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## Review

# Anthropogenic volatile organic compounds in ambient air and natural waters: a review on recent developments of analytical methodology, performance and interpretation of field measurements

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### Abstract

This review focuses on a number of specific elements in recent developments of the analysis of volatile organic compounds (VOCs) in ambient air and natural waters. The first element that is discussed is the current status of the sampling methods. Recent advances in sorbent sampling, cryogenic sampling and the combination of both methods for sampling VOCs in ambient air are discussed. Next, some infrequently used sampling techniques are mentioned. As far as the analysis of VOCs in natural waters is concerned, the paper focuses on recent applications of liquid–liquid extraction and the dynamic headspace technique, and on new techniques such as the application of membranes. Secondly, the paper deals with the performance of the analytical techniques. General and specific elements affecting the analytical quality are discussed. In current measurements of VOCs in ambient air and natural waters, control of the analytical performance is not carried out in a systematic way. Finally, the possibilities of using the current techniques in field sample analyses are discussed. Information obtained using the analytical methods provides insights into the concentration levels of VOCs and their sources. By investigating relationships between concentration data of VOCs and environmental factors affecting these concentrations, it is now possible to explain observed variances in the concentrations of VOCs in the environment. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Reviews; Water analysis; Air analysis; Volatile organic compounds

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## 1. Introduction

The technical development of gas chromatography (GC) has undoubtedly contributed to the current analytical possibilities of measuring volatile organic compounds (VOCs) in the environment. This field of application of analytical techniques is one of growing interest because of awareness of the impact of VOCs on several aspects of the global environmental system. Indeed, several effects of VOCs are recognized, such as their contribution to stratospheric ozone depletion, tropospheric photochemical ozone formation, toxic and carcinogenic human health effects, enhancement of the global greenhouse effect and accumulation and persistence in the environment of recalcitrant pollutants [1–3]. Chromatographic methods have led to a better understanding of the importance of the occurrence of VOCs in the global environment, as well in the atmosphere, water bodies as in solid compartments.

It is clear that field applications of an analytical procedure do not imply only the analysis *in sensu strictu*, i.e. the separation and detection of compounds. This can be seen from the topics investigated in research papers published during the last five to ten years on the measurement of VOCs in the environment. In most of them, the performance of GC systems in combination with flame ionisation detectors (FIDs), electron capture detectors (ECDs), photoionisation detectors (PIDs) and mass spectrometers (MSs), proved to be acceptable for separating and quantifying VOCs at environmental back-

ground concentration levels (ppb and ppt) [3,4]. It is noticed from recently published work that more research has been carried out on developing appropriate sampling and preconcentration techniques. This is also clear from the diversity of sampling and preconcentration methods that have been developed.

Next to the topic of sampling, it can be seen from the recent literature that attention has been paid to analytical quality assurance. However, approaches to assess and guarantee the overall quality of measurements of VOCs in environmental samples have not been implemented systematically. Nevertheless, reported results of field measurement campaigns have been proven to be valuable in obtaining a better understanding of the environmental occurrence and behaviour of VOCs.

The purpose of this work is to present an overview of recent methodological developments in the field of analysis of VOCs in ambient air and natural waters. In studying recent literature on the analysis of VOCs in both air and water, it can be found that these two research fields have a number of common elements. For example, parallels can be found at the preconcentration, separation and detection stages. Emphasis in this overview will be placed on the sampling and preconcentration step rather than on separation and detection techniques. Following on from this, the use of parameters and methods to assess and to guarantee analytical performance will be discussed. Finally, by giving an overview of recent applications of the techniques in the field, the information that has been generated will be illus-

trated by interpretation of the analytical results. The literature discussed in this overview is mainly information published during the last four to five years in international peer-reviewed journals in the field of analytical and environmental organic chemistry.

## 2. Sampling of VOCs

For the determination of VOCs both in ambient air and natural water matrices, in almost all applications, VOCs are first preconcentrated, either at the sampling location or after transport of the whole sample matrix to the laboratory. In a second step, GC analysis is performed to separate, identify and quantify the VOCs. However, it has to be mentioned that, for the determination of VOCs in air, the use of optic techniques has been mentioned recently [5–8]. Differential optical absorption spectroscopy (DOAS) operates at wavelengths between 230 and 270 nm, which enables the measurement of BTX compounds (benzene, toluene and xylenes) [5–7]. The accuracy of the technique is not yet fully controlled [7]. This is illustrated by an intercomparison study in the city of Göteborg where the DOAS method was compared to sorbent sampling and GC analysis [6]. The author concluded that the results obtained for BTX compounds using the DOAS technique were unsatisfactory. It was found that, at zero concentrations, the DOAS technique generated measured concentrations of 34 and 44  $\mu\text{g m}^{-3}$  for benzene and toluene, respectively.

### 2.1. Air

The most widely applied preconcentration techniques are the sorbent sampling technique, the cryogenic sampling method and canister sampling [3]. To a lesser extent, passive sampling has been reported. Essentially, canister sampling is not a preconcentration technique. It requires a subsequent sorbent or cryogenic concentration stage at the laboratory. The major advantage of canister sampling is that it allows one to analyse a single collected sample several times, which is not the case for a cryogenically collected or sorbed sample. For these latter sampling methods, all collected VOCs have to be introduced simultaneously into the GC. Critical

points in the canister sampling technique (humidity, wall adsorption, conditioning) have been discussed previously [3]. In addition, canister sampling involves a relatively high cost (e.g. transportation) and requires sophisticated equipment for the cleaning procedure [9].

After preconcentration, either cryogenically or by sorption, all VOCs have to be brought into the GC instrument in a rapid and quantitative way. Samples collected on sorbents can be introduced by thermal or solvent desorption. If thermally desorbed, a second preconcentration step may be necessary in order to achieve good chromatographic separation. This is frequently done by cryogenic trapping. Cryogenically concentrated samples can be introduced into the GC instrument immediately by rapid heating of the trap.

#### 2.1.1. Sorbent sampling at ambient temperature

Preconcentration of VOCs in ambient air on solid sorbents has been reported frequently in the literature recently. An ideal sorbent for preconcentrating VOCs from an air matrix need to have four main properties, i.e. infinite breakthrough volume (BTV) for the compounds to be sampled, complete desorption of the target compounds at moderate temperatures, no generation of artefacts and no retention of water vapour. Moreover, it must be possible to seal the sorbent completely from the atmosphere so that contamination before and after sampling can be excluded. No single available sorbent material meets all of these criteria. The determination of the BTV of sorbent materials has been discussed in a number of recent papers [10–15]. The BTV problem can generally be solved by selecting a sorbent material appropriate for the range of target VOCs. In this respect, we noticed that there is a tendency to use multiple sorbents, which allows one to focus on a wide range of VOCs [16–28].

A more difficult issue is the retention of water on the sorbents. It has been shown that some sorbent materials that have high BTVs for VOCs do retain large quantities of water vapour (e.g. Carbosieve SIII) [29,30]. Several options to reduce the amount of water that is brought into the GC system via the sorbent materials are found in the literature. A first possibility is to avoid the use of sorbent materials with high water retention [20]. A second strategy to

reduce interference by water is to minimise water retention at the sampling stage. This can be done by installing a tube with hygroscopic salts [ $K_2CO_3$ ,  $MgCO_3$ ,  $Mg(ClO_4)_2$ ] in front of the sampling tube [31]. Another possibility is the use of a water-sorbing polymer (Nafion) in front of the sampling tube. It has to be mentioned that loss of VOCs can be caused by the use of this hygroscopic polymer [17,32,33]. The approach of Haunold et al. [23], however, counteracts (at least partially) the retention of VOCs on the Nafion material. The authors inserted the Nafion tube between two sampling tubes instead of placing the dryer in front of the sampling tube(s). In this set-up, the positioning of the first, less water-retaining sorbent material (Tenax) in front of the Nafion tube allowed them to sample less volatile VOCs without the loss caused by the Nafion tube. A second sorbent tube with a higher affinity for water (Molsieve and Carbosieve), placed after the Nafion dryer, was used to sample the more volatile compounds ( $C_2$  to  $C_5$  compounds). In a third option, water can be prevented from entering the analytical instrument at the sample injection stage. For example, Knobloch et al. [34] used a dry helium purge (2 min,  $70^\circ C$ ) in order to remove water from a Carbotrap C/Carbotrap tube. However, since they realised that loss of VOCs could occur in this way, they directed the purge gas to a Carboxen 569 tube, which was subsequently also subjected to a dry purge (4 min,  $80^\circ C$ ). Control of the water removal method showed no losses of VOCs, except for  $C_1$  and  $C_2$  hydrocarbons. Dewulf et al. [21,35] reduced water interference by leading the gas stream with VOCs (and water) desorbed from a Carbopack B/Carbosieve SIII trap to a condensing trap ( $-10$  to  $-15^\circ C$ ) before adsorbing the VOCs onto a second sorbent trap.

