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Review

Trace level analysis of micropollutants in aqueous samples using gas chromatography with on-line sample enrichment and large volume injection

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Abstract

In this review article an overview of methods for the analysis of aqueous samples with capillary gas chromatography is presented. The methods can be classified into two approaches: a direct approach in which water is directly introduced onto the GC column, and an indirect approach in which water is eliminated, i.e., by liquid–liquid extraction or solid-phase extraction, prior to introduction of the analytes onto the GC column. The emphasis is on methods in which sample preparation and GC analysis are combined on-line. An outline of methods for large volume injection is also presented as the use of on-line systems often involves the introduction of large volumes of sample extract.

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1. Introduction

The presence of organic microcontaminants in various compartments of the environment constitutes a growing source of concern for human health and the natural environment. As a consequence there is a rapid increase in the demand for the determination of these micropollutants in air, soil and sludge, and water. In this respect especially the analysis of water samples is of utmost importance as many of the organic contaminants of interest are either directly introduced into the aquatic environment or eventually turn up in this compartment due to aquatic runoff of agricultural and industrial sites or transfer from the atmosphere into surface water. As surface water is a vital source of drinking water, water quality has received considerable attention in environmental legislation and stringent regulations for surface water as well as drinking water were issued by legislation agencies. For example, current European Union (EU) directives dictate that the concentration of, e.g., individual pesticides in drinking water should not exceed a maximum admissible concentration of $0.1 \mu\text{g/l}$ [1]. Quantitative analysis of such levels is already a challenging task for analytical chemists. More stringent regulations which will without any doubt be issued in the not too distant future will force analysts to develop new methods for the accurate and reliable determination of even lower concentrations of contaminants in aqueous samples.

Due to the complex nature of aqueous environmental samples, powerful separation methods, such as for example capillary gas chromatography (GC) or high-performance liquid chromatography (LC), are indispensable for the analytical determination of contaminants. A pre-

ferred arrangement is a combination of the separation method with an identification technique, such as for example mass spectrometry (MS). The high efficiency, the favourable speed of analysis and the ease of combination with spectrometric detection devices render especially capillary GC a powerful analytical technique in water analysis. In this respect one of the most important advantages of GC over any of the other separation methods clearly is the availability of a wide range of sensitive and selective detection devices. The combination of the excellent separation capability of capillary GC with sensitive selective detection enables the measurement of low concentrations of different components in complex sample matrices. Selective detectors have become increasingly popular in recent years due to the fact that they partially eliminate the need for laborious and time-consuming sample preparation. Moreover, selective detection also reduces the risk of false-positive identifications. Finally, the use of selective detection, at least in principle, simplifies the demands that have to be posed on the separation itself. If selective detection is applied, target compounds can be determined while other co-eluting components are not sensed. The most powerful selective detector is the mass spectrometer which allows a truly positive identification of target compounds whereas selective detectors merely reveal the presence of certain hetero-atoms in the eluting molecules. A survey of some of the characteristics of a number of selective GC detectors frequently used in environmental analysis is presented in Table 1 [2].

The minimum detectable amounts for the various detectors presented in Table 1 represent the quantity of a component required to obtain a peak with a signal-to-noise ratio of three under

Table 1
Overview of detection limits and linear dynamic ranges of various GC detectors [2]

Detector	Minimum detectable amount (g)	Linear dynamic range
Flame ionization detector (FID)	$5 \cdot 10^{-11}$	10^6
Electron-capture detector (ECD)	10^{-12}	10^4
Nitrogen-phosphorus detector (NPD)	10^{-11}	10^3
Flame photometric detector (FPD)	$5 \cdot 10^{-12}$	10^3 ^a
Mass spectrometer (MS)		
Full scan	10^{-10}	10^3
Single ion monitoring (SIM)	10^{-12}	10^3

^a Linearized response from quadratic output.

