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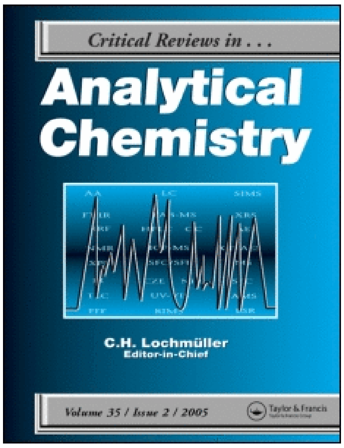

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ORGANIC POLLUTANTS IN WATER

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I. INTRODUCTION

The analysis of organic pollutants in water is a subject of very large scope that can include a description of all analytical techniques known at this moment. A large number of papers with respect to the field have been published in the last 20 years. Many reviews are written on minor aspects of this subject. In Europe, the Commission of the European Community started a project entitled "Analysis of Organic Micropollutants in Water" with the aim of coordinating all relevant research in this field in the participating countries. In 1981, they organized a symposium with review papers in areas such as sampling methodology by Josefsson,[1] selective detectors in gas chromatography (GC) by Mantica,[2] process technology by Venema,[3] selective detectors for high-performance liquid chromatography (HPLC) by Poppe,[4] sampling techniques for capillary GC by Grob,[5] mass spectrometry (MS) by Cornu,[6] software systems for MS by Henneberg,[7] identification of nonvolatile organic compounds by Crathorne and Watts,[8] organic halogens (sum) by Wegman,[9] and phenols by Renberg.[10] In 1983, another symposium with review presentations was organized.[11] In the U.S., the American Chemical Society also organized symposiums with presentations regarding the state of the art of the analysis of organics in water. Keith[12,13] edited two volumes based on the papers of one of these symposiums.

Thus, it is impossible to review completely a subject such as the analysis of organic pollutants in water. In this review paper, only the highlights of the last 4 years, with emphasis on extraction techniques, will be discussed. For detection techniques, we refer to other reviews. Excellent extended summaries in this field are published every 2 years in *Analytical Chemistry*.[14,15] In selecting the papers that should be reviewed, a very restrictive selection was made from 10 to 15 scientific journals.

The reliability of any analytical measurement is directly coupled to the uncertainties of the sampling process, sampling storage, preservations, isolation from aqueous matrix, and the extraction process prior to analysis. In any stage of the analytical process, errors may be introduced. Sampling is the first, and probably the most essential, step in the analysis. Unless precautions are taken to assure that a sample is representative, even the most careful analysis will be misleading.

Knowledge about the nature of the water is important. The presence of particulate matter influences the distribution of organic compounds in the water system. Volatilization from the water body is, to a great extent, dependent on oxygen content, temperature, hydrodynamics, etc. The characteristic of the water (groundwater, waste water, etc.) must be considered in the selection of sampling methods.

Table 1
SIMPLIFIED VERSION OF MASTER ANALYTICAL SCHEME

Sample handling	—	Collection Storage/preservation Water quality scouting Measurements	—	Purgeables Extractables Other ionic compounds

- Addition of internal standards
- Isolation from aqueous matrix
  - Neutral, water soluble, low molecular weight, heated purge and trap
  - Extractables
    - pH 1.0
    - pH 8.0 (three techniques)
  - Other ionic compounds
    - Ion-exchange resins
- Extract processing
  - Derivatization
  - Clean up (silica column)
  - Evaporation/concentration
  - Addition of external standards
- GC-MC analysis
- Qualitative analysis
- Quantitative analysis

An analytical method consists of a series of operations. It is desirable to use as few operations as possible as every step means the possibility of error introduction. There are very few methods where the water sample is directly accessible to measurement. Organic compounds are generally present in trace amounts at the microgram-per-liter level or less and as a part of a complex mixture. Thus, before separation and identification can be attempted, compounds usually must be isolated from a very dilute aqueous solution. Due to the wide variety of chemicals present in water, no single extraction technique is capable of isolating all organics from the water sample. After isolating all organics from the water sample, generally the analytes should be separated from other organics. The ideal technique should have a high resolving power and sensitivity of detection for separated compounds. In addition, there should be no need for derivatization prior to analysis, and the technique should not alter the organics during separation. After separation, a technique is necessary to give information about the identity and the quantity of the analyte. To reach the sensitivity of the detector technique, a concentration step is often necessary.

Environmental analyses seem to be moving increasingly into the lawyer's domain. This makes it necessary to improve the accuracy and reliability of quantitative data, and this can be accomplished through quality assurance/quantity control programs and the use of more sophisticated quantitative methods, such as the use of multiple internal standards. The use of isotope dilution methods seems to be especially attractive.

A first effort in developing a comprehensive qualitative-quantitative scheme to include organic compounds of all volatile classes of all functional group types in samples from any water type was developed by the Environmental Protection Agency (EPA) and described by Garrison et al.[16] A Master Analytical Scheme (MAS) for the analysis of priority pollutants in any type of water was presented. A simplified version is given in Table 1. The overall objective of the MAS is to develop and validate analytical techniques that can be combined in a comprehensive protocol. A high degree of importance has been attached to quality assurance.

II. ISOLATION AND CONCENTRATION TECHNIQUES

For organic pollutant residue analysis of water samples, several isolation and concentration techniques are available, e.g., liquid-liquid extraction (LLE), use of polymeric resins such as Amberlite® XAD, and head-space analysis (HSA). The choice of isolation and concentration procedures depends on the analytical goal, the nature of the organic pollutants, the water-sample type, and the method of detection. A good approach for selecting an isolation and concentration technique for pesticides was described by Lee et al.,[17] Chau et al.,[18] and Sirons et al.[19] Detailed discussion on each of the isolating and concentration techniques mentioned in the reviewed literature is given below.

A. Direct Aqueous Injection

Direct injection of a water sample into a gas chromatograph or high-performance liquid chromatograph is the most simple and fastest analytical procedure for the analysis of organic pollutants in surface water. However, most of the columns are not water resistant and, e.g., with GC-FID (flame ionization detector), immediately after the injection, the flame is extinguished. Grob[20] reviewed the development of glass capillary GC with special emphasis on application to water analysis, in particular to the deactivation of columns for direct injection of aqueous solution. His conclusions were with respect to:

1. The influence on columns — in most columns, support surfaces or stationary phases hydrolyze; resisting column types are polyglycols, e.g., Carbowaxes® on a $BaCO_3$ surface; however, water is very strongly retained and inert columns with immobilized silicone coatings (apolar) that have almost no retention for water must be used.
2. The influence on a detector that the FID flame will be extinguished, the electron capture detector (ECD) ground current will effectively be quenched by water, and all potential causes of retarded water elution will have to be avoided.
3. The influence on solute bands that water is a poor solvent for most organics analyzed by GC injection, where splitting gives no problems. On-column injection gives no problems with strongly water-soluble (fully trapped) solutes, little or negligible problems with water-insoluble solutes (nontrapped), and problems with solutes of intermediate solubility (partially trapped). Splitless injection can only be used for strongly soluble solutes.

Melcher and Caldecourt[21] developed a gas chromatographic/concentration apparatus for direct determination of organic compounds in water. Organic compounds were retained on a collection precolumn and after venting the water (10 to 200 μℓ), the precolumn was heated in a few seconds. The method is especially useful for compounds that are difficult to extract or to purge from water. The apparatus was used in combination with GC-FID, ECD, N/P AFID, and photo-ionization detectors (PID).

Boyce and Hornig[22] found different yields of $CHCl_3$ by GC analysis by the direct aqueous injection and LLE methods. Under acidic and neutral conditions, high concentrations of a variety of trichloromethyl-substituted intermediates were identified in addition to $CHCl_3$ by the direct injection method.

Joshipura et al.[23] had poor reproducibility and correspondence between observed and actual values of concentrations of acetonitrile using GC-FID. Better results were obtained with a thermal conductivity detector and by using 2-methoxy-ethanol as the internal standard. Kawahara et al.[24] described a new monitor for hydrocarbons, which made it possible to measure aromatics, crude oil, and oil products dispersed in water directly in the water sample which is flowing through a capillary column without solvent extraction or further treatment of the sample.

Grob and Grob[25] and Grob and Habich[26] used a very thick film (1 to 8 μm) with a high loading capacity, which was especially useful for direct injection.

Zlatkis et al.[27] injected large-sized aqueous samples (as much as 400 μℓ) onto a bonded hydrophobic-phase capillary column. Trace substances were adsorbed from the water when the sample passed through the capillary column at room temperature and were subsequently thermally desorbed, trapped, and analyzed gas chromatographically by using either the same column or one in series. Utilizing a single column with a FID, concentrations at the microgram-per-liter level and at the nanogram-per-liter level using two columns with an electron capture detector were determined.

Knuth and Hoglund[28] used a Tenax-GC column in combination with a FID for the analysis of 68 organic compounds, e.g., alcohols, acetates, ketones, ether, etc., with good results.

Simmonds[29] described a novel and simple method of direct aqueous injection GC whereby water was selectively removed by diffusion across a permaselective membrane prior to the sample entering the GC column. Injection volumes were 1 to 20 μℓ.

