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Review

Methods of isolation and determination of volatile organohalogen compounds in natural and treated waters

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Abstract

Volatile organohalogen environmental pollutants and their sources and the routes of entry into various elements of the environment are described. Comprehensive literature data on the concentrations of these pollutants in natural and treated waters and in wastewaters in various countries are tabulated and discussed. A wide selection of the techniques for the isolation and preconcentration of the above pollutants are presented and discussed. Direct aqueous injection into a capillary column, liquid–liquid extraction, solid-phase extraction and headspace analysis are emphasized.

Keywords: Reviews; Water analysis; Environmental analysis; Sample preparation; Volatile organic compounds; Organohalogen compounds

Contents

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1. Sources of environmental pollution by volatile organohalogen compounds

Water pollutants can be divided into physical, radioactive, inorganic and organic. This paper discusses only water pollution by anthropogenic organic compounds.

Most organic compounds in water are of natural origin. These compounds are predominantly non-toxic, but can be precursors of toxic compounds in the process of water treatment. Anthropogenic organic compounds present the main hazard to the life and health of humans and flora and fauna. Approximately one third of all organic compounds produced end up in the environment, including water.

Volatile organohalogen compounds are particularly important pollutants among organic compounds as a result of their common use, persistence in the environment and toxicity. They are primarily anthropogenic. Volatile organohalogen compounds are used mainly as solvents, cleaning and degreasing agents, blowing agents, polymerization modifiers and heat-exchange fluids. As wastes, they find their way into lakes and rivers, and then into seas and oceans. Their concentrations in waters and air are very variable and depend upon atmospheric conditions due to washing by rain and evaporation from water during long periods of warm weather. It is estimated that the annual global production of organohalogen solvents alone amounts to several million tons [1].

One of the most important sources of organohalogen compounds, particularly volatile compounds, is water disinfection by chlorination [1–78]. The actual disinfecting agent is hypochlorous acid formed by the disproportionation reaction that takes place when chlorine dissolves in water. During chlorination, humic and fulvic compounds (so-called precursors), harmless and naturally occurring in water, are converted into toxic organohalogen compounds. The largest group of compounds formed during chlorination are trihalomethanes (THMs), that is, trichloromethane (chloroform, the most abundant compound), bromodichloromethane, dibromochloromethane and tribromomethane [1–78]. Organobromine compounds are formed when the water being chlorinated contains a large amount of bromides or when the chlorine used for disinfection is contaminated with bromine [1,8,10,15–18,45,49,57–59,73,81–83]. Hypobromous acid formed in the reaction of bromide ions with hypochlorous acid reacts with an organic matrix about 200 times faster than does hypochlorous acid [57]. The amount and kind of organohalogen compounds formed depend on the water pH, the amount of chlorine used and the content of organic matrix [total organic carbon (TOC)] in chlorinated water [8,9,15,36–46,49,77,78].

Trihalomethanes are not the only organohalogen compounds formed in the course of chlorination. Other volatile organochlorine compounds, such as tetrachloromethane, chloroethylene, 1,1-dichloroethylene, 1,1,2-trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane and 1,2-dichloroethane [1,4,5,12,17,20,26–29,50–60,83–89], are also commonly found in

chlorinated water. In addition, chlorination of humic substances and organic water pollutants yields a variety of other derivatives, of which over 100 have already been identified, including chlorinated acetone, chlorinated acetonitrile, chloropicrin, chloral, chloroacetic acids, chlorinated ethers, chlorophenols and chlorinated ketones [1,4,7,12,15,18,21,22,24,28,43–53,60,82–88]. Koch and Krasner [51] estimated that among organohalogen compounds formed during chlorination of water, 77% are trihalomethanes, 15% are haloacetic acids, 3% are halonitriles, 4% is trichloroacetaldehyde hydrate and 1% are the remaining compounds.

The kind and amounts of compounds formed depend primarily on the composition of water being chlorinated and on the dose of chlorine. In the case of intense chlorination of water in public swimming pools, these compounds become a serious health hazard to users of the pools [89–102].

Recently, papers documenting the biogenic origin of organohalogen compounds have also been published [103–106]. The presence of organohalogen compounds, measured as adsorbable organic halogen (AOX), has been established in groundwater thousands of years old. The content of organohalogen compounds is frequently estimated as the ratio of AOX to isolated fulvic acids, AOX/FA. The ratio varies from 730 to 8600 μg AOX per gram of organic matrix in surface waters, in soils it ranges from 210 to 1400 μg/g and in old groundwater it varies from 230 to 370 μg/g [103]. Organohalogen compounds have also been found in deep layers of marshes and peat bogs [103]. This demonstrates the substantial natural production of these compounds.

Organohalogen compounds can be produced by organisms living in soil, water and air or can be formed in the course of chlorination of fulvic acids with chlorine generated by the oxidation of chloride ions. Chlorine substitution is catalysed by certain enzymes (haloperoxidases), e.g., chloroperoxidase of the fungus *Caldariomyces fumago* [103].

However, the largest bioproducers of organohalogen compounds are marine macroalgae, sponges and bacteria, and particularly red, brown and green algae, which produce about 250 of compounds that have until recently been considered exclusively synthetic (e.g., dibromomethane, tribromomethane, chloroform, tetrachloromethane, tetrabromomethane). The macroalgae not only contain these compounds but also release them into seawater at rates of nanograms to micrograms of each compound per gram of dry algae per day [104]. Since organohalogen compounds are toxic, cases of deaths of entire algal colonies grown artificially have been reported [104]. It is estimated that only chloromethane makes a significant contribution to the atmospheric input ($5 \cdot 10^6$ tons/year) [104] and only about 1% of organohalogen compounds in the atmosphere are of natural origin [106].

2. Occurrence of volatile organohalogen compounds in surface and tap waters

Organic compounds undergo a variety of transformations in nature [2,75,76,107–111]. Anthropogenic organic compounds enter the atmosphere, soil or water. Volatile organic compounds evaporate to the atmosphere, from where they can be transported again to soil and surface waters in the form of wet or dry deposition. From water and soil, organic pollutants can enter living organisms either directly or through the food chain [108]. The latter route is particularly dangerous for the organisms at the end of the food chain, such as predators or humans, since their food contains a large dose of pollutants that has already been concentrated. In the environment, organic compounds undergo a number of transformations, such as hydrolysis, biodegradation, oxidation, photolysis, biotransformation and metabolic reactions in living organisms.

The stability of organic compounds in the environment is characterized by their half-lives or times of degradation [108,109]. Organohalogen compounds are very persistent in the environment and in many cases (chloroform, tetrachloromethane) their half-lives are of the order of several thousand years.

Table 1
Concentration of volatile organohalogen compounds in tap water in various locations (μg/l)

Country	Site	Year	Ref.	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
Portugal	Porto	1992	[154]	0.1–65.5	0.1–24.2	n.d.[a]–13.5	n.d.–13.5	0.1–116
Iran	Tabriz-Mean	1994	[153]	3.9		0.7		
Spain	Barcelona	79/81	[17]	1.9–156	11–60	9.3–129	n.d.–85	
USA	13 towns	1981	[35]	n.d.–540	n.d.–125	n.d.–250	n.d.–190	n.d.–695
USA	Kansas	1986	[41]	0.1–92	0.1–43	0.1–25	0.1–31	0.2–154
USA	35 intakes	1988–89	[18]	9.6–15	4.1–10	2.6–4.5	0.3–0.9	30–44
Italy	Sulcis	1986	[25]	1.6–46.5	6.6–30.5	11.6–20	0.7–25.8	37.8–94
Egypt	Cairo	1989	[67]	4.2–63.1	7.6–72.4	0.1–5.1	0.0–5.2	18–131
Canada	10 cities	1982	[141]	2.0–56.1	n.d.–5.0	n.d.–1.2	n.d.–0.1	3.3–57.3
Finland	Turku	1980	[142]	55.2	9.5	1	0.06	65.8
Spain	Santiago de Compostella	1987	[120]	6.3–121	3.0–54.7			
Spain	Prov. Lugo	1988	[112]	1.5–174	3.5–25	0–7.1		
Saudi Arabia	Dammam	1985	[19]	0.4	1.1	2.6	10	
Thailand	Bangkok	1984	[118]	n.d.–58	n.d.–14	n.d.–4	n.d.	n.d.–72
Poland	Gdańsk	1993–94	[293]	n.d.–42.7	n.d.–12.6	n.d.–2.3	n.d.–0.5	0.1–51.1
Israel	Jerusalem	1978	[57]	n.d.–3.6			n.d.–117	n.d.–133

[a] n.d. = Not detected.

As a result of the large-scale production and high stability of the groups of compounds discussed in this review, they are present in all kinds of water. Volatile organohalogen compounds have been determined primarily in tap water [2,4,6–80,86,108,112–155] (Table 1) and wastewater [11,23,126,155–164], but also in surface water [1,3,84,85,109,114,115,119,122,124,132–134, 136,140,143,163–184] (Table 2), groundwater [109,109,126,148,185–199], rainwater [168,175, 199–201] and seawater [23,62,165,122,184, 202–205], or even in water and ice of polar regions [204,205]. They have also been determined in biological material, human milk, urine and blood [1,93,108,142,148,155,173,206]

3. Methods for the isolation and determination of organic compounds in water

3.1. Total parameters as a measure of water quality

The data on hazards caused by organic compounds, and organohalogen compounds in particular, presented so far substantiate the need for continuous monitoring of levels of these contaminants in tap and surface water. Owing to the possibility of bioaccumulation of organic compounds, even low concentrations can result in poisoning of an organism. In practice, analysts have to deal with an enormous number of individual compounds, of which only a fraction can be identified and determined quantitatively. Using GC–MS, Coleman et al. [207] identified approximately 460 organic compounds in Cincinnati drinking water. In spite of this, it is estimated that only about 10% of the total organohalogen content is determined in surface waters, of which 3% are trihalomethanes, 6% are other volatile compounds and ca. 1% are chlorophenols, pesticides, PCBs, etc. A larger fraction of organohalogen compounds, namely about 25%, is determined in drinking water, of which 20% are trihalomethanes and 5% are other organohalogen compounds [207]. Consequently, a determination can exclude strongly toxic compounds whose presence in and analysed water sample has not been anticipated. Also, the determination of individual compounds is not always possible or required owing to limitations in the instrumentation available or costs of analy-