optimum experimental conditions. For reliable peak integration, especially in case of real-life samples, peak heights of approximately 25 times the noise level are required which results in *determination* limits which are approximately 10 times higher than the *detection* limits specified in Table 1. From this it is clear that in order to meet the detection limits dictated by the EU regulations, a total analyte content of at least an equivalent of ca. 0.1 to 1 ml of water has to be introduced into the GC system. The direct introduction of aqueous samples of this size suffers from a number of experimental difficulties. First, upon evaporation, the water sample forms a very large volume of vapour. Discharge of this vapour volume via the column is a tedious and time consuming process. Moreover, because of the polar nature of water, the stationary phase is essentially non-wettable by water which makes water a poor solvent with regard to the creation of a solvent film required for band focusing. Thirdly, large volumes of water can have an adverse effect on the deactivation layer and the stationary phase of the chromatographic column due to hydrolysis of siloxane bonds. Finally, water is not compatible with most of the flame-based detection devices frequently used in GC nor with spectroscopic identification systems such as infrared detectors.

To eliminate the problems encountered in the *direct* methods for water analysis, various *in-direct* methods were developed. In these methods the compounds of interest are isolated from the water sample prior to introduction into the

GC column. Basically, three approaches for the indirect analysis of water samples can be distinguished. Gas phase stripping is applied in techniques such as, e.g., (dynamic) headspace analysis or purge and trap techniques. In headspace analysis the gas phase in equilibrium with the aqueous phase is analyzed. In the purge and trap technique a purge gas is used to strip volatile analytes from the water sample. The components isolated from the sample are then collected in a cryotrap and reinjected into the chromatographic column. Purge and trap analysis as well as other (gas stripping) techniques for the determination of volatile components in aqueous samples are nowadays well developed and frequently used in water quality control laboratories all over the world. For a review of methods for the analysis of volatiles in water the reader is referred to two excellent recent papers [3,4] and the literature cited therein. In the present review the authors restrict themselves to a survey of methods for the determination of contaminants with unfavourable water–gas distribution coefficients due to either a too low volatility or a too polar nature. These solutes can not be isolated from the water sample using gas phase stripping techniques but require the use of other isolation methods such as those described below.

A second group of techniques for the isolation of analytes from aqueous samples relies on transfer of the analytes of interest from the aqueous phase into an organic solvent with more favourable properties for GC sample intro-

duction. This procedure, which is generally called phase switching, can be performed using either liquid–liquid extraction (LLE) or solid-phase extraction (SPE). In both methods the water is eliminated prior to the injector of the GC. Very often a phase-switching step yields an additional advantage, viz. preconcentration, because fairly large volumes of water can be extracted using a much smaller volume of the organic solvent.

A third method for water elimination is based on sorption of the analytes of interest from the aqueous phase onto a solid sorbent or an immobilised liquid with subsequent thermal desorption. In solid-phase micro-extraction (SPME), one of the sorption–thermal desorption techniques for water elimination, the water is eliminated prior to introduction of the compounds of interest into the GC instrument. In other techniques SPE with subsequent thermal desorption takes place within the injector of the GC. A schematic representation of the various methods for water analysis is shown in Fig. 1.

Most of the sample preparation methods described above can be performed in an on-line as well as an off-line fashion. On-line combination of the sample preparation and the chromatographic analysis has a number of significant advantages over an off-line approach. First, as no intermediate sample handling step is required, the risk of sample contamination or analyte loss is reduced. Moreover, on-line

combination greatly simplifies automation thereby allowing the construction of a fully automated pretreatment module connected on-line with the gas chromatograph. Additionally, an on-line set-up generally yields improved detection limits since the total amount of component introduced into the analytical system is actually transferred to the chromatograph. Despite the inherent advantages of on-line sample pretreatment–chromatographic analysis, this technique is not yet widely accepted in water analysis. In part this is due to the lack of commercial instrumentation. Besides, analytical chemists in many water quality control laboratories obviously are not familiar with the state-of-the-art in on-line water analysis.

In the present paper an overview of the various direct and indirect methods for the analysis of water samples is presented. Each of the various techniques shown in Fig. 1 will be discussed in detail in subsequent sections. Emphasis will be on methods in which sample preparation and analysis are combined on-line. Because many of the on-line systems for indirect analysis rely on the introduction of large volumes of organic solvents into the GC system, an outline of methods for large volume sampling is presented in a first section.