Guillemin et al.,[30] Kohei et al.,[31] and Teply and Dressler[32] used steam as the carrier gas in the gas chromatograph. The sensitivity was 10 μg/ℓ for hydrocarbons. The FID gave a constant and reproducible response, which, however, was lower than under conventional gas chromatographic conditions.

Hu and Weiner[33] determined trihalomethanes by a direct aqueous injection method in combination with GC.

From the papers reviewed, it follows that it is almost always important to avoid direct contact of the water with the gas chromatographic column. Attractive solutions of this problem that removed the water are given by Melcher and Caldecourt[21] and Simmonds.[29] The direct aqueous injection technique is a simple and useful method for determination at relatively high concentrations.

B. LLE

For enrichment, LLE is a simple and conventional technique. The classes of compounds which can be extracted from water samples depend on a number of factors, such as type of water sample (presence of particulate matter, ionic strength of the water), pH, type of extraction solvent (polarity of the solvent is a main factor), solvent-water ratio, and extraction procedure. After the extraction, a great loss of the more volatile compounds is possible if the method includes a concentration step by evaporation. Concentration of the extraction solvent subsequently requires the availability of very pure solvents. Extraction at approximately pH 7 can be inefficient for some classes of compounds, e.g., phenols, which means that for some classes of compounds the pH of the water samples has to be adjusted before extraction or else consecutive extraction at different pHs may be advisable. A low solvent/water ratio can lead to the formation of an emulsion, and extraction may take a long time because of the slow kinetics to reach equilibrium, especially for high molecular weight organic compounds. If a high solvent/water ratio is applied, a concentration step is usually necessary in order to make the method sensitive. For extraction, a suitable immiscible solvent has to be used.

Several techniques have been utilized for years, such as those described below.

Batch LLE (BLLE) — This technique involves shaking or stirring the water sample with a small volume of solvent in an extraction vessel. A modification is the so-called high speed stirring technique used by Blanchet.[34] The extraction of a water sample with a very low volume of solvent is possible in a vessel with a narrow neck.

Flow-under continuous LLE — By this method, organics are extracted by bringing the sample and solvent into contact without breaking the interface between the two phases. Stirring the aqueous layer prevents the process from being diffusion limited, and the distillation feature cycles fresh solvent into contact with the sample.[35]

Continuous LLE — An automated continuous LLE apparatus has been constructed for use in the field by Ahnhoff and Josefsson.[36] The extraction unit is based on the mixer-settler principle and can be used with solvents lighter than and heavier than water. The apparatus consists of two extractors in series for serial extraction and can be applied at different depths. The units are loaded with about 200 mℓ of solvent and have a capacity to extract some 100 ℓ of water, depending on the solvent used.

Murray[37] described a continuous extraction apparatus which consists of three inverted 250-mℓ volumetric flasks. A vibratory mixer was used for vigorous shaking of all three flasks. A 10-ℓ sample was siphoned through the apparatus in about 4 hr and extracted, with a total solvent volume of 10 mℓ. The advantage is that no concentration step is involved.

In all the papers reviewed, simple batch extraction was mostly used. Otson and Williams[38] evaluated the simple one-step LLE method for a representative group of 41 semivolatile organic pollutants. Extractions were completed by shaking the bottles for 30 min, storing for 3 days at 25°C, and transferring the organic phase into autosampler vials. Recovery studies were carried out at the 1-, 5-, 20-, or 100-μg/ℓ level. Six solvent systems were evaluated. Their extraction efficiency decreased in this order: pentane $\geqslant$ hexane $>$ hexane saturated with methanol $>$ iso-octane $>$ 15% (v/v) acetone in hexane $\geqslant$ benzene. Pentane and hexane showed the least interference with standard peaks during GC. Hexane was selected as the extraction solvent since the volatility of pentane makes it difficult to handle, particularly when it is used with an automatic injector. The solvent/water ratio was 1:40. They concluded that the single-step LLE procedure, although considered to give quantitative results for studies involving a limited number of compounds, has some limitations when applied to water samples containing large numbers of compounds. Analytical results for the latter type of sample are likely to be semiquantitative and will require careful evaluation. The hexane extraction procedure is, however, very useful as a simple, rapid screening method that can be applied in order to complement other methods for the analysis of organic pollutants in potable water.

The solvent/water ratio used by Otson and Williams[38] will certainly give problems in the analysis of more foaming samples like discharge water. The amount of solvent has to be increased. The use of large volumes of organic solvents and the high concentration factor (10^2 to 10^4) subsequently requires solvents of very high purity. Concentration by evaporation gives a loss of volatile compounds and is laborious.

Peters[35] compared five different continuous extractors: a heavier-than-water solvent liquid-liquid extractor, a steam codistillation extractor, a steam distillation extractor, a flow-under extractor, and a flow-over extractor, using a synthetic mixture of ten chemicals in water at 50 μg/ℓ each (see Section II.E). Erickson et al.[39] evaluated the common solvent evaporation techniques to determine which are acceptable for use in pollutant analysis. Techniques for solvent reductions from 200 to 10 mℓ (macro) and 8 to 0.2 mℓ (micro) were evaluated.

The macro-concentration techniques included

1. Kudema-Danish evaporative concentrator equipment with a Snyder or Vigreux column
2. Rotary evaporation, equipped with a bump trap, under vacuum at ambient temperature
3. Evaporation on a hot plate in an Erlenmeyer flask whereby the solution is heated at 30°C
4. Heated nitrogen blowdown in an Erlenmeyer flask whereby the solution is heated at 30°C with a gentle stream of nitrogen

The micro-concentration techniques included

1. Micro Kudema-Danish concentration
2. Nitrogen blowdown without column
3. Nitrogen blowdown with a modified Snyder column whereby solution is heated at 30°C

A series of model compounds covering a wide range of boiling points (bps) (108 to 323°C) and polarities was used for the recovery experiments.

From the macro-concentration techniques, the best results were obtained with nitrogen blowdown. Kuderna-Danish gave the lowest recoveries. The time required ranged from 10 min (Kuderna-Danish) to 120 min (nitrogen blowdown). The recoveries improved markedly with the experience of the analyst. From the micro-concentration techniques, the nitrogen blowdown with column was signficantly superior using dichloromethane as the solvent. For 15% dichloromethane/hexane, Kuderna-Danish gave the best results.

C. Adsorption

Sorbent extraction is based on the distribution of the dissolved compounds between the solid sorbent and water. In 1979, Dressler[40] reviewed a number of papers. The base factors that make the use of organic porous polymers advantageous for the extraction of organic compounds from water are

1. The partition coefficients of compounds in a polymer-water system reach to infinity if the correct polymer is selected for the types of contaminants present.
2. Adsorption of water itself on the polymer is minimal.
3. The wettability of the polymer with water makes possible the satisfactory transport of the substance towards the polymer surface.
4. The polymer is inert.

Usually the water sample is pumped through a column packed with a sorbent. The adsorbed compounds are then desorbed from the sorbent and analyzed chromatographically. The presence of mineral oil in the water at the parts-per-million level decreases considerably the adsorption of compounds on the sorbent. This problem can be solved using an extra layer of inert material at the entrance of the column.

On passing water containing organic compounds through the column, a chromatographic process occurs and, after a certain time, a breakthrough also occurs. The ideal state is reached if the trapping of organic compounds is 100%. This depends on a number of factors: sorbent, structure of the analytes, composition of water sample, and original concentration of the analytes in water. Adsorption theory is very complicated, especially when water matrix effects are involved. Water characteristics may vary widely, and recovery studies are difficult to carry out. The water content of particulate matter and the way the organics are stuck to the particles are important. The nature of the active sites determines the ability of the organics to be extracted.

When the water is first filtrated, colloidal and small particles will still pass through the filter and bring part of the organics, more or less unaffected, through the extraction column. When the water is not filtrated, the adsorbent columns are easily clogged, resulting in channeling. Even pores may sometimes be blocked. A problem is the necessity to obtain resins of high purity and an optimal adsorption capacity. An extended clean-up procedure for trace analysis is strictly necessary; this procedure can be automated. An example of such a procedure is given by Noordsij et al.[41] Before cleaning, the resin is stored for 2 weeks in an alcohol-lye solution.

Procedure for purifying XAD-4 resin:

1. Washing with a diluted solution of sodium hydroxide (ten times)
2. Washing with a diluted solution of hydrochloric acid (ten times)
3. Washing with a diluted solution of distilled water (ten times)
4. Washing with methanol (two times)
5. Extraction with heated methanol for 24 hr

6. Washing with ethanol (three times)
7. Extraction with a mixture of ethanol/cyclohexane for 24 hr
8. Washing with methanol (double distilled) to remove all cyclohexane

Desorption of the compounds from the sorbent can be performed either by a liquid[42,43] or by heating.[44,45] Solvents that are used are diethylether, *n*-hexane, acetone, isopropanol, methanol, methylisobutyl ketone, and pyridine. Also important is the solvent strength, e.g., in a stream containing activated carbon the solvent strength increases in this sequence: water < methanol < ethanol < acetone < propanol < diethylether < butanol < ethyl acetate < *n*-hexane < benzene.

