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Review

Environmental analysis of volatile organic compounds in water and sediment by gas chromatography

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Abstract

Considerable attention is still devoted to the analysis of volatile organic compounds (VOCs) owing to their occurrence in various fields and also harmful effects on health. The techniques used for their analysis are also manifold. The use of headspace techniques in the analysis of VOCs in various matrices has been well reviewed several times, but other techniques have been discussed only very briefly. The aim of this review is to give a brief survey of all techniques used in the environmental analysis of volatiles in water and sediment with emphasis on new trends and the applicability of these techniques in the analysis of water and sediment samples.

Keywords: Reviews; Environmental analysis; Water analysis; Sediment; Extraction methods; Volatile organic compounds

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1. Introduction

Water is a necessary condition for life on Earth. It is not possible to substitute it and its supplies are also limited. Water is closely related to sediment in a water column. The pollution of the water and sediment causes problems for humans and other living organisms dependent on the water. The quality of water and sediment must conform to the requirements for various areas of their use, especially health regulations; therefore, the analysis of water and sediments has great importance for our communal health. It imposes increased requirements on analytical chemists and on laboratory instrumentation owing to the low concentration levels and the great number of pollutants occurring in the environment.

This review gives a brief survey of all the techniques used in the environmental analysis of volatiles. Attention is focused on new trends, new techniques and the applicability of these techniques in the analysis of water and sediment samples, especially during the last decade.

2. Definition and toxicity of volatiles

Some of the most common pollutants are volatile organic compounds (VOCs). The compounds considered as volatiles are insoluble or only slightly soluble in water with boiling points up to ca. 200°C [1] and with molecular masses in the range ca. 16–250. Recently, the number of monitored volatiles was increased from 60 to 84 by addition of some more polar compounds [2].

Some of these compounds are mutagens, teratogens or carcinogens [1] and are resistant to microbial or photochemical degradation. It has been reported that carcinogenic and mutagenic effects have been induced in animals by several volatile halocarbon compounds (VOX) [3]. Several studies have confirmed the carcinogenicity of chloroform in mammals [4,5]. This is a correlation between the toxicity of VOX and their electron affinity. These compounds interrupt the transport of electrons in the living cell, which damages the metabolism inside the cell. On inhalating VOX, an anaesthetic effect can occur in cases of acute intoxication. Chronic intoxication causes irreversible neurological damage to the central nervous system. Trihalomethanes (THMs) in particular are harmful to the liver, the kidneys and the blood [6]. If halogenated organics enter the human body through the food chain or respiration, they tend to accumulate in fatty issues [7]. The carcinogenic and mutagenic effects of specific VOX are given in Table 1.

Exposure to aromatic hydrocarbons can also cause serious health problems. Benzene is known as the leukaemic agent in humans [8]. The toxic properties of toluene, ethylbenzene and xylenes have also been frequently studied [9,10]. Some volatiles, especially polar compounds, are responsible for the degradation of organoleptic parameters such as taste and odour of the water, which affect its quality [11].

Table 1
Carcinogenic and mutagenic effect of specific VOX (from Ref. [6])

Compound	Carcinogenic	Suspected of being carcinogenic	Mutagenic
Dichloromethane			+
Trichloromethane	+		+(?)
Tetrachloromethane	+		
1,2-Dichloromethane			+
1,2,2,2-Tetrachloroethane	+		+
1,1-Dichloroethane		+	+
trans-1,2-Dichloroethane	+		
Trichloroethane	+		+
Tetrachloroethane		+(?)	
Bromodichloromethane		+	
Tribromomethane		+	

3. Sources of contamination by volatiles

The sources of pollution by volatile organic compounds can be divided according to their origin into two basic groups: (1) man-made sources, e.g., municipal waste, traffic, industrial and agricultural sources; and (2) naturally occuring sources.

From the municipal sources, various commercial products containing organic solvents contribute to pollution. This is the way by which volatile aromatics (benzene, toluene, ethylbenzene and xylenes, BTEX) and halogenated volatiles enter the environment [12]. Another source of VOX is the treatment of water with chlorine or oxidizing agents such as ozone [13]. Fulvic and humic acids are considered as precursors of chlorine and ozone reaction products [6]. The functional groups, which are present in large numbers in poly-heterocondensation, form intermediates of trihalomethanes (THMs: $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$) [14]. In municipal waste waters there are various types of surfactants that are non-volatile, but they increase the solubility of organic compounds in water and thus the solubility of volatiles [15].

Traffic causes an increased content not only of some toxic gases such as CO and NO_x in the environment, but also the content of VOX and alkylbenzenes as result of complex reactions during the combustion of petrol in vehicles [6,12,16,17]. VOX can be successively transported via rainwater into the aquatic environment. One of the important sources of contamination is the leakage of petrol and diesel fuel from underground storage tanks [18]. This is another way for BTEX to enter the aquatic environment owing to their better solubility in water in comparison with other compounds in petrol. Oilfield brines can be also considered as a traffic source of pollution. They are applied to roads to control the formation of ice in winter months. The presence of BTEX was revealed in this material, which sometimes resulted in a state regulatory agency mistakenly accusing an adjacent property owner of contaminating subsurface soils with VOCs [12]. As a traffic source one can classify the pollution of water by accidents during transport of petroleum products on giant sea tankers and during their manipulation in ports. Hence the extensive contamination of groundwaters near ports is not surprising [12].

The industrial sources are first of all the enterprises producing fumes, which are transported by rain or by airborne particles to the water or soil. It has been reported that contamination from industrial sources makes chloroform a common air pollutant. It was found together with carbon tetrachloride in the rain water in Kobe [19]. Moreover, VOX can be found in aquifers as a result of diffuse seepage into the soil during their use by companies, from acci-

dents and during storage and transport [12]. The important industrial sources of volatiles are waste waters from the petrochemical industry, which contain large amounts of BTEX.

Pesticides are a possible source of agricultural pollution. They are often diluted with petroleum distillates that again contain BTEX. They can be washed from soil by rain water and transported to the aquatic environment. Sewage sludges are another source of volatiles in aquifers. They have been added in many regions to agricultural soils to increase the organic content of the soil. Sewage sludges have a high adsorption capacity for, among others, volatiles [12]. Volatiles can be extracted from these sludges by rain water and transported into aquifers.

The second source of organic compounds in water is biota. Volatile aromatics have been known since 1966 to be naturally occurring in soil. These aromatics come from humic and fulvic acids which contain benzene in their structure and are naturally occurring in soil and in water [12]. The presence of some gaseous hydrocarbons in soils which can be converted by hydrolysis of the β-carbon of straight-chain alkanes by the enzyme monooxygenase during the β-oxidation metabolic pathway into polar compounds is known. For example, propane can be converted into acetone, which is soluble in water [12]. Some of VOX are also of natural origin. Monochloromethane, monobromomethane, dichloromethane, tribromomethane and chloroform are metabolically active products of marine organisms. This leads to the assumption that VOX are used by marine organisms for protection against decay [6].

4. Sampling and preservation of water and sediment

Proper sampling is a necessary condition for obtaining reliable analytical results. The purpose of sampling is to reduce the mass or volume. Analysts achieve this reduction by selecting constitutive elements from among those that compose the parent batch. Constitutive elements are well defined units, such as solid fragments or individual molecules, that belong to the sought-after batch composition [20]. The sampling process can be divided into two main stages: primary and secondary sampling. Primary sampling includes all steps that are performed outside the analytical laboratory. The result of primary sampling is a sample that is small enough to be transported to an analytical laboratory. Secondary sampling incorporates all steps performed within the analytical laboratory. It includes the extraction of one or several test portions from the laboratory sample for processing and analysis.

The theory of sampling has been widely discussed by Gy [21,22]. Some practical aspects of sampling of gas, soils and waters have been discussed [12]. Any deviation from the rules of correct sampling results in both a deviation from accuracy and an increase in the overall sampling variance.