Table 2
Concentration of volatile organohalogen compounds in surface water and groundwater at different locations (ng/l)

Site	Year	Ref.	$CHCl_3$	CCl_4	$C_2H_3Cl_3$	C_2HCl_3	C_2Cl_4
Antarctica: Lake water	1988–91	[205]	–	0.6–7.6	–	1.2–20	0.2–4.3
Ice water				2.5–15	–	2.6–40	1.1–9.9
Seawater				1.8	–	3.8	0.7
Italy (Milan)	1988	[198]	n.d.[a]–161 000	n.d.–49 000	n.d.–171 000	n.d.–4 000 000	n.d.–60 000
Estuary and seawater (UK)	1992	[333]	<10–11 500	<25–102	<10–602	<10–269	<10–274
Industrial wastes (Sweden)	1978	[23]	760 000	–	–	2800	1400
Aurajoki River (Finland)	1980	[142]	1300	30	n.d.	40	10
Crawford Lake (Canada)	1981	[12]	58	3.8	5.9	32	9
Avon River (UK)	1984	[168]	2.6	1.1	9.7	15.2	14.7
Rainwater (UK)	1983	[168]	1.1	0.7	1.4	15	1.1
Tama River (Japan)	1983	[122]	590			140	
Aburatsubo Bay (Japan)	1983	[122]	300			20	
River Rhine (Koblenz, Germany)	1983	[175]	5900	750		340	940
St. Clair River (Canada)	1985	[178]	5–4482	2–2411	5–4174		2–740
Municipal sewage (Nantes, France)	1985	[160]	6200	420	1270	3140	7800
Elbe River (Czech. Republic)	1989	[164]				n.d.–30 000	n.d.–8600
Groundwater, max. conc. (Birmingham, UK)	1990	[186]	5000	1000	780 000	5 500 000	460 000
Groundwater (Modena, Italy)		[148]	2200	<1000	26 000	32 000	136 000
Reservoir (Straszyn, Poland)	1990	[166]	500	120		340	
Vistula River (Kiezmark, Poland)	1990	[166]	430	130		730	
Borowo Lake (Poland)	1990	[166]	220	80		120	

[a] n.d. = Not detected.

ses. These factors have resulted in the introduction into analytical techniques of basic and group total parameters [2,208–212]. Parameters such as total organic carbon (TOC), dissolved organic carbon (DOC) and suspended organic carbon (SOC) are used to characterize the content of organic compounds in water. Other parameters are defined in terms of the method of isolation of an organic fraction from water: volatile organic carbon (VOC) or purgeable organic carbon (POC), extractable organic carbon (EOC) and adsorbable organic carbon (AOC). However, total parameters measuring the carbon content in an organic fraction are not particularly suitable as an estimate of anthropogenic water pollutants and their hazard to human health, since a decisive majority of organic compounds in water are biogenic.

Conversely, organohalogen compounds are mostly anthropogenic and highly toxic to humans, animals and plants. As a result, total parameters describing water pollution by organohalogen compounds have found wide application. Similarly to the parameters characterizing carbon content in the organic fraction dissolved in water, group parameters related to the halogen content in the organic fraction are also determined. These include volatile organic halogen (VOX) or purgeable organic halogen (POX) [156,211–245], adsorbable organic halogen (AOX) [71,156,211–216,218–226,246–264] or extractable organic halogen (EOX) [71,211–215,217,219,224,229,248,265–267]. In addition, there are other parameters, such as non-purgeable organic halogen (NPOX), non-adsorbable organic halogen (NAOX) and non-extractable organic halogen (NEOX). Only the addition of these complementary parameters results in total organic halogen (TOX), although in many papers it is considered as being equal to AOX or EOX. In most cases, the discussed parameters are closely related to an analytical procedure,

solvent or sorbent being used, temperature, water pH and ionic strength, interferents, etc. As a result, analytical procedures used to determine these parameters require a detailed and precise description.

A different type of group parameter is total trihalomethanes (TTHM) (trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane), which is obtained by adding contents of individual compounds determined separately. This parameter is used mostly to determine the content of products of chlorination of humic substances in water disinfected by chlorination.

3.2. General procedure for the determination of organic compounds in water

Except for some wastewaters, volatile organohalogen compounds and pesticides occur in water at relatively low concentration levels. Hence, in the majority of cases the determination of both individual compounds and total parameters has to be preceded by the isolation of organic compounds from a complex aqueous matrix and preconcentration of the analytes.

Recently, a shift in the approach to the analysis of organic water pollutants has been observed among analysts. More and more emphasis is placed on the initial stages of analysis, that is, on sampling, isolation and preconcentration of the analytes and their preparation for the final determination. The importance of the initial stages of an analytical procedure, and especially of isolation and preconcentration methods, is reflected by numerous papers [33,71,111, 128,134,156,176,268–288] and conferences [145] dealing with the topic. The results of a survey taken by *LC · GC International* among analytical laboratories are also interesting [284]. According to participants of the survey, the contributions of various analytical steps in the total time of analysis were as follows:

sampling	6%
sample pretreatment	61%
analysis proper	6%
data handling	27%

These data clearly indicate that sample pretreatment, including isolation and preconcentration of the analytes, is an essential step of trace analysis.

The methods for the isolation and preconcentration of organic compounds in water are closely associated with the kind of analytes, their volatility, polarity, stability, water solubility, solubility in organic solvents, etc. Numerous techniques for the isolation and enrichment of organic analytes have been developed, the most common ones being solvent extraction, solid sorbent extraction, techniques utilizing the distribution of solute among the liquid and the gaseous phase (headspace, purging), and also less commonly used freezing-out, lyophilization, vacuum distillation, steam distillation and membrane processes (reverse osmosis, ultrafiltration, dialysis) [275–278,289]. A schematic diagram of the utilization of various isolation techniques for the determination of organic compounds in water is shown in Fig. 1 [209].

3.3. Determination of volatile organohalogen compounds by direct aqueous injection and electron-capture detection (DAI–ECD)

The only method for the determination of organohalogen compounds in water avoiding the

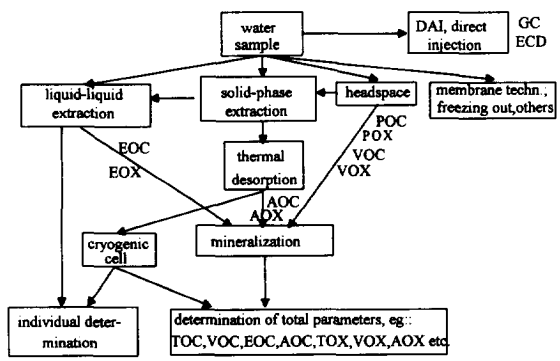

Fig. 1. Classification of techniques for the isolation and determination of organic compounds in water [209].

isolation and preconcentration step uses direct injection of an aqueous sample on to a GC column and an electron-capture detector [direct aqueous injection–electron-capture detection (DAI–ECD)] [59,98,131,138,154,244,290–295]. The method requires a special injector allowing cold on-column injection and special capillary columns. Cooling of the injector prevents sample evaporation from the needle of a syringe prior to its withdrawal. The DAI–ECD technique has been successfully used for the determination of volatile organohalogen compounds containing one or two carbon atoms [the products of chlorination of humic substances (THMs)] in tap water [59,131,138,290–294] and surface water [291,296]. The method avoids the problems associated with incomplete recovery of the analytes during their isolation from the aqueous phase, the effect of potential contaminants when using solvent or solid-phase extraction and losses of the analytes during the enrichment step.

During the chromatographic process, water is eluted before the analytes owing to the use of an inert column coated with a possibly thick layer (up to ca. 5 μm) of non-polar stationary phase which results in rapid and complete elution of water and sufficient retention of the analysed organohalogen compounds. Methylsilicones (DB-1, SE-30) are used as non-polar stationary phases. To improve separations, the methylsilicone stationary phases are modified with phenyl and/or vinyl groups (SE-54, 5% phenyl and 1% vinyl groups; PS-255, 1% vinyl groups). In practice, capillary columns 25–30 m × ca. 0.5 mm I.D. are used. Longer columns provide an improved resolution but at the expense of sensitivity. Isothermal runs at about 103–105°C are commonly employed. Non-volatile inorganic and organic compounds can gradually accumulate at the column inlet, which will deteriorate the resolving power of the column. To prevent this, readily exchanged, deactivated, non-coated precolumns connected to the analytical column through a zero dead-volume fitting are used [244,290,292]. Following a specified number of analyses, the precolumn can be completely exchanged or a part of it can be broken off. The precolumns play another important role; they serve as a so-called retention trap, narrowing chromatographic bands of the analytes [244]. As a result of the high sensitivity of ECD, the stationary phase in the analytical column should be immobilized through cross-linking and chemical binding to the column wall or support.

The electron-capture detector is usually operated at 300–350°C, which minimizes the residence time of water in the detector, thus improving the sensitivity of the detector. For the identification of the analytes and for quantitative analysis of other organic compounds, GC–MS and GC–FT-IR spectrometry are used [297].

The main advantages of DAI–ECD include its simplicity (no isolation and preconcentration methods are necessary), repeatability, reduction of the possibility of sample contamination and low detection limits (0.015–6 μg/l depending on the percentage of halogen in the compound). The detection limit of the method is related to the amount of the analyte in the sample injected on to the column and the volatility of the analytes.

3.4. Methods for the isolation of volatile organic compounds from water employing the distribution of analytes between the liquid phase and the gaseous phase (headspace techniques)

Headspace method are typically used for the determination of volatile compounds and utilize the distribution of analytes between the liquid and the gaseous phase. The analytes in a liquid sample are thus determined by measuring their concentration in the gaseous phase being in thermodynamic equilibrium with the sample. The methods are rapid and straightforward. They eliminate the effects of matrix components which could interfere with the determination, and contaminate the GC injector, detector and column. The problems associated with the blank contributed by the solvents in liquid–liquid extraction methods or by the sorbents in solid-phase extraction methods are also eliminated. Hence, headspace techniques are suitable for the analysis of samples with a high content of inorganic compounds (e.g., seawater, wastewater), high-molecular-mass organic compounds (polymers,

humic substances) or non-homogeneous mixtures (blood, other physiological fluids, colloids, wastewater), which would other wise require complex sample purification and treatment procedures. Fig. 2 presents the classification of headspace methods used for the determination of total parameters and individual compounds.