Sometimes the desorbed compounds are led directly into the chromatographic column of a HPLC, e.g., Goewie et al.,[46] Ogan et al.,[47] and Wolkoff and Creed.[48]

In thermal desorption, the column is situated before the analytical column of the GC, similar to HSA.

In order to eliminate peak broadening, the first portions of the chromatographic columns are usually cooled. The temperature must be such that all compounds contained in the sorbent are transferred from it to the gas chromatograph in a reasonable amount of time. If the temperature is too high, the substances can decompose. In Table 2, applications of sorbent for water extraction are summarized. The classes of compounds that were extracted are also given.

From Table 2, it follows that a wide scope of organic compounds can be extracted from the water sample with different resins, however, extraction of volatile compounds with a resin was not described. A new trend is the use of an analytical scheme. Noordsij et al.[41] developed an analytical method for both chemical and biological analysis. The procedure is a combination of a gas stripping technique for the volatiles and a number of adsorption steps. The water sample is led through the XAD-4 resin. The organics that passed the XAD can be isolated from the XAD effluent by means of a freeze-drying concentration. Generally, the lipophilic compounds are isolated with XAD-4 at pH 7 and the hydrophilic compounds with XAD-4 at pH 2.

Giabbai et al.[49] developed an isolation-fractionation scheme in which organic compounds with different functional groups and sorption parameters were separated and concentrated in fractions with similar behavior, which permitted instrumental analysis. Experiments were carried out with 22 model organics. XAD-8, AG MP 50, cation-exchange resin, and Carbopack® B were used as resins. They concluded that the proposed scheme appeared to allow the identification and quantitation of a wide range of organic substances. However, as several other organic classes still could not efficiently be recovered, the investigation of other isolation and concentration methods as an integral part of the scheme would be suggested. Purge and trap (P and T) and/or closed-loop stripping analyses (CLSA) may be used for the highly volatile compounds (e.g., chloroform), whereas freeze-drying and/or reverse osmosis may be utilized for the highly water-soluble compounds (e.g., furfural, glucose).

In the last few years, more attention has been given to on-line trace enrichment in HPLC using a precolumn. Werkhoeven-Goewie et al.[50] developed a specific HPLC method for the trace analysis of chlorinated aromatic compounds. The method consists of an on-line preconcentration and a postcolumn reaction step. On-line preconcentration of mono- and dichlorophenols from aqueous samples was performed using PRP_1, a divenylbenzene-styrene copolymeric sorbent, as packing material for both analytical and precolumn. Enrichment factors of over 300 were obtained. The method is suitable for the analysis of effluent water samples. The potential of this technique for automation was demonstrated by using a microprocessor-controlled column switching unit. Later, this method was applied by Zygmunt et al.[51] to other compounds, e.g., 1-methyl-2,4-diaminobenzene.

Table 2
SUMMARY OF APPLICATIONS OF SORBENT EXTRACTION TECHNIQUES

Sorbent	Organic compounds	Ref.
XAD-2	Pesticides, PCBs	53, 54
	PCBs	55
	Alkylbenzenes, phthalates	56
	Carbamates	57
	Azaarenes	58
	Aldicarb, aldicarbsulfox	59
XAD-4	Chloroethers, haloalkanes	42
	Acids	43
	Fenitrothion	60, 61
	Phenols, humic acids	62
	Aminocarb	63
	Bases	64
XAD-7	Aminoacids, PAHs	65
	Fenitrothion and metabolites	61
	Organochlorine compounds, PCBs	54
	4-Amino-3-methylphenol	63
XAD-8	Brominated alkylphenol polyethoxy-carboxylates	66
	Phenols/humic acids, TOCl	62, 67
	Pyridine, quinoline, acridine	68
Graphitized carbon black	Organochlorine compounds (pesticides)	69
	Hydrocarbons	70
	Humic compounds, phenols	62, 71
	Acids	72
	Herbicides	73
	Malathion	74
	Nitrobenzene	75
	Octadecane, P,P'-DDT	76
	PAHs	77
Chromosorb 102	Chlorobenzenes	78
Tenax-GC	HCH, naphtalene, PAHs	79
	Chlorobenzenes	80
	Organohalides	45
	PAHs	81
Ambersorb XE-340	Nitrosamines	82
Chromosorb T	Humic acids	83
Molecular sieve SA	Animal-vegetable oils	84
Carbopack® B	Chlorinated pesticides	85
Sep-pak® C_{18}	PAHs	47
	Aromatic amines/phenylurea herbicides	46
	Phenols	86
	PAHs	48
	Pesticides, e.g., carbofuran, thiram, azinphosmethyl, benomyl, diuran, PCP, simazine	87
	Rhodamine B_1/WT	88
	PCBs	89
	Aliphatic carboxylic acids	90
	Fenvalerate	91
	Pyrazon	92
Polypropylene	PAHs	93

A precolumn, when used for preconcentration, generally serves for sample clean-up and also as a guard column at the same time. A guard column serves to protect the valuable analytical HPLC column against contamination by sample, mobile phase constituents, and grit released by the chromatographic equipment, including the injector. In summary, the requirements that have to be met by a precolumn are the following:

1. The amount of material should be sufficient for the preconcentration of the desired amount of analyte from a given volume of water sample.
2. The precolumn has to be as small as necessary to prevent peak-broadening and has to have a high-pressure capability. It should not present back-pressure limitations during sampling at high flow rates, should be easily replaceable and easy to repack, and has to be compatible with all eluents generally used in HPLC.
3. Field sampling and automated sampling handling must be feasible.

The geometric volumes varied from 24 to 500 μℓ. Goewie[52] evaluated several stationary phase materials for the preconcentration of chlorophenols from aqueous solutions. Preconcentrations were performed on both C_{18} and carbonaceous sorbents. The amount of solution that could be sorbed without loss was dependent on the number of chlorine substituents and varied from some milliliters for monochlorophenols to several liters for pentachlorophenol on a 2.2 × 4.6-mm I.D. precolumn packed with carbon material. Preconcentration on C_{18}-type materials was less efficient than on carbon. For mono- and dichlorophenols, better results were obtained with PRP_1. Combined preconcentration and postderivatization techniques in the (automated) LC analysis of trace organics in complex aqueous solutions have a high potential. For many problems, small (i.e., 2 to 5-mm long and about 2-mm I.D.) precolumns packed with C_{18}-modified silica can be used to increase the sensitivity of the LC method 10- to 1000-fold as compared to that obtained with the conventionally used 10 to 100 μℓ loop injection.

D. HSA

1. General Aspects

By analyzing the gas phase, which is in equilibrium with the water phase, instead of the water phase, one can eliminate many drawbacks present in the usual methods of preconcentration (e.g., LLE). Determination of trace organic volatiles in the gas phase above the water sample has been called HSA. The techniques of HSA can be divided into two groups (also see Table 3).

"Static head-space" — The sample for chromatographic analysis is taken from a closed vessel where the material under study comes into equilibrium with its vapor at a predetermined temperature. Experimental conditions that can influence the results are the temperature and the sample withdrawal technique. The concentration of the analytes in the gaseous phase can be increased by raising the temperature, adding an electrolyte, and varying the pH. Solutes with low vapor pressures cannot be detected.

"Dynamic head-space" — A stream of inert gas (helium or nitrogen) strips the volatile compounds from the water and passes through a sorbent or cryogenic trap. The volatiles are eluted from the sorbent with a solvent or are thermally desorbed and brought into the gas chromatograph or another instrument. The technique can be applied in an open system where the stripping gas is vented to the atmosphere or in a closed circuit where the gas phase is recycled through the water and trap (CLSA). An extended review paper was written by Nũnez et al.[136]

2. Static Head-Space Techniques

Kolb et al.[102] described the quantitative determination of volatile halogenated hydrocarbons by static head-space and the use of internal and external standards to improve the reproducibility. He suggested the use of the multiple head-space extraction (MHE), which is based on a stepwise gas extraction with intermediate HSA. A simple two-step procedure is adequate for practical applications. Friant[95] studied the interactive effects of temperature, salt concentration, and pH on HSA for isolating volatiles in water samples. The optimum static HSA-sampling conditions of pH 7.1, 50°C, and 3.35 *M* sodium sulfate were determined

Table 3
HEAD SPACE ANALYSIS (HSA) (NUMBERS REFER TO REFERENCES)

	Dynamic headspace				
	Purge and trap (P&T) (open system)		Closed-loop stripping analysis (CLSA)		
			Activated carbon		
Static headspace	**Trap packed with solid sorbent**	**Cryogenic trap**	**Solvent elution**	**Thermal desorption**	**Other sorbents**
94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105,	Thermal elution: Tenax-GC: 106, 107, 108, 109, 110, 111, 96, 112, 113, 129, 114, 115, 116, 117, 118 Chromosorb W-AW (+ coating): 109 Other: 119, 120, 121, 122, 123, 124, 125, 126 Solvent elution: Activated carbon: 127	122, 124	112, 128, 129, 130, 131, 132, 133	134	Porapak® W: 135 Tenax-GC: 109

from a statistical design. At the optimum conditions of this design, enrichment factors of the vapor phase of up to 66 times were achieved as compared to a reference state of pH 7.1, 30°C, and without electrolyte addition.