2. Fundamentals of large volume injection

In order to be able to meet the required determination limits for micropollutants in water analysis, the total amount of analyte in 0.1 to 1 ml of water will have to be transferred to the GC instrument. With a typical GC injection volume of 1 μ l this would imply that the volume ratio of water over organic solvent used in the phase switching procedure should be between 1:100 and 1:1000. This means that 100 to 1000 μ l of water have to be extracted with only 1 μ l of organic solvent. In daily practice, these ratios are impractically large due to (partial) miscibility of the organic solvent and water in case of LLE and the unfavourable extraction yields obtained at such large ratios, or due to the large dead volumes of the packed sorbent beds in SPE cartridges. Most of the extraction methods cur-

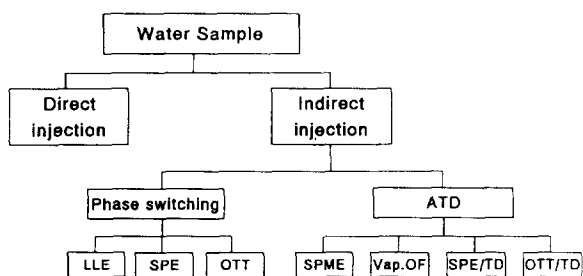


Fig. 1. Schematic representation of methods for the analysis of aqueous samples. ATD = adsorption–thermal desorption; LLE = liquid–liquid extraction; SPE = solid-phase extraction; OTT = extraction with open tubular traps; SPME = solid-phase microextraction; Vap.OF = vapour overflow; SPE/TD = solid-phase extraction–thermal desorption; OTT/TD = open tubular trapping–thermal desorption.

rently in use in water analysis rely on the use of large volumes of extraction solvents. The required preconcentration is obtained by means of time consuming evaporation which easily causes losses of volatile compounds [5]. The introduction of a larger fraction of the extract is an attractive alternative.

In recent years several injection techniques have been developed that allow the injection of samples of up to at least 100 μ l in capillary GC. Techniques that have been developed to this end — and have also been used to couple column liquid chromatography on-line with GC, i.e. for LC–GC [6] — are partially concurrent solvent evaporation (PCSE) using an on-column interface [7], fully concurrent solvent evaporation (FCSE) with a loop-type interface [8] and, the programmed temperature vaporizer (PTV) injection technique.

Optimization of the processes during and after the actual injection is the key to successful large volume injection. Essentially, these processes are the same for each of the large volume injection techniques referred to above. During injection of the sample most or all of the solvent is evaporated and as little solvent (vapour) as possible should reach the stationary phase in the analytical column. It is evident that increasing the retention power at the site of evaporation during the solvent elimination step will greatly improve the recovery of volatile analytes. Although in principle several routes are open to achieve increased retention, creation of a temporary solvent film on the wall of an uncoated capillary column acting as injection zone, or on the wall of the injector liner is of most interest. During injection this solvent film is an efficient trap for the volatile analytes, while, once evaporated, it leaves behind a bare wall with low retention. In case of PTV injection cooling of the injection zone to sub-ambient temperatures is often used.

Furthermore, in order to speed up the evaporation process and to protect the detector from the large solvent cloud, the solvent vapour is generally released from the GC system through an exit, either via a split vent as with PTV sampling or via an early solvent vapour exit as

with the other two injection techniques. For the PTV injection system the exit is part of the injector itself, while for large volume injection with both the on-column and the loop-type interface the exit is positioned after an uncoated capillary. Generally, a short piece of coated GC column, the so-called retaining precolumn [9] is installed between the uncoated capillary and the solvent vapour exit which prevents the volatile analytes from being vented with the solvent. However, especially with on-column injection it is still necessary to optimize the time of “solvent release system open” after completion of the injection in order not to lose the early eluting compounds and at the same time to transfer an as small as possible amount of solvent to the analytical column and detector. A detailed discussion of the three techniques applied for large volume sample introduction will be presented below.

2.1. On-column injection

Large volume injection through an on-column injector became possible due to the development of deactivated uncoated fused-silica or glass capillaries, so-called retention gaps [10,11]. The introduction of the analyte-containing solvent has to take place at a temperature below the solvent boiling point, in order to prevent back flush of solvent vapour into the injector. The introduction speed is usually above the evaporation rate. This guarantees the formation of a solvent film on the surface of the retention gap provided, of course, that the retention gap can be wetted by the liquid.