3.4.1. Static headspace methods

The simplest version of the headspace technique is static headspace [63,72,102,112–121,156,174,175,206,244,276–280,288,298–304]. It involves the analysis of the gaseous phase being in thermodynamic equilibrium, at a constant temperature T, with the analysed liquid sample. If the volume of the liquid phase is V_L and that of the gaseous phase is V_G, the initial analyte concentration in the liquid phase is c_L^0 and the equilibrium analyte concentrations in the liquid and gaseous phases are c_L and c_G, respectively, then the mass balance equation describing the equilibrium will be

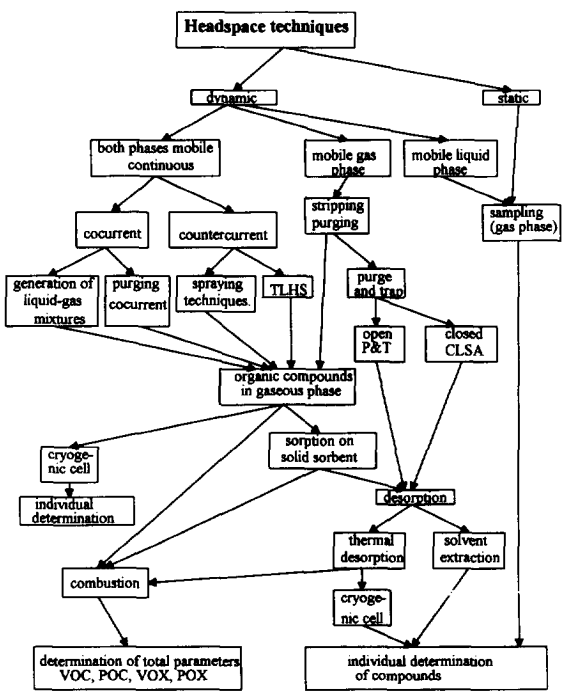

Fig. 2. Classification of headspace techniques.

$$c_L^0 V_L = c_G V_G + c_L V_L \quad (1)$$

Introducing the definition of the distribution coefficient of a compound i between the liquid and gaseous phase, $K_i = c_L / c_G$ (where c_L and c_G are expressed in grams per cm^3 of liquid and gas, respectively) and of the volume ratio of gaseous and liquid phases $r = V_G / V_L$, Eq. 1 can be rearranged as follows:

$$c_L^0 = c_G \cdot \frac{K_i V_L + V_G}{V_L} = c_G (K_i + r) \quad (2)$$

Eq. 2 is the basis of all quantitative determinations by the headspace technique. The most favourable conditions (the highest concentration in the gaseous phase) are obtained with the smallest possible V_G and K_i values.

The distribution coefficient can also be expressed in terms of physical-chemical parameters [305]:

$$K_i = \frac{RTd_L}{gp_i^0 M_L} \quad (3)$$

where R is the perfect gas constant, d_L is the density of the liquid phase at temperature T, g_i and p_i^0 are the Raoult-law activity coefficient and saturated vapour pressure of component i, respectively, and M_L is the molecular mass of the liquid phase, all the above quantities referring to an absolute temperature of the system T. Based on the experimentally determined K_i values, other fundamental thermodynamic parameters of the analyte can be found from Eq. 3.

In order to carry out quantitative analysis by headspace GC, the analyte has to be identified and its distribution coefficient determined or eliminated. The latter task can be accomplished by the following methods [244,270]:

- temperature method;
- model reference system (calibration method);
- standard addition method;
- method of successive extractions;
- continuous extraction method;
- variable volume method.

Guidelines for the selection of an optimum variant of static headspace are compiled in Table 3.

The equipment necessary to carry out static

Table 3
Guidelines for selection of an optimum mode of static headspace [244,270]

Headspace variant	Applicability range for K	Recommended r values	Remarks
Temperature method	$K < r$ at ca. 70°C	$1 < r < 10$	Used for compounds for which K decreases strongly with increase in temperature in the range 20–70°C
Model reference system (calibration)	Any K value	$0.01 < r < 100$	Difficult to reproduce the real matrix in standard solutions
Standard addition method	Any K value	$0.01 < r < 100$	Standard addition should cause about a twofold increase in c_G
Method of successive extraction	$K < 100$	$0.01 < r < 100$	If $K/r < 1$, then two extractions are sufficient
Continuous extraction method	$K > 100$	$0.01 < r < 100$	Should be used when $K/r_0 < 1$ and $K/r > 1$
Variable volume method	$0.1 < K < 10$	$0.01 < r < 100$	The procedure should be carried out in such a way that $r_1 < K < r_2$, where $r_1 = V_{G1}/V_L$ and $r_2 = V_{G2}/V_L$

headspace analysis is very simple and permits the automation of sample injection into a GC column. The design of headspace accessories has been described in a number of papers [112–114,244,275,277,301–307] and the accessories are now available commercially from numerous sources, such as Perkin Elmer (HS-6B; HS-100; HS-101), Hewlett-Packard (HP 19395A), Carlo Ebra (presently Fisons HS 250) and DANI (HSS 3950).

The detection limits of static headspace GC depend primarily on the sensitivity of the GC detector used, the boiling point of the analyte and its distribution coefficient between the liquid and the gaseous phase. Using a flame ionization detector and injecting a 1-ml gaseous sample, a detection limit of the order of 1–10 μg/l is obtained. For organohalogen compounds, the detection limit can be lowered to 0.1 μg/l by using an electron-capture detector. Besides increasing the temperature, the distribution coefficient can be decreased for certain compounds by as much as two orders of magnitude by salting out the liquid sample (mostly with NaCl solution) or by varying its pH, thus improving the detection limit [116,117,277,298,299]. The static headspace technique is suitable for volatile compounds with boiling points up to 200°C. The major advantages of static headspace GC include simplicity and rapidity, high sensitivity and precision, the removal of most of the solvent and inorganic and non-volatile organic compounds from the sample injected into a gas chromatograph and the possibility of automation of the final determination.

An original variant of static headspace has been proposed by Comba and Kaiser [132]. After heating a closed container with the analysed aqueous sample, the gaseous phase over the sample was sucked into a collecting vial cooled with liquid nitrogen which had been previously evacuated. Basically, this is a vacuum distillation method combined with trapping the distillate in a cryogenic cell. The final determination was carried out by GC–ECD following evaporation of the analytes from the cryogenic cell.

3.4.2. Headspace techniques employing immobile gaseous phase and mobile liquid phase

Among dynamic headspace techniques, the one most closely resembling static headspace involves the measurement of the analyte concentration in the immobile gaseous phase being in equilibrium with the mobile liquid phase being analysed [308]. The apparatus for such a measurement has been described first by Przyjazny et al. [309] and used by Biziuk and Polkowska [246]

to determine breakthrough volumes of solid sorbent beds. The apparatus allows monitoring of the variations in the analyte concentration in the analysed liquid sample as a function of the volume of sampling passing through the system.

3.4.3. Headspace techniques employing immobile liquid phase and mobile gaseous phase

These techniques fall into two categories. A stream of gas can pass over the surface of the analysed liquid sample or it can be bubbled through the sample (stripping, purging). By the term "immobile liquid phase" one should understand the liquid sample which is not being replenished, since in both categories the liquid phase is vigorously stirred either by a magnetic stirrer or by a gas stream.

An example of an apparatus in which a stream of purified gas was passed over the surface of a vigorously stirred and thermostated aqueous sample was described by Klöpffer et al. [310]. The liberated volatile compounds were then frozen out in a Dewar flask cooled with a mixture of acetone and solid carbon dioxide along with water vapour. However, the method has limited applicability because, despite stirring, the contact between the liquid and the gaseous phase is insufficient.

A substantially increased interface is achieved by passing a stream of gas in the form of tiny bubbles through the liquid phase. An example of a device based on this principle and used for the determination of the concentration of volatile organochlorine compounds in model solutions [244,246] is shown in Fig. 3. The device consists of a thermostated 100-ml glass vessel equipped with a frit (4 in Fig. 3), the inlet of the analysed sample which can be shut off by a valve, the inlet of the purge gas (2 in Fig. 3) and the outlet of the purge gas (3 in Fig. 3). The determination of the concentrations of volatile organochlorine compounds in model solutions was carried out by pouring 25-ml aqueous samples into the stripping vessel thermostated at 70°C and passing a stream of purified air at 200 ml/min for about 30–40 min. The liberated volatile organochlorine compounds were transported with the air stream to a quartz tube heated to 900°C and combusted. The chloride ions formed in the course of combustion were washed from the combustion tube with an aqueous solution of 2-propanol (1:1) with a small addition of perchloric acid (16 ml per 2 l of solution) into a coulometric cell and determined by coulometric argentometric titration. The addition of 2-propanol lowered the solubility of silver chloride while perchloric acid improved the conductivity of the solution. In this method, an organochlorine compound was determined as chloride ion and 1 mg of chloride ions resulting from the combustion of volatile organochlorine compounds (VOCl or, more correctly, POCl) corresponded to a charge of 2721.6 mC. In the case of analysis of model solutions, the identification of compounds was not required and the method, in addition to determining POCl, could also be used to determine the concentration of

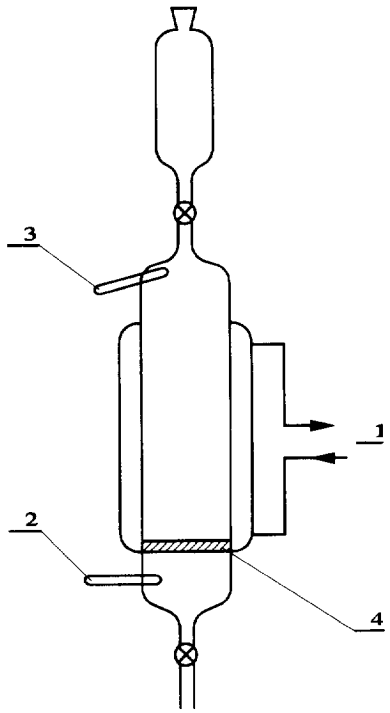

Fig. 3. Device for the removal of volatile organic compounds from the aqueous phase by stripping: 1 = Thermostat; 2 = inlet for purified air; 3 = outlet for air with liberated analytes; 4 = glass frit.

the analyte. In the analysis of natural samples, the concentrations of individual compounds cannot be determined by this procedure, but it can still be used for the determination of POX [210,211,215,216,220–228]. In almost all of the papers cited above, volatile organohalogen compounds were purged with a stream of purified gas, combusted and the resulting halides were determined by coulometric titration. Commercially available POX analysers, such as the Dohrmann total organic halide analysers DX-20 and DX-20A, Mitsubishi total organic halogen analyser TOX-10, Metrohm AOX, POX analyser and DANI or Ströhlein (Coulomat 702 CL) analysers, employ the same principle.