3. *P and T Techniques*

By these dynamic procedures, the volatile compounds can be enriched to reach the detection limit of the chromatographic system. The trap packed with a solid sorbent can be considered as a chromatographic column. When the volume of the inert purge gas through the column becomes equal to the retention volume of the analyte (at T), it breaks through and elutes from the column. Knowledge of these breakthrough volumes is necessary. The breakthrough value depends on the form and size of the trap tube, specific area and particle size of adsorbent, temperature, flow-rate of the stripping gas, original concentration of the analyte in the water sample, chemical structure of the analyte, and the purge gas.

Bertsch et al.[137] determined the breakthrough volume for various organic volatile compounds in water using Tenax-GC as sorbent. Murray[138] found that trap tubes with an I.D. of over 0.5 cm and a sorbent with a mesh range of 35 to 70 should be avoided as they require too high flow-rates, which give high pressure drops.

Elution of the volatiles from the trap are performed with small volumes of organic solvents like methanol, isopropanol, acetone, etc. Often it is necessary to reach the detection limit to concentrate the eluate by evaporation. Drawbacks of solvent elution are the introduction of artifacts by the solvent, glassware, and gas; the solvent peak in the chromatogram washing the volatile organic compounds; and loss of volatiles by evaporation.

Desorption of the volatiles from the sorbent of the trap can also be carried out thermally. It is then necessary that the sorbent have thermal stability and that no reactions of the volatiles with the sorbent take place.

For thermal desorption, more complicated equipment is necessary as compared to elution with a solvent.

A suitable choice of the sorbent is essential for a successful result. Before analysis, several types of sorbents have to be evaluated. However, no sorbent has universal properties. Nũnez et al.[136] summarized a great number of sorbents, such as activated carbon, graphitized carbon black, and porous polymers, which exhibit a characteristic low capacity for water and do not show irreversible adsorption or decomposition phenomena, e.g., Porapak®, Chromosorb, Amberlite® XAD resins, Tenax-GC, Spheron, Synachrom, and Cehachrom. Tenax-GC is most widely used due to its thermal stability, in spite of its lower specific surface area.

Another type of dynamic head-space is the technique in which a stream of inert gas is passed over the water sample and led through a trap This method is similar to the strip-and-trap method. However, the equilibrium between the water and gas phase depends on the flow of the stripping gas. The surface contact is much smaller than in the purge technique. This technique can be applied to water samples with considerable foaming.

With P and T systems, problems were also encountered. Hu and Weiner[33] described problems with the original sparging apparatus of Bellar and Lichtenberg,[139] i.e., sample foaming and the inability to add standards to the system without losses. A modified version of the apparatus was developed. Rose and Colby[111] reduced sample foaming in the P and T apparatus by means of a heat gun (heat-dispersion method). Solutions of volatile organics such as dichloromethane in water are difficult to prepare, however, because of their high volatility and their low solubility in water. Generally, water-soluble carriers such as methanol or acetone are used. For P and T, substantial quantities of purgeable organics (the carrier) can interfere with the analysis. Ligon and Grade[140] suggested the use of polyethylene glycol as the diluent for preparation of standards. The compound is freely miscible with water and is completely nonpurgeable. It can be made free of purgeable impurities by heating at 100°C under vacuum for 0.5 hr. Purified helium or nitrogen can be obtained by means of silver oxide at 100° C.[110]

4. CLSA

In 1973, Grob[141] developed a method by which compounds with appreciable vapor pressure over water are removed from the sample by purging with gas and passing the stripping gas through an adsorption tube. A 0.5 ℓ of stripping gas is recycled continuously through the water sample. The adsorption trap (1.5 mg of activated carbon) is extracted with 10 μℓ of CS_2. Thomason and Bertsch[112] evaluated the applicability of a closed-loop stripping apparatus for the determination of trace organics in water. The effects of extraction solvent, stripping time, stripping temperature, pH, and salt content on the close-loop system were tested. The solvents studied were carbon disulfide, methanol, and dichloromethane; the stripping time was varied from 1 to 3 hr and the temperature from 25 to 60°C. Spiked water samples containing 0.5 and 1.0 mℓ of sodium chloride per liter of water were evaluated. The pH was adjusted by means of a sodium hydroxide solution and varied from 8 to 11. The organics were base neutrals, e.g., dichlorobenzenes, hexachloroethane, acenaphthene, PAHs, and *bis*(2-chloroethyl)ether.

Ramstad and Nestrick[109] recommended Tenax-GC because of its thermal stability and ample sampling capacity. Borén et al.[130] pointed out that the range of compounds that can be measured is somewhat limited. Peaks of highly volatile compounds are hidden by the peak of the extraction solvent, and moderately or extremely polar organic series are either poorly purged or not recovered at all. The CLSA technique has been most often used for screening of large numbers of compounds; its outstanding concentration factor without the need of an evaporation step makes the system useful, even when only a few compounds are of interest. After 3 months of routine use of the CLSA system, many contaminant blank peaks appeared. A modification of the closed system to an open system allowed the use of the stripping technique without a decrease of sensitivity or capacity, but with very few blank peaks in the gas chromatogram. Grob[142] commented to these critiques, "The major source of possible contamination is a damaged adsorbent filter. The carbon powder thus produced procedure that should be a more suitable response to contamination than switching to an open system that sacrifies the advantages of the closed loop.

In 1984, Grob et al.[143] discussed further the contamination problems. The application of the CLSA method was broadened to more polar substances, which showed a greater tendency to produce contamination problems. They distinguished two contamination problems: (1) a mechanically damaged charcoal filter that contaminates pump and connecting lines and (2) the quality of the charcoal filter, which can give unacceptable blanks when the filter continuously releases substances interfering in the volatility range of interest. Even a repeated extraction with solvents such as carbon disulfide, dichloromethane, ethanol, toluene, and dichlorobenzene failed to produce a clean filter. The only solution is an oxidation treatment of the filter with a hydrogen-peroxide solution.

Graydon et al.[134] had a solution for one of the limitations of the CLSA technique, i.e., its inability to determine compounds that elute under the gas chromatographic peak of the solvent (carbon disulfide). They introduced thermal desorption CLSA. However, in the course of developing thermal desorption CLSA, they observed significant breakthroughs of highly volatile compounds. The problem was solved by incorporating a 2-cm section of silanized chromosorb filled into the 15-cm trapping loop. However, they found that to achieve optimum performance it was necessary to focus on a narrow range of compounds, to adjust the gas volume during adsorption and desorption, and to optimize the temperature of the carbon filter. An application to raw waste water from a chemical plant means that care must be taken to ensure that the adsorbent is not overloaded. Quantitative work becomes especially critical when determining a very broad spectrum of compounds because of the displacing effect of the lighter materials by the heavier ones.

5. *Comparison of Methods*

Otson et al.[96] compared dynamic (P and T) and static head-space and solvent extraction techniques for the determination of trihalomethanes in water. Tenax-GC was used as the sorbent. The three analytical techniques gave comparable trihalomethane values for tap water samples. The P and T technique was the most sensitive, solvent extraction gave comparable precision, and the static head-space technique showed relatively poor precision and sensitivity.

Melton et al.[144] reported a comparison of experimental results from the analysis of drinking water before and after water treatment with granular activated carbon at the Cincinnati Water Works. The following methods of organic analysis were used: (1) Grob CLSA; (2) Bellar (P and T); (3) BLLE with dichloromethane; and (4) XAD-adsorption with ethylether extraction (XAD-EEE). The compounds were measured by capillary GC-MS. Of the 183 different organic compounds that were measured by the methods, 6 organic compounds were detected by the P and T method, 107 by the CLSA method, 90 by BLLE, and 58 by XAD-EEE analysis. The CSLA method with the carbon trap (with CS_2 elution) gave the best results, except that the recovery for highly volatile compounds such as chloromethane, vinylchloride, dichloromethane, and chloroform was poor.

A direct comparison of the closed-loop stripping and the P and T methods with Tenax-GC was performed by Thomason and Bertsch[112] on a surface water sample. Carbon disulfide and dichloromethane were found to have comparable extraction recoveries for base neutrals. Methanol has a poor extraction efficiency. By raising the stripping temperature from 25 to 40°C, increased recoveries were observed for base neutral compounds. At 60°C, the recoveries were not improved; water condensed at the charcoal filter. Variation of the stripping time from 1 to 3 hr at 25°C gave no recovery enhancement. Also, repetitive stripping had no effect, the pH had no influence on the recoveries, and the addition of salt to the water sample gave no changes in stripping efficiency. The recoveries for the two methods are comparable. The closed-loop system showed a better recovery for the compounds eluted earlier. This can be attributed to the breakthrough of these compounds in Tenax-GC. A drawback of the closed-loop system is that the most volatile compounds are masked by the solvent peak. The effect of temperature on the desorption of the EPA neutral-base priority pollutants from Tenax-GC was studied. The desorption temperature was varied from 200 to 300°C at 25°C intervals. At increased temperatures, more compounds were recovered (30 of 39). Nineteen compounds gave recoveries of 90% or better. Curvers et al.[145] investigated the possibilities, the limitations, and the quantitative performance of dynamic head-space sampling, particularly CLSA, for various classes of organic substances in aqueous samples. The results were compared with a theoretical model. The recovery was shown to be independent of concentration in a wide range (from 200 ng/ℓ to 20 μg/ℓ). For components that do not interact strongly with water, overall recoveries corresponding to a standard deviation of 10 to 15% were found. A detection limit of 10 ng/ℓ and enrichment factors of up to 5000 could easily be obtained for nonpolar compounds with bps up to 350°C for a 1-ℓ sample.