Until recently rather long retention gaps, viz. 10 meters or longer, were used, in order not to allow the liquid film to reach the stationary phase of the analytical column. The developments reported by Munari et al. for eluent transfer from LC to GC under PCSE conditions [12] opened the route to the injection of much larger volumes. In PCSE some 90% of the solvent injected is evaporated during the injection. Because only a minor part is introduced as a liquid, which floods the retention gap, retention gaps could be drastically decreased in

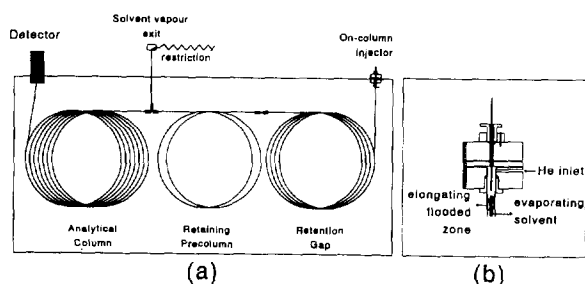


Fig. 2. (a) Schematic representation of a set-up for on-column injection consisting of an on-column injector, a retention gap, a retaining precolumn, an early solvent vapour exit and the separation column. (b) The process of partially concurrent solvent evaporation; volatile analytes are retained in the elongated flooded zone.

length [13]. A system for on-column large volume injection is schematically depicted in Fig. 2. The main advantage of the on-column interface is that it can be used for non-volatile as well as volatile analytes, while alternative techniques for large volume sampling such as those described below are restricted to compounds eluting at relatively high temperatures.

After large volume on-column injection the analytes are spread out over several meters of uncoated capillary. These broad bands are refocused by solvent trapping and phase-ratio focusing [14–16]. With solvent trapping relatively volatile solutes are re-concentrated because the solvent film evaporates from the rear to the front and the analytes are retained by the liquid film, i.e., analytes start to migrate with evaporation of the rear end of the film but are trapped again in the liquid film ahead. Less volatile compounds do not evaporate with the solvent and remain spread out over the wall of the retention gap. These compounds are re-concentrated by phase-ratio focusing. The difference in migration speed in the retention gap and in the coated GC column causes the rear end of the zone to catch up with the front end. As soon as the front end of the zone reaches the stationary phase, its migration speed is reduced to nearly zero, while the remaining part, which is still in the retention gap, continues to migrate at the initial, higher speed.

Solvent peaks can be rather broad, which can

not be tolerated by all GC detectors. It is therefore necessary to release the solvent vapour via a solvent vapour exit. The period of time this exit is left open after injection has to be optimized experimentally. The major part of the evaporating solvent film will then be sent to waste, i.e., it will not enter the analytical column. However, this process can not be unduly prolonged, since delayed closure of the solvent vapour exit will result in loss of volatile compounds. A delayed closure of the solvent vapour exit in the order of a few seconds only, already caused a complete loss of the most volatile compounds.

For optimizing large volume injection using the PCSE technique and the on-column interface two parameters have to be determined, i.e., the evaporation rate and the length of the flooded zone; furthermore, the maximum speed of injection and/or the length of the retention gap have to be adjusted so that the solvent film will not reach the stationary phase of the GC column. Additionally, it is very important that during injection of the sample the temperature of the GC oven is below the (pressure-corrected) boiling point of the solvent used. At too high temperatures the solvent will start to boil, which can create backflush into the injector and eventually into the carrier gas lines. Two relevant examples of calculating the length of retention gap and the maximum injection volume in the on-column injection technique are presented in Table 2.

The recent introduction of commercial instruments for large volume on-column injection will help this technique to become applied in routine analysis. If the optimization has been carried out carefully, very reproducible results can be obtained at low concentration levels. An optimization strategy was described by Vreuls et al. [13]. The same authors used 100- μ l injections with an autosampler for confirmatory GC-MS with full scan acquisition of various compounds at the sub- μ g/l level in water extracts [17]. Polycyclic aromatic hydrocarbons could be detected in surface water samples at the 5 ng/l level after extraction of 1 l of sample with two times 0.8 ml of *n*-hexane. The presence of