Regarding the sampling of waters and sediments for the analysis of volatiles, the requirements on correct sampling are even higher. In the sampling of waters, the basic rule is to fill up a container without a headspace and to keep it at about 4°C. Also, it is useful to invert the sampling flask to prevent any losses of volatiles. All samples should be collected in duplicate. The water sampled in this way should be transported and analysed within 24 h if no stabilizers are added. When stabilizers are added, the sample can be analysed within a few days. When sodium azide as a stabilizer at a concentration of about 1 g/l is used, water samples can be analysed for purgeable components within 58 days without loss of compounds [23]. The commonly used preservatives hydrochloric acid and mercury(II) chloride (200 μl of 50% HCl or 100 μl of a 24 g/l aqueous solution of $HgCl_2$ in 40-ml vials) [12,24,25] are less recommended because of their corrosive properties and adverse environmental effects [23]. If samples contain residual chlorine, and measurements of the concentrations of disinfection by-products (THMs) at the time of sample collection are desired, the addition of ascorbic acid (about 25 mg in a 40-ml vial) or sodium thiosulfate (3–100 mg in a 40-ml vial) to the sample before filling is recommended [26,27].

In sampling of sediments and soils, the collection of small-volume soil core samples is considered to be a reasonable means of minimizing VOC losses. It is considered less reliable to place soil in larger containers which require later subsampling, and which will be subject to resultant volatile losses during handling [12]. However, in this case the sample representativeness can be questionable [28]. One of the possible approaches to overcoming these problems is field sampling of volatiles. Good results have been obtained when volatiles from water and sediment samples have been preconcentrated in the field on various polymer sorbents such as Carbotrap 300 [29]. For sediments, a possible way of suppressing losses and microbial degradation of volatiles is to introduce the sample directly into an organic solvent such as methanol [7,12] or, as in the case of waters, to add a stabilizer (e.g., sodium azide). Samples for the analysis of gasoline-range volatiles (mostly aromatics and non-polar compounds) preserved in methanol can be held for up to 28 days at 4°C with no apparent losses [12]. No significant decrease after 50 days for the most VOX except more volatile compounds (trichlorofluoromethane, 1,1-dichloroethylene, dichloromethane), CCl_4, tetrachloroethylene and 1,3-dichloropropenes (6–14% decrease in relation to the initial recovery values) was observed when methanol was used as a preservative [30]. The results regarding the sample holding time are summarized in Table 2.

The collected sample of water or sediment must be carefully protected from possible contamination. The basic rule is to carry out the analysis in laboratory free of any target compounds. This rule is essential when the organic solvents are used as preservation or extraction agents. The organic solvents act as excellent absorptive traps with a very high affinity for airborne volatiles. The detectable amounts of volatiles can be observed over time as the bottle is opened and reopened. If the laboratory is located near areas that use organic solvents for cleaning or other purposes, the only possibility to avoid contamination is to minimize air exposure and purge the bottle with clean inert gas while withdrawing solvent. These problems can be encountered especially when analysing halogenated compounds using electron-capture detection (ECD). The same problem can occur if the samples of water and sediment are opened in such an environment and left with some headspace for a longer time.

The gas purity is critical, especially in dynamic headspace techniques. The purge gas must be at least 99.999% pure, high-purity regulators with stainless-steel diaphragms and non-fluorocarbon seals should be used and clean stainless-steel or copper tubing and unions are required; any plastic tubing or ferrules must be eliminated because they act as excellent source of VOCs [31]. Halogenated solvents are commonly used to degrease piping, fittings, manifolds, regulators,

Table 2
Sample holding times (days) for VOCs preserved with addition of sodium azide, methanol, mercury(II) chloride or stored on polymeric adsorbent (for details see text)

VOCs	Matrix	Sample preserved with sodium azide	Sample preserved with methanol	Volatiles stored on Carbotrap 300 desorption tubes	Sample preserved with $HgCl_2$
VOX	Water	58 [23]	–	14 [29]	–
	Sediment	–	50 [30]		
Aromatics	Water	58 [23]	–	–	39 [24]
	Sediment	–	28 [12]	–	39 [24]
Non-polar	Water	58 [23]	–	–	–
	Sediment	–	28 [12]	–	–
Polar	Water	58 [23]	–	–	–
	Sediment	–	–	–	–

valves and cylinders in specialty gas fill plants. Their removal from metal surfaces is difficult. Methylene chloride adsorbs strongly on copper and steel surfaces. Trace levels of halocarbon detectable by GC–ECD can be removed only by prolonged purging with a hot, purified gas. The cleaning of bellows valves from 1,1,1-trichloroethane by drying with a stream of nitrogen and baking at 100°C overnight was insufficient to drive trace levels of solvent from the valve surfaces [32]. Extraneous peaks can appear as contamination from previous injections (carryover) [32] or as decomposition products of the trap material when adsorbent traps are used [31].

The purity of "blank" water for standard preparation is also important. Several water sources were tested (listed from best to worst): deep-well groundwater; triply distilled water from a neighbouring inductively coupled plasma (ICP) laboratory; deionized water from a deionization cartridge; HPLC-grade water; and city tap water. No peaks were detected in well water, whereas distilled water was contaminated with fairly large amounts (several hundred ppb) of chloroform. The deionized water contained aromatics and chloroform [31]. HPLC-grade water was also contaminated with chloroform (several ppb) and aromatics [33]. The city water showed a typical pattern of chlorohydrocarbons from the municipal water-treatment process [31]. The distillation of well water in conjunction with helium stripping produced blank water of sufficient purity to permit the analysis of VOCs at low ppt levels [33].

When all these aspects are taken into account, the sample can be analysed by means of available techniques for the determination of volatiles. To obtain data of known quality, the validation of applied methods should be documented if standard methods were not applied. The problems associated with quality control are discussed in more detail in the literature [12,26,34].

5. Volatiles in water

From the point of view of the analysis of water as an environmental matrix, it can be stated that water represents a less complicated matrix than sediment owing to its better defined composition and homogeneity. Some problems can be encountered when analysing water samples with a high organic content, especially when headspace techniques are used [35].

5.1. Analytical techniques

Techniques for the analysis of the volatiles in water can be subdivided into several groups according to extraction agent: gas extraction; liquid extraction; solid-phase microextraction; membrane extraction; distillation techniques; and direct injection.

5.1.1. Gas extraction

The determination of VOCs in water samples at the ppb level requires the preconcentration of volatiles prior to GC analysis. One of the possible ways is to use the gas as the extraction agent. Gas extraction is cost efficient and non-hazardous, requires few consumable items and can be automated. The advantage is that in the preconcentration step no extraction medium has to be removed because analytes are extracted directly into the carrier gas. Thus, no potential interferents are introduced. With appropriately designed instruments, analytes as large as n-C_{40} can be extracted and analysed using gas extraction [36].

Two modes of gas extraction can be distinguished: static headspace and dynamic headspace. The physico-chemical aspects, methodology and applications of both techniques with emphasis on quantification were reviewed by Drozd and Novák [37].

5.1.1.1. Static headspace. Static headspace is often called equilibrium headspace sampling. Volatiles are extracted from the gas phase (headspace) which is in equilibrium with the matrix in a closed system. This means that the concentrations of analytes do not change with time. The equilibrium can be disturbed only during sampling, and therefore this step must be carefully controlled [28]. The theoretical principles and quantification by static headspace have been

