 and 120% for all VOCs and surrogates except for chloroform (72.2%), benzene (185.0%), toluene (53.8%), [$^2H_8$]toluene (133.8%), 1,4-dichlorobenzene (64.1%), 1,3,5-trichlorobenzene (69.9%) and 1,2,3-trichlorobenzene (68.4%). In the case of dichloromethane, no value is given as the amount recovered was lower than the amount found in the non-fortified sample.

### *3.3.3. Analytical quality control for routine analysis of marine water samples*

All results obtained during method validation, as well as a detailed description of all steps involved in sample collection, pretreatment and analysis were written down in a standard operating procedure (SOP). The manual includes a working scheme for routine analysis of samples, to further guarantee the

Table 4
Standard addition test: analysis of a laboratory fortified matrix (LFM) and determination of the recovery of the amount added to the original sample S15 ($n=1$)

| Compound | S15 (ng $l^{-1}$) | Added amount (ng $l^{-1}$) | LFM (ng $l^{-1}$) | Recovery (%) |
|---|---|---|---|---|
| 1,1-Dichloroethene | 3.16 | 18.20 | 19.31 | 88.8 |
| Dichloromethane | 178.34 | 19.88 | 134.50 | – |
| *trans*-1,2-Dichloroethene | 0.47 | 18.78 | 18.18 | 94.3 |
| 1,1-Dichloroethane | 1.80 | 17.61 | 18.91 | 97.2 |
| [$^2$H]Chloroform | 115.85 | 22.50 | 137.79 | 97.5 |
| Chloroform | 70.26 | 22.34 | 86.40 | 72.2 |
| 1,1,1-Trichloroethane | 4.34 | 19.65 | 25.79 | 109.2 |
| Cyclohexane | 38.88 | 11.69 | 51.03 | 104.0 |
| Tetrachloromethane | 1.64 | 23.90 | 27.05 | 106.3 |
| 1,2-Dichloroethane | 34.22 | 18.80 | 53.58 | 103.0 |
| Benzene | 1.47 | 13.19 | 25.87 | 185.0 |
| Trichloroethene | 21.12 | 21.96 | 42.91 | 99.2 |
| 1,2-Dichloropropane | 1.27 | 17.37 | 18.74 | 100.5 |
| [$^2H_8$]Toluene | 66.31 | 14.16 | 85.26 | 133.8 |
| Toluene | 36.37 | 13.01 | 43.37 | 53.8 |
| 1,1,2-Trichloroethane | 22.94 | 21.53 | 42.30 | 90.0 |
| Tetrachloroethene | 42.78 | 24.33 | 64.97 | 91.2 |
| [$^2H_5$]Chlorobenzene | 82.42 | 17.36 | 96.41 | 80.6 |
| Chlorobenzene | 30.96 | 16.59 | 45.46 | 87.4 |
| Ethylbenzene | 3.71 | 13.01 | 16.87 | 101.2 |
| *m*/*p*-Xylene | 9.65 | 25.89 | 32.74 | 89.2 |
| *o*-Xylene | 3.78 | 13.22 | 15.99 | 92.4 |
| 1,3-Dichlorobenzene | 3.85 | 19.32 | 20.09 | 84.0 |
| 1,4-Dichlorobenzene | 5.49 | 30.01 | 24.71 | 64.1 |
| 1,2-Dichlorobenzene | 4.00 | 19.58 | 20.70 | 85.3 |
| 1,3,5-Trichlorobenzene | 0.36 | 30.01 | 21.33 | 69.9 |
| 1,2,4-Trichlorobenzene | 2.80 | 21.83 | 21.59 | 86.1 |
| Hexachloro-1,3-butadiene | 0.47 | 25.22 | 24.39 | 94.9 |
| 1,2,3-Trichlorobenzene | 1.21 | 30.01 | 21.72 | 68.4 |

analytical quality of generated sets of data. The working scheme is presented in Fig. 4.

In order to maintain an accurate estimate of the long term bias and precision, replicate analyses of LRM are performed at the beginning of each batch of samples. If the results fall within the acceptable limits, defined from the previously constructed control charts, the routine analysis of samples can start. If not, the process is not under control. The source of systematic error is investigated and the findings recorded in a log book. Furthermore, less than 10% RSD should be observed between both replicates.