Artefacts can be generated in different ways by the sorbent sampling technique. First of all, the sorbent material itself can generate artefacts by degradation. This is of particular importance for polymer-type sorbent materials such as Tenax [36]. Clausen and Wolkoff [36] observed different degradation products of Tenax after exposure to  $O_3$ ,  $NO_2$  and limonene. Among other unidentified degradation products, benzaldehyde, phenol, acetophenone, benzoic acid, dibutyl phthalate, 2,6-diphenyl-*p*-benzoquinone and 2,6-diphenyl-*p*-hydroquinone were found. A second

way in which artefacts can be generated is by the conversion of compounds from the sampled air at the sorbent sampling stage. This mechanism is of key importance in sampling unsaturated compounds (e.g. styrene, cyclohexene and monoterpenes) with Tenax, due to reaction with ozone during sampling [37–40]. This results not only in artefacts but also in loss of the compounds to be quantified. A recent review discusses several ozone removal techniques in order to minimise this interference [41]. Reported ozone removal techniques combined with the sampling of VOCs are the use of  $Na_2S_2O_3$ ,  $K_2CO_3$ ,  $MgSO_4$ , KI and Ni. A recent application of KI for  $O_3$  removal in the measurement of volatile oxygenated hydrocarbons has been mentioned [42].

A wide range of solid sorbents have been used in the measurement of VOCs in ambient air, such as activated carbon, graphitized carbon blacks (Carbotrap, Carbopack, Carbograph, Graphtrap, Graphon, Spheron), porous carbons (Carb, Hypercarb), carbon molecular sieves (Carbosieve, Carboxen, Purasieve, Sphero carb, Sortophase, Carbosphere, Saran Carbon, Ambersorb) and carbon-based porous polymers (Tenax, Chromosorb, Porapak, Hayesep, Amberlite resins) [43,44]. Nevertheless, research on the development of new types of sorbents has been reported [10,12,45–49]. Slovakian investigators evaluated the use of pyrolysis products of saccharose and cellulose (pyrolysis in the presence of silicagel) as sorbent materials combined with solvent desorption (carbon disulphide or pentane) [46–48]. Other materials investigated are new graphitized carbon blacks [12], activated carbon manufactured from pith with a low ash content [45], carbon molecular sieves made by dehydrohalogenation of poly(vinylidene chloride) [45] and, especially, cleaned crosslinked styrene [45]. Basically, all of these sorbents are not new types of sorbent materials: they can be classified in one of the categories mentioned in the preceding reviews [43,44]. The polydimethylsiloxane (PDMS) polymer, however, is basically a new type of sorbent since it is based on an absorption process [10,49]. The PDMS polymer has some possible advantages when compared to the other materials. First, water retention is low. Secondly, the degradation products of the polymer are usually not compounds that are to be detected in ambient air sampling. Furthermore, since PDMS is a widely used polymer in GC,

information about sorption equilibria can be gained from research work done in the field of GC (e.g. Kovats indices as estimates for gas/polymer equilibrium coefficients). The main limitation however in the development of PDMS as a sorbent material is the mass transfer velocity of the compounds from the air matrix to the polymer. Whereas the absorption process in capillary GC with PDMS stationary phases is carried out with gas flow-rates of 1–5 ml min<sup>-1</sup>, ambient air sampling is usually performed with flow-rates of 100–500 ml min<sup>-1</sup>. Compared to previous evaluations of PDMS in air sampling [50,51], the recent work of Baltussen et al. [10] investigated the possibilities of using particulated PDMS materials instead of capillary tubes. PDMS particles with an average length of 0.63 mm were prepared by grinding silicone tubing (0.3 mm I.D.; 0.63 mm O.D.). This sorbent material allowed them to sample air at a flow-rate of 460 ml min<sup>-1</sup> through a single sampling tube in a field application (total sample volume, 52.4 l). The mentioned work focused on less volatile compounds (decane, 1-octanol, 2-nonanone, dodecane and polycyclic aromatic hydrocarbons).

Another trend in the development of sorbent sampling techniques is to place the sorbent trap in an on-line position with the subsequent analytical sequence. This can be done with micro-traps (with I.D.s about 0.5 mm), which allow rapid heating of the sorbent and immediate on-line injection of the VOCs into a GC detector system [52–55]. This configuration can give new possibilities in the on-site monitoring of VOCs. However, due to the limited quantities of adsorbent material that can be used (e.g. 0.02 g [55]), limited sample flow-rates and sample volumes are obtained, resulting in operations at the ppmv level. Nowadays, typical on-site monitoring methods involve cryogenic- or sorbent-trapping combined with a second (pre)concentration step, which allow detection at sub-ppbv levels [56].

### 2.1.2. Cryogenic sampling

The cryogenic sampling technique has been discussed recently [3]. Compared to the sorbent sampling technique, cryogenic sampling prevents the generation of artefacts caused by the sorbent trap material. However, artefact formation due to reaction of the compounds to be sampled with ozone during

the sample stage can occur [41]. In addition, the cryogenic technique has to deal with water interference, even more so than the sorbent sampling technique because cryogenic preconcentration is carried out at very low temperatures ( $\leq -150^{\circ}\text{C}$ ) so that water vapour can be trapped quantitatively. Interference by water can be handled during the sampling stage in front of the cryogenic unit [57]. An alternative method consists of two subsequent cryoconcentration steps. The first cryogenic unit is heated slowly after sampling so that the bulk of the water vapour trapped during the first stage is prevented from being transferred to the second trap [58,59]. A specific field of application of the cryogenic preconcentration technique is the measurement of sulphur compounds because application of the sorbent sampling technique is difficult due to weak trapping efficiency and desorption recovery from sorbent materials [60,61].

### 2.1.3. Sorbent sampling at reduced temperature

According to recent literature, sorbent sampling is also done at reduced temperatures [23,31,62–67]. Basically, this approach is a sorbent sampling technique and has to be distinguished from cryogenic techniques that involve only solid glass beads in order to improve heat and mass transfer [68–70]. However, the possibility that higher boiling compounds simply condense, either on the sorbent or on the inner surface of the cryogenic device, cannot be excluded.

Ciccioli et al. [62] investigated the possibility of using cryogenic microtraps (1 mm I.D.) filled with Carboxpack B graphitized carbon. Water interference was prevented by installing a Nafion membrane in front of the enrichment trap, which allowed the collection of 2-l samples. It was concluded that the system was able to determine C<sub>2</sub> to C<sub>7</sub> hydrocarbons in ambient air at levels of 0.01 ppbv. Haunold et al. [23] reported that C<sub>2</sub> compounds could be sampled by means of Carboxisieve SIII/Molsieve traps cooled down to  $-30^{\circ}\text{C}$ . A Peltier element, which was cooled by means of cooling water at the warm site of the element, was used for cooling. The use of dry ice to cool down a Hayesep Q resin to  $-60^{\circ}\text{C}$  to sample volatile halogenated hydrocarbons and small polar alcohols, which, in general, have smaller BTVs was reported by Kivi-Etelälä et al. [31] (total sampled

volumes  $\leq 3$  l). Activated charcoal traps at  $-15$  to  $-20^\circ\text{C}$  allowed  $\text{C}_2$  to  $\text{C}_6$  compounds, with total sample volumes of 1.2 L, to be sampled, with the limitation being the breakthrough of ethane [63–65]. Moschonas and Glavas [66] reported improved retention of  $\text{C}_2$  compounds (ethane, ethylene and acetylene) by introducing Carbotrap in a glass bead cryotrap at  $-180^\circ\text{C}$ . However, the recovery of *o*-xylene was reported to decrease by 22–46% due to insufficient desorption. A microloop cryogenic sample loop (50 or 100  $\mu\text{m}$  I.D.) coated with different silicone materials has been tested by Borgerding and Wilkerson [67] at the laboratory level for 10 ppbv mixtures.