6. *Conclusions/Recommendations*

The static head-space procedure is the simplest one and can be applied to organic compounds with a high vapor pressure and a low solubility in water. With this technique, only simple equipment is necessary, and there are no great problems with impurities. However, the method is relatively insensitive because only a part of the vapor can be injected and an enrichment procedure is not present. The sensitivity can be improved by optimizing the conditions. The method can be automated. A new development is the MHE.

The P and T technique has a higher sensitivity than the static method and also compounds with a lower vapor pressure can be determined. Special equipment is necessary. The method is used on a large scale in drinking water analysis for the determination of trihalomethanes. The technique is semiautomated.

With CLSA, it is possible to determine the widest scope of compounds. However, this technique has some practical problems such as contamination of the filter or system. A new development is thermal desorption. For the analysis, special equipment is necessary and the technique is semiautomated.

E. Steam Distillation

For exhaustive enrichment, LLE is usually used. This technique is laborious and generally needs concentration of the solvent by evaporation. Solvent impurities can disturb the analysis to a large extent. Micro-extraction procedures eliminate these problems, but are often not quantitative. Nickerson and Likens[146] developed a continuous gas-phase extraction apparatus. Godefroot et al.[147] transformed the apparatus in a micro-version for essential oil extraction. This micro-apparatus also appeared to be useful for the analysis of organochlorine pesticides and polychlorinated biphenyls (PCBs) at submicrogram-per-liter level. Small water samples (10 to 100 mℓ) can be concentrated to 1 mℓ of pentane. For organochlorine pesticides, the mean recovery was nearly 100% and for PCBs 95%. The main advantage of the system is a high recovery in a short time. The pentane extract can be directly injected into the GC-ECD without clean-up.

Wegman and Hofstee[148] described the use of a Bleidner apparatus for the extraction of aromatic amines from water samples. Also, in this system, a continuous steam distillation/continuous LLE was carried out and good recoveries were obtained (over 90%). The extraction solvent was *n*-iso-octane and the extraction time was 2 to 3 hr, but the technique is not laborious.

Rijks et al.[149] reported a theoretical model that described the recovery of different classes of organic compounds as a function of the process time. The quantitative performance of steam distillation extraction was investigated for different types of organic substances at levels of 10^{-7} to 10^{-9} g. Good results were obtained within 20 min.

Ramstad and Nicholson[106] described a method for the determination of acetonitrile at levels of 10^{-10} g. This method combines steam distillation, elevated P and T technique, and nitrogen-specific detection.

Norwitz and Keliher[150] studied the effect of acidity and alkalinity on the distillation of phenol. The phenols were determined by the 4-aminoantipyrine (4-AAP) spectrophotometric method. The distillation of phenol was quantitative over the range from about pH 1 to 6. The interference of aromatic amines could be considerably reduced by distillation from a strongly acidic solution (10 mℓ of concentrated sulfuric acid per 500 mℓ); for large amounts of aromatic amines, double distillation was necessary.

Rennie[151] developed a method based on sample distillation followed by bromination of the phenol in the distillate. Donkin and Evans[152] obtained recoveries of over 80% for petroleum hydrocarbons.

Janda and Krijt[153] used a continuous steam distillation/continuous LLE for the isolation of phenols from water. The recovery for a concentration range of ~0.1 to 30 mg/ℓ approached 100%, using acidification and strong salting of the water sample.

Goodwin and Marton[154] improved a distillation apparatus for continuous use for the determination of phenol in waste water.

Peters[35] compared five different continuous extractors:

1. LL Extractor — a commercial extractor in which a heavier-than-water solvent is dripped through the sample (dichloromethane).
2. Steam codistillation extractor — this unit allows simultaneous condensation of a steam distillate and an immiscible extraction solvent, e.g., dichloromethane.
3. Steam distillator extractor — this extractor passes a sample steam distillate through an immiscible lighter-than-water solvent, e.g., hexane.
4. Flow-under extractor — in this extractor, the heavier-than-water solvent (dichloromethane) and water sample do not mix but only contact at the interface.
5. Flow-over extractor — this is an extension of the flow-under extractor in which a lighter-than-water solvent (hexane) is used.

The extraction time of each of the extractors was 18 hr. The water samples (1 ℓ) were fortified with 50 μg/ℓ of chlorobenzene, phenol, chlorophenol, pentachlorophenol, nitrophenol, tetrachlorobenzene, dimethylphthalate, and naphthalene. The solvents were concentrated by means of Kuderna-Danish. An internal standard was used.

In general, the steam distillation extractor, the flow-under extractor, and the flow-over extractor appear to be the most used. However, the other techniques also gave good results for most of the components. Steam distillation results in a "cleaner" extract and reduces the build-up of residue at the front of the gas chromatographic column. The small volumes of solvent normally used in steam distillation techniques facilitate solvent concentration and minimize interferences due to solvent impurities.

F. Other Techniques

1. Freezing Techniques

Freeze concentration, a process in which dissolved organics are concentrated in the unfrozen portion after freezing the water sample, has not been reported on recently. Another cryogenic technique is freeze-drying (lyophilization) in which the water sample is frozen and the water is removed by sublimation under vacuum. Watts et al.[155] and Crathorne et al.[156] identified parts-per-billion levels of organohalogen compounds in drinking water by freeze-drying (Edwards High Vacuum Ltd., Speedivac model 30Pz) 50-ℓ samples. The solid residue was extracted with methanol and the extract was then concentrated to 1 mℓ by rotary evaporation. Recoveries varied from 18 to 80%. The process is not suitable for the more volatile organic constituents, and another disadvantage is the difficulty of recovering the organic material from the inorganic precipitates. Moreover, the method is very time consuming (>1 week) and requires large water samples.

Small sample volumes have been analyzed by Klockow et al.[157] They determined several lower carboxylic and sulphonic acids in the micromole-per-liter range in 10 mℓ of synthetic rainwater after derivatization (carboxylic acids to their tetra-*n*-butylammonium salts, sulphonic acids to their corresponding silver salts) and freeze-drying (model 10-010 VirTislo, Inc., Gardiner, N.Y., U.S.). Before GC, the carboxylic acid salts were esterified to their benzyl carboxylates and the sulphonic acids to their *n*-butyl esters.

Ehntholt et al.[158] introduced a new concept for extracting trace levels of organic compounds from water. They used supercritical fluid carbon dioxide (pressure, ±2500 psi; temperature, 45°C) to isolate and concentrate at the parts-per-billion level 23 spiked organic substances in synthetic natural water. The use of CO_2 avoids the introduction of organic solvents or contaminants associated with other methods. The method is based on the solubility of organics in supercritical CO_2. Three hundred liters of CO_2, compressed to 2500 psi and heated to 45°C, were passed through a 400-mℓ water sample in an extraction vessel. After reduction to atmospheric pressure, the extracted organic substances were trapped in a system consisting of a set of three sequential U-tubes maintained at −76°C. The technique was demonstrated to work for most of the organics studied, such as biphenyl compounds, phthalates, phenols, aldehydes, ketones, and anthraquinone. Recoveries varied from 0 to 84%.

2. *Reverse Osmosis and Ultrafiltration*

These processes involve the migration of molecules across membranes by molecular diffusion. In reverse osmosis, water is forced under pressure greater than the osmotic pressure. The water sample is enriched in small molecules (inorganics) as well as large molecules (organics with a molecular weight >200). Reverse osmosis is used mostly for removal of inorganics, e.g., seawater desalinization, rather than concentration and has not been reported recently for the latter purpose.

Ultrafiltration is a process in which large molecules (molecular weight >1000) are separated from solution by filtration through the membrane. The technique involves membranes with larger pore sizes than those used for reverse osmosis and operates at a relatively low differential pressure. The efforts of various experimental conditions on the results obtained by using ultrafiltration for the separation and fractionation of fulvic and humic substances in fresh waters have been reported by Buffle et al.[159] They used the Amicon system and concluded that the most useful membranes are the Amicon membranes UM05, UM2, and PM10. The results depend greatly on the interactions of the organic matter with other dissolved molecules, with the membrane, and with each other. Le Cloirec et al.[160] have made an analytical scheme for the determination of nitrogenous substances in natural waters used for drinking water production. Macromolecular compounds such as humic substances, chlorophylls, and proteins were separated by ultrafiltration.