Table 2
Examples of adjusting parameters when using the on-column interface

Length of retention gap for 100 μl injection?		Maximum injection volume in 150 cm retention gap?	
Evaporation rate	55 $\mu\text{l}/\text{min}$	Evaporation rate	55 $\mu\text{l}/\text{min}$
Injection speed	120 $\mu\text{l}/\text{min}$	Injection speed	60 $\mu\text{l}/\text{min}$
Flooded zone	10 $\text{cm}/\mu\text{l}^{\text{a}}$	Flooded zone	20 $\text{cm}/\mu\text{l}^{\text{b}}$
Residual liquid per min	65 $\mu\text{l}/\text{min}$	Maximum amount as liquid (150/20) \approx 7.5 μl	
		Residual liquid per min (60 – 55) \approx 5 μl	
		Maximum injection volume (7.5/5) \times 60 \approx 90 μl	
Length required \rightarrow (65 \times 10 \times 0.83) \approx 540 cm			

^a Typical value for 0.53 mm I.D. retention gap.

^b Typical value for 0.32 mm I.D. retention gap.

atrazine was confirmed in drinking water at a level of 0.05 $\mu\text{g}/\text{l}$ after off-line SPE of 100 ml of sample with subsequent desorption with 2 ml of ethyl acetate. In both cases, the injection volume was 100 μl .

By adapting the insertion depth of the syringe needle in the autosampler vial, it is also possible to perform in-vial extraction. To that end Venema and Jelink [18] added 1 ml of *n*-pentane to a 2.5-ml autosampler vial containing 1 ml of aqueous sample, which was then closed with a crimp-cap. The contents was shaken for 3 min and placed in the autosampler; 140 μl of the extract were injected. With this procedure the authors were able to detect hexachlorobutadiene and hexachlorobenzene at 6 ng/l using MS with selected ion recording (R.S.D. about 10%). At higher levels the R.S.D. values were significantly better, viz. 2–3%. A similar approach was used for the determination of phenolic compounds in water [19].

2.2. Loop-type injection

A second interface that can be used for large volume sample introduction in capillary GC is the loop-type interface [8], which was originally designed for on-line LC–GC. This interface is schematically shown in Fig. 3. The heart of this interface is a 10-port valve with two loops, one being used for injection of the sample and the other for adding an internal standard or a wash solvent. The carrier gas supply line and the

retention gap are attached to other parts of this valve. When both loops are filled, the valves are switched and now the carrier gas pushes the eluent into the part of the retention gap located inside the GC oven, which is kept at a temperature slightly above the solvent boiling point. The pressure built up by the evaporating solvent will stop the plug of liquid from further penetration into the retention gap. Using these FCSE conditions, the solvent is thus evaporated during transfer into the GC system. Volumes of up to several millilitres can be transferred in a relatively short period of time, the maximum being 20 ml in less than 20 min [9]. Since there is no liquid film on the capillary wall, volatile compounds will be lost together with the solvent. As a result, the set-up can only be used for the determination of compounds with rather high GC elution temperatures, i.e., compounds eluting at temperatures some 100–120°C above the

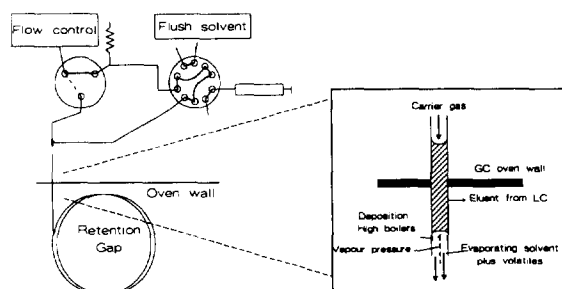


Fig. 3. Schematic representation of the loop-type interface consisting of two valves, a flow control system, and a retention gap.

transfer temperature. Refocusing of the analytes occurs due to phase-ratio focusing.

To increase the carrier gas pressure during eluent evaporation to a pre-determined level, the pneumatic system consists of a pressure and a flow regulator in series (see Fig. 3). The pressure set on the pressure regulator in front of the flow regulator determines the maximum inlet pressure during introduction of the liquid sample. During GC analysis, the gas supply is flow regulated. The inlet pressure is relatively low, and increases with the oven temperature. In principle, there is only one parameter which has to be optimized, viz. the transfer temperature. When the temperature is too low, liquid will enter the GC column, which will result in broad and distorted peaks [20]. When the transfer temperature is too high, excessive analyte losses will occur rendering the application range very narrow. Furthermore, the evaporation process will be more difficult to control due to delayed evaporation. If the temperature needed for correct transfer is lower than the retention gap has to be longer. For many GC amenable solvents and solvent mixtures, Grob and Läubli [21] have determined minimum transfer temperatures for FCSE conditions which allow the liquid to penetrate a 3-m retention gap for 1–1.5 m.