#### 2.1.4. Passive diffusive sampling

A limited number of studies on the use of passive diffuse sampling followed by solvent desorption can be found [71,72]. This way of sampling allows atmospheric concentrations averaged over longer periods (e.g. several weeks) to be monitored. However, some drawbacks of this sampling method have to be mentioned. Air concentrations have to be calculated based on an average uptake rate coefficient, so that variations in the concentration level can give rise to bias. In addition, wind speed may influence the uptake rate. The effect of wind can be counteracted by providing a shelter [71,72], although the effect cannot be totally excluded. Monn and Hangartner [72] reported that wind speeds between 0.5 and 3.0  $\text{m s}^{-1}$  were smoothed in the shelter box to 0.2 to 0.6  $\text{m s}^{-1}$ . Furthermore, blank levels of unexposed monitors have to be considered [71]. This means that data from exposed samplers have to be corrected with these blank levels. Begerow et al. [71] stated that it is necessary to correct concentrations from exposed samplers with data from unexposed monitors from the same series of purchased samplers since the blank levels can depend on the production batch of samplers. When compared to a dynamic sampling system, systematic underestimation by 1.7  $\mu\text{g m}^{-3}$  for benzene and overestimation by 0.6  $\mu\text{g m}^{-3}$  for toluene were observed during passive diffuse sampling at concentrations of 1–4 and 15–40  $\mu\text{g m}^{-3}$ , respectively [72].

## 2.2. Water

For the determination of VOCs in water, a wide

range of techniques have been developed, as discussed in a number of recent reviews [2,4,73]. Direct aqueous injection of the sample, static headspace techniques, dynamic headspace techniques, liquid–liquid extraction, solid-phase extraction, membrane techniques, solid-phase microextraction and distillation techniques are used as sample preparation techniques. The number of techniques applicable for natural waters, however, is limited, mainly because of the low concentrations of VOCs in these types of water bodies (ppb to ppt levels). Therefore, high preconcentration factors are required in sample preparation. This is not accomplished with direct liquid injection. Also, the preconcentration factors obtained in the static headspace and solid-phase microextraction techniques are too limited to be able to determine VOCs in most natural waters. Ketola et al. [74] concluded from a comparative study that detection limits of the static headspace technique are 10- to 100-times higher than those of the purge and trap technique. The most frequently used techniques investigated in the determination of VOCs in natural waters are liquid–liquid extraction and dynamic headspace (purge and trap technique). Next, the development of some recent new techniques are mentioned.

#### 2.2.1. Liquid–liquid extraction

The liquid–liquid extraction technique with the use of an organic solvent is an efficient preconcentration technique because of the apolar character of a large number of VOCs. Recent applications for natural waters are mentioned in Refs. [75–80]. There are three main drawbacks to the extraction technique. First of all, the occurrence of the solvent in the chromatogram can limit the range of VOCs that can be measured. Next, the volatile character of the compounds to be extracted is a limitation. Whereas in a number of applications of the technique for less volatile compounds further concentration is achievable by partial evaporation of the solvent, this is not the case for the analysis of VOCs. This is clear from the work of Desideri et al. [78], who observed losses of 43–46% for xylenes when 5 ml of *n*-hexane extracts were evaporated to volumes of 50–100  $\mu\text{l}$ . The third disadvantage of the technique is the limited fraction of solvent that can be injected, resulting in moderate limits of detections. Due to this disadvantage, the extraction technique has been mainly

applied in combination with the highly sensitive ECD detector. It has to be mentioned that the development of large volume injections allows one to increase the injected volumes of solvent up to several hundreds of microliters [81,82]. This technique is a proper sample introduction method for semi-volatile organic compounds, such as pesticides [83–87], polycyclic aromatic hydrocarbons [88] and extractable chlorinated organic compounds (e.g. hexachlorobenzene) [89]. However, due to the volatility of the compounds considered in this paper, large volume injection in combination with solvent vaporization is questionable due to potential losses of the target compounds during the vaporization process. Grolimund et al. [90] mentioned a loss of about 12% for toluene when a large volume of pentane was injected. Therefore, it may be questionable whether this technique is suitable for eluting VOCs in front of toluene or not.

### 2.2.2. Dynamic headspace (purge and trap technique)

A wide number of applications of the dynamic headspace technique can be found in recent literature [35,80,91–102]. Here, VOCs are extracted by purging a water sample with an inert clean gas stream. The purging is usually performed by bubbling the gas stream through the water matrix. However, Hino et al. [103,104] performed the purging by leading the inert gas stream only through the headspace of the sample vial.

The gas stream leaving the purge vial and being enriched with the volatiles is then led through a unit where the volatiles are retained, whether by cryofocussing or on a sorbent material (purge and trap). Subsequently, the VOCs are brought onto the GC column by heating the cryo- or sorbent trap. When sorbent-sampling is used, cryogenic refocusing after thermal desorption is often done in order to obtain sharp peaks on the chromatogram. Zygmunt [102] reported the development of a sorbent micro-trap as a refocusing unit.

The major advantage of the purge and trap technique is that all VOCs present in the analysed sample can be transferred to the cryo- or sorbent trap and subsequently to the GC unit, resulting in low detection levels. In a similar manner to that used in the preconcentration of VOCs from ambient air, sorbent concentration is performed at a reduced temperature.

Ekdahl and Abrahamsson [98] evaluated five sorbent materials at temperatures of between 5 and  $-10^{\circ}\text{C}$ . The reduced temperature allowed the use of packed traps of smaller dimensions. Furthermore, the dynamic headspace technique can be automated more readily than liquid–liquid extraction.

The major drawbacks of the dynamic headspace technique are twofold. First, it requires complex instrumentation, including a purge gas device, purge gas, a sample vial and a sorbent or cryogenic trapping unit, equipped with a heating device. When compared to the liquid–liquid extraction technique, the dynamic headspace technique results in longer analysis times, which is typical for headspace techniques, whether they are static or dynamic. It must be stated that the analysis time is not only affected by the preconcentration technique, but also by the subsequent GC analysis. Next, the more complex equipment may give rise to possible sources of contamination. In this regard, the static headspace method is a simpler technique. In addition, the liquid–liquid extraction technique is less subject to contamination generated by equipment. In this technique, however, impurities in the solvent may contribute to inaccurate quantification.

The second disadvantage of the dynamic headspace technique is related to the water vapour generated at the purge stage. Water vapour can interfere with the subsequent separation and detection. Therefore, some authors mention the insertion of a water-removing trap between the aqueous sample and the cryo- or sorbent trap. Water removal has been performed using hygroscopic membranes (Nafion) [80,99,100,102,105], magnesium perchlorate [98],  $\text{CaCl}_2$  or  $\text{NaCl}$  [91], condensation [35,95–98] or a dry purge stage [74,106]. A dry purge stage for a Tenax adsorbent at temperatures of between 40 and  $80^{\circ}\text{C}$  resulted in recoveries of between 63 and 78% for three compounds investigated, i.e. toluene, chlorobenzene and *m*-xylene [106].

### 2.2.3. Recent new techniques

Some new trends in the development of techniques for the measurement of VOCs in natural waters can be found in the literature. Most of this recent work dealt with the development of the analytical technique at the laboratory, field applications of the new analytical methods being rather limited.

The use of membrane materials in the analysis of

VOCs in water has been investigated [107–111]. In this approach, VOCs at ppb concentrations were allowed to permeate from a water sample stream through a polysiloxane capillary into a gas stream. Subsequently, the compounds were collected in a sorbent microtrap [107,110] or in a cryotrap [108,110]. Limits of detection in the ppt range have been achieved with FID detection for monocyclic aromatic hydrocarbons and 1,1,1-trichloroethane [111].