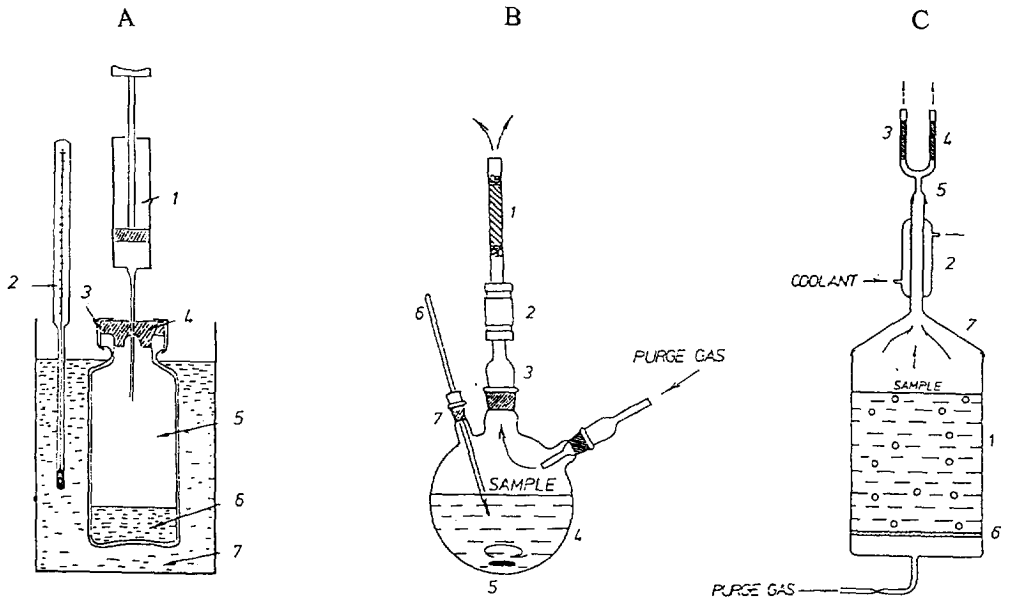

Fig. 1. Comparison of headspace techniques (A) Static headspace (from Ref. [39]): 1 = syringe; 2 = thermometer; 3 = screw-cap; 4 = septum; 5 = headspace vessel; 6 = sample; 7 = constant-temperature liquid bath. (B) Dynamic headspace when the purge gas flows over the sample (from Ref. [60]): 1 = trap; 2 = PTFE union; 3 = reducer; 4 = 100-ml round-bottomed flask; 5 = magnetic stirring bar; 6 = thermometer; 7 = thermometer adapter. (C) Dynamic headspace when the purge gas passes through the sample (purge and trap technique) (from ref. [60]): 1 = sampler body; 2 = condenser; 3, 4 = trap tubes; 5 = tube holder; 6 = glass frit; 7 = reducer.

clearly described in several papers [12,38–40]. One of the possible types of apparatus for static headspace is shown in Fig. 1.

This technique has several advantages. It is not very expensive, does not required complicated instrumentation and can be automated. Because of this, it is favoured in the analysis of food and beverages and in biomedical applications [41]. The disadvantage of the technique is its relatively low sensitivity compared with dynamic headspace. As a result, static headspace is suitable for the analysis of samples with higher contents of volatiles such as waste or municipal waters. Several papers have been published describing the application of static headspace to the analysis of VOX in environmental samples [6,27]. Vitenberg et al. [42] reported the use of static headspace in the analysis of polar compounds such as phenol and *o*-, *m*- and *p*-cresol.

Pare et al. [43] reported a comparison of static headspace with microwave isolation of BTEX and dichlorobenzenes followed by GC. Selective vaporization of the analytes that were then transferred into the gas chromatograph was achieved. Compared with static headspace, the proposed method offered enhanced sensitivity. The time required for equilibration was shortened to 1 min by the use of the proposed microwave-assisted process (MAP).

Considerable efforts have been devoted to the automation of static headspace in combination with high-resolution capillary GC. The major difficulty encountered in this combination is the rapid transfer of the gas phase from the vial to the column owing to the low carrier gas flow-rates through the capillary column. The slow transfer of the headspace gas causes an unacceptable decrease in analytical system efficiency [44]. This topic has been discussed in several papers [45–47]. The drawback of this approach is the necessity for major modification of the instrument. Moreover, these devices allow complete automation only when working with a single sample. Poy and Cobelli [44] used an improved

programmed-temperature vaporizer (PTV). This technique allows the complete transfer of large amounts of the headspace gas without any loss of efficiency, eliminates splitting techniques and, when coupled with an automatic headspace sampler (HSS), up to 24 unsupervised sampling operations can be performed. The static headspace determination of a volatile analyte requires the determination of the partition coefficient, K [41], but the value of K is generally not known for most practical headspace applications. Without the value of K, quantitative calibration techniques can be used only if a homogeneous sample can be prepared and, in the case of the external standard method, if the sample matrix can be reproduced. The problems and various approaches concerning this topic have recently been reported [6,48–50].

The so-called multiple headspace extraction technique (MHE) provides a possible solution to this problem [51–53]. This technique was preceded by discontinuous gas extraction, a simplified version of MHE [54]. MHE is an absolute quantitative method used in static headspace GC. In principle it is dynamic gas extraction carried out stepwise with the establishment of equilibrium conditions in each step. The concentration of the analyte in the headspace decreases exponentially during the series of extraction steps and, by proper mathematical extrapolation, the total amount of the analyte present in the original sample can be obtained. However, some disagreement regarding the mathematical development of MHE occurred. The problems related to this topic have been discussed in the literature [55–59].

5.1.1.2. Dynamic headspace. In the dynamic headspace method, the gaseous phase over the sample is permanently purged with carrier gas, which carries the analytes to the trapping medium. This technique enables lower detection limits to be achieved. It is possible to determine the solutes with a lower vapour pressure and the possibility of contamination from the septum is removed. In principle, purge gas can pass through or over the material. The arrangement when purge gas passes through the sample is often called the purge and trap technique. Both arrangements are shown in Fig. 1.

This technique can be applied in two ways: with open-loop stripping and closed-loop stripping.

Open-loop stripping. In open-loop stripping (OLS), the stripping gas passes through the sample and the trap and is vented to the atmosphere. The concentrations of the analytes in open systems decrease continuously with time in both phases and approaches zero asymptotically. The deviation from equilibrium is more or less pronounced, although it may be assumed that even under these non-stationary conditions the gas in the bubbles leaving the condensed phase is practically equilibrated [60]. OLS is favoured owing to its simplicity when compared with closed-loop stripping, but suffers from two drawbacks: (a) it is necessary to determine the breakthrough volume, i.e., the volume of stripping gas when the least sorbed analyte is eluted from the sorbent, and (b) there are higher requirements on the purity of stripping gas owing to the higher volumes of stripping gas used. The breakthrough volume depends on different parameters: (a) the form and the size of the trap tube; (b) the porosity, specific surface area, amount used and inertness of the adsorbent towards the analytes; (c) the flow-rate of the stripping inert gas, affected by its purity and temperature; and (d) the original concentration and the molecular structure of the analytes in the sample and the complexity of the mixture [60]. The determination of the breakthrough volume for various types of sorbents has been widely reported [61–69].

OLS was originally introduced by Bellar et al. [70]. During the initial purge and trap (P&T) development work, chloroform and other THMS were discovered in treated drinking water in Cincinnati, OH, USA, and, subsequently, in many other chlorinated drinking waters in the USA [34]. Recognition of the development work on the P&T method was published in 1974 [70,71].

Bertsch et al. [72] applied P&T to the trace organic analysis of volatiles in water. In several studies in which P&T was used, the evaluation of

various types of chromatographic columns and phases was investigated in order to optimize the separation of volatile priority pollutants [73–78]. The complete separation of the 60 volatile organochlorine priority pollutants has been achieved by coupling two different liquid-modified adsorption chromatographic columns and using two temperature programmes [79]. The reason for the good separation obtained here and the extremely critical effect of temperature on the elution of each compound lies in the driving mechanism of the process called gas–liquid–solid chromatography, which is based on adsorption. In such a process, the heats of adsorption are much greater than those of a solution in the liquid phase and the change in retention volumes with temperature is much higher. The nature of the adsorption process means, furthermore, that the chromatographic behaviour of the various compounds is influenced more by their steric molecular structure and by their electron distribution than by their vapour pressure.

Ho [27] reported using a P&T system for the analysis of 58 VOX and aromatic organics in drinking water. The separation of all compounds, except *p*- and *m*-xylene, was achieved on the single wide-bore column using photoionization detection (PID) and electrolytic conductivity detection (ELCD) in a series configuration. ELCD was used for halogenated compounds and PID for aromatics.

OLS was evaluated for the determination of alkylbenzenes, halogenated hydrocarbons, alkanes and some polar compounds using charcoal filters by Kristiansen et al. [23]. The recoveries of target compounds and the variance in recoveries caused by the use of several analytical charcoal filters were discussed.