As described earlier for large volume injection via the on-column interface, an early vapour exit can be installed after the retention gap and a retaining precolumn to speed up solvent evaporation. For standard use of the loop-type interface it is not very critical to close the solvent vapour exit exactly in time. Compounds retained in the retention gap and on top of the retaining precolumn during the actual transfer into the GC system are not lost when the solvent vapour exit is kept open for a few more minutes after the injection has been completed. However, when applying the co-solvent trapping technique [22,23] the moment of closing the solvent vapour exit becomes very important. This technique is used to reduce losses of volatile analytes normally encountered with FCSE. To the main solvent a co-solvent is added. The co-solvent should have a boiling point which is higher than that of the main solvent. Further the co-solvent should

be miscible with the main solvent and wet the retention gap. While the main solvent evaporates during introduction into the GC, a layer of co-solvent remains in the retention gap which serves as a temporary stationary phase in which the volatile analytes are trapped. With evaporation of the co-solvent, the volatile analytes are no longer retained and lost if the solvent vapour exit is not closed in time.

Recently, large volume injection using the loop-type interface has successfully been combined with GC-atomic emission detection (AED) [24–28]. The technique was used for the confirmation of GC-MS data and for element specific screening, with limits of detection below 1 $\mu\text{g/l}$. Ground, tap and surface water samples were analyzed.

2.3. Programmed temperature vaporizing injection

The use of temperature-programming techniques for sample introduction in capillary GC was proposed in 1964 by Abel [29]. In 1979 Vogt and co-workers [30–32] constructed a PTV injector and used it to introduce large sample volumes (up to 250 μl) in biomedical and environmental studies. In 1981 Schomburg [33] and Poy et al. [34] demonstrated that temperature-programmed sample introduction offers many advantages compared with hot injection techniques. Injection into a cold chamber greatly reduces the discrimination of less volatile components. Moreover, thermal degradation is minimized, because the residence time of the components at elevated temperatures is reduced compared with conventional split and splitless injection. The quantitative performance of PTV injection systems appears to be comparable to that of on-column injection while at the same time column contamination due to the presence of residue components in the sample, which is frequently observed in on-column sample introduction, is absent [35]. Despite the good results obtained by Vogt using the PTV injector in early large volume sampling experiments, there was hardly any interest in the PTV injector for large

volume sampling in the decade following that publication. PTV injection has, however, received considerable attention as a means of discrimination-free injection or for the injection of thermally unstable molecules.

Large volume sampling using PTV injectors is based on selective elimination of the solvent from the liner of the PTV injector while simultaneously trapping the components with a much lower volatility in the cold liner. When solvent elimination has reached completion, the components are transferred to the column in the splitless mode by rapid temperature-programmed heating of the injector.

A schematic representation of a PTV injector is given in Fig. 4. The basic set-up of a PTV injector closely resembles that of a conventional split/splitless injector. As in conventional split/splitless injectors the liner is the heart of the injection system. The main difference between conventional split/splitless injectors and PTV injectors is in the temperature control. In PTV injectors the vaporization chamber can be heated or cooled rapidly. Temperature control is provided by a sophisticated control box that allows controlled heating and cooling of the liner.

Heating can be performed either by direct or indirect resistive heating, by using heater cartridges or by means of preheated compressed air. Cooling can be performed using cold air, a Peltier element, expanding CO₂, or liquid nitrogen. Temperature programmable injectors are highly flexible injection devices for capillary GC. Various injection modes including cold and hot split and splitless operation can all be performed using the same injector.