Another approach is the direct combination of membranes with mass spectrometry. VOCs are allowed to move from an aqueous matrix into a mass spectrometer system, without the need for any pre-concentration. The possibilities of this membrane inlet mass spectrometry (MIMS) technique are outlined in Ref. [74,112]. The insertion of a jet separator between the membrane and the MS detector has been investigated [113], and Mendes et al. [114] investigated the possibility of inserting a cryotrap between the membrane and the MS detector. Ojala et al. [115] reported the measurement of volatile sulfur compounds with limits of detection below the ppb level by means of MIMS. In situ measurement of VOCs on the sampling site has been reported [116]. The combination of purging water samples and membrane MS has been reported by Kostianen et al. [117]. In this method, the purge gas with VOCs is directed to a sheet membrane module, allowing the permeation of the compounds from the gas phase through the membrane towards the MS. The major advantage of the membrane techniques in comparison with the purge and trap technique is that the selectivity of the preconcentration is better, due to the apolar character of the membranes, resulting in less problems with interferences from water. However, this weak polarity of the membrane simultaneously limits the number of target compounds; it is not suitable for the analysis of more polar VOCs.

Another MS application in the field has been reported by Davis et al. [118]. VOCs were purged out of ground water at the site and were transferred via a PTFE line to a direct sampling ion-trap mass spectrometer, equipped with a capillary restrictor. Limit of detections were in the ppb range. MS detection was based on single ions, therefore, it is subjected to incorrect identification and hence quantification.

Also a purge and spray technique has been

investigated. Similar to the purge and trap technique, VOCs are transferred from an aqueous sample via a gas phase towards an adsorbent trap [119–121]. The gas–liquid exchange in the spray and trap technique is enforced by a spray contact instead of gas bubbling, as in the purge and trap technique. The major advantage of this technique is that it can be applied to the analysis of water samples with high contents of surfactants.

### 3. Analytical performance

#### 3.1. General aspects

In order to evaluate the analytical performance of an elaborated analytical technique, several criteria should be mentioned. The performance of a technique can be validated by considering a number of specific analytical characteristics, as mentioned in Table 1. The overall analytical performance of a technique, however, does not depend only on such particular analytical criteria. It also depends on a number of general measures. The analytical work has to be carried out by experienced and qualified staff members and with an adequate technical structure. Next, general rules of good laboratory practice, including sample and data treatment, have to be implemented in a systematic way. The availability of protocols for the identification of samples and for analyses, written standard operating procedures and structured data records can enhance the assurance of the quality of the analyses. Since the measurement of VOCs in ambient air and natural waters is increasingly applied on a routine basis, general procedures applied in the analytical quality control and assessment of routine analyses can be integrated in order to

Table 1  
Specific elements in the validation of an elaborated analytical technique

Limit of detection
Limit of quantification
Reproducibility
Repeatability
Accuracy
Calibration curve
Specificity
Range of application



improve the quality of the analysis of VOCs in the environment.

### 3.2. Specific aspects

The developed analytical procedure has to be assessed on the basis of a number of specific parameters of the analysis in *sensu strictu* (Table 1). Reported research in the field of analysis of VOCs in ambient air and natural waters generally includes the assessment of such parameters as reproducibility or repeatability, and limits of detection of the technique, as illustrated in previous review papers [3,4,73]. However, the limit of quantification is usually not mentioned.

The quality of the analysis is also related to the traceability of the compounds in the matrix. For example, at urban sites, concentrations of atmospheric VOCs can be in the ppbv range, whereas measurements at remote continental or marine sites show levels in the pptv range. This results in relative standard deviations better than 10%, and up to 20 to 30% if concentrations are in the pptv range [3].

The accuracy of the reported techniques is a more difficult element to assess. Bias in the quantification can be caused either by inaccurate integration of the results obtained for the sample or by applying an incorrect calibration reference. Inaccurate integration of a sample can be due to the contributions of non-blank levels. This point has been assessed in ambient air analysis by several authors [17,21,25,66,122,123].

A second source of inaccurate integration of the VOCs in the sample is incorrect identification of the compounds. This means that the specificity of the technique is unsatisfactory. It can be the case when one single non-selective detector is used. In order to ensure identification, structural information given by MS detection is a useful tool, either used as a routine detector or as a confirmation tool, for e.g. ECD and FID detection. Another possibility is to analyse samples on different types of GC columns so that the availability of different specific retention times enhances the means of peak identification [124,125]. The use of MIMS without previous GC separation can cause inaccurate quantification, as illustrated by Ketola et al. [74] for the analysis of VOCs in water. In a comparative study in which MIMS, static and

dynamic headspace techniques were investigated, it was shown that overestimation of concentrations with the MIMS technique was observed for some real samples. The authors explained this overestimation as being due the contributions of fragment ions of minor unidentified compounds to the mass spectrum.

Furthermore, incorrect calibration tools can cause bias in the quantification. In general, the preparation of calibration mixtures of VOCs in a water matrix is easier to achieve than in air matrices. Aqueous mixtures can be prepared by liquid dilutions (e.g. via intermediate acetone or methanol solutions) and can contain as many (liquid) target VOCs as have to be calibrated. The preparation of reference materials for calibration of VOCs in ambient air is more complex. The main reason is that gas mixtures containing a wide range of VOCs at ambient air concentrations in the pptv to ppbv range are not easily available or cannot easily be prepared. In this respect, it has to be noted that, in a large number of papers, calibration is merely mentioned [3]. A number of papers report the use of liquid injection into the GC detector system as a calibration approach [3]. However, this is basically not a gas calibration technique. Most reported calibration materials are dilutions of pure liquid compounds or purchased gas mixtures, whether used after dilution or not. Methods that are mentioned less often are the use of permeation tubes [42,126] and calibration by means of headspace from closed two-phase systems [21,35]. Dilution methods, whether starting from pure liquid compounds or from gas mixtures, are subjected to bias due to interaction of the compounds with the used materials. Wall adsorption in canisters under specific conditions is a known phenomenon [33,127,128]. Also sorption processes in Tedlar bags have been described [31,129]. The major advantage of dilution methods is that a wide number of VOCs can be involved. Borowiak and De Saeger [130] used calibration mixtures containing 26 compounds, whereas the calibration standards of Oliver et al. [25] and McClenny and Colon [24] contained 41 compounds. In addition, mixtures made by dilutions can be freshly prepared. Purchased mixtures at ppbv levels, however, are usually limited in the number of VOCs that they contain. Moreover, they are guaranteed for a limited period. The major obstacle to employing

purchased mixtures are the high costs and the limited number of compounds in the mixture. The undiluted mixtures used by Knobloch et al. [34] and Laurila and Hakola [131] contained only *n*-butane and benzene. This means that, for quantification of other compounds, relative quantification methods are needed. Some authors prefer quantification on a ppb C approach [132], whereas others use relative response factors from literature data [23]. It is clear that all of the ways of calibrating VOCs in ambient air have limitations and may contribute to bias.

Finally, incorrect calibration can be generated by non-linearity if the standard calibration materials being used have concentrations that are an order of magnitude higher (or lower) than those present in the sample. The range of application of the technique is not systematically investigated. In calibrating the measurement of VOCs in water, investigation of linearity is frequently reported in the development of techniques [74,98–100,110,111,113–115,118–120]. In the analysis of VOCs in ambient air at low pptv levels, however, non-linearity can give rise to bias, since preparation of calibration mixtures at pptv levels is usually not done. Greenberg et al. [59] noted that mixing ratios below 15 pptv are unachievable because of concentration levels in the zero gas stream used for dilution.

### 3.3. Control of analytical performance

Next to the enhancement of the analytical quality by awareness of the previously discussed elements, analytical performance can be assessed by investigation of additional specific tools, e.g. standard addition tests, the use of surrogate compounds and the setting up of quality control charts. The ultimate way to validate the developed in-house analytical performance is comparison with other laboratories.