The subambient cooling of the separation system represents another approach to the complete separation of volatiles by GC. Bianchi and Cook [80] described such a system using an automated thermal desorber. They used a temperature programme ranging from −35 to 300°C to analyse the complex mixtures containing compounds from ethylene to substituted benzenes. They found that at temperatures lower than −35°C, all components with boiling points between those of methane and *cis*-2-butene exhibited excessive band spreading and comparatively small relative peak areas. They attributed this effect to condensation on the column and breakdown in the internal flow dynamics.

At present, however, neither of these efforts for the separation of such large numbers of pollutants in a single run may be sufficient because, as mentioned before, the number of analytes in the standard EPA Method 524.2 was recently increased from 60 to 84 [2] by addition of some more polar analytes.

Bianchi et al. [81] also reported a method for the analysis of kerosene, white spirit, regular leaded gasoline and two common aromatic solvent mixtures (Solvent 100 and 150) using a system similar to that described previously [80], without subambient cooling of the separation system. The results obtained can be useful from the point of view of pollution control, where the chemist is often required to fingerprint the identity of the entire hydrocarbon mixture rather than to identify the individual compounds within the mixture in order to identify the source of pollution.

Hazard et al. [18] reported the analysis of gasoline, kerosene, fuel oil and diesel fuel in water and soil using a dynamic thermal stripper and four-bed absorbent tube for effective adsorption of the analytes in the presence of water and for subsequent removal of water in the tube during the purge and dry stages.

For pollution control purposes a paper by Hirz and Rizzi [82] describing gasoline-type samples and their weathering and ageing could be useful. They derived and tested semi-empirical equations which correlate the composition of samples after evaporation with the composition of the original material. This procedure can be helpful for tracing back the composition of the liquid remaining to that of the original unweathered liquid. The losses of original gasoline-type samples, however, should not be higher than 50%.

Recently, Voice and Kolb [83] discussed the differences between the European and American approaches to VOC analysis in water and soil. In the analysis of water samples they compared static headspace, which is more firmly established

in Europe, with the P&T technique, which is prevalent in the USA. They stated that static headspace was more precise that P&T. The reason for this was the tailing of all P&T peaks which resulted in variations in the integration routine. The tailing results from the thermal desorption process. This effect is commonly observed with commercial thermal desorption equipment. For this reason, many manufacturers have developed two-stage processes in which the analyte is cryofocused after desorption from the solid sorbent.

Recent trends in the P&T technique were described and evaluated by Abeel et al. [84]. The trends include improvements in P&T techniques that attempt to make the preconcentration part of the overall analysis. These techniques include methods and hardware capable of handling a wide array of sample matrices encountered, minimizing matrix interferences inherent within the technique and efficiently transferring the concentrated sample to the GC system for separation and subsequent detection.

One of the modern trends in P&T techniques is the effort to meet today's increasing needs for the rapid analysis of purgeable organics in water and soils. The analysis of the vapour headspace over a well by using a portable gas chromatograph with PID was presented by Jerpe and Davis [85]. Progress in this area permitted the recent development of a fast microchip gas chromatograph in high-speed GC [86], suitable for use in the field. In connection with a portable sample concentrator introduced by Sherman et al. [87], improved field application of the P&T technique is possible. The development of a simple field P&T method for analysing purgeable organics at ppb levels in water and soil samples was published by Yan et al. [88]. Schnable et al. [89] described the use of an inexpensive modified P&T system which allowed the continuous on-line automatic analysis of VOCs in small (0.1–70 ml) water streams.

Closed-loop stripping. In the closed-loop stripping (CLS) the gaseous phase is recycled through the sample and trap. CLS has two variants depending on whether the process is performed until the least sorbed component in the trap does not break through (so-called conservation trapping) or the most sorbed component in the trap comes into equilibrium with the gaseous phase (equilibrium trapping). The latter arrangement has the advantage of removing the problem with the breakthrough of most volatile compounds because the analytes in gaseous phase are recycled into the sample and the whole system is in equilibrium. The CLS was originally described and introduced into analytical practice by Grob and co-workers [90–93]. They compared this method with solvent extraction and found that (a) the detection limit with the P&T method in a closed circuit is ten times lower for volatile substances, whereas solvent extraction is more sensitive for heavy materials, (b) the quantitative reproducibility is better in a closed circuit and (c) there is no essential difference between the methods in sensitivity depending on the polarity of the analyte. Narang and Bush [94] used a similar system for the determination of arenes, vinyl chloride and some other VOX in water. The only components modified were absorbent, eluting solvent and separation system (packed column).

Bruchet et al. [95] reported a comparison of CLS and simultaneous distillation extraction (SDE) for volatile and semi-volatile constituents of the soluble organic matter from an underground water sample. This study revealed that, although the total extract is four times less abundant with SDE, the extraction process is more efficient with more polar substances, e.g., alcohols, ethers, pyridines, ketones, carboxylic acids, amines and heavier non-polar alkanes. CLS is better for other classes of pollutants, e.g., aliphatic aldehydes, terpenes and iodo-THMs. It can be concluded that these two methods appear to be complementary rather than concurrent.

Guardiola et al. [96] used CLS in the analysis of Barcelona tap water and untreated water from the Llobregat river. The main compounds identified were toluene, C_2–C_4 alkylbenzenes, which reflect petrogenic dumping, and C_{10}–C_{13} alkylbenzenes, which are a complex mixture of isomers manufactured for the production of anionic surfactants of the linear alkylbenzene sulphonate (LAS) type. Phthalates, phosphates and poly-

ethoxylated nonylphenol non-ionic surfactants with degree of polyethyoxylation $n = 0–3$ have also been found in raw water and their brominated derivatives in tap water. The tap water showed smaller seasonal variations in concentration ranges than the river water.

Rosell et al. [97] studied by CLS and by charcoal and polyurethane foam adsorption the distribution of VOCs in river waters and in urban-influenced air. In both types of samples, $C_1–C_5$ alkylbenzenes and *n*-alkanes constituted the two major VOC groups, indicating a predominance of petroleum products in these two environmental compartments. Of chlorinated compounds, they found polychlorobenzenes, polychloronaphthalenes and hexachlorobutadiene in water, whereas tetrachloroethene was the predominant chlorinated airborne VOC.

5.1.2. Liquid extraction

Another way to preconcentrate volatiles from water samples is their extraction into a small volume of organic solvent. The advantages of this procedure are its simplicity, speed, few requirements as to special equipment and low solvent consumption. With one injection it is possible to analyse wide range of compounds, not only volatiles. The disadvantages are possible solvent overlapping with some more volatile compounds and, at low concentration levels (ppb, ppt), the introduction of uncertainty, not only in the complete quantitative isolation of the compounds but also in the qualitative analysis, as other substances in this concentration range can be present in the solvent or enter into the sample from the surroundings [60].

The preconcentration is based on the favourable distribution coefficient of the analyte compound in a water–organic solvent system and on the high value of the ratio of water sample volume to organic phase volume. This procedure is suitable especially for non-polar compounds. The extraction recoveries of polar compounds using hydrophobic solvents are negligible at trace concentration levels. They can be increased by salting-out or by changing the pH value, provided that the compounds are acidic or basic [98]. Another possibility is the addition of a polar compound to the extraction agent. This compound must be virtually insoluble in water and must form readily extractable complexes with analytes. These requirements are fulfilled, for example, by 3-octylphosphine oxide, which was used with methyl-*tert.*-butyl ether for the analysis of trace levels of phenols [99], acetic acid [100] and acrylic acid [101].

In liquid extraction, it is necessary to evaluate properly the choice of the most suitable extraction agent, its volume and the recovery of extraction. The extraction agent must have, as mentioned before, a favourable distribution coefficient for the analyte in a water–organic solvent system, must not form an emulsion with water, must be free from impurities and must be as insoluble in water as possible. Concerning the volume of extraction agent and the recovery, it can be stated that the higher the volume of extraction agent used, the higher is the recovery that can be achieved, but the concentration factor decreases. Therefore, it is better to use smaller volumes of extraction agent. Theoretically, the recovery is influenced only by the value of the distribution coefficient and by the ratio of phase volumes [102]. In practice, however, the value of the distribution coefficient at trace concentration levels can be dependent on concentration [103]. Therefore, in a quantitative analysis, calibration over the entire concentration range used is needed.