3. *Conclusions and Recommendations*

In 1981, Crathorne and Watts[8] reviewed papers on the identification of nonvolatile organic compounds in water. They described the more commonly used techniques such as freeze-drying, reverse osmosis, activated carbon adsorption, and XAD-resin adsorption. They concluded, "A satisfactory comparison of the isolation methods in use is impossible due to the wide range of water samples examined and the variety of methods used to analyse the organic extracts." Although reverse osmosis and freeze-drying result in extracts containing the widest range of organic compounds, for ease of operation, particularly when processing

Table 4
CONCENTRATION TECHNIQUES

Method	Principle	Type of organic compound concentrated	Advantages	Drawbacks
Freeze-concentration	A portion of water is frozen; higher concentration in unfrozen portion	Nonvolatiles polar and nonpolar (e.g., m-cresol)	Low contamination	Slow and comparatively expensive, volatiles are lost, concentrate also contains inorganics
Reverse-osmosis	Water is forced through a membrane, water sample is enriched	Polar and nonpolar molecular weight >200	Large volumes, continuous	Release of contamination by membranes, adsorption to the membrane, concentration of inorganics, necessity of extraction step
Ultrafiltration	Water sample is filtered under pressure (through a membrane, compounds retained on membrane)	Molecular weight > 1000 (humic material)		Concentration of inorganics, loss of lower molecular weight; organics, results dependent on interaction by molecules
Vacuum distillation	Evaporation at reduced pressure	Nonvolatiles	High concentration factor, low contamination	Concentration of inorganics, labor-intensive
Lyophilization (freeze-drying)	Water sample is frozen; water is removed by sublimation under vacuum	Nonvolatiles	Low temperature, high concentration factor, low contamination	Concentration of inorganics, loss of volatiles, time consuming
Supercritical fluid CO_2	Compressed CO_2 is passed through a water sample; after reduction to atmospheric pressure, the organics are trapped at −76°C	Biphenyls, phthalates, phenols, aldehydes, ketones, anthraquinone	No introduction of organic solvents or contaminants	Little experience

large volumes of water, a column concentration technique may be preferred. With the freeze-drying technique, a large number of organics of high polarity are obtained. Many of those compounds are not absorbed by a XAD-resin.

Jolley[161] also discussed some concentration techniques.

In Table 4, the advantages and drawbacks of the techniques are summarized. A new development is the technique using supercritical fluid CO_2.

G. Applications to Specific Classes of Compounds

The selection of an isolation and/or concentration technique depends largely on the class of compounds that have to be analyzed. Sometimes it is necessary to analyze simultaneously a wide variety of chemical compounds in the water sample. Application of a series of techniques can be the solution.

In order to give an impression about the selection of isolation and/or concentration techniques for some classes of compounds, the results of a survey of the literature are summarized in Table 5. Besides "normal" classes of compounds such as volatile hydrocarbons, phenols,

Table 5

SUMMARY OF ISOLATION AND CONCENTRATION TECHNIQUES FOR SEVERAL CLASSES OF ORGANIC COMPOUNDS (NUMBERS REFER TO REFERENCES)

Concentration techniques	Direct aqueous injection	Liquid-liquid extraction	Adsorption	Headspace analysis	Steam distillation	Freezing techniques	Ultrafiltration	Derivative extraction
Compounds								
Volatile halocarbons	22, 29, 33, 162, 163	22, 33, 113, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173	42, 131	33, 95, 96, 98, 99, 100, 101, 102, 104, 105, 109, 110, 113, 116, 119, 120, 122, 125, 131, 134, 135, 136, 140, 142	175			
Other halocarbons	26	78, 176, 177, 178, 179	54, 78, 80, 180	100, 108, 120				
Polynuclear compounds		181, 181, 183, 184, 185	58, 77, 79, 83, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195	127				
Polychlorinated biphenyls		179, 196, 197	53, 54, 55, 89, 198					
Phenols	199, 200, 201, 202	171, 199, 203, 204, 205, 206, 207, 208, 218	50, 62, 86, 209, 210, 211, 212	109	150, 151, 153, 154			213, 214, 215
Aliphatic hydrocarbons	24, 32	171, 176, 216, 217	84	114, 126, 224	31, 152, 220			
Aromatic hydrocarbons		221, 222, 223	132, 222, 224	97, 120, 123, 126, 132, 222	152, 225			
Aromatic amines			68, 198, 226		148			
Nitrosamines			82					
Other organic nitrogen compounds	23		65, 75, 227	106	106		160	
Organic acids		228, 229, 230	43, 66, 72, 90, 231, 232			157		232
Phthalates		197	190, 198					

Table 5 (continued)
SUMMARY OF ISOLATION AND CONCENTRATION TECHNIQUES FOR SEVERAL CLASSES OF ORGANIC COMPOUNDS (NUMBERS REFER TO REFERENCES)

Concentration techniques	Direct aqueous injection	Liquid-liquid extraction	Adsorption	Headspace analysis	Steam distillation	Freezing techniques	Ultrafiltration	Derivative extraction
Surfactants		233, 234, 235	236	237				233, 234, 235
Dioxines		238, 254, 295, 296						
Organophosphorus pesticides		34, 239	60, 61, 74					
Chlorophenoxy acids		168, 240, 241						
Phenylurea pesticides	242	243, 244	46, 73					
Organochlorine pesticides		172, 176, 245, 246, 247	54, 69, 76, 79, 85, 191	127				
Other pesticides	248	38, 156, 196, 249, 250, 251, 252, 253, 255, 256, 257, 258, 259, 260, 261, 262	53, 57, 59, 63, 87, 92, 156, 263, 264, 265		264			215, 265
Fulvic/humic substances			62, 266				159, 160	
Nonvolatiles		267				155, 156, 263, 269		
Organosilicon	270, 271	270, 271						
Organometal compounds	233	272, 273	274	118	272			275
Priority pollutants	200, 276	166, 196, 246, 277	51, 80	101, 117				
Polar compounds	28, 32, 105							
Sumparameters	277, 278	48, 267, 279, 280, 282	48, 69, 132, 180, 228, 279, 281, 282	48, 282				

etc., the group "priority pollutants" defined by the EPA is also given because in some papers the group as a whole is mentioned. From this table, it follows that freezing techniques and ultrafiltration are used on a very small scale and are restricted to only a few classes of compounds.

An extended review for the analysis of a number of classes of compounds has recently been written by McIntyre and Lester.[283]

III. CLEAN UP

The applied concentration and/or isolation technique has a great influence on further clean-up procedure. HSA techniques such as static head-space and P and T with thermal desorption have the advantage that no further clean up is necessary. These techniques are restrictred to the class of volatile compounds. A high selectivity of the concentration and/or isolation technique decreases the necessity of a further clean-up procedure. By a proper selection of the extraction solvent or the sorbent, the analytes can be extracted and separated simultaneously from the majority of coextractives. Also a derivatization procedure can increase the selectivity of the method.

For clean up, the following procedures can be used.

1. Liquid-liquid partitioning — liquid-liquid partitioning between two immiscible phases will separate compounds of different solubilities. Thus, if the extract is a nonpolar solvent such as petroleum ether or hexane, it is partitioned with a polar solvent such as acetonitrile.
2. Liquid-solid chromatography — liquid-solid chromatography is the most widely used technique to clean up sample extracts. Silicagel, alumina, and Florisil® are the most commonly used adsorbents. The adsorbent should be free of organic contaminants, inert to the analytes, effective in removing interferences, and uniform in activity from batch to batch. Column chromatography can also be used for preliminary fractionation of sample extracts, e.g., separation of PCBs from organochlorine compounds such as described by Wegman and Hofstee.[284] Extended experience with clean-up procedures is present in the analysis of pesticide residues.[17-19]
3. Gel permeation chromatography — gel permeation chromatography, or size-exclusion chromatography, has been used on humic or fulvic acids in water. This technique is frequently applied in the analysis of fatty samples, as described by Tuinstra et al.[285] Also Lee et al.[17] described some applications in the analysis of fish and wildlife. Gel permeation chromatography is a very effective method based on differences in molecular weight. Large molecules are excluded from the pores of the gels and are eluted first. It is a good technique for cleaning environmental samples of their fat or lipid content and can easily be automated. However, after gel permeation chromatography for fractionation, extra liquid-solid column chromatography is still necessary. Thus there is little advantage in using gel permeation chromatography for the clean up of low fatty or nonfatty samples such as water.
4. HPLC — HPLC can be used as a clean-up technique. One of the biggest advantages of HPLC is the possibility of automation. However, HPLC analytical columns can be deactivated by sample coextractives, and regeneration of the columns is time consuming. A solution is to use small precolumns in series with the analytical column; this minimizes the effect, as described by Goewie in her thesis.[52] Good results were obtained for chlorophenols and other aromatics (also see Section II.C).

In Table 6, some examples of clean up are given for several classes of compounds. From this table, it follows that for clean up the adsorption technique is very attractive. A new development is HPLC, however, often in combination with a small precolumn.