A method blank is analysed daily. Blanks are considered acceptable with respect to the analytical goals defined in this study as long as the peak area of each analyte does not exceed 5% of the peak area corresponding to the internal calibration standard. This way, blank levels up to 1.98–7.97 ng $l^{-1}$ can be encountered depending on the analyte, except for 1,2-dichloroethane (11.12 ng $l^{-1}$) and hexachloro-1,3-butadiene (15.57 ng $l^{-1}$). This measure was not applicable for dichloromethane and benzene as higher background levels were always found. Therefore these compounds where not considered when evaluating the blank. LODs were re-evaluated batchwise.

A calibration material was analysed at the end of each day to provide response factors for the calculation of concentration levels. Response factors are compared at regular time intervals to check the stability of the analytical instrument. Blanks, laboratory reference materials and calibration materials are prepared using natural seawater in order to avoid interferences caused by the use of different matrices.

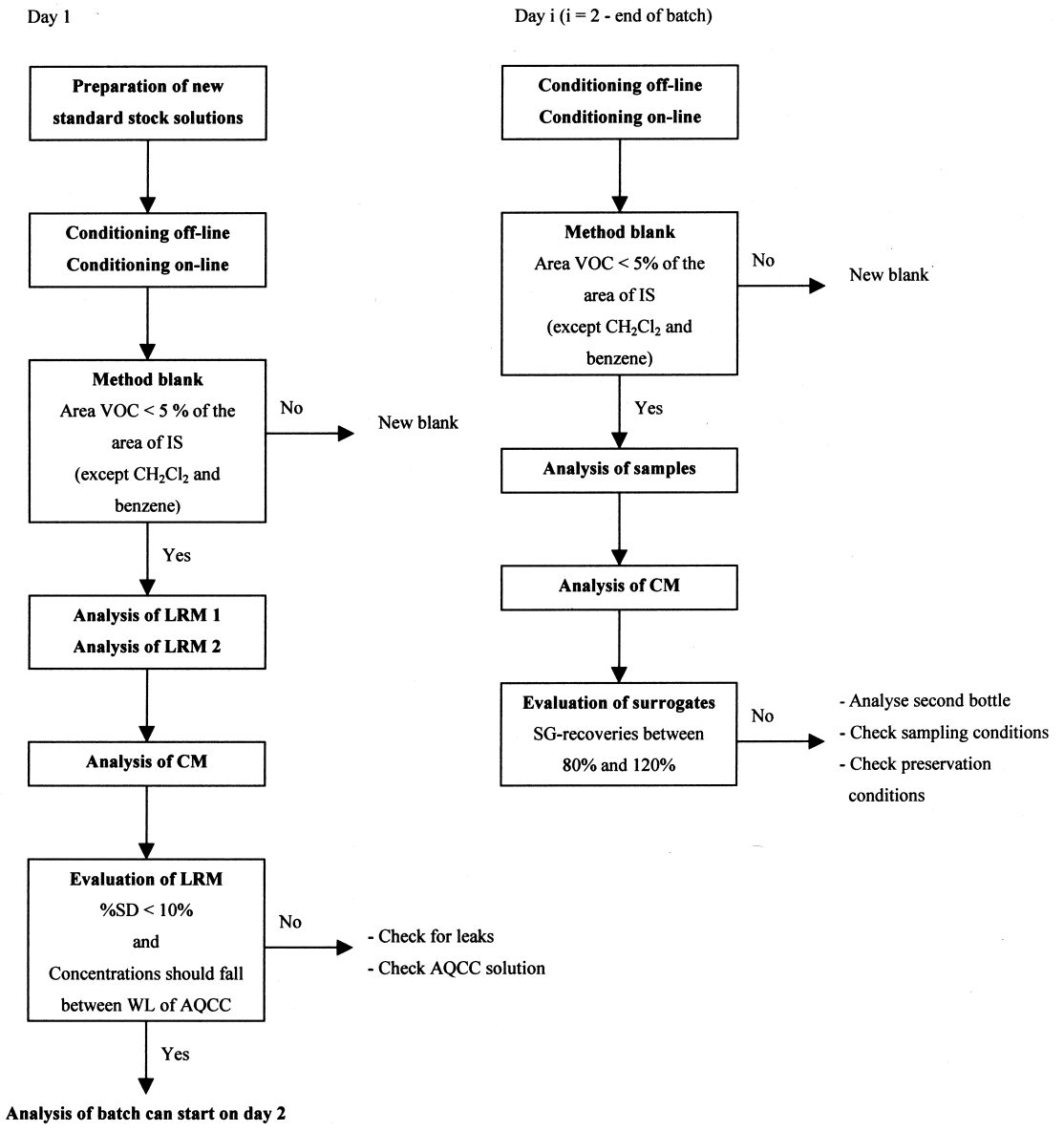


Fig. 4. Guidelines for routine analysis of volatile organic compounds in marine water samples.