The important factor in liquid extraction is to ensure as good a contact of the water with the extraction agent as possible. From a comparison of techniques (manual shaking, stirring, ultrasonic and low-frequency vibrations), intensive manual shaking was shown to be the best choice [91]. The extraction time is very different, and fluctuates from 30 s to several tens of minutes [104].

The use of liquid extraction as a standard method has been described [105]. According to this procedure, El-Dib and Ali [106] analysed waters in various stages of the treatment process. They stated that the concentrations of THMs and some unknown VOX had progressively increased as the water passed through the various treatment processes. The storage of filtered water in a

clear well usually had enhanced the formation of THMs, which reflects the effects of post-chlorination and extended contact time with chlorine. Liquid microextraction using *o*-xylene as an extraction agent was used by Adachi and Kobayashi [19] in the analysis of some VOX in rain water. Chloroform and carbon tetrachloride were confirmed in all samples regardless of the distance from the highway, hence these compounds were not thought to be derived from air pollution due to motor vehicles.

The occurrence of THMs in water supplies from different points in the distribution network after their disinfection by chlorination using extraction with pentane have been investigated by Ibarluzea et al. [13]. They supported the results obtained by El-Dib and Ali [106].

5.1.3. Solid-phase microextraction

Solid-phase microextraction is one of the newest approaches in the analysis of volatiles. In this procedure, a small-diameter optical fibre coated with polymeric phase is placed in an aqueous sample. The analytes partition into the stationary phase and are then thermally desorbed, on-column, in the injector of a gas chromatograph. Since the coatings used are almost always viscous liquids, the extraction is, in effect, liquid–liquid extraction with the convenience that the "organic phase" is attached to the fibre. The fibre is contained in a syringe which protects it and simplifies introduction of the fibre into the GC injector [107]. The apparatus for solid-phase microextraction is shown in Fig. 2.

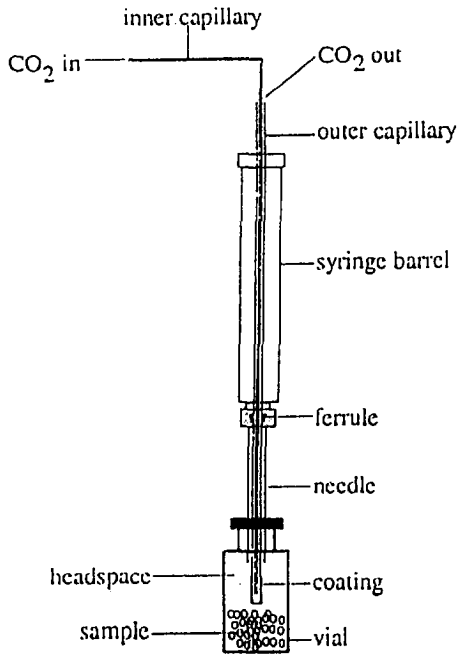

Fig. 2. Apparatus for solid-phase microextraction (SPME) with internally cooled fibre coating (from Ref. [114]).

The most common polymer coating is poly(dimethylsiloxane), but uncoated fibres can also be used [108] in addition to a variety of common chromatographic phases [109] in order to enhance the selectivity and detection limits for classes of compounds or specific analytes. This technique meets most of the criteria for an ideal sample preparation method [110]. It is fast, sensitive, inexpensive, portable and solvent-free. It can be used for gaseous and liquid samples in combination with any gas chromatograph or gas chromatograph–mass spectrometer and can be completely automated. Moreover, the technique can be applied to volatile and non-volatile compounds and meets the detection limits specified by EPA methods and the Ontario Municipal/Industrial Strategy for Abatement programme [110]. No special sample work-up is required and sampling times are also short, typically 2–15 min. The mathematical model of the technique and the effects of the matrix, the extraction temperature and chromatographic conditions on the precision and accuracy of automated SPME have been described [107].

An interesting trend in the use of SPME is its combination with spectral techniques without gas chromatographic separation. Wittkamp and Tilotta [111] published a method for determination of BTEX in water that combines SPME and spontaneous Raman spectroscopy. The SPME step affords a preconcentration of the analytes which effectively increases the sensitivity of the Raman measurement (2–3 orders of magnitude) without adding complexity to the experimental step. Raman spectroscopy provides molecular recognition of the extracted compounds directly in the extraction medium (coating on the fibre). Moreover, it is a non-destruc-

tive detector so that the sample can be further analysed using other detection systems. The disadvantage is the relatively high detection limits for BTEX (1–4 ppm).

A similar system, in principle, was used by Krska et al. [112] for the determination of chlorinated hydrocarbons in water. As a stationary phase they used low-density polyethylene attached to polycrystalline silver halide fibres to enrich the VOX within the evanescent wave and to exclude the IR-absorbing water from the measurement. After extraction the coated silver halide fibres were inserted inside the flow cell of an FT-IR spectrometer and then carefully adjusted in the focal point of the parabolic mirror. This procedure permitted the simultaneous in situ detection of the most common chlorinated hydrocarbons in water; however, the detection limits, between 1 and 50 mg/l, are too high. The same team [113] continued in this area by investigating eight polymers [low-density polyethylene (LDPE), propylene copolymer (E/co), poly-1,2-butadiene (PBD), polyisobutylene (PIB), oxidized polyethylene (PEox), chlorinated polyethylene (PEcl), ethylene–vinyl acetate copolymer (E/Vco) and poly(4-methyl-1-pentene) (PMP)] as coating materials for SPME from aqueous solution in combination with IR spectrometry. PIB and E/Pco showed both high enrichment and relatively fast response times compared with LDPE.

SPME can be used also for the analysis of the headspace phase, not only aqueous. The development of an internally cooled SPME device to achieve quantitative extraction for benzene, toluene, ethylbenzene and xylene isomers from gas, water and soil in combination with simultaneous heating of the sample was recently reported [114].

5.1.4. Membrane extraction

The use of semi-permeable membranes is another of the newest approaches to the extraction of VOCs from aqueous samples. In this process, the aqueous sample is contacted with a membrane and the VOCs permeate selectively through the membrane into a gaseous phase on the other side. The principle can be understood from Fig. 3.

The membranes can be non-porous or porous. With non-porous membranes, VOCs migrate from the aqueous phase to the surface of the membrane and dissolve in the inside surface layer of the membrane. Then dissolved analytes migrate through the bulk membrane under a concentration gradient. The next step is evapora-

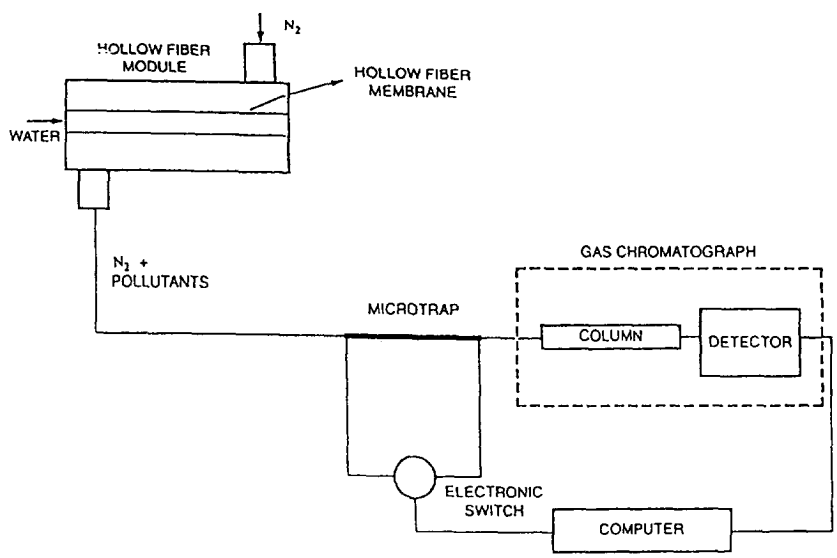

Fig. 3. Schematic diagram of the on-line membrane extraction and microtap GC system (from Ref. [115]).

tion or stripping of the VOCs from the outer membrane surface into the stripping gas [115]. In the case of microporous membranes, the VOCs diffuse directly through pores.