A different approach involves the combustion of liberated organohalogen compounds in a hydrogen–oxygen flame (Wickbold burner) [244] and, following condensation of the combustion products, the determination of halides, e.g., by nephelometry [215,224].

The purge technique described above can also be used for the determination of individual volatile compounds. To this end, the following approaches can be employed (see Fig. 2):

(a) the liberated organic compounds are trapped in a cryogenic cell, converted into a liquid and injected into a GC column;

(b) the purged compounds can be trapped directly inside a cooled GC column [purge with whole-column cryotrapping (P/WCC)];

(c) the liberated compounds can be adsorbed on a solid sorbent using an open purge-and-trap (P&T) system;

(d) the liberated compounds can be trapped on a solid sorbent using a closed-loop stripping system [closed-loop stripping analysis (CLSA)].

In the first approach, the freezing out of the purged compounds takes place in a capillary tube cooled with liquid nitrogen. Water is removed in a drier (a piece of Nafion tubing passing through a container filled with molecular sieve 5A) [153,168]. After the trapping process is completed, the cryogenic cell is rapidly heated and the released compounds are introduced into a GC column as a plug [168].

In the P/WCC method [311–315], volatile organic compounds are stripped from an aqueous sample with a stream of gas and, after removing water vapour (e.g., by using Nafion tubing), introduced directly into a GC column cooled with liquid nitrogen to −80°C. When the stripping/trapping process is completed, the GC column is rapidly heated to the starting point of the temperature programme and a normal GC analysis is performed.

The P&T method involves the removal of volatile organic compounds by a stream of gas passing through the liquid phase maintained at an elevated temperature and adsorption on a solid sorbent [4,9–15,92,122–129,137,157,162,164, 169, 170, 177, 200–202, 213, 218, 275, 277, 316–333]. The method has found wide applicability in the determination of volatile organohalogen compounds in tap water [4,9–15,122,123,125,129,137, 162,318,319], surface water [92,111,122,124,137, 164,170,177,202,326], seawater [122,202], wastewater [11,126,164], water in swimming pools [92], rainwater [200,201] and biological samples [322]. Helium, argon or nitrogen is usually used as a purge gas, and the most common sorbents are Tenax [11,12,92,122,123,125,126,129,137,162, 164,200–202,319–326], activated charcoal [13,167, 213,218,326,329,330,334], XAD [10], Chromosorb 106 [318], Spherocarb [318] or a combination of Tenax with carbon molecular sieve and silica gel [14,111,177]. The adsorbed analytes are usually released by thermal desorption at 180–280°C and, to focus the chromatographic bands of the analytes, they can be trapped in a cryogenic cell before the GC analysis takes place [14,127,129,200–202,323,324,328]. The adsorbed analytes can also be extracted from the sorbent bed with an organic solvent, e.g., with pentane from XAD-2 [10] or with carbon disulfide from activated charcoal [13], and the extract analysed by GC. In the case of sorption on activated charcoal, the total parameter POX can also be determined by combusting the entire sorbent bed with the trapped analytes in one of the commercially available TOX analysers (a Dohrmann DX-20 TOX analyser in the work cited here [213]).

The CLSA method, which was originally proposed by Grob and Zürcher [335], is a modification of the P&T method. In CLSA, the

headspace gas of the gas–liquid system is recirculated through the liquid sample and the sorbent bed [1,60,134,149,158,172,217,275,277,335,336]. Such a closed system reduces the danger of introducing artifacts into the system and the possibility of removal of the analytes from the system if they partially break through the sorbent bed. Charcoal filters containing 1.5 or 5 mg of charcoal were usually used as traps. The concentrated analytes were recovered by extracting the filter with 5–15 ml of carbon disulfide. The entire extract was then injected into a gas chromatograph. When using sample volumes from 0.5 to 2 l and flow-rates of the stripping gas from 1.0 to 2.5 l/min, the stripping time varied from 1 to 3 h. If only volatile compounds with low molecular mass are to be determined, the time can be reduced to 15 min.

In the majority of papers using CLSA, the procedure introduced by Grob (i.e., charcoal as the sorbent, extraction with CS_2 or dichloromethane [1,133,134,149,171,172] and GC final determination) were employed. However, similarly to the P&T technique, when the preconcentration step is completed, other approaches can be used. Hence, the preconcentrated analytes can be desorbed thermally [60,155,158,337] and determined individually by GC, or the entire sorbent bed with the preconcentrated analytes can be combusted in a stream of oxygen and CO_2 at 800°C (Dohrmann DX-20 TOX analyser) and the total parameter VOX determined coulometrically [217].

The major advantages of CLSA include:

rapidity and simplicity;

high sensitivity (detection limits for volatile compounds are from 1 to 10 ng/l, depending on the detector used);

elimination of the possibility of sample contamination during analysis.

elimination of matrix effects in the GC analysis;

The main problems with CLSA are:

the possibility of losses of the analytes and sample contamination by components of the air caused by leaks in the system or permeation through the walls of system connections;

adsorption of the analytes on the loop materials resulting in losses of the analytes and the "memory" effect of the system;

transfer of water droplets to the charcoal filter causing filter plugging and its contamination by non-volatile organic and inorganic compounds;

condensation of water in the sorbent pores, significantly reducing its sorption capacity;

irregularity of sorbent particles and their packing inside the filter, which can reduce the sorption capacity of the filter and make extraction difficult.

3.4.4. Headspace techniques with mobile liquid and gaseous phases

These techniques involve the transfer of volatile organic compounds from the mobile aqueous phase to the gaseous phase moving in a countercurrent [230–232,234–243,338–346] or a cocurrent sense [233,347–349]. The techniques have found wide application for the removal of volatile organic compounds from tap water, and especially toxic organohalogen compounds formed in the water treatment process. The removal is usually accomplished in stripping towers or columns in which the water being purified and a stream of air run countercurrently, and the volatile organic compounds are stripped from the aqueous phase. Many devices operating on a technological scale have been described in the literature along with calculations of mass transfer coefficients for individual compounds as a function of the kind and concentration of the compound, the ratio of flow-rates of water and air and the height and type of packing [338–343].

The devices used for the determination of volatile organic compounds in water are based on similar principles. Vernon et al. [344] proposed such a device employing a packed column with the aqueous sample and air flowing in countercurrent for the determination of volatile organic compounds in cooling water. After drying, the gas stream with the stripped compounds was directed to a detector (TLV Sniffer; Bacharach Instrument).

A number of different approaches have been proposed for the determination of volatile organic compounds, and particularly organo-

halogen compounds, in natural and treated water, including:

thin-layer countercurrent headspace (TLHS) [166,230,244,277,234–243];

spray extraction with the countercurrent gas flow [231,232,277,345,346];

generation of a water–gas mixture with the cocurrent gas flow [233,277];

continuous purging with the cocurrent [347–349] or countercurrent [347] gas flow.

The efficiency of removal of volatile compounds from the aqueous phase depends on the interfacial area, the temperature, the flow-rates of the two phases, the type of compounds and the nature of the matrix. The four approaches are discussed below along with the proposed applications and the results of determinations in real samples.

3.4.4.1. Methods employing thin-layer countercurrent headspace (TLHS). The TLHS method involves the transfer of volatile organic compounds from a thin layer of the aqueous phase flowing through a spirally wound thermostated glass tube to a stream of purified air flowing countercurrently. A diagram of such a device, patented by Kozłowski et al. [230], is shown in Fig. 4. The vertical, spirally wound and thermostated glass tube is about 2 m × 7 mm I.D. The analysed solution is introduced at the top of the tube through an inlet allowing instantaneous development of the gas–liquid interface, after which the sample flows down the tube as a thin layer into a U-shaped outlet. This design allows a certain positive pressure to be maintained inside the device and prevents the air with the released analytes from escaping outside the analytical system. The air used as a stripping gas was prepurified by passing it through Körbl catalyst [350] heated to 500°C, which removed organic compounds and also organosulfur or organohalogen compounds. The analytes released from water were introduced in the air stream into the final determination system.

Depending on the method of final determination used, TLHS can be applied to the determination of volatile organic or inorganic compounds in water by periodic or continuous

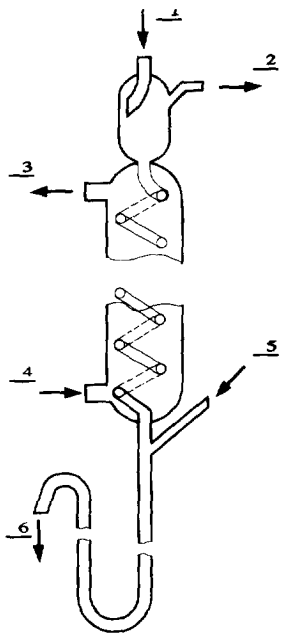

Fig. 4. Column for countercurrent TLHS in a spiral tube. 1 = Sample inlet; 2 = outlet for gas stream containing the liberated analytes (to the combustion tube); 3,4 = outlet and inlet for water from thermostat, respectively; 5 = inlet for purified air; 6 = sample outlet.

techniques and also to the removal of these contaminants from water. So far, the TLHS technique has found applications in the following analytical methods:

(1) periodic assay for VOX with coulometric final determination of halides [230,231,244];

(2) continuous assay for VOX with counductimetric final determination of halides [234,244];

(3) continuous assay for VOX with potentiometric final determination of halides [236–238];

(4) continuous assay for VOCl with spectrophotometric final determination of chlorides [244,235];

(5) periodic assay for VOX with the trapping of organohalogen compounds on a solid sorbent, followed by thermal desorption and coulometric final determination;

(6) continuous assay for VOCl, VOBr and VOI with spectrometric [atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP)] final determination [243].