Possible losses of target compounds during storage and sample treatment are detected by calculating the amount of surrogate recovered after analysis. Recoveries between 80 and 120% are considered acceptable. If not, a sample aliquot from the other bottle is analysed.

### *3.3.4. Interlaboratory comparison exercises*

Interlaboratory comparison exercises provide laboratories with opportunities to obtain independent assessments of the quality of their analytical capability. Interlaboratory tests for VOCs in water are rather scarce compared to other pollutants such as trace metals, nutrients or PCBs. To our knowledge, only QUASIMEME provides round robin tests for VOC measurements in marine waters. The VOCs included in the test consist of the halocarbons chloroform, tetrachloromethane, 1,2-dichloroethane,

1,1,1-trichloroethane, trichloroethene and tetrachloroethene. The performance is assessed by calculating *Z*-scores [47]:

$Z$ = (deviation from assigned value)/

(maximum allowable deviation)

The magnitude of the maximum allowable deviation depends on the maximum allowable error $E_T$%:

$$E_T\% = E_P\% + 0.5(E_C/[C]) \cdot 100$$

The calculation of the maximum allowable error $E_T$% depends on the assigned value [$C$] and includes a proportional ($E_P$%) and constant ($E_C$) error term. The constant error term is related to the limit of detection of the analytical method used. The proportional component makes up all of the assigned error when the concentrations of the determinands are far above the LOD, whereas the contribution of the constant component increases as the concentrations tend towards the limit of detection.

Results yielded by the participation to the QUASIMEME intercomparison exercise 383 (QVC009SW and QVC010SW) are summarised in Table 5. The exercise was attended by seven out of eight laboratories who agreed to participate. For all VOCs $E_P$% was defined by QUASIMEME as 12.5% and $E_C$ as 0.10 μg $l^{-1}$, except for 1,2-dichloroethane ($E_C$ = 1.00 μg $l^{-1}$) [48].

The results of QVC010SW met the QUASIMEME quality demands: all results fell within $\pm 2E_T$%. In the case of QVC009SW the requirements were almost fulfilled: 83% of the *Z*-scores were below 2, while 17% fell between 2 and 3. Strictly speaking, the data produced was not under control as the target value of 95% was not achieved. However as the *Z*-score of −2.04 obtained for trichloroethene is a rather marginal value, the results obtained for QVC009SW were considered satisfactory.

The number of VOCs proposed by QUASIMEME is rather limited and should be extended towards other VOCs of environmental importance, e.g., VOCs listed as additional priority substances at the Third International Conference on the Protection of the North Sea [10].

### 3.4. Field measurements

In order to prove its applicability towards real sample analysis, the method was used for measuring the target VOCs along the River Scheldt, from Breskens to Temse (Antwerp). The Scheldt estuary constitutes a significant source of pollution towards the marine environment as most VOCs were found at concentration levels much higher than those observed in the North Sea. As a more in-depth investigation on the data acquired will be given elsewhere, only a few findings will briefly be discussed here. Results of the monitoring campaign for cyclohexane, tetrachloroethene, toluene and chlorobenzene are given in Fig. 5. In the case of tetra-

Table 5
Results obtained in QUASIMEME laboratory performance study AQ-6 Volatile Organochlorines in Seawater, Round 15-Exercise 383 (October 1998 to January 1999)[a]