The harmonisation work of the European Reference Laboratory of Air Pollution showed that the results of an intercomparison test for atmospheric ozone measurements with nine participants from seven countries were within a tolerance limit of 5% [130]. Round robin results for the determination of VOCs in ambient air, however, were much weaker [130]. The results for 26 hydrocarbons at 5 to 50 ppbv with 21 laboratories routinely dealing with air quality measurements showed deviations of about

20%, using one compound within the mixture as a reference compound. The round robin results of an air sample with concentrations below 5 ppbv showed mean deviations of about 50%. The authors concluded that systematic errors can be due to the sampling method employed, and to analytical and calibration procedures. Better results are presented for C<sub>2</sub> to C<sub>5</sub> compounds in ambient air by Laurila and Hakola [131]. Comparison of data from (only) two groups showed deviations that were usually below 10% for concentrations above 200 pptv. For concentrations below 200 pptv, deviations could be up to 40%. Apel et al. [133] concluded from an intercomparison test that the analytical performance of laboratories all over the world for the analysis of VOCs in ambient air is unsatisfactory. Reticence to interpret atmospheric concentrations of VOCs based on measurements carried out by different laboratories can be found in the work of Rudolph et al. [134]. These authors did not include measurements from other laboratories in the study of concentrations of tetrachloroethylene in the atmosphere. In the EMEP programme, air samples collected at sites all over Europe are transferred to and analysed in a single laboratory [132].

Interlaboratory tests for the analysis of VOCs in water have also been reported [135–137]. The participation of 20 laboratories for the analysis of VOCs at ppbv levels with solid-phase microextraction, and static and dynamic headspace analysis showed deviations below 30%. However, the concentrations were of the order of those observed in ground water and drinking water instead of those in natural surface waters. Wells and Cofino [136] mentioned that an interlaboratory test for six chlorinated VOCs in sea water consisted of only nine participating laboratories, which may scientifically (and financially) be too low to be viable. Gardner et al. [135] observed, from the UK interlaboratory tests, that the achieved accuracy of the analysis of six chlorinated VOCs in sea water at a concentration >10 ng l<sup>-1</sup> met a maximum tolerable error of 50%.

In conclusion, the available intercomparison results suggest that the interlaboratory tests are not carried out systematically and on a large international scale for VOCs in ambient air and natural waters. The results of the analytical tests show that the analytical performance of laboratories is capable of

improvement. The implementation of a standard approach, in which all aspects of analytical quality are investigated in a systematic way, could enhance the analytical quality of the data produced, improving the possibilities of interpretation.

#### 4. Interpretation of field measurements

Although it is clear from the previous paragraphs that the development of analytical techniques that can be used to determine VOCs in ambient air and natural waters is not finalised, a large number of applications in the field are published. Some of them are single casual measurements, just illustrating the capabilities of the developed technique under field conditions. Others provide larger sets of data, acquired according to a predefined sampling strategy, allowing a more profound interpretation of the measurement results. The results of these campaigns can be interpreted on two levels. On the first level, the analytical data provide information on concentration levels at a specific site. Spatial location with respect to the sources of the measured VOCs can be integrated in the discussion. On the second level, sources of variations for the measured concentrations at single sampling sites can be investigated.

##### 4.1. Interpretation of observed concentration levels

###### 4.1.1. Ambient air

The influence of the proximity of anthropogenic sources on the level of concentrations of VOCs in ambient air at remote sites has been illustrated in a previous paper [3]. Recent illustrations of the effect of the proximity of anthropogenic sources are clear from several field measurements [5,22,34,35,64,71,72,132,138–143]. Specific anthropogenic activities have been mentioned to explain observed concentrations, such as industrial activities [16,70,140,141,144], vehicle exhaust in highly populated areas [5,22,34,71,72,132,141,144–148], solvent use [71,141] and fuel evaporation and spillage [132]. Chattopadhyay et al. [142] concluded that BTX patterns measured in Calcutta (India) were generated by emissions from coal-burning cooking stoves.

###### 4.1.2. Natural waters

Concentrations of VOCs observed in estuaries and rivers can be affected by nearby industrial sources and densely populated areas [35,80,93,96,101,149]. Generally direct discharges are assumed as sources of VOCs. However, anthropogenic inputs via atmospheric transport are also reported as an input mechanism [35,97,150,151]. At remote sites, very low concentrations ( $\text{ng l}^{-1}$  level and lower) can be explained by the absence of nearby sources [77,80,152,153]. In explaining the concentrations of VOCs at marine sites, contributions of biogenic sources have to be taken into account in the interpretation [35,97,98,154].

Bianchi and Varney [97] investigated several types of VOCs in the Southampton Water estuary. They observed ratios for the monocyclic aromatic hydrocarbons ethylbenzene-*p*-xylene-*m*-xylene-*o*-xylene of 1.4:1.0:3.5:1.9, these being typical ratios found in the volatilised fraction of gasolines, light fuel oils and distillates used in industrial, domestic and marine fuels. Marinas and boat traffic are also suggested as being important sources of aromatics. For the measured levels of alkanes and alkenes, the authors mentioned the semi-industrialised character of the estuary, next to shipping and boating activity and biogenic sources. Various uses and applications of chlorinated VOCs by man are reported in order to explain estuarine concentration levels. Alcohols and ketones (e.g. methyl isobutyl ketone) are mainly anthropogenic in origin, with highest concentrations being found near industrial complex and raw sewage outfalls. The anthropogenic sources of aldehyde- and sulfur-containing VOCs are reported to be of minor importance to the observed levels in the estuary, when compared to biogenic sources.

##### 4.2. Interpretation of variations in observed concentration levels

###### 4.2.1. Ambient air

A first source of variation of observed concentrations of VOCs at a single sampling site is the analytical work itself. Spicer et al. [139] showed that the variability in measurement generally contributed 10 to 25% to the total variance of measured ambient concentrations of VOCs in Columbus (USA). A

second source of variation can be fluctuations in the intensity of the sources [5,132,141,144,145]. This is illustrated by diurnal patterns of aromatic hydrocarbon levels at urban sites where the patterns of the measured compounds followed the intensity of traffic during the day [5,141]. Cheng et al. [144] suggested that higher summer concentrations could be partially explained by increased industrial emission rates from storage tank evaporations.

Meteorological factors also affect the observed concentration levels. When air masses of different origins can be sampled at a single site, high fluctuations are observed depending on the wind direction [16,17,35,70,131,138,140,143]. This is well illustrated at coastal sampling sites, where continental and remote marine air masses can be sampled [17,35,70,138]. The level of atmospheric turbulence can also affect the dilution of emitted air masses with more uncontaminated air masses [17,144]. Limited dilution of emitted VOCs is observed with periods of inversion [72,139,141,142]. Higher concentrations at night were explained by concentration build-up due to trapping of VOCs in air layers beneath low-lying nocturnal inversions [139,141].

Next to these direct meteorological effects, the meteorological conditions influence the atmospheric stability of compounds. This results in diurnal variations due to faster atmospheric degradation during daytime than at night [57]. Seasonal cycles caused by enhanced degradation in summer and slower degradation in winter have also been noted [5,34,59,131,132,142,144,146,155]. This is of special importance for compounds that are easily degradable by reaction with OH-radicals, such as alkenes [64].

#### 4.2.2. Natural waters

Several causes giving rise to variations in concentrations of VOCs in natural waters at a given site can be mentioned. First, fluctuations in the source contributing to the observed concentration levels have to be mentioned. Changes in the emissions of VOCs were indicated to explain variation in the concentrations of VOCs in urban rivers on a diurnal basis and on a time scale of days [101]. Long-term variations in source intensity have been studied by Bianchi and Varney [151]. Concentrations of aromatic VOCs at the Southampton Water estuary in the last decade (e.g. mean toluene concentration,  $5 \mu\text{g l}^{-1}$ ) were reduced when compared with measure-

ments reported in the seventies (e.g. mean toluene concentration, about  $200 \mu\text{g l}^{-1}$ ), due to significant improvements in emission control technologies employed by the petrochemical industries. Levels of 1,1,1-trichloroethane and Freon-113 proved to be reduced when compared to data from the eighties, possibly due to international regulations for their use. In contrast, trichloroethylene and tetrachloroethylene showed increased concentrations, suggesting larger usage of these substances.

On a second level, variations in the degree of dilution at one site can explain variations in the levels of VOCs in natural waters. This can be found at estuarine sites where salinity can be used as a measure of the degree of dilution of fresh water [96,97,105,151].