Membranes are most frequently used in combination with MS or GC–MS systems. The membrane can serve as a direct interface between the sample and the vacuum system of the mass spectrometer without GC separation [membrane inlet mass spectrometry (MIMS)]. If a hollow fibre membrane is being used, two inlet geometries are possible: "flow-over", when the inside of the hollow fibre is exposed to MS vacuum and the outer surface is exposed to the sample [116], and "flow-through", when the sample flows through the inner volume of the hollow fibre while the outer surface is exposed to the MS vacuum [117]. A comparison of these arrangements and evaluation of the influence of membrane thickness and temperature on permeation rates were reported by La Pack et al. [118]. The "flow-through" arrangement showed improved permeation rates.

The utility of MIMS has been demonstrated in various fields where on-line monitoring and detection of low levels of VOCs are in water and air are required [118–121]. Bauer and Solyom [122] showed MIMS to be a valuable tool for analysing chlorinated drinking water samples for trihalomethanes. The possibilities of the use of MIMS to detect ppqd concentration levels of toluene and *trans*-1,2-dichloroethene in water without preconcentration were demonstrated by Soni et al. [123]. Lauritsen and Gylling [124] described the use of MIMS for on-line monitoring of biological reactions.

An analysis system which combines membrane extraction with GC has also been used [115,125–128]. The introduction of analytes into the gas chromatograph after their permeation through the membrane is the critical part of this system. The possible solution is the use of gas sampling valves [125,126]. Their disadvantage is that only a small volume can be injected. Therefore, these systems have high detection limits and are not effective in monitoring at trace levels. The on-line membrane extraction microtrap (OLEMEM) system used by Xu and Mitra [115] seems to be more suitable for the analysis of VOCs at the low ppb level (see Fig. 3). The combination of the semi-permeable membranes with purge and trap GC–MS for the analysis of polar, volatile organic compounds from water, particularly those compounds not amenable to purge and trap GC, was reported by Shoemaker et al. [129]. They used a flat-sheet semipermeable membrane positioned between the two Plexiglas plates of a dialyser. In the groove of one plate, the water sample is pumped over the membrane. In the groove of the second plate, helium sweeps the permeated compounds on to the top of a trap from which the analytes are desorbed into a capillary column GC–MS system. This configuration permits the detection of analytes such as 2-propanol, 2-methyl-1-propanol and 1,4-dioxane at concentrations below 100 ppb.

5.1.5. Distillation techniques

The use of distillation as a preconcentration step prior to GC analysis of water distillate is suitable especially for polar substances, the isolation of which from water by other preconcentration techniques is difficult [98]. Distillation techniques were, among others, also discussed in a review of sample preparation for chromatographic separations by Poole et al. [130].

5.1.5.1. Steam distillation. In steam distillation extraction (SDE), sometime called gas-phase liquid–liquid extraction under reflux conditions [131], the isolation of volatiles consists of two successive steps: continuous distillation and continuous or discontinuous extraction. The distillate is extracted with a suitable extraction agent and, after extraction, the distillate is recycled back to the distillation flask with the water sample. The extraction agent can be regenerated (continuous extraction) or not (discontinuous extraction). A possible apparatus for continuous distillation–discontinuous extraction [132] is shown in Fig. 4. The vapour of steam volatiles after condensation flows through the layer of extraction agent (density lower than that of water) where the extraction is realized. The extracted distillate is returned to the distillation flask. After achievement of equilibrium, the

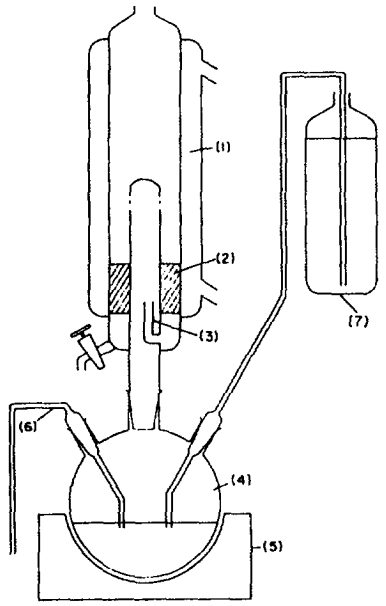

Fig. 4. Continuous steam distillation–discontinuous extraction apparatus (from Ref. [132]). 1 = Condenser; 2 = solvent layer; 3 = water overflow; 4 = boiling flask; 5 = heating mantle; 6 = overflow; 7 = sample reservoir.

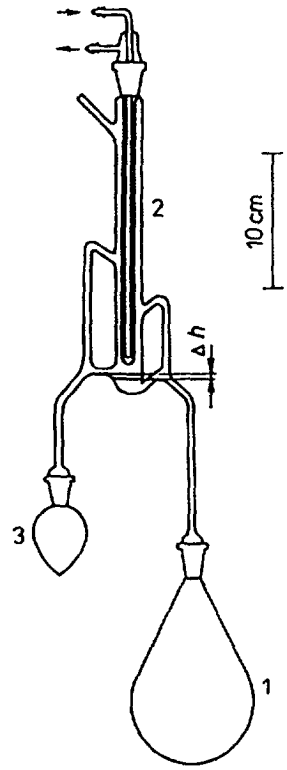

Fig. 5. Continuous steam distillation–continuous extraction apparatus (from Ref. [98]). 1 = Boiling flask; 2 = condenser; 3 = flask with extraction agent; Δh = difference between the levels of water and extraction agent.

extracted distillate still contains a reasonable concentration of the analyte compound corresponding to its equilibrium concentration with the organic solvent in the extraction space. Therefore, if a higher extraction recovery is required, the extraction agent must be refreshed (continuous extraction). This can be achieved by simultaneous distillation of the water sample and extraction agent, as is clear from Fig. 5 [98]. Generally, to achieve high recoveries with this technique some assumptions need to be fulfilled: the analyte creates an azeotropic mixture with water under the minimum boiling point, the volume of the water in the central part of apparatus, where extraction is realized, is as small as possible and the extraction agent has as low as possible a boiling point and a similar polarity to the analyte [98].

The steam distillation technique was originally used in the analysis of food and agricultural products [133,134], but it has also found use in the analysis of waters [135].

5.1.5.2. Vacuum distillation. Vacuum distillation was developed as an alternative technique for the determination of VOCs in non-aqueous environmental matrices. Despite this fact, this technique has also found application in the analysis of water samples. The greatest advantage of this procedure is the capability of handling of larger water samples (up to 1 l) [136] that enables lower detection limits to be achieved. Moreover, the technique is useful when analysing waters with a high organic content (about 20%) [35]. The technique came through several refinements, including the elimination of an adsorbent trap and direct interfacing of the apparatus with a GC–MS system [76]. The removal of the adsorbent trapping material eliminated a major source of problems that plagued volatile compound determination [137]. Its utilization was not recommended by Núñez et al. [60] at ppb or ppt levels, but recently published recovery and preci-

sion data regarding the utilization of vacuum distillation in the analysis of volatiles in waters are reasonable [35]. The vacuum distillation procedure used in the mentioned study is currently in the approval process for becoming an EPA test method. The apparatus used in this technique is shown in Fig. 6.

5.1.6. Direct injection

In this technique, the sample is injected directly into the GC column. The advantage of this procedure is a rapid and simple preparation of the sample without any pretreatment. However, the contamination of the injector and GC column with sample matrix (non-volatile compounds, salts, etc.) is a serious disadvantage and requires frequent maintenance of the injection port. Also, attaining a stable baseline is often difficult [41]. The detection limits depend especially on the detector sensitivity for target compounds and on amount of sample injected. For an injection volume of 10 μl, the upper limit acceptable in capillary GC, the detection limits are in the range 0.1–1 mg/l for flame ionization detection (FID), 0.01–1 μg/l for ECD [98] and 0.1–0.0001 μg/l for PID [138].