Table 6
SUMMARY OF CLEAN-UP METHODS USED FOR DIFFERENT CLASSES OF ORGANIC POLLUTANTS (NUMBERS REFER TO REFERENCES)

Clean-up techniques Compounds	Liquid-liquid extraction	Adsorption	HPLC
Volatile halocarbons			
Other halocarbons		177, 179	
Polynuclear compounds	185	182, 183, 286, 287	190
Polychlorinated biphenyls		179, 197	
Phenols	151, 288, 289	290	291
Aliphatic hydrocarbons		152, 216, 286	
Aromatic hydrocarbons		152	
Aromatic amines		226, 292	293
Nitrosamines			
Other organic nitrogen compounds		75, 81	
Organic acids	43	228	
Phthalates		197	190
Surfactants	234, 236	294	
Dioxines		295, 296	
Organophosphorus pesticides			297
Chlorophenoxy acids			
Phenylurea pesticides		243	46, 298
Organochlorine pesticides		300	
Other pesticides	299	249, 251, 252, 256, 257, 258, 260, 300, 301, 302, 303, 304	291, 305
Fulvic/humic substances		266	
Nonvolatiles			
Organosilicon			
Organometal compounds		273	
Priority pollutants		51, 277	
Polar compounds			
Sumparameters	282	282	

IV. DERIVATIZATION

Several types of derivatization techniques can be mentioned:

1. Chemical derivatization as a prerequisite for the method of analysis, e.g., acylation of chlorophenols; it must meet all requirements associated with a practical usable analytical method, such as reproducibility, good recovery, no interferences, etc.
2. Chemical derivatization confirmatory test; the demands are less severe since the mean criteria are: speed, size of operation, and acceptable yield
3. On-column derivatization (GC)
4. Precolumn derivatization (HPLC)
5. Postcolumn derivatization (HPLC)
6. Clean-up reaction, chemical reactions to clean up or remove specific interferences.

Chemical derivatizations can have advantages such as increase in volatility, thermal stability, sensitivity, more selectivity, and improvement of peak shape and/or separation behavior.

A special aspect in HPLC analysis is the appearance of postchromatographic techniques[306]

Table 7
DERIVATIZATION REAGENTS USED IN ANALYSIS OF ORGANIC POLLUTANTS IN WATER

Derivatization reagent	Organic compound	Analytical method	Ref.
Diazomethane	Trichloroacetic acid	GC-microwave plasma emission detector	241
	Humic and fulvic acids	GC-microwave plasma emission detector	307
	Pentachlorophenol, chlorophenols	GC-MS, GC-ECD	203, 288
	Acids	GC	308
Acetic anhydride	Chlorophenols	GC-ECD	213, 215, 309, 310, 311
	Aminophenol, aniline	GC-ECD	312
	Nitrophenols	GC	310, 313
Chloro/dichloroacetic acid	Chloroanilines	GC-ECD	314
	ETU		265
Trifluoro acetic acid	Chlorophenols	GC-MS	311
	Glutamic acid	GC-MS	315
Heptafluoro butyric anhydride	Anilines	GC-ECD	292, 315, 316
	Phenols	GC-MS	205, 317
	Phenylurea herbicides	GC/HPLC	318
Pentafluorobenzylbromide	Chlorophenols	GC-MS	311
2,6-Difluorobenzylbromide		GC-MS	311
Pentafluorobenzoyl chloride	Chlorophenols	GC-MS	311
2,4-Dinitro fluoro benzene	Chlorophenols	GC-MS	311
	Matacil	GC-ECD	299
$NaNO_2$ in buffer (diazotation)	Phenols	Raman spectrometry	319
Alkylhalide	4-Nitrophenol	HPLC	320
Acetone	Hydrazine	GC-AFID	321
Methylen blue alkyl	Alkylbenzene sulphonates	GC-MS	234, 322
4-Amino antipyrine	Phenols	Spectrophotometric	154
Complex Na picrate	Nonionic surfactants	Spectrophotometric	234, 235
1-(4-Nitrobenzyl)4-(4-diethylaminophenylazo)	Anionic surfactants	Spectrophotometric	235
Pyridinium bromide	Pentachlorophenol	GC/HPLC	290
N-nitroguanidine/diazoethane			
β-Napthtal	Alkylhalides	HPLC-fluorescence	323
Ortho-phthalaldehyde	Amino acids	HPLC-fluorescence	160
n-Bu-Grignard reagent	Tetra alkyl lead compounds	Induced microwave-plasma detector	273
Salicyl aldehyde diphenylboron chelate	Primary amines	HPLC-fluorescence	324

and postcolumn reaction detectors. The lack of suitable detectors in LC for trace and ultratrace analysis of complex matrices has catalyzed this trend. The major advantage of postcolumn reaction detectors is the absence of artifact formation, and the only requirement is good reproducibility. A disadvantage is the great influence of the mobile phase on the reaction medium. A good review on chemical derivatization in analytical chemistry is edited by Frei and Lawrence.[306]

In Table 7, the derivatization reagents and the analytes are listed from the reviewed papers. From this table, it follows that most of the applications, especially in GC, are conventional.

Chemical reactions for clean up (not given in the table) are especially interesting in the analysis of organic compounds at very low concentrations in water samples contaminated with many interfering compounds. An example is the analysis of dioxin in water samples of a wash water circuit during incineration of chlorine-containing industrial wastes, as described by Brenner et al.[296]

Postcolumn chemical reaction detectors were applied in past years in pharmaceutical analysis. The use in environmental analysis is, up until the present, only done on a small scale. One of the remarkable features of reaction detectors is their ability to fit into automated analytical systems. Their selectivity and sensitivity in the reaction itself will often permit decreasing drastically the amount of sample preparation or the requirements for a powerful separation. A problem can be the aspect of band broadening and interference of the detection signal with the reagent.

V. DETECTION

A wide range of analytical detection techniques are available for the determination of organic pollutants. These techniques are not specifically designed for water analysis and can also be used for many other matrices. In order to restrict the volume of this paper, only a short description of the different detectors in GC and HPLC will be given. For further detailed information with respect to detection techniques, complete scientific journals and a large number of books are available.

A. GC

GC is used on a large scale in the analysis of organic pollutants in water samples. The introduction of capillary columns, selective detectors, and new sample introductory techniques was important. In Table 8, a number of detectors used in the analysis of water samples are summarized.

In 1981, Mantica[2] reviewed all papers with respect to GC detectors. He concluded, "In the last years no development of special interest was reported in this field; only a limited number of detectors was introduced, but none of them reached a reasonable distribution in the analytical world. However their performances have enhanced concerning sensitivity, selectivity, linearity of response and ease of operation. With the introduction and development of the low inner volume detectors, studied purposely for use with capillary columns, the improvement of the sample introduction techniques and the quality of the capillary columns, the introduction of derivatising reagents and the introduction of multidetection systems, very highly efficient and sensitive systems for the analysis of trace organic pollutants in water samples were made available to the analysts."

Sandra[310] reviewed papers with respect to new developments in selective detection in capillary GC. Some interesting developments were capillary GC-FTIR (Fourier transform infrared), multiple simultaneous detection, multidimensional GC, and selective sample introduction.

The main benefit of multiple detection is the simultaneous registration of specific and selective items by a single injection, drastically reducing the analysis time. Destructive detectors can be mounted directly on nondestructive (see Table 8). Multidimensional GC enhances selectivity.[325] Interesting peak groups from a complex mixture, eluting from a first capillary or packed column, can be transferred to a second column of a high selectivity. An application of multidimensional head-space capillary GC in waste water analysis is described by Merz et al.[326] Two capillary columns of different polarity were used for the analysis of volatile compounds in waste water. Schneider et al.[327] used a parallel capillary column technique for the analysis of chlorinated pesticides and PCBs. The use of specially dedicated columns is important.[328]

Smith[329] compared two separation identification techniques, capillary GC-MS and capillary GC-FTIR. Capillary GC-MS is well established and routinely used in many areas of analytical

Table 8
DETECTORS FOR GAS CHROMATOGRAPHY

Detector	Elemental or molecular information	Destructive character	Minimal detectable amount	Linear dynamic range	CGC* compatibility	Remarks
Ionization detectors						
Electron capture detector (ECD)	Electron affinity, halogens, nitrocompounds, conjugated carbonyls	No	10^{-14}—10^{-12} g aldrin/sec	10^4	+ + +	High sensitivity; sample clean up very important
Photo-ionization detector (PID)	Aromatic compounds	No	10^{-12} g	10^7	+	Selectivity can be obtained by utilizing UV lamp with different photo-energies
Alkali flame ionization detector (AFID)	Nitrogen/phosphorus	Yes	10^{-13}—10^{-14} g N or S; 2.10^{-13}—2^{-15} g P/sec	10^4—10^5	+ +	Can also be used for halogens, sulfur, As, Sb, Sn, Pb
Electrochemical detectors						
Coulometric detector (CD)	Halogens (except F)	Yes	10^{-9} g Cl			Operation not simple
Hall-electrolytic conductivity detector (HECD)	Nitrogen, sulfur, halogens	Yes	10^{-9} g	10^4		Operation not simple
Spectroscopic detectors						
Flame ionization detector (FID)		Yes	0.02 Coulomb per gram of carbon	10^6—10^7	+ + +	Most universal detector; sensitivity can be strongly improved by adding nitrogen make-up gas
Flame photometric detector (FPD)	Phosphorus/sulfur	Yes	10^{-12} g P/sec 5.10^{-12}—10^{-10} g S/sec	10^8—10^4 (P) 10^2—10^3 (S)	+ +	Excessive flame noise; can also be used for halogens, CN groups, heavy metals
Microwave-induced plasma detector	Selective mode: C, H, D, S, F, Cl, Br, I, Hg, V, Ci, Mn, Fe, Co, Ni	Yes	10^{-9} g		+ +	Problems with O, P, and N
Atomic absorption spectrometric detector (AASD)	Monofunctional Hg	Yes	10^{-10} g Hg		+ +	Expensive