A third major process is the exchange of the VOCs from the natural water body to adjacent environmental compartments, i.e. sediment and the atmosphere [35,96,150,151]. Sorption onto sediment is generally considered to be of less importance. Sorption of VOCs on to solids was estimated to be responsible for a maximum of 5% of the removal of VOCs in the Southampton estuary [151]. This is related to the unfavourable sediment–water partitioning equilibrium of VOCs [156].

Water-to-air fluxes for the Scheldt estuary were estimated to be between 0.1 and 8.6 tonnes year<sup>-1</sup> for 13 individual chlorinated and monocyclic aromatic compounds [96], whereas the total flux of VOCs (about 130 compounds) amounted to up to 0.3 tonnes day<sup>-1</sup> in summer and 2.0 tonnes day<sup>-1</sup> in winter at the Southampton Water estuary [151]. Air–water exchange can result in seasonal cycles because air–water equilibrium partitioning of VOCs varies with temperature [150]. Biziuk et al. [80] suggested that fluctuations in wind speeds (and, hence, in air–water exchange velocities) within one week may explain the large differences observed in concentrations of VOCs in river waters. Finally, degradation has to be mentioned, as e.g. in the work of Krysell et al. [157], although for various subgroups of VOCs, this process is of rather limited importance [4].

## 5. Conclusions

The current status of the analytical methods determining VOCs in ambient air and natural waters

allows field determination at background concentrations. However, it can be seen that new developments are continuing, especially for ambient air sampling, indicating that no ‘standard method’ is available at the moment. Although the currently applied techniques are not employed on a routine basis and there are no specific guidelines available to ensure analytical performance, more attention could be paid to the analytical quality assurance in a systematic way. Comparing in-house analytical results with those obtained by other laboratories is not used systematically to validate measurement methods of VOCs in ambient air and natural waters.

Nevertheless, the value of the analytical techniques has been made clear in field applications. Not only do they allow one to observe the concentration patterns of VOCs, but, by bringing in environmental factors in the interpretation, they provide a better understanding of the sources and dynamics of VOCs in the environment.

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## References

- [1] R.G. Derwent, *Iss. Environ. Sci. Technol.* 4 (1995) 1–15.
- [2] P. Kuran, L. Sojak, *J. Chromatogr. A* 733 (1996) 119–141.
- [3] J. Dewulf, H. Van Langenhove, *Atmos. Environ.* 31 (1997) 3291–3307.
- [4] J. Dewulf, H. Van Langenhove, *Water Res.* 31 (1997) 1825–1838.
- [5] D. Brocco, R. Fratarcangeli, L. Lepore, M. Petricca, I. Ventrone, *Atmos. Environ.* 31 (1997) 557–566.
- [6] G. Barrefors, *Sci. Tot. Environ.* 196 (1997) 99–104.
- [7] P.A. Siskos, E.B. Bakeas, M.P. Baya, *Biosensors for Direct Monitoring Environmental Pollutants in Field*, D.P. Nikolelos, U.J. Krull, J. Wang, M. Mascini (Eds.), Kluwer Academic Publishers, The Netherlands, 1997, pp. 17–25.
- [8] Compendium Method TO-16, Long-path open-path Fourier Transform Infrared monitoring of atmospheric gases, EPA/625/R-96/010b. Compendium of methods for the determination of toxic organic compounds in ambient air, second edition. U.S. Environmental Protection Agency, Cincinnati, 1997, 40 pp.
- [9] E. Woolfenden, *J. Air Waste Manage. Assoc.* 47 (1997) 20–36.
- [10] E. Baltussen, H.-G. Janssen, P. Sandra, C.A. Cramers, *J. High Resolut. Chromatogr.* 20 (1997) 385–393.
- [11] G. Bertoni, R. Tappa, *J. Chromatogr. A* 767 (1997) 153–161.
- [12] A.R. Mastrogiacono, E. Pierini, L. Sampaolo, F. Bruner, *J. Chromatogr. A* 810 (1998) 131–139.
- [13] R.H. Brown, *Analyst* 121 (1996) 1171–1175.
- [14] J.F. Pankow, W. Luo, L.M. Isabelle, K.M. Hart, D.F. Hagen, *J. Chromatogr. A* 732 (1996) 317–326.
- [15] SIS (1995) <http://www.sisweb.com/index/referenc/resins.htm>.
- [16] A.P. Bianchi, M.S. Varney, *J. Chromatogr.* 643 (1993) 11–23.
- [17] H. Boudries, G. Toupance, A.L. Dutot, *Atmos. Environ.* 28 (1994) 1095–1112.
- [18] D. Helmig, J.P. Greenberg, *J. Chromatogr. A* 677 (1994) 123–132.
- [19] D. Helmig, W. Pollock, J. Greenberg, P. Zimmerman, *J. Geophys. Res.* 101 (1996) 14697–14710.
- [20] P. Ciccioli, E. Brancaleoni, A. Cecinato, R. Sparapani, *J. Chromatogr.* 643 (1993) 55–69.
- [21] J. Dewulf, D. Ponnet, H. Van Langenhove, *Int. J. Environ. Anal. Chem.* 62 (1996) 289–301.
- [22] I.L. Gee, C.J. Sollars, *Chemosphere* 36 (1998) 2497–2506.
- [23] A. Haunold, E. Rosenberg, M. Grasserbauer, *Int. J. Environ. Anal. Chem.* 67 (1997) 157–172.
- [24] W.A. McClenny, M. Colon, *J. Chromatogr. A* 813 (1998) 101–111.
- [25] K.D. Oliver, J.R. Adams, E.H. Daughtrey Jr., W.A. McClenny, M.J. Yoong, M.A. Pardee, *Atmos. Environ.* 30 (1996) 2751–2757.
- [26] K.D. Oliver, J.R. Adams, E.H. Daughtrey Jr., W.A. McClenny, M.J. Yoong, M.A. Pardee, E.B. Almasi, N.A. Kirshen, *Environ. Sci. Technol.* 30 (1996) 1939–1945.
- [27] T. Seko, N. Onda, *Anal. Sci.* 13 (1997) 437–442.
- [28] S. Suzuki, *Anal. Sci.* 11 (1995) 953–960.
- [29] C.A. McCaffrey, J. MacLachlan, B.I. Brookes, *Analyst* 119 (1994) 897–902.
- [30] D. Helmig, L. Vierling, *Anal. Chem.* 67 (1995) 4380–4386.
- [31] E. Kivi-Etelälä, O. Kostiaainen, M. Kokko, *J. Chromatogr. A* 787 (1997) 205–214.
- [32] W.F. Burns, D.T. Tingey, R.C. Evans, E.H. Bates, *J. Chromatogr.* 269 (1983) 1–9.
- [33] J.P. Hsu, G. Miller, V. Moran, *J. Chromatogr. Sci.* 29 (1991) 83–88.
- [34] Th. Knobloch, A. Asperger, W. Engewald, *Fresenius’ J. Anal. Chem.* 359 (1997) 189–197.
- [35] J. Dewulf, H.R. Van Langenhove, L.F. Van Der Auwera, *Environ. Sci. Technol.* 32 (1998) 903–911.
- [36] P.A. Clausen, P. Wolkoff, *Atmos. Environ.* 31 (1997) 715–725.
- [37] E.D. Pellizzari, K.J. Krost, *Anal. Chem.* 56 (1984) 1813–1819.
- [38] E. Pellizzari, B. Demian, K. Krost, *Anal. Chem.* 56 (1984) 793–798.
- [39] T. Hoffmann, *Fresenius’ J. Anal. Chem.* 351 (1995) 41–47.
- [40] A. Calogirou, B.R. Larsen, C. Brussol, M. Duane, D. Kotzias, *Anal. Chem.* 68 (1996) 1499–1506.
- [41] D. Helmig, *Atmos. Environ.* 31 (1997) 3635–3651.