The periodic assay for VOX with coulometric final determination of halides was the first described application of TLHS [230]. In this approach, the liberated organohalogen compounds were combusted in an empty quartz tube heated to 900°C in a stream of humid air, and the resulting halides were washed out from the outlet of the combustion tube and determined coulometrically (see Section 3.4.3). The result of VOX determination was calculated in terms of VOCl. The detection limit of the coulometric method for a sample volume of 2 l was 4 μg/l as VOCl.

In the continuous assay for VOX with conductimetric final determination [244,234], the volatile organohalogen analytes liberated by TLHS were also combusted, and the combustion products were washed out with doubly distilled water from the outlet of the combustion tube to a flow-through conductimetric cell. The principle of determination is based on the direct proportionality between the electrolytic conductivity of the washing solution containing the combustion products and the amount of mineralized organohalogen compounds released into the air stream by TLHS. In contrast to the coulometric method, which is absolute, this technique requires the preparation of a calibration graph.

The continuous assay for VOX with potentiometric final determination [236–238] involves the combustion of volatile organohalogen compounds liberated by TLHS, washing the combustion products with a solution containing 114 ml of acetic acid and 55 ml of aqueous ammonia in 1 l of water, deaeration of the washing solution containing the combustion products and potentiometric determination of halide ions in a flow-through potentiometric cell using an Ag/AgCl indicator electrode and a double-junction Ag/AgCl reference electrode. The potential of the indicator electrode is a linear function of the concentration of halide ions in the wash solution, and hence also a linear function of the VOX content in the analysed water sample. Hydrogen halides occurring in the combustion products can be converted quantitatively into their iodine equivalents by passing the combustion gases through a microreactor packed with silver oxyiodide (the reagent introduced by Kozłowski [351]) and heated to 180°C, followed by the reduction of iodine to iodide ions using ascorbic acid or sodium sulfite and potentiometric final determination of the iodide ions using an ion-selective electrode selective for iodides or an Ag/AgI indicator electrode [237,238]. In this case, the wash solution was 0.01 *M* ascorbic acid or sodium sulfite.

The continuous assay for VOCl with spectrophotometric final determination [244,235] utilizes a colour-producing reaction of formation of iron(III) thiocyanate in the presence of chlorides produced after combustion of volatile organochlorine compounds liberated by TLHS. The wash solution has the following composition (per litre of solution): 0.62 g $Hg(SCN)_2$, 30.3 g $Fe(NO_3)_3$, 4.72 g HNO_3 and 150 ml ethanol. The principle of determination is based on the following reactions:

$$Hg(SCN)_2 + 2Cl^- = HgCl_2 + 2SCN^-$$

$$3SCN^- + Fe^{3+} = Fe(SCN)_3$$

In the periodic assay for VOX with coulometric final determination, volatile organohalogen compounds are liberated by TLHS, sorbed from the air stream onto a solid sorbent at the sampling site, transported to the laboratory, thermally desorbed, combusted and determined by coulometric titration.

The organic compounds liberated by TLHS can also be introduced directly into an ICP spectrometer [243], where they are combusted, atomized and individual atoms excited, which allows the observation of emission (ICP) or absorption (AAS) lines characteristic of the analysed elements. Preliminary experiments demonstrated the applicability of this technique to the determination of volatile organochlorine, organobromine and organoiodine compounds with ICP detection. However, the method requires expensive and complex instrumentation which offsets the simplicity and low cost of TLHS.

3.4.4.2. Methods employing spray extraction with a countercurrent gas flow. Examples of devices

employing this technique are shown in Fig. 5. The main element of these devices is a spray extraction chamber (1 in Fig. 5), which allows the formation of a very large gas–liquid interface. The analysed aqueous sample is pumped with a piston pump (4 in Fig. 5) through a thermostated heat exchanger (3 in Fig. 5) in which the sample is heated to the desired temperature and then sprayed on the walls of the chamber through a 15-hole (0.5 mm diameter) spray ring (2 in Fig. 5). A stream of purified air is passed countercurrently to a thin layer of water flowing down the chamber walls, stripping the analytes, which are then introduced into the system for the final determination. In the work cited here [231,232,277], the device shown in Fig. 5 were used for the determination of VOX; hence, as described above [230,244], the liberated organohalogen compounds were combusted in a stream of humid air in an empty quartz tube heated to 900°C, and the resulting halide ions were washed from the tube outlet into a coulometric cell and determined by argentometric titration.

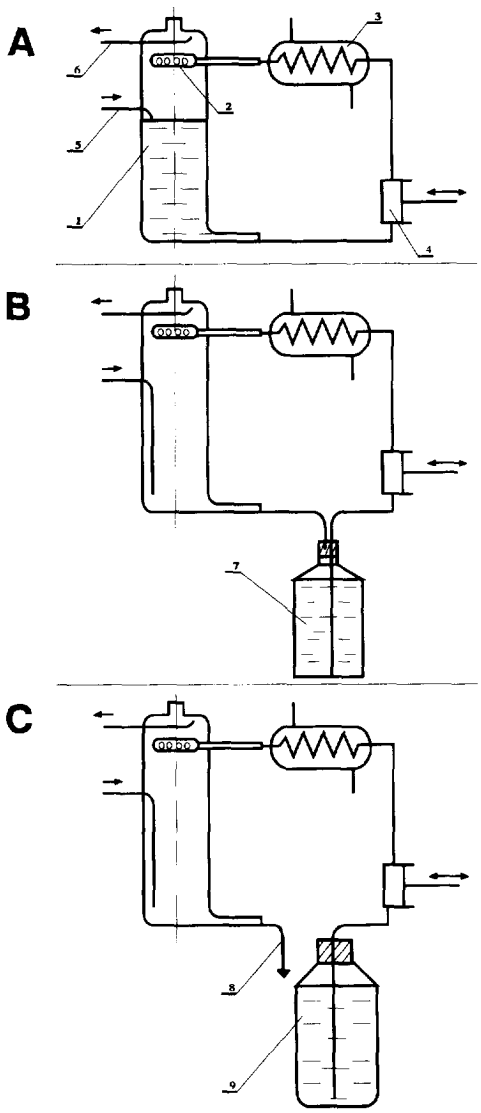

Fig. 5. Three approaches to using the spray extraction technique for the isolation of volatile organic compounds from water. (A) Periodic method: 1 = spray extraction chamber; 2 = 15-hole spray ring; 3 = heat exchanger; 4 = piston pump; 5 = inlet for purified air; 6 = outlet for air with analytes. (B) Periodic method with an external container: 7 = external container. (C) Continuous method: 8 = sample outlet; 9 = analysed water.

Fig. 5 presents three variants of the discussed principle [231]:

(A) An internal periodic system. The analysed sample (ca. 400 ml) is placed inside the spray extraction chamber and pumped through the spray ring in a closed system.

(B) An external periodic system. The analysed sample (1–2 l) is placed in an additional external container connected in a closed system with the pump and the spray extraction chamber.

(C) A continuous system. The analysed water sample is pumped through the spray extraction chamber in a continuous manner without returning the water into the chamber.

In all three variants, the flow-rates of the sample and the air and the temperature of the heat exchanger can be adjusted [231,232].

The spray extraction devices described above made use of piston pumps and connections associated with them, which can result in sample contamination, analyte losses or a "memory" effect of the system. These disadvantages are eliminated by the device shown in Fig. 6. The main element of this device is a thermostated vessel for the expansion of the surface of the gas–liquid interface (1 in Fig. 6) equipped with a chamber (2 in Fig. 6) with a PTFE-coated stirring bar (3 in Fig. 6). The chamber is connected through a tangentially positioned glass

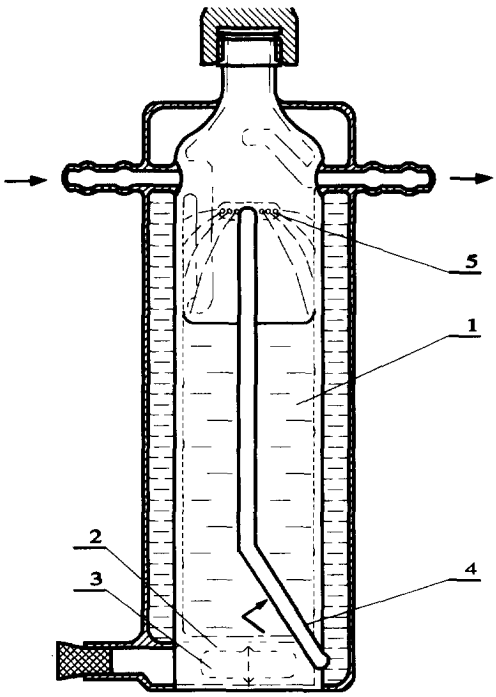

Fig. 6. Pumpless spray extraction device: 1 = Thermostated vessel with the analysed sample; 2 = chamber with stirring bar; 3 = PTFE-coated stirring bar driven by a magnetic stirrer (not shown); 4 = glass tube; 5 = 15-hole spray ring.

tube (4 in Fig. 6) with a spray ring (4 in Fig. 6), whose design was described previously. The device is placed on a magnetic stirrer. The rotating stirring bar acts as a rotor of a centrifugal pump, forcing the analysed solution through the spray ring and on the vessel walls at a flow-rate of about 250 ml/min. Since the stirring chamber is connected with the main body of the vessel, the analysed sample undergoes multiple passes through the spray ring. A stream of purified air flows countercurrently to the liquid sample at a flow-rate of 250 ml/min. The entire device is thermostated at 90°C. The liberated analytes were introduced in a stream of stripping gas into the system for the final determination (combustion and a coulometric titration of the resulting chlorides) [232].