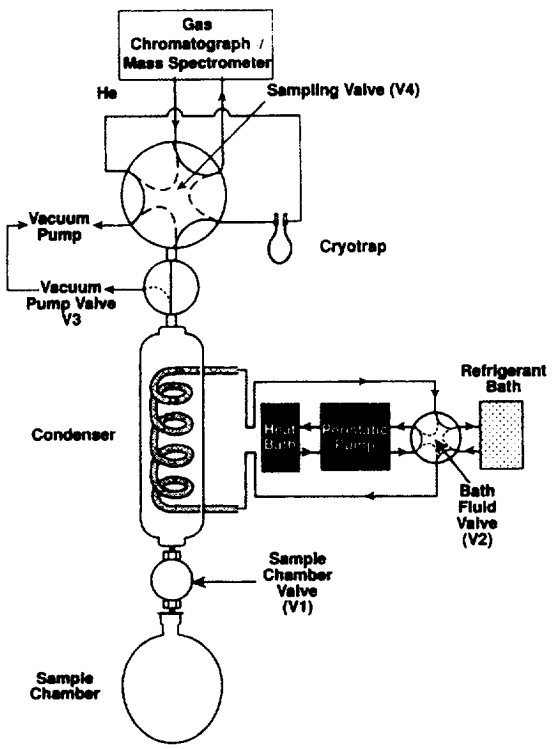

Fig. 6. Vacuum distillation apparatus (from Ref. [35]).

This technique has been applied mainly in the analysis of halogenated compounds in water samples using ECD [139,140]. The problems in using this combination were the lack of suitable columns, especially capillary columns, which would allow the separation of water from VOX, and the loss of the detector sensitivity due to large amount of water eluting from the column. When analysing samples with varying water contents, a shift of the retention times, especially on polar stationary phases, can be observed [98]. The solution to these problems was described by Grob and co-workers [141–143]. They stated that the problems with water were not caused by the detector, but other parts of chromatographic system, mainly by an insufficiently deactivated column, dead volumes in the injector ports and the use of unsuitable stationary phases. The main advantage is on-column injection into a non-polar immobilized polysiloxane capillary column with a thicker film, but after a certain period it is necessary to break the front part of the column to remove the deposits.

The comparison of direct aqueous injection followed by GC–ECD with the continuous-flow thin-layer headspace (TLHS) technique followed by electrochemical detection in the analysis of VOX was reported by Kozlowski et al. [144]. In the TLHS technique, volatiles are isolated from the aqueous phase in a thermostated spiral tube (TLHS column), where the sample flows in the form of a thin film countercurrent to a stream of purified air. The isolated compounds are mineralized in an empty quartz tube at 900°C, and the mineralization products are washed with distilled water. The conductivity of the wash solution is proportional to the VOX concentration. The principles and theory of TLHS have been discussed in detail [145,146].

Reasonable results in the analysis of priority pollutants and polar compounds such as alcohols, free carboxylic acids, aliphatic amines and phenols at the sub-nanogram level by the use of direct injection of aqueous solutions into a

graphite layer open-tubular (GLOT) column were reported by Bruner et al. [147]. The preparation of the column was described. The problems with detectors (FID, ECD, MS) were discussed.

The use of a packed column with mixed stationary phases consisting of potassium fluoride crystal hydrate and a conventional organic liquid stationary phase for direct aqueous injection GC analysis of polar compounds was described by Polanuer [148].

A possible way to increase the sensitivity in direct injection analysis could be to use large-volume injection with a deactivated retention gap and secondary cooling to avoid the loss of separation efficiency for volatile compounds.

6. Volatiles in sediments

Water and sediments are two matrices closely related to each other in a water column. Many methods for the determination of organic compounds in ground and surface waters have been described, but their direct application to the determination of VOCs in sediments is infrequent [28]. In the analysis of sediments it is necessary to take into account factors such as the content of organic carbon, the considerable composition variability of various types of sediments, the particle size distribution and the representativeness of the collected sample.

Organic pollutants are mostly hydrophobic, which indicates that these substances have a low affinity for solution in water, and are much more soluble in apolar liquids. These pollutants are readily taken up in the organic matter of sediments. Their tendency to become sorbed is related to the distribution coefficient of the compound between water and an apolar liquid, such as octanol. This distribution coefficient between octanol and water (K_{ow}) is highly correlated with the distribution coefficient between organic carbon and water K_{oc} [149,150]. Karickhoff [149] suggested for selected chlorinated hydrocarbons, chloro-*s*-triazines, carbamates, organphospates and phenylureas the relationship $\log K_{oc} = \log K_{ow} - 0.35$ and Schwartzenbach and Westall [150] propose $\log K_{oc} = a \log K_{ow} + b$, where a and b are the regression coefficients, which depend on the analysed group of pollutants. The values of the octanol–water distribution coefficients have been widely reported [151–155]. Log K_{oc} refers to partitioning between water and a 100% organic carbon phase; the actual distribution coefficient for the soil or sediment is then obtained as $K_d = K_{oc} f_{oc}$, where f_{oc} is the fraction of organic carbon [156]. When sediment contains more than 0.1% of organic carbon, the sorption of non-ionic organic chemicals is wholly attributed to organic carbon [156]. Below this value, sorption on non-organic solids can become relatively important [156], which depends on the particle size distribution. Thus, the organic pollutants can be easily preconcentrated in sediment and, with a change of aquifer conditions (pH, temperature variations, increased concentration of surfactants, etc.), can be released back to the water.

6.1. Analytical techniques

The techniques used in the analysis of sediments are in principle the same as those for the analysis of waters, except the direct injection technique. Generally, there is less published work in this area, and therefore the following text is not subdivided as fully as for the analysis of waters.

6.1.1. Gas extraction

6.1.1.1. Static headspace. As mentioned before, quantification by the static headspace procedure requires a thermodynamic equilibrium between the gas phase and the sample. This prerequisite is readily fulfilled by liquid samples of relatively low viscosity. This also holds for the applicability of the standard addition quantification method. However, if solid samples are analysed, thermodynamic equilibrium is not attained very easily; moreover, the standard addition method cannot be applied [58]. The possible utilization of this technique is for systems that behave as though

the volatiles are "dissolved" in the solid (monomer-in-polymer systems) [157].

When the sediment represents an adsorption system, then the distribution of the volatiles is determined by adsorption coefficients, which are usually function of concentration or are constant over a small concentration range [55]. Therefore, the static headspace and even multiple static headspace technique (MHE) can fail. The MHE technique can be applied, but with some other approaches [55].

The first consists in exhausting MHE, when the peak area of the analyte is measured step-by-step until no peak is found. The sum of peak area is proportional to the total amount of the analyte present in the sample. The second approach consists in the modification of the adsorption system to a partition system, by adding a displacer (usually water) to the headspace vial. Then static headspace can also be applied. This approach has been described in several papers [24,158–161]. The third method is a suspension approach [162] in which the sample is suspended in a water-miscible solvent such as ethylene glycol monomethyl ether. The solvent will displace water from the sediment and dissolve it. However, some problems still remain, because in the analysis of solid samples relatively high temperatures are often needed to release the volatiles from the sample, which can cause problems when using septum-closed vials [58], such as adsorption of the analyte on the septum, restriction of the desorption temperature owing to use of a rubber septum, contamination from the septum and the risk of secondary reactions in the gas phase during the equilibration [58]. Despite these facts, reasonable results were published for recoveries and reproducibilities of volatiles from solid matrices by static headspace [83]. This technique, followed by isotope ratio monitoring GC–MS, was also used in the determination of dissolved methane in sediments [163].

6.1.1.2. Dynamic headspace. Dynamic headspace has a great advantage in that equilibrium between the gas phase and the sample is not needed. The desorption time can be chosen in such a way that all volatiles are released from the sample, determined by repeated analysis of the same sample. Quantification can be carried out simply by external standard method.