- [42] E. Leibrock, J. Slemr, *Atmos. Environ.* 31 (1997) 3329–3339.
- [43] V. Camel, M. Caude, *J. Chromatogr. A* 710 (1995) 3–19.
- [44] E. Matisova, S. Skrabakova, *J. Chromatogr. A* 707 (1995) 145–179.
- [45] M. Harper, *Analyst* 119 (1994) 65–69.
- [46] S. Skrabakova, E. Matisova, E. Benicka, I. Novak, D. Berek, *J. Chromatogr. A* 665 (1994) 27–32.
- [47] E. Matisova, M. Strakova, S. Skrabakova, I. Novak, *Fresenius' J. Anal. Chem.* 342 (1995) 660–666.
- [48] E. Matisova, S. Skrabakova, *Anal. Chim. Acta* 309 (1995) 181–188.
- [49] E. Baltussen, F. David, P. Sandra, H.G. Janssen, C.A. Cramers, *J. High Resolut. Chromatogr.* 21 (1998) 332–340.
- [50] J. Roeraade, S. Blomberg, *J. High Resolut. Chromatogr.* 12 (1989) 138–141.
- [51] M.S. Krieger, R.A. Hites, *Environ. Sci. Technol.* 26 (1992) 1551–1555.
- [52] S. Mitra, C. Yun, *J. Chromatogr.* 648 (1993) 415–421.
- [53] S. Mitra, A. Lai, *J. Chromatogr. Sci.* 33 (1995) 285–289.
- [54] S. Mitra, Y.H. Xu, W. Chen, A. Lai, *J. Chromatogr. A* 727 (1996) 111–118.
- [55] C. Feng, S. Mitra, *J. Chromatogr. A* 805 (1998) 169–176.
- [56] T. Maeda, S. Onodera, H. Ogino, *J. Chromatogr. A* 710 (1995) 51–59.
- [57] P.D. Goldan, W.C. Kuster, F.C. Gehsefeld, S.A. Montzka, *J. Geophys. Res.* 100 (1995) 25945–25963.
- [58] J.P. Greenberg, B. Lee, D. Helmig, P.R. Zimmerman, *J. Chromatogr. A* 676 (1994) 389–398.
- [59] J.P. Greenberg, D. Helmig, P.R. Zimmerman, *J. Geophys. Res.* 101 (1996) 14581–14598.
- [60] H. Tang, P. Heaton, M. Hadley, *Int. J. Environ. Anal. Chem.* 64 (1996) 59–69.
- [61] Y.C. Chen, J.G. Lo, *Anal. Sci.* 13 (1997) 199–204.
- [62] P. Ciccioli, E. Brancaleoni, R. Mabilia, A. Cecinato, *J. Chromatogr. A* 777 (1997) 267–274.
- [63] A.C. Lewis, K.D. Bartle, J.B. McQuaid, M.J. Pilling, P.W. Seakins, P. Ridgeon, *J. High Resolut. Chromatogr.* 19 (1996) 686–690.
- [64] A.C. Lewis, K.D. Bartle, D.E. Heard, J.B. McQuaid, M.J. Pilling, P.W. Seakins, *J. Chem. Soc. Faraday Trans.* 93 (1997) 2921–2927.
- [65] J.B. McQuaid, A.C. Lewis, K.D. Bartle, *J. High Resolut. Chromatogr.* 21 (1998) 181–184.
- [66] N. Moschonas, S. Glavas, *J. Chromatogr. A* 790 (1997) 117–123.
- [67] A.J. Borgerding, C.W. Wilkerson Jr., *Anal. Chem.* 68 (1996) 701–707.
- [68] R. Koppmann, F.J. Johnen, C. Plass-Dülmer, J. Rudolph, *J. Geophys. Res.* 98 (1993) 20517–20526.
- [69] R. Koppmann, F.J. Johnen, C. Plass-Dülmer, J. Rudolph, *Eur. Comm. Report EUR 15609/1 EN*, Office for Official Publications of the European Communities, Luxembourg (1994) 417–423.
- [70] T.S. Clarkson, R.J. Martin, J. Rudolph, B.W.L. Graham, *Atmos. Environ.* 30 (1996) 569–577.
- [71] J. Begerow, E. Jermann, T. Keles, T. Koch, L. Dunemann, *J. Chromatogr. A* 749 (1996) 181–191.
- [72] C. Monn, M. Hangartner, *Environ. Technol.* 17 (1996) 301–307.
- [73] M. Biziuk, A. Przyjazny, *J. Chromatogr. A* 733 (1996) 417–448.
- [74] R.A. Ketola, V.T. Virkki, M. Ojala, V. Komppa, T. Kotiaho, *Talanta* 44 (1997) 373–382.
- [75] K. Abrahamsson, A. Ekdahl, *J. Chromatogr.* 643 (1993) 239–248.
- [76] N.K. Kristiansen, M. Froshaug, K.T. Aune, G. Becher, *Environ. Sci. Technol.* 28 (1994) 1669–1673.
- [77] L. Zoccolillo, M. Rellori, *Int. J. Environ. Anal. Chem.* 55 (1994) 27–32.
- [78] P.G. Desideri, L. Lepri, L. Checcini, D. Santianni, *Int. J. Environ. Anal. Chem.* 55 (1994) 33–46.
- [79] I. Harrison, R.U. Leader, J.J.W. Higgs, J.C. Tjell, *J. Chromatogr. A* 688 (1994) 181–188.
- [80] M. Biziuk, J. Namiesnik, J. Czerwinski, D. Gorlo, B. Makuch, W. Janicki, Z. Polkowska, L. Wolska, *J. Chromatogr. A* 733 (1996) 171–183.
- [81] H.G.J. Mol, H.G. Janssen, C.A. Cramers, U.A.T. Brinkman, *Trends Anal. Chem.* 15 (1996) 206–214.
- [82] H.G.J. Mol, H.G.M. Janssen, C.A. Cramers, J.J. Vreuls, U.A.T. Brinkman, *J. Chromatogr. A* 703 (1995) 277–307.
- [83] C. Charreteur, R. Colin, D. Morin, J.J. Peron, *Analisis* 26 (1998) 8–14.
- [84] J. Beltran, F.J. Lopez, M. Forcada, F. Hernandez, *Anal. Chim. Acta* 356 (1997) 125–133.
- [85] R.J.C.A. Steen, I.L. Freriks, W.P. Cofino, U.A.T. Brinkman, *Anal. Chim. Acta* 353 (1997) 153–163.
- [86] A. Termonia, M. Termonia, *J. High Resolut. Chromatogr.* 20 (1997) 447–450.
- [87] H.G.J. Mol, M. Althuizen, H.G. Janssen, C.A. Cramers, U.A.T. Brinkman, *J. High Resolut. Chromatogr.* 19 (1996) 69–79.
- [88] P.L. Morabito, T. McCabe, J.F. Hiller, D. Zakett, *J. High Resolut. Chromatogr.* 16 (1993) 90–94.
- [89] A. Venema, J.T. Jelink, *J. High Resolut. Chromatogr.* 19 (1996) 234–236.
- [90] B. Grolimund, E. Boselli, K. Grob, R. Amado, G. Lercker, *J. High Resolut. Chromatogr.* 21 (1998) 378–382.
- [91] Dj. Djozan, Y. Assadi, *J. Chromatogr. A* 697 (1995) 525–532.
- [92] N.K. Kristiansen, E. Lundansen, M. Froshaug, G. Becher, *Anal. Chim. Acta* 280 (1993) 111–117.
- [93] V.J. Dawes, N.J. Waldoek, *Mar. Pollut. Bull.* 28 (1994) 291–298.
- [94] L. Dunemann, H. Hajimiragha, *Anal. Chim. Acta* 283 (1993) 199–206.
- [95] J. Dewulf, H. Van Langenhove, *Int. J. Environ. Anal. Chem.* 61 (1995) 35–46.
- [96] J. Dewulf, H. Van Langenhove, M. Everaert, H. Vanthourout, *Water Res.* 32 (1998) 2941–2950.
- [97] A.P. Bianchi, M.S. Varney, *Water Res.* 32 (1998) 352–370.
- [98] A. Ekdahl, K. Abrahamsson, *Anal. Chim. Acta* 357 (1997) 197–209.
- [99] I. Silgoner, E. Rosenberg, M. Grasserbauer, *J. Chromatogr. A* 768 (1997) 259–270.