The investigation of the dynamics of stripping of trichloromethane, trichloroethylene, chlorobenzene, dichlorobenzene and their mixture has shown that after 30 min of operation of the device the recovery of the analytes ranged from 92 to 97%.

A device utilizing the spray extraction technique with a countercurrent gas flow was also described by Baykut and Voigt [345,346]. Water samples were pumped through a special nozzle into an extraction chamber at about 450 ml/min, forming a cone of tiny liquid droplets. A stream of carrier gas (at 150 ml/min) passed through the droplets, extracting the analytes. Following the extraction, the gas passed through a sorption tube packed with Tenax TA. After the sampling period, the trapped analytes were thermally desorbed and introduced into a gas chromatograph. The analytes studied included benzene, toluene, *p*-xylene, acetone, *tert.*-butylbenzene, *p*-dichlorobenzene, dichloromethane, trichloroethylene, naphthalene, tetrachloroethylene, 3-pentanone and 4-heptanone. Linear calibration graphs were obtained for the investigated compounds with a low detection limit ranging from 10 to 30 ng/l.

The methods for the isolation of volatile organic compounds from water described in this section are characterized by good precision and high accuracy. The continuous method can be used for the on-line monitoring of volatile organics in water. Depending on the method of final determination, the described isolation techniques can also be utilized for the determination of VOC or VOS (volatile organic sulfur), or for the determination of individual compounds by GC, following the purge-and-trap enrichment and solvent extraction.

3.4.4.3. Methods employing generation of a water–gas mixture with a cocurrent gas flow. The design of devices for the isolation of volatile organic compounds by the generation of a water–gas mixture is based on the principle of operation of a Mammoth-type micropump. An example of such a device for the periodic determination of volatile organohalogen compounds is shown in Fig. 7 [233,277]. The volume of the glass cell is 300–400 ml, which permits the analysis of a 200-ml sample. A stream of purified air is passed at 200 ml/min through a capillary (9 in Fig. 7) into the tube of the micropump (10 in

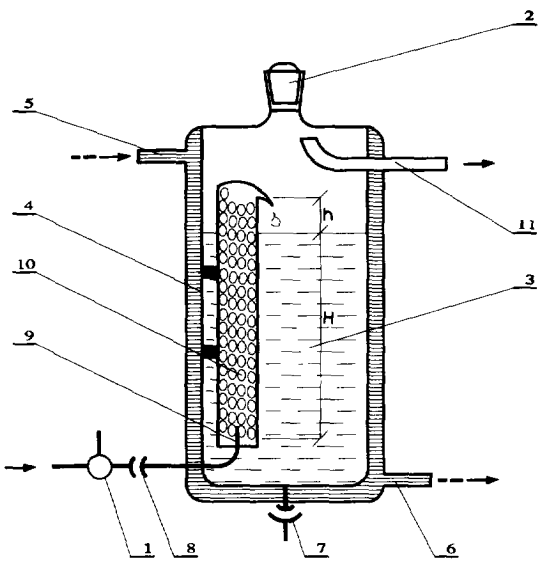

Fig. 7. Device for the isolation of volatile organic compounds from water by the generation of a water–gas mixture. 1 = Three-way stopcock; 2 = ground-glass stopper; 3 = analysed water sample; 4 = water jacket; 5,6 = thermostated water inlet and outlet, respectively; 7 = draining valve; 8 = ground-glass joint; 9 = capillary gas inlet; 10 = micropump tube; 11 = outlet for gas with analytes.

Fig. 7). This results in the generation of a water–gas mixture with a density lower than that of water, raising the liquid level in the tube above the upper edge of the outlet and pumping of the solution through the tube. In this way, the entire solution in the cell passing through the tube is in multiple contact with the gas stream in a system with a very large interfacial area. The volatile organohalogen compounds liberated from the aqueous phase were then combusted and the halide ions formed were assayed by coulometric titration. Using this approach, total parameters were determined in model solutions (VOCl) and natural samples (VOX). Studies of the dynamics of the recovery of individual compounds as a function of temperature revealed that the time necessary to obtain a VOCl recovery close to 100% decreases from 35 min at 25°C to 8 min at 90°C.

The above method of isolation of volatile organic compounds from the aqueous phase can also be performed in a continuous mode which allows the use of larger water samples, thus resulting in a decrease in detection limits. A diagram of such a device is shown in Fig. 8 [233]. The analysed water sample is pumped at 45 ml/min through a preliminary heat exchanger (7 in Fig. 8) to an inner tube of the device (5 in Fig. 8) thermostated at 90°C, in which the water–gas mixture is generated. Purified air is introduced at 250 ml/min into the inner tube through a three-way stopcock (1 in Fig. 8) and a capillary (3 in Fig. 8). During pumping of the water–gas mixture through the inner tube, volatile organic compounds are transferred from the aqueous to the gaseous phase. After stripping of the analytes, the aqueous phase is removed through an outer chamber (4 in Fig. 8) and an outlet (9 in Fig. 8). The final determination of VOCl or VOX is carried out in the same way as for the periodic method. Model investigations of this technique revealed that at 90°C a recovery of the analytes close to 100% is achieved at a flow-rate of the analysed solution below 55 ml/min.

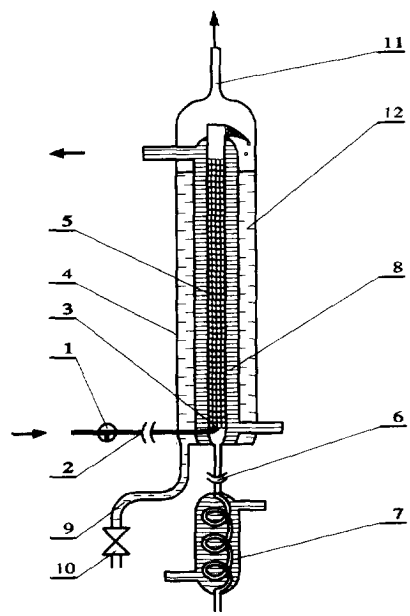

Fig. 8. Device for the isolation of volatile organic compounds from water by the continuous generation of a water–gas mixture. 1 = Three-way stopcock; 2,6 = ground-glass joints; 3 = capillary gas inlet; 4 = glass tube; 5 = water–gas mixture; 7 = heat exchanger; 8 = water jacket; 9 = sample outlet; 10 = draining valve; 11 = gas stream outlet; 12 = water sample outlet.

The methods described in this section are characterized by good precision (the relative standard deviation ranges from 1.6 to 4.1% for the periodic mode and from 1.4 to 3.6% for the continuous mode) and a high recovery (the average recovery varies from 96.4 to 99.7% for the periodic mode and from 91.6 to 96.5% for the continuous mode). High concentrations of inorganic salts (simulated seawater) or of surfactants had no effect on the analytical process [233]. The periodic mode described here is superior to other periodic methods of isolation of volatile organic compounds from water in terms of the time required to remove the analyte completely from the sample. In combination with continuous methods of final determination (e.g., conductimetric or potentiometric), it allows the monitoring of water pollution on a continuous basis.

3.4.4.4. Methods employing continuous purging of volatile organic compounds from water with a cocurrent or countercurrent gas flow. A device for the continuous purging of volatile compounds from a flowing aqueous phase into a cocurrently flowing stream of inert gas (nitrogen, helium) is manufactured by Siemens [348,349]. An aqueous sample is heated to 58°C, fluorobenzene is added as an internal standard and then the sample is pumped through a frit into a headspace chamber at a flow-rate of 4 l/h. A stream of helium (or nitrogen) is passed cocurrently through the chamber at a flow-rate of 1.5 l/h. The helium stream is then dehydrated in a condenser and introduced into a gas chromatograph through a six-port valve and a sample loop. GC is carried out isothermally with a flame ionization detector. The following detection limits were obtained: 2.8 mg/l for trichloromethane, 2.0 mg/l for fluorobenzene, 2.3 mg/l for tetrachloroethylene and 1.4 mg/l for toluene. In this approach, continuous isolation of organic compounds from the aqueous phase was combined with a periodic method of final determination (GC).

Devices based on a similar principle and used for the isolation of volatile hydrophobic compounds (chlorobenzenes, toluene and mercury) from the aqueous phase directly in the water reservoir or by using a pump were described by Sproule et al. [347]. In the device operating directly in a water reservoir, a stream of purified air was introduced through a frit into the lower end of an open Teflon column immersed in the water reservoir and passed at a flow-rate of 50–150 ml/min through water present inside the column. The air stream containing the stripped compounds was then directed into an absorber packed with Tenax GC. Mercury was trapped on metallic gold. The water inside the Teflon column was exchanged naturally during the sampling period. After the isolation was completed, volatile organic compounds trapped on the Tenax bed were desorbed thermally and transferred directly into a GC column. In the second device, the analysed water was pumped to the top of a column at 340 ml/min and a stream of air was pumped countercurrently through a frit at the bottom of the column at 240 ml/min. The water was removed from the column through a side-arm (overflow) and the air with the stripped compounds was passed through two absorbers filled with 200 ml of hexane each. After the isolation of volatile organic compounds was completed, the hexane from each of the absorbers was evaporated to a volume of 1–2 ml and GC analysis was carried out using an electron-capture detector.

All the headspace techniques discussed in this section are necessarily suitable for the isolation of volatile and semivolatile compounds, which constitutes their major limitation. However, the techniques have one major advantage, which is the possibility of separation of the analytes from a complex inorganic and organic matrix. This significantly reduces the chance of contamination of chromatographic columns and detectors, and enables much simpler chromatograms to be obtained, thus facilitating identification of the analytes and lowering their detection limits. The apparatus used for headspace techniques is relatively simple and permits the automation of determinations and their performance in a continuous or semi-continuous mode.