Table 8 (continued)
DETECTORS FOR GAS CHROMATOGRAPHY

Detector	Elemental or molecular information	Destructive character	Minimal detectable amount	Linear dynamic range	CGC[a] compatibility	Remarks
Fourier-transform infrared detector (FTIR) on line	Functional group information	No	10^{-9} g	10^{1}—10^{3}	+	Expensive; discrimination between isomers
Mass spectrometric detection (MS)	Elemental and/or molecular information	Yes	10^{-9}—10^{-12} g benzofenon		++	Expensive; optimal specificity/sensitivity ratio
Far UV-absorbance detector (FUV)		No			+	Little information available
Thermal conductivity detector (TCD)		No	10^{-7} g	10^{5}		Not sensitive, nonspecific

[a] CGC = capillary gas chromatography.

chemistry. The other, capillary GC-FTIR, is a technique for which few applications have been reported. He concluded, "In the last few years, capillary GC-FTIR has developed into an on-line technique whereby spectral data can be obtained in a short period of time even for difficult samples. The sensitivity of both techniques is compatible with capillary columns."

Due to the widely varying IR absorptivities of different types of compounds, different chromatographic systems in GC-FTIR may be required for different samples. Generally, the capillary columns with higher capacity columns are useful in GC-FTIR. While both techniques can be applicable, considerably more sample is necessary for the GC-FTIR analysis. To solve indentification problems, use of GC-MS and GC-FTIR gives advantages and decreases total analysis time. A complete comparison was made by Shafer et al.[330] for the analysis of waste soil samples. Of the 35 compounds detected by both techniques, 12 were identified by GC-MS and 26 by GC-FTIR.

For the isomeric aromatic compounds, the IR data yielded exact identifications, while the MS data yielded the compound type. The solution was reversed for the hydrocarbons.

Details of GC-MS and GC-FTIR instrumentation are reviewed by Holland et al.,[331] Van de Heuvel et al.,[332] and by Griffits et al.[333]

B. HPLC

HPLC has become a major analytical technique for the analysis of a wide range of compounds too involatile or too thermolabile for analysis by GC. An excellent introduction to HPLC is given by Snyder and Kirkland.[334] The analytical application of HPLC depends to a high degree on the availability of suitable detectors. The main requirements for these detectors are high sensitivity and adequate selectivity. The latter requirement is generally much more important here than in GC. In water analysis, the gas chromatographer can at least be sure that compounds with a high molecular weight will not generate peaks in the chromatogram of the analytes with a lower molecular weight. Interference of high molecular weight material is an omnipresent problem in trace analysis with HPLC. Selectivity can be improved by selective extraction, matrix removal, high efficiency of separation by the suitable choice of phase system or multicolumn operation, and by selective selection. Important parameters that are in use for selective HPLC detection are[4] UV wavelength choice, simultaneous multiwavelength (photodiode array), fluorescence, electrochemistry, atomic spectrometry, electron capture, homogeneous postcolumn reaction, and postcolumn reaction with extraction. Recent developments in detection techniques have recently been reviewed by White.[335,336] In our paper, the analysis of organic pollutants in water samples is described; thus we restricted the scope to analytical problems directly related to water analysis. As an example, in Table 9, the detectors are summarized that are used in water analysis.

New techniques that are very promising in the analysis of water samples are[337]

1. Application of columns with large plate numbers. A large number of theoretical plates can be generated by decreasing the theoretical plate height, by recycling, or by increasing the length of the column. In focus are coupling of micro-bore columns.
2. Multicolumn operation. The whole multicolumn operation can be executed on- or off-line.[156]
3. Selective detection systems.

It can be concluded that the significant improvement of the column technology and the new stationary phases and detection systems during the last 10 years turned HPLC into a suitable method for trace analysis of organic micropollutants. However, the separation power of common HPLC columns is insufficient for very complex mixtures. The applicability of packed micro-bore columns of about 0.5 to 1-mm I.D. is now the subject of much interest. Especially important is the development of a reliable on-line LC-MS combination. Recent

Table 9
DETECTORS FOR HPLC

Detector	Compounds	Sensitivity (g/mℓ)	Dynamic linear range	Remarks
UV-vis absorbance	Aromatics	2.10^{-10}	10^5	Many applications, high reliability, simple operation
Fluorescence	PAHs, phenols, pesticides	10^{-11}	10^3	Derivatization often necessary, high specificity
Amperometric	Oxidizable and reducible compounds	10^{-12}	10^6	Contamination of detector; reversed-phase chromatography; ion-exchange chromatography
Conductivity detector	Ions	10^{-5}	10^4	
Refractometric index	Alkanes	10^{-7}	10^4	Universal detector
Infrared	Macromolecules	10^{-6}	10^4	
Radioactivity	Labeled compounds		$>10^6$	Very restricted scope

progress in LC-MS is described by Games et al.[338] On-line coupling of LC with MS will be an attractive tool for analysis of low volatile organic compounds in water samples. However, a clean up of the sample prior to LC-MS analysis will be very necessary. Although the sensitivity is not yet comparable with that obtained by capillary GC-MS combinations, recent advances in combined LC-MS have improved the range of compounds amenable to study and have decreased the detection limits. At the present time, there is no universal LC-MS system for all types of compounds. Current systems have considerable potential for extending the range of identification of organic pollutants in water.

A relatively new technology is field-flow fractionation (FFF). This technique is applicable to the characterization and separation of macromolecules and particulate species with an effective molecular weight of 10^3 to 10^{18}.[339,340]

FFF is the general name of a family of separation techniques that use fields of gradients that can interact with solute macromolecules to force them differentially into the slow streamlines of a flowing fluid. Separations take place in thin open channels of a rectangular cross section under conditions of laminar flow. A field is applied perpendicularly to the face of the channel so that solutes form narrow layers against the channel wall based on their field-induced velocity and counteracting ability to diffuse away from the channel wall. The rate of elution of the layers is greater for solutes that, by virtue of weak interaction with the field, can diffuse higher into the parabolic flow profile. In many cases, the degree of interaction of the macromolecules can be calculated, which makes it possible to use the degree of retention in an FFF channel for characterizing a solute. The passing of the continuous stream of eluate through an appropriate detector gives a fractogram, i.e., a plot of detector response vs. elution volume.

Two advantages are controlled retention by external fields, which can be varied, and low surface area exposed to the solute.

The following FFF techniques can be applied

1. Thermal FFF — a thermal gradient is maintained by heating the upper plate of the channel and cooling the lower plate to separate macromolecules by thermal diffusion. This technique cannot be applied to water-soluble macromolecules.
2. Electrical FFF — a semipermeable membrane is used for the channel walls and a voltage is applied to electrodes placed in electrolyte reservoirs on either side of the channel. This technique has not been developed as the thermal mode. However, the technique has the potential for separation and characterization, especially in the area of macromolecules of biological origin (proteins).
3. Sedimentation FFF — a gravitational or centrifugal field is used. With this technique, it is possible to characterize the molecular weight. Aqueous solutions are used as carriers.
4. Flow FFF — an apparatus similar to that used in electrical FFF is constructed with semipermeable membranes. A separate pump forces the carrier solution across the membranes, forming a cross-flow field. Retention is based only on frictional drag related to molecular size. This technique has been used exclusively for water-soluble species.

A complete FFF apparatus consists of a pump to drive the carrier solution, a channel, the field-of-gradient generating components, a detector, flow-measurement, and a fraction collector. The collected samples can be identified and/or subjected to subsequent analytical steps using spectroscopy, electron microscopy, or biological detection. It can be concluded that in the future FFF technology could be a handsome tool for the analysis of macromolecules in water samples.

VI. CONCLUSIONS AND RECOMMENDATIONS

A number of concentration and isolation techniques are applied on a large scale for the analysis of volatile compounds. Techniques that are capable of isolating and separating nonvolatile organics in water have limited application and only a few laboratories are actively involved. The development of methods for the identification of nonvolatile organics is an urgent and important task. For example, an accurate assessment of human health associated with the long-term exposure to organics in water cannot be made until more is known about the nonvolatile compounds present.

On-line coupling of LC-MS will be an attractive tool for analysis of low volatile organic compounds in water samples. However, a clean up of the sample prior to HPLC-MS analysis will most likely be necessary.

An interesting technology will be FFF for larger molecules.

Extraction methods based on adsorbents such as XAD are suffering from contamination problems. The purity of solvents is far easier to control.

In GC, it is now technically feasible to place two or more detectors in parallel or series to obtain dual or multiple detection systems that can simultaneously detect compounds belonging to different chemical classes.

More attention has to be given to particulate matter in the water samples. Many compounds are adsorbed to these particles. Particulate matter in the water causes systematic errors.

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