| Determinand | QVC009SW | | | | QVC010SW | | | |
|---|---|---|---|---|---|---|---|---|
| | $C_{Ass}$ (μg $l^{-1}$) | $C_{Lab}$ (μg $l^{-1}$) | $E_T$% (%) | $Z$ (–) | $C_{Ass}$ (μg $l^{-1}$) | $C_{Lab}$ (μg $l^{-1}$) | $E_T$% (%) | $Z$ (–) |
| Chloroform | 0.78 | 0.69 | 18.9 | −0.60 | 1.54 | 1.33 | 15.7 | −0.88 |
| 1,1,1-Trichloroethane | 1.17 | 0.93 | 16.8 | −1.23 | 2.32 | 2.48 | 14.7 | 0.48 |
| Tetrachloromethane | 0.79 | 0.56 | 18.8 | −1.55 | 1.55 | 1.58 | 15.7 | 0.12 |
| 1,2-Dichloroethane | 2.74 | 2.02 | 30.7 | −0.85 | 5.41 | 3.52 | 21.7 | −1.61 |
| Trichloroethene | 1.18 | 0.78 | 16.7 | −2.04 | 2.33 | 1.78 | 14.6 | −1.60 |
| Tetrachloroethene | 0.93 | 0.68 | 17.9 | −1.47 | 1.83 | 1.50 | 15.2 | −1.17 |
| % *Z*-scores | | | | | | | | |
| <2 | | | | 83 | | | | 100 |
| 2–3 | | | | 17 | | | | 0 |
| >3 | | | | 0 | | | | 0 |

[a] $C_{Ass}$ = Assigned value; $C_{Lab}$ = laboratory value; $E_T$% = maximum allowable error.

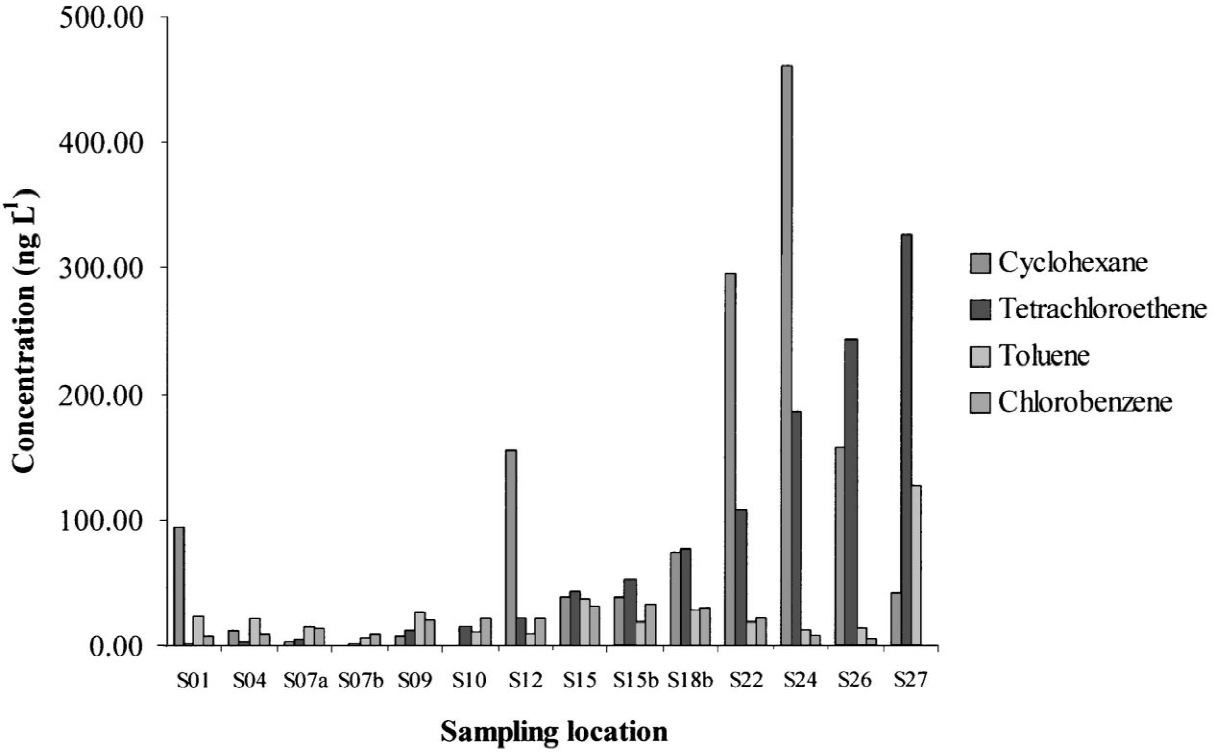


Fig. 5. Concentration profiles of cyclohexane, tetrachloroethene, toluene and chlorobenzene along the Scheldt estuary, from Breskens to Temse (Antwerp) (ng $l^{-1}$).