3.5. Application of liquid–liquid extraction methods for the isolation of organic compounds from the aqueous phase

Liquid–liquid extraction is one of the oldest methods for the isolation of organic compounds from the aqueous phase [4,86,128,205,271,272, 275–278,288,352,353]. It is based on a favourable partition coefficient of the analytes between the aqueous phase and an organic solvent with which the analytes are extracted. This principle also determines the applicability of liquid–liquid extraction. Organic solvents used for the extraction have to be immiscible with water (i.e., relatively non-polar) and the analytes have to dissolve better in the solvent than in water. The most favourable case for the analyst is a close to 100% transfer of the analytes into the organic phase. This can be achieved by proper selection of the solvent, by adjusting the pH of the aqueous phase or by adjusting its ionic strength. If the extraction into the organic phase is not close to 100%, a correction factor has to be introduced or an internal standard with properties similar to those of the analytes has to be added to the sample. This does not ensure, however, reliability of the results owing to the error in determining the correction factor and the effect of the matrix and temperature on the partition coefficient. The extraction proper is carried out by adding an organic solvent immiscible with water to the aqueous sample (typically in a 1:10 to 1:100 ratio) and vigorously stirring or shaking the two phases.

Numerous papers have dealt with the extraction with pentane of volatile organohalogen compounds that are the products of chlorination of humic acids in the course of water treatment [15–23,86,171,144,159,203,354]. Besides pentane, other solvents such as diethyl ether [15,43,44], hexane [69,139,205,355], methylcyclohexane [109], isooctane [167], dichloromethane [1,356] and other solvents and their mixtures [52,140,142,336] have been used. In most of the cases cited above, the isolated volatile organohalogen compounds were separated and determined by GC–ECD. The cleaned extracts were also used to determine EOX, following their combustion and coulometric determination of the resulting halide ions [265–267].

To expedite the extraction process, especially for larger volumes of aqueous samples, a number of devices and procedures have been developed allowing continuous extraction using solvents both lighter and heavier than water [163,173, 176,275,357,358].

The liquid–liquid extraction methods, although simple and not requiring sophisticated apparatus, have a number of drawbacks. They require the use of large volumes of expensive, and possibly toxic, solvents, which are then evaporated, thus creating the problem of storage of hazardous waste. Working with these solvents may require the use of personal protection devices, such as respirators. The solvents used for extraction should be of very high purity, free from traces of the analytes and other potential interferents, otherwise a large solvent background is obtained, frequently precluding the determination. The formation of emulsions is yet another problem with liquid–liquid extraction. Considering all these disadvantages, solid-phase extraction seems to be better suited for the isolation of organic compounds from water.

3.6. Methods for the isolation of organic compounds from the aqueous phase based on sorption on solid sorbents (solid-phase extraction)

Sorption on solid sorbents is currently the most common technique for the isolation of organic compounds from water [273–279,359]. The process is based on partitioning of organic compounds dissolved in water between a solid sorbent and the aqueous phase. The retention of substances on solid adsorbents is predominantly due to van der Waals forces. The technique has many advantages:

it allows isolation and preconcentration on the sorbent bed of both volatile and non-volatile organic compounds present in water, which permits the determination of both individual analytes and total parameters (TOC, TOX, TOS, etc.);

water and inorganic compounds are minimally retained and readily removed from the bed during washing and drying following the sorption step;

for properly selected adsorbents, the partition coefficients of the analytes between the sorbent and water approach infinity;

wettability of a sorbent by water results in satisfactory transport of the analytes toward the sorbent surface;

sorbents do not react chemically with the preconcentrated analytes and can be readily regenerated, which extends their lifetimes to several years;

in contrast to liquid–liquid extraction, the problems associated with using large volumes of expensive and toxic solvents of high purity, generating hazardous waste, the formation of emulsions and the effect of solvent background on the results of analyses are largely minimized;

the analytes trapped on a sorbent can be transported and stored, the final determination being performed at a convenient time;

the enrichment process is rapid and straightforward and can be readily automated.

Preconcentration can be carried out by passing the analysed aqueous sample through a column packed with a sorbent or in a batch mode, by agitating the aqueous sample with a sorbent added to it and then separating the sorbent by filtration. Following preconcentration of the analytes, further analysis can be carried out as follows (see Figs. 1 and 2):

the whole sorbent bed is combusted and the total parameters of water pollution are determined (in the case of carbon sorbents only);

the trapped analytes are solvent extracted and, following the extract clean-up, individual analytes are determined by chromatography, or the extract is combusted and the total parameters are determined;

the trapped analytes are thermally desorbed, combusted and the total parameters determined, or, following the desorption step, the analytes are frozen out in a cryogenic cell, released and individual compounds determined chromatographically.

In analytical practice, a variety of adsorbents have been used for the isolation of organic compounds from water, and new sorbents are being developed, better suited for specific matrices, methods of final determination or selective isolation of a particular group of compounds. The most common kinds of sorbents along with their functional groups, matrices and possible mechanisms of interactions with the analytes have been tabulated [276]. In the following text, we discuss the sorbents most often used for the isolation of volatile organohalogen compounds and pesticides from water.

3.6.1. Activated charcoal

Powdered activated charcoal (PAC) or granulated activated charcoal (GAC) have been used for the longest time for the isolation of organic compounds from water. This sorbent has found the widest applicability as a result of its high sorption capacity and thermal stability and the possibility of combustion of the entire sorbent bed. The drawbacks of activated charcoal include incompleteness of sorption and desorption, the possibility of reactions of the sorbent with the analytes and a relatively high background. In the assays for organohalogen compounds, charcoal (mostly GAC) is commonly used for the determination of AOX, frequently treated as TOX. The analytes are preconcentrated on the sorbent by shaking PAC with the analysed water sample [57,212,216,219,223,255,256,260,360] or by passing the sample through a column packed with GAC [32,55,71,156,207,211,214,218,220–222,225, 226,249,253,254,257–259,261,361–366]. Prior to use for trace analysis, activated charcoal has to be cleaned. An example of a clean-up procedure can be found in Ref. [361]. When activated charcoal is used in a batch mode, about 1 g of the sorbent per 10 l of sample [367,368] or 50 mg of the sorbent per 100 ml of sample [250,251] are typically added and the sample is shaken or stirred for 1 h. In order to prevent the sorption of inorganic chlorides, the analysed sample is sometimes acidified with nitric acid and sodium nitrate is added [57,255,256]. After filtering out the sorbent, the residual adsorbed inorganic chlorides are removed by washing the bed with an acidified sodium nitrate solution

[71,216,255,256,260], followed by drying the bed and its combustion at 1000°C in a stream of moist air. The resulting HCl is determined coulometrically by argentometric titration or potentiometrically using ion-selective electrodes. For each batch of activated charcoal, the blank has to be determined and subtracted from the result of determination.

The second approach, i.e., passing the analysed water sample through a column packed with GAC, has been utilized in commercially available AOX and TOX analysers, including the DANI Type 70.10 AOX analyser, Mitsubishi Model TOX-10 analyser and Dohramann DX-20A TOX analyser. In this approach, 10–150 ml of the analysed water sample are passed at 3 ml/min through the sorbent bed. The bed is then washed with 2 ml of 0.5% $NaNO_3$ solution. The entire bed is next transferred to a boat which is placed in a furnace. The activated charcoal with the trapped analytes is combusted at 800°C in a stream of oxygen and the halide ions formed from organohalogen compounds are determined by coulometric titration.

3.6.2. XAD porous polymeric sorbents

Amberlite XAD macroporous resins have found wide application for the isolation of organic compounds from water. Their basic physical properties have been described elsewhere [274,275]. Like activated charcoal, XAD resins also have to be pretreated prior to their use in trace analysis [274].

XAD-2 and XAD-4 (styrene–divinylbenzene copolymers) have been used most frequently because of their hydrophoibicity and lack of adsorption of inorganic ions. XAD-2 has been utilized for the preconcentration of volatile organohalogen compounds [24,45,50,146,176] and other groups of compounds. The sorbent was also used to remove organic compounds from drinking water and to prepare extracts of these compounds to study mutagenic properties of drinking water [83,145,369,370].

Solvent extraction is the most common method of desorption of trapped analytes from the sorbent bed. The solvents used for desorption included diethyl ether, ethyl acetate, methanol, acetone, acetonitrile, cyclohexane, *n*-hexane, dichloromethane, ethanol or a mixture of two solvents.

XAD-4 has a higher thermal stability (250 vs. 200°C) and a larger specific surface area (750 vs. 330 m^2/g) than XAD-2. It has been used for the preconcentration of volatile organohalogen compounds [64,98,167,246,247,371] and other compounds. XAD-4 has also been applied in the removal of chlorinated pesticides, phenols, chlorinated aliphatic hydrocarbons and BTX (benzene, toluene and xylenes) from wastewater [372]. The solvents used for the recovery of the trapped analytes included pentane, dichloromethane, diethyl ether, ethanol, acetone, methanol and hexane.

Other XAD resins have found much more limited application [274,276,277]. XAD-7 and XAD-8 (methyl methacrylate polymers) have also been utilized for the isolation and enrichment of volatile organohalogen compounds [50,264].

Some procedures for the isolation of organic compounds from water employ a combination of sorbents, e.g, XAD-4–XAD-8 for the determination of THMs, PAHs, aliphatic hydrocarbons and dibenzofurans [366], XAD-2–XAD-7 for the determination of organic compounds in surface water [373] and XAD-8–GAC for the determination of 780 compounds [87].

Final determinations of the analytes were typically performed by GC with flame ionization or mass spectrometric detection [24,64,83,176, 373], but selective detection methods, such as ECD and electrolytic conductivity detection for organohalogen compounds, nitrogen–phosphorus detection for organonitrogen and organophosphorus compounds and flame photometric detection for organosulfur compounds have also been used.

Thermal desorption is the other method for liberation of the trapped analytes. As a result of the relatively low thermal stability of XAD-2, thermal desorption is not usually used for this sorbent. Chang and Fritz [146] proposed a double-sorption procedure based on the sorption of the analytes on XAD-2, followed by their thermal desorption and sorption on another sorbent

(Tenax GC), from which the analytes were desorbed directly into a GC column and determined. A similar procedure for XAD-4 was described by Ryan and Fritz [374].