- [100] A. Wasik, W. Janicki, W. Wardencki, J. Namiesnik, *Analisis* 25 (1997) 59–64.
- [101] K. Yamamoto, M. Fukushima, N. Kakutani, K. Kuroda, *Environ. Pollut.* 95 (1997) 135–143.
- [102] B. Zygmunt, *J. Chromatogr. A* 725 (1996) 157–163.
- [103] T. Hino, S. Nakanishi, T. Hobo, *J. Chromatogr. A* 746 (1996) 83–90.
- [104] T. Hino, S. Nakanishi, T. Maeda, T. Hobo, *J. Chromatogr. A* 810 (1998) 141–147.
- [105] M. Krysell, P.D. Nightingale, *Cont. Shelf Res.* 14 (1994) 1311–1329.
- [106] L. Wolska, W. Janicki, J. Namiesnik, *Analyst* 120 (1995) 2781–2786.
- [107] Y.H. Xu, S. Mitra, *J. Chromatogr. A* 688 (1994) 171–180.
- [108] M.J. Yang, S. Harms, Y.Z. Luo, J. Pawliszyn, *Anal. Chem.* 66 (1994) 1339–1346.
- [109] M.J. Yang, M. Adams, J. Pawliszyn, *Anal. Chem.* 68 (1996) 2782–2789.
- [110] B.V. Burger, W.J.G. Burger, I. Burger, *J. High Resolut. Chromatogr.* 19 (1996) 571–576.
- [111] S. Mitra, X. Guo, *Anal. Lett.* 31 (1998) 367–379.
- [112] P.S.H. Wong, R.G. Cooks, M.E. Cisper, P.H. Hemberger, *Environ. Sci. Technol.* 29 (1995) 215A–218A.
- [113] P.S.H. Wong, R.G. Cooks, *Anal. Chim. Acta* 310 (1995) 387–398.
- [114] M.A. Mendes, R.S. Pimpim, T. Kotiaho, M.N. Eberlin, *Anal. Chem.* 68 (1996) 3502–3506.
- [115] M. Ojala, R. Ketola, T. Mansikka, T. Kotiaho, R. Kostianen, *J. High Resolut. Chromatogr.* 20 (1997) 165–169.
- [116] V.T. Virkki, R.A. Ketola, M. Ojala, T. Kotiaho, V. Komppa, A. Grove, S. Facchetti, *Anal. Chem.* 67 (1995) 1421–1425.
- [117] R. Kostianen, T. Kotiaho, I. Mattila, T. Mansikka, M. Ojala, R.A. Ketola, *Anal. Chem.* 70 (1998) 3028–3032.
- [118] W.M. Davis, M.B. Wise, J.S. Furey, C.V. Thompson, *Field Anal. Chem. Technol.* 2 (1998) 89–96.
- [119] G. Baykut, A. Voigt, *Anal. Chem.* 64 (1992) 677–681.
- [120] G. Matz, P. Kesners, *Anal. Chem.* 65 (1993) 2366–2371.
- [121] M.R. Lee, J.S. Lee, W.S. Hsiang, C.M. Chen, *J. Chromatogr. A* 775 (1997) 267–274.
- [122] D. Helmig, *J. Chromatogr. A* 732 (1996) 414–417.
- [123] X.L. Cao, C.N. Hewitt, *J. Chromatogr. A* 688 (1994) 368–374.
- [124] D.R. Blake, N.J. Blake, T.W. Smith Jr., O.W. Wingenter, F.S. Rowland, *J. Geophys. Res.* 101 (1996) 4501–4514.
- [125] O.W. Wingenter, M.K. Kubo, N.J. Blake, W.S. Tyrrel Jr., D.R. Blake, F.S. Rowland, *J. Geophys. Res.* 101 (1996) 4331–4340.
- [126] U. Hofmann, D. Weller, Ch. Ammann, E. Jork, J. Kesselmeier, *Atmos. Environ.* 31 (1997) 1275–1284.
- [127] A.R. Gholson, R.K.M. Jayanty, J.F. Storm, *Anal. Chem.* 62 (1990) 1899–1902.
- [128] R.W. Coutant, US Environmental Protection Agency, Research Triangle Park, NC, EPA/600/R-92/055 (1992) 39p.
- [129] Y. Wang, T.S. Raihala, A.P. Jackman, R. St. John, *Environ. Sci. Technol.* 31 (1996) 3115–3117.
- [130] A. Borowiak, E. De Saeger, *Analyst* 121 (1996) 1247–1248.
- [131] T. Laurila, H. Hakola, *Atmos. Environ.* 30 (1996) 1597–1607.
- [132] S. Solberg, C. Dye, N. Schmidbauer, A. Herzog, R. Gehrig, *J. Atmos. Chem.* 25 (1996) 33–66.
- [133] E.C. Apel, J.G. Calvert, F.C. Fehsenfeld, *J. Geophys. Res.* 99 (1994) 16651–16664.
- [134] J. Rudolph, R. Koppmann, Ch. Plass-dülmer, *Atmos. Environ.* 30 (1996) 1887–1894.
- [135] M.J. Gardner, J.E. Dobson, A.H. Griffiths, M.A. Jessup, J.E. Ravenscroft, *Mar. Pollut. Bull.* 35 (1997) 125–132.
- [136] D.E. Wells, W.P. Cofino, *Mar. Pollut. Bull.* 35 (1997) 146–155.
- [137] T. Nilsson, R. Ferrari, S. Facchetti, *Anal. Chim. Acta* 356 (1997) 113–123.
- [138] P.G. Simmonds, R.G. Derwent, A. McCulloch, S. O'Doherty, A. Gaudry, *Atmos. Environ.* 30 (1996) 4041–4063.
- [139] C.W. Spicer, B.E. Buxton, M.W. Holdren, D.L. Smith, T.J. Kelly, S.W. Rust, A.D. Pate, G.M. Sverdrup, J.C. Chuang, *Atmos. Environ.* 30 (1996) 3443–3456.
- [140] K.L. Yang, J.G. Lo, *Chemosphere* 36 (1998) 1893–1902.
- [141] R. Mukund, T.J. Kelly, C.W. Spicer, *Atmos. Environ.* 30 (1996) 3457–3470.
- [142] G. Chattopadhyay, G. Samanta, S. Chatterjee, D. Chakraborti, *Environ. Technol.* 18 (1997) 211–218.
- [143] D.R. Blake, T.Y. Chen, T.W. Smith Jr., C.J.L. Wang, O.W. Wingenter, N.J. Blake, F.S. Rowland, E.W. Mayer, *J. Geophys. Res.* 101 (1996) 1763–1778.
- [144] L. Cheng, L. Fu, R.P. Angle, H.S. Sandhu, *Atmos. Environ.* 31 (1997) 239–246.
- [145] E. Grosjean, D. Grosjean, R.A. Rasmussen, *Environ. Sci. Technol.* 32 (1998) 2061–2069.
- [146] T. Morikawa, S. Wakamatsu, M. Tanaka, I. Uno, T. Kamiura, T. Maeda, *Atmos. Environ.* 32 (1998) 2007–2016.
- [147] B. Rappengluck, P. Fabian, P. Kalabokas, L.G. Viras, I.C. Ziomas, *Atmos. Environ.* 32 (1998) 2103–2121.
- [148] W.H. Ding, J.L. Wang, *Chemosphere* 37 (1998) 1187–1195.
- [149] H.R. Rogers, B. Crathorne, C.D. Watts, *Mar. Pollut. Bull.* 24 (1992) 82–91.
- [150] S. Klick, *Limnol. Oceanogr.* 37 (1992) 1579–1585.
- [151] A.P. Bianchi, M.S. Varney, *Water Res.* 32 (1998) 371–379.
- [152] T. Yamasaki, N. Oki, T. Okuno, *Water Sci. Technol.* 25 (1992) 33–39.
- [153] M. Krysell, *Mar. Chem.* 39 (1992) 297–310.
- [154] K. Abrahamsson, A. Ekdahl, *J. Sea Res.* 35 (1996) 73–79.
- [155] H.B. Singh, A.N. Thakur, Y.E. Chen, M. Kanakidou, *Geophys. Res. Lett.* 23 (1996) 1529–1532.
- [156] J. Dewulf, T. Dewettinck, A. De Visscher, H. Van Langenhove, *Wat. Res.* 30 (1996) 3130–3138.
- [157] M. Krysell, E. Fogelqvist, T. Tanhua, *Geophys. Res. Lett.* 21 (1994) 2511–2514.