chloroethene concentration levels significantly decrease from Temse (S27) (326 ng $l^{-1}$) to Breskens (S01) (1.61 ng $l^{-1}$). The exponential curve suggests the existence of other removal mechanisms besides dilution. Volatilisation is very likely to occur while sorption of tetrachloroethene onto riverine sediment is not considered a major sink because of its low log $K_{ow}$ value [49] ($K_{ow}$ = octanol–water partition coefficient). For cyclohexane, toluene and chlorobenzene concentration profiles are less obvious to explain. Concentration levels for toluene and chlorobenzene ranged from 6.67 to 125 ng $l^{-1}$ and 5.16 to 31.5 ng $l^{-1}$ at each sampling station, while several peaks in the vicinity of Antwerp were noticed for cyclohexane.

The recovery of the surrogates was 103.7±10.3% (9.9% RSD) for [$^2$H]chloroform (96.2 ng $l^{-1}$ added), 94.7±12.0% (12.7% RSD) for [$^2H_8$]toluene (60.5 ng $l^{-1}$ added) and 96.3±8.2% (8.2% RSD) for [$^2H_5$]chlorobenzene (74.2 ng $l^{-1}$ added). The samples had been kept at 4°C for ±3 months prior to analysis. No losses due to diffusion, microbial or chemical degradation have occurred during this time.

## 4. Conclusions

This paper describes the evaluation of purge-and-trap–high-resolution gas chromatography–mass spectrometry for the simultaneous determination of 27 chlorinated alkanes and alkenes, monocyclic aromatic hydrocarbons and chlorinated monocyclic aromatic hydrocarbons in marine water samples at the ng $l^{-1}$ concentration level. The organics included ranged from 1,1-dichloroethene (786 kPa; 25°C) to hexachloro-1,3-butadiene (0.2 kPa; 25°C), covering a wide range of volatile organic compounds of environmental interest. The reliability and performance of the analytical method were checked by determining limits of detection, precision and accuracy. All

VOCs could be measured at concentration levels below 6.57 ng $l^{-1}$, except for dichloromethane (41.07 ng $l^{-1}$), chloroform (19.74 ng $l^{-1}$), benzene (22.05 ng $l^{-1}$) and 1,4-dichlorobenzene (20.43 ng $l^{-1}$). At a concentration level of 25.97 to 66.68 ng VOCs $l^{-1}$, the method proved its applicability towards the analysis of all VOCs, except benzene and dichloromethane. Lack of precision and accuracy for these compounds were attributed to the relatively high concentrations found in method blanks as compared to the concentration levels investigated. In the case of dichloromethane the laboratory environment acted as a source of contamination. The presence of benzene in method blanks was attributed to artefact formation from the sorbent material Tenax TA. The use of different trapping materials, compared to the monitoring of 13 VOCs in marine water, allowed the measurement of a broader range of volatile organic compounds, but was accompanied with a considerable increase of LOD for benzene, hence affecting its precision and accuracy. Lowering the desorption temperature would certainly diminish artefact formation. However care must be taken not to alter the desorption efficiency of the target compounds, especially for the high boiling chlorinated aromatics.

Adequate quality assurance and quality control measures were implemented. Analytical quality control charts were constructed at a concentration level of 25.97 to 66.68 ng VOCs $l^{-1}$, and a standard addition test was performed. The analytical control charts of dichloromethane and benzene were not considered satisfactory according to QUASIMEME guidelines at respective concentrations of 44.17 ng $l^{-1}$ and 29.30 ng $l^{-1}$. New charts should be constructed for both compounds at higher concentration levels, while re-evaluating precision and accuracy to find out at which concentration levels reliable measurements can be obtained. The charts were incorporated in a working scheme containing guidelines to ensure the quality of future measurements during routine analysis of water samples. An independent quality assessment of the analytical method was obtained by participating to interlaboratory tests proposed by QUASIMEME concerning the determination of organochlorines in seawater. At a concentration level of 0.78 to 5.41 μg $l^{-1}$ the results of this exercise were considered satisfactory for all organochlorine compounds present.

Samples were taken along the Scheldt estuary, from Breskens to Temse. Concentration levels ranged from 0.33 ng $l^{-1}$ (1,2-dichloropropane) to 461 ng $l^{-1}$ (cyclohexane) near Antwerp. The river Scheldt is known to act as an important source of pollution towards the North sea as enhanced concentrations were found for almost all analytes compared to the adjacent marine water.

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