Thermal desorption of organohalogen compounds trapped on XAD-4, followed by their combustion and coulometric final determination of the resulting halide ions, have formed the basis for the determination of AOX [98,166,246,247]. This parameter can also be determined by sorbing the analytes on a solid sorbent, followed by solvent extraction (using acetone or diethyl ether), combustion of the extract and coulometric determination of the halide ions formed [248,264].

XAD-4 resin has been used for the determination of VOX in tap water [247], surface water [166,247], seawater [247], and water from a swimming pool [98]. The procedure involved passing a water sample through the sorbent bed, followed by thermal desorption of the analytes at 200°C, their combustion and coulometric determination of the halide ions formed.

In many cases a total parameter (such as VOX) is not a sufficient measure of water quality. Preconcentration of the analytes on solid sorbents also allows their individual determination, following thermal desorption with cryofocusing or solvent extraction and GC separation and quantification. Using XAD-4 as a sorbent, solvent extraction with pentane and GC–ECD of the extract, volatile organohalogen compounds and pesticides were determined in model solutions, tap water, surface water and water from a swimming pool [98,166]. Studies of this procedure revealed that XAD-4 is suitable for preconcentration of organohalogen compounds owing to its high thermal stability, sorption capacity and chemical inertness. The effect of the inorganic matrix is eliminated, which permits the determination of organo-halogen compounds in the presence of large amounts of inorganic chlorides, e.g., in seawater. Isolation of the analytes on a solid sorbent allows one to carry out sampling in the field and storage of the analytes either trapped on the sorbent or as an extract of the sorbent bed. Both volatile and non-volatile organohalogen compounds can be determined simultaneously.

3.6.3. Solid-phase microextraction

Although solid-phase extraction has a number of attractive features, it also has a number of limitations, such as low recovery, plugging of the cartridge or blocking of the pores in the sorbent by solid components, which result in small breakthrough volumes, high blank values and batch-to-batch variations of the sorbents. Because SPE involves a multi-step procedure, including concentration of the extract, it is limited to the analytes with relatively low volatility with boiling points above those of the solvent.

One solution to these disadvantages is to improve the geometry of the sorbent by coating it on a fibre or a wire made of fused silica. The cylindrical geometry of such a solid-phase microextraction (SPME) system allows rapid mass transfer during sorption and desorption, prevents plugging, eliminates the use of solvents and facilitates the introduction of the analytes into analytical instruments [355,375–385].

Commercial SPME devices are manufactured by Supelco (Bellefonte, PA, USA). In such a device, the fused-silica fibre coated with a suitable GC stationary phase (see Table 4) is connected to a stainless-steel tube to increase the mechanical strength of the fibre assembly. The stainless-steel tubing is then contained in a specially designed syringe. During SPME, the fibre is first withdrawn into the syringe needle, then lowered into the sample vial. The fibre coating is exposed for a predetermined time to extract analytes from the sample. Once sampling is completed, the fibre is directly transferred into a GC injector. Analytes are thermally desorbed from the fibre coating and quantitatively determined by GC.

SPME consists of two processes: partitioning of analytes between the coating and the sample and desorption of preconcentrated analytes into an analytical instrument, typically a gas chromatograph. Thus far, SPME applications have focused on extracting organic compounds from various matrices, such as air, water and soils.

SPME retains all the advantages of solid-phase extraction, such as simplicity, low cost, ease of automation and on-site sampling. At the same time, it eliminates the drawbacks of SPE such as

Table 4
Application of different fibre coatings for solid-phase microextraction [393]

Type of fibre for SPME	Application
Uncoated	PCBs BTEX (benzene, toluene, ethylbenzene, xylenes)
Coated with polyimide	Volatile organohalogen compounds (1,1,1-trichlorethane, trichloroethylene, tetrachloroethylene)
Coated with 85-μm polyacrylate[a]	Phenol and derivatives N and P herbicides
Coated with liquid crystals	PAHs (polynuclear aromatic hydrocarbons) Dioxin congeners
Coated with 7-μm polydimethylsiloxane[a]	PAHs Phthalates Organochlorine pesticides
Coated with 100-μm polydimethylsiloxane[a]	BTEX Volatile organohalogen compounds (1,1,1-trichlorethane, dichloromethane, tetrachloromethane, 1,1,2,2-tetrachloroethane, 1,2- and 1,3-dichloropropane, chloroform, bromodichloromethane, dibromochloromethane, bromoform, tri- and tetrachloroethylene) Flavour components PAHs S and P pesticides
Carbon fibre	N and P pesticides

[a] Fibres commercially available.

plugging and the use of solvents. No special thermal desorption module is required and no modification of gas chromatographs is needed. SPME completely eliminates organic solvetns from extraction and injection, and it combines both processes into a single step. The geometry of SPME allows one to place the sorbent in a sample (gas or liquid) or the headspace above the sample to extract the analytes. By sampling from the headspace, very complex matrices can be analysed.

3.7. Methods for the isolation of organic compounds from the aqueous phase using membrane techniques

Separation techniques employing membranes for the preparation of samples for chromatographic analysis have been introduced fairly recently. In the past, the membrane techniques have found wider applications in industrial processes, such as water deionization. Owing to the progress in polymer research, the applicability of membranes in analytical chemistry has been increasing [37,289,386–392].

Briefly, a membrane is a selective barrier between two phases. The separation process is based on the ability of a membrane to allow a much more rapid transfer of some components from the donor to the acceptor phase than others, although the membrane is never an ideal semipermeable barrier. Classification of membranes can be based on a number of criteria, such as their origin (biological or synthetic), structure, applicability or the mechanism of separation.

With respect to their structure, membranes generally fall into two categories, porous and non-porous. Non-porous membranes are typically thin films of a liquid or of a polymer in which a molecule has to dissolve to be transferred. Hence, the driving force for the transport of molecules across non-porous membranes is the partition coefficient between the donor phase

and the membrane and the partition coefficient between the membrane and the acceptor phase. Non-porous membranes are relatively selective. Ion-exchange membranes represent a special kind of membrane of this type.

Porous membranes allow the transport of any molecules with appropriate sizes. The transport is primarily based on diffusion of molecules through pores of the membrane, although sometimes dissolution of compounds in the membrane material is also observed. Porous membranes can be further classified into symmetric and asymmetric. The geometric characteristic of symmetric membranes in the same along the entire path of a molecule through the membrane, whereas asymmetric membranes consist of two layers: a thicker, rigid layer of porous polymer (up to 250 mm) and a thinner (0.1–0.5 mm) layer of a membrane covering the polymer. Both layers can be made of the same or different materials.

Membranes can be used in a planar, supported form. Although such supported membrane sheets were used in many early methods, hollow fibres have replaced them in most recent membrane extraction techniques [389,390]. The hollow fibre is self-supporting and has a significantly higher surface are to volume ratio, which allows greater mass transfer rates and thus a more efficient extraction.

The passage of substances through a medium can be generally called permeation. Permeation consists of different means of transport resulting from different driving forces. The most important thermodynamic driving forces include concentration gradient, electric potential gradient and pressure gradient. A theoretically possible temperature gradient did not play a significant role in the membranes used so far.

Dialysis and osmosis both take place owing to the concentration gradient across the membrane, but in dialysis the solute is transported through the membrane whereas in osmosis the solvent molecules ar the species being transferred. In filtration, both the solvent and the solute molecules are transported across the membrane owing to the pressure gradient. With respect to the pore size of membranes, filtration can be divided into hyperfiltration (pore sizes 0.1–1 nm), ultrafiltration (1–100 nm) and microfiltration (100–1000 nm). Electrodialysis and electroosmosis take place owing to an external electric potential. In electrodialysis, the species transported across the membrane is the solute whereas in electroosmosis the solvent is transferred from one side of the membrane to the other.

Disadvantages of membrane techniques include the slow response of the membrane to changes in concentration and a very limited capability to separate very polar compounds because of a lack of commercially available polar hollow-fibre membranes.

Methods of isolation of organic compounds using membrane techniques have already found applications in the analysis of environmental pollutants, such as pesticides, amines, chlorophenols and other compounds in water, plasma, milk, urine and biological material [289].

Devices and procedures for the determination of THMs in water using PTFE membranes [37,386] or of chlorobenzenes using silicone membranes [388] have also been described. These techniques allow automation of the isolation process and on-line operation [37,386].

4. Conclusion

The analysis of organic environmental pollutants is a formidable task considering the very low concentrations of analytes, their diversity and their different physical and chemical properties, and the much higher concentrations of interfering compounds. Consequently, environmental analysts have to have a number of techniques available for the isolation, separation and final determination of different groups of pollutants, taking into account their characteristics, concentration level and the sample matrix. In addition to methods aimed at determining total parameters (TOC, VOC, TOX, VOX, etc.) based mainly on combustion of a sample, followed by final determination of the inorganic products of combustion, individual pollutants can be determined by gas and liquid chromatographic techniques using a variety of detectors. It must be realized, however, that even the most powerful instrumentation is not enough. Proper sampling,

sample storage, isolation and preconcentration of the analytes and the preparation of samples for final analysis are just as important. The latter activities take up to 60% of the total time of analysis and can contribute about 30% to the errors of analysis. Hence water analysis for organic pollutants should be carried out by analytical experts.

Abbreviations

AOC	adsorbable organic carbon
AOX	adsorbable organic halogen
BTEX	benzene, toluene, ethylbenzene, xylenes
CLSA	closed-loop stripping analysis
DAI	direct aqueous injection
DOC	dissolved organic carbon
ECD	electron-capture detection
EOC	extractable organic carbon
EOX	extractable organic halogen
FA	fulvic acids
GAC	granulated activated charcoal
NPOX	non-purgeable organic halogen
NAOX	non-adsorbable organic halogen
PAC	powdered activated carbon
P&T	purge and trap
POC	purgeable organic carbon
POX	purgeable organic halogen
SOC	suspended organic carbon
SPE	solid-phase extraction
SPME	solid-phase microextraction
TOC	total organic carbon
TOCl	total organic chlorine
TOX	total organic halogen
TOS	total organic sulfur
TTHM	total trihalomethanes
THMs	trihalomethanes
TLHS	thin-layer countercurrent headspace
VOC	volatile organic carbon
VOCl	volatile organic chlorine
VOX	volatile organic halogen
VOS	volatile organic sulfur

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