Dynamic headspace analysis of sediments is usually carried out in two ways: with and without the addition of water prior to the analysis. With closed-loop stripping, these two approaches have been investigated by Amin and Narang [164]. The recoveries of various halogenated volatiles after various combinations of spiking and stripping arrangements showed no significant differences, only practical limitations make some methods better than others. The advantage of the approach with additional water is that the system turns to a partition type and the sample can be stripped at room temperature. Such purging, however, usually causes foaming of the samples [164]. This problem does not occur when no water is added, and, moreover there is no need to prepare interference-free water, but care must be taken when spiking such sediment. To achieve a good spike, it is important for the sediment to be coated uniformly with the various analytes. It is reasonable to use enough aqueous solution of the analytes to wet the whole sediment. Amin et al. observed that 1.5 ml of water is sufficient to wet completely 5 g of sediment.

The problems with recoveries of VOCs from sediments as to effect of sediment type, analyte and conductivity of the desorbing solution on recovery have been discussed [165]. The results of this study show that neither sediment mass and type nor the conductivity of the desorbing solution have an effect on the recovery of the P&T method. The ability of the method to desorb compounds from sediments, however, is affected by particular analtyes, and therefore cross comparisons of data are valid for different sediments and sample masses, but not for different analytes [165]. This conclusion is slightly in contradiction with the results presented by Voice and Kolb [83]. Perhaps a larger set of well characterized sediment types would be needed to clarify this topic.

Problems also arise with the preparation of blank organic-free sediment suitable for spiking experiments. This topic has been discussed in several papers [1,166,167].

The approach of adding water to sediment prior to stripping, but in an open-loop stripping system, was used by Bianchi et al. [1]. In this exhaustive study, the separation over 100 VOCs found mainly as trace contaminants or naturally occurring compounds was achieved. They studied, among others, the effects of stripping temperature, boiling point, vapour pressure and solubility on recovery. A temperature of 60°C was found to be optimum. Above this temperature, there is the risk of thermal degradation or subsequent reaction with other analytes. The relationship between recovery and boiling points was found to be strongly dependent upon the functional organic compound class. Non-polar volatile compounds (alkanes, aromatics, organohalogens) exhibit a more consistent and liner relationship than the polar alcohols and ketones. The relationship between vapour pressure and recovery is not as well established (correlation coefficient $r = 0.715$) as that between boiling point and recovery; in general, the higher the vapour pressure, the better is the recovery [1]. The solubility of selected VOCs in water has been found to be a reasonable guide to their recovery, second to the boiling points.

The analysis of VOCs in water and sediments from the Morava and the Danube rivers using a P&T open-loop stripping system was reported by Al-Rekabi et al. [168]. Sediment samples were mixed with organic-free water in a ratio of 3:1 wet mass sediment to water and then purged. The average concentrations of volatile *n*-alkanes (C_6–C_{13}) in water and sediments were found to be 0.02–1.33 μg/l and 0.04–105 μg/kg wet mass, respectively, and those of volatile aromatics were found to be 0.07–3.62 μg/l and 0.08–290 μg/kg wet mass, respectively. The reported method detection limits were in range 0.02–0.04 μg/l.

The procedure with additional water has also been applied [18] in the analysis of soils around leaking underground storage tanks.

6.1.2. Liquid extraction

The use of liquid extraction in the analysis of volatiles has a greater importance than in the analysis of waters. The reasons for this are the problems with the poorer quantification with regard to precision and recovery when using gas extraction techniques [160,161], especially dynamic techniques, when compared with the headspace method [30]. The origin of these problems seems to be in volatilization losses occurring during sample transfer from the storage vial to the purging vessel. Attempts to minimize these volatilization effects by reduction of soil, water and glassware temperatures have been unsuccessful [161]. In some cases the heterogeneity of sediment can be a source of poor precision [28].

One of the possible ways to overcome these problems is to collect sediment directly into preweighed vials with an organic solvent [30]. Moreover, when methanol is used as the solvent, the microbial degradation of the contaminants is suppressed by its toxic effects [28]. The possibilities of the loss of very volatile compounds and of contamination of the extract are solved by minimizing the free space over the solvent [12,31].

Various extraction agents such as *n*-hexane [3,169], *n*-pentane [170] *n*-pentane–2-propanol [170] and isooctane [171] have been used in combination with direct injection into the GC system. Methanol as an extraction agent has been used in several studies in combination with subsequent P&T of the extract diluted in blank water [12,28,30].

Kuráň et al. [28] compared dynamic headspace and P&T techniques with methanolic extraction (MeOH–P&T) for the determination of trace amounts of BTEX in river sediments. They stated that the MeOH–P&T method with an external standard method gave a better representativeness of the analysed portion, higher precision and lower detection limits.

When the internal standard method was applied, the precision and detection limits strongly increased (about fourfold) and the results obtained by both techniques were then comparable. Low recoveries were related to the short purging time. Surprisingly, higher recoveries were obtained for heavier analyses. A similar discrepancy was observed by Voice and Kolb [83]. They observed that higher recoveries had been found for the heavier analytes and the more sorptive matrices, and lower recoveries for light-

er analytes and the least sorptive matrices. Hence it can be concluded that the poor recoveries in the mentioned cases result primarily from volatilization losses due to the spiking procedure used (standard added directly on the surface of the sediment). Better recoveries were found when the standards were added in the liquid phase [12,30].

Generally, liquid–liquid extraction, especially when methanol is used, seems to be particularly useful in applications where long distances between the site of study and the instrumental equipment do not allow immediate determination of volatiles. Using the MeOH–P&T method, no significant decrease in concentration after 50 days of storage for some very volatile halogenated compounds (dichloromethane, 1,1-dichloroethene, chloroform) [30] and after 28 days for gasoline-range volatiles [12] was observed.

6.1.3. Solid-phase microextraction

As mentioned in Section 5.1.3, solid-phase microextraction (SPME) is one of the newest approaches to the analysis of volatiles. From the principle of this technique, for the analysis of sediments it results that the recovery, precision and detection limits will be influenced by similar parameters to those for the static headspace method. The possibilities of using headspace SPME with an internally cooled device in the analysis of sludges and soils involving procedures with heating up the sample or turning the adsorption system into a partition system by adding water have been widely discussed by Zhang and Pawliszyn [114]. The same device was used in the analysis of different types of soils [172]. It can be noted, however, that despite cooling of the SPME device, the recovery of more volatile compounds is problematic.

6.1.4. Membrane extraction

The use of membrane extraction in the analysis of sediments is problematic owing to the principle of this technique. The possibilities of membrane extraction in the analysis of sediments were briefly outlined by Cisper et al. [121], where an aqueous solution of methanol was added to soil. This mixture was filtered through glass-wool to remove large grains of soil that would block the membrane fibre. The filtrate can then be used in conventional way as described in Section 5.1.4.

6.1.5. Distillation techniques

6.1.5.1. Steam distillation. In the analysis of sediments, steam distillation is used in combination with stripping techniques with either an open-loop stripping system [18] or a closed-loop stripping system [164] after addition of water to promote distillation. The studies in which this combination has been used were discussed in Section 6.1.1.2.

6.1.5.2. Vacuum distillation. As stated before, vacuum distillation was developed as an alternative technique for determining VOCs in non-water environmental matrices. The capability of this techniques in the analysis of volatiles has been demonstrated for some special matrices such as algae [173], fish tissue [76,174] and cod liver oil [35]. Regarding the sediments, this technique gives greater recoveries than P&T for the individual VOCs and appears to be free from interferences due to sediment matrices and moisture content [174].

7. Conclusions

Volatile organic compounds constitute a potential risk factor to health. They enter the aquatic environment from both man-made and naturally occurring sources. To fulfil the requirements regarding health regulations and quality of water, it is necessary to monitor the level of VOCs in aquifers.

In the analysis of VOCs in water and sediment, headspace techniques are still widely used although reasonable results have been obtained by several other techniques such as solid-phase microextraction and vacuum distillation.

The trends in this field consist in efforts to automate the analysis of VOCs, improving portable systems for field GC of VOCs and optimizing the parameters affecting the analysis by

minimizing matrix interferences, efficient transfer of the preconcentrated sample to the GC system, selecting the proper trapping medium and GC inlet interface and the use of a suitable analytical column with more detectors connected in parallel or in series to separate as many VOCs as possible in a single run.

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