In the injection mode that is used for the introduction of large sample volumes, the solvent elimination injection mode, enrichment of the analytes occurs in the liner of the injector. First, the liquid sample is introduced into the liner of the injector at a controlled rate. Speed-controlled sampling is necessary because the capacity of the liner to retain liquid is limited. Upon introduction the solvent is selectively eliminated and solvent vapours are discharged via the split line while less volatile solutes are retained in the liner. During sample introduction the liner temperature is well below the boiling point of the solvent. Next, the components retained in the liner are transferred to the column in the splitless mode. The initial inlet conditions have to be carefully optimized to avoid (or minimize) losses of volatile sample constituents [36]. For optimum performance the speed of sample introduction should equal the rate of solvent elimination [37]. If the sample introduction rate exceeds the evaporation rate, the excess liquid will accumulate in the liner which eventually will result in flooding or overloading of the liner and, thus, in severe losses of both volatile and non-volatile components via the split exit. Contrary to this, too low sample introduction rates will result in a lengthy sampling procedure and in severe losses of volatile sample constituents. The use of liners packed with an adsorbent has been reported to be an efficient means to minimize losses of volatiles [38].

The large number of experimental parameters involved in PTV-based large volume sampling makes optimization of the sampling process, especially with regard to minimizing losses of volatile compounds by co-evaporation with the

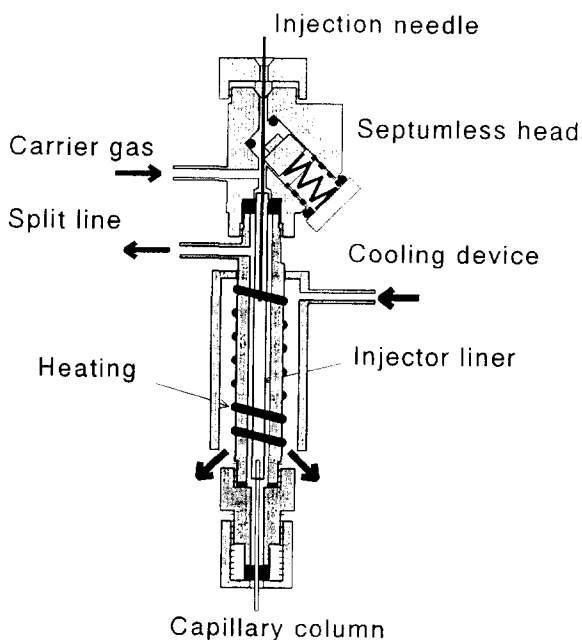


Fig. 4. Schematic representation of a PTV type injector.

solvent, a tedious and time-consuming process. Optimization of PTV large volume injection has been the subject of a number of studies. Herraiz and co-workers reported on the use of chemometrical strategies for the optimization of, e.g., sample volume, initial PTV temperature, speed of sample introduction, carrier gas flow-rate during sample introduction, and the nature of the adsorbent packed in the liner [39,40]. Further work by this group focused on large volume PTV injections in food analysis [40,41]. Reliable determinations of volatile alcohols and ethyl esters of fatty acids at sub- $\mu\text{g/l}$ concentrations were obtained using a flame ionization detector without the need for prior enrichment of the analytes [39]. Samples of up to ca. 500 μl of ethanol–water (1:1, v/v) were introduced at an initial PTV temperature of 9°C and a sample introduction rate of 11 $\mu\text{l/s}$. Losses of volatiles were avoided by using a liner packed with a mixture of Tenax TA and Gas Chrom 220.

A theoretical model to predict the optimum combination of speed of sample introduction, initial liner temperature and carrier gas flow-rate was proposed by Staniewski and Rijks [37]. The solvent elimination flow-rate was shown to depend on, amongst others, the vapour pressure of the solvent, the liner temperature and the design of the liner. It was found that the solvent elimination rate could be increased by increasing the carrier gas flow-rate through the injector during sampling and/or by a decrease in the inlet pressure. Enlargement of the gas–liquid contact area in the liner by packing the liner with glass wool was found to improve the process of saturation of the purge gas with solvent vapour which resulted in higher maximum allowable sampling rates. With a special porous-bed liner components with a boiling point equal to or higher than that of dodecane were quantitatively recovered from a 250- μl sample of test components in hexane introduced at a sampling rate of 25 $\mu\text{l/min}$ and at a PTV initial temperature of –30°C [42]. The half-open liner was found to yield optimum conditions for wetting and evaporation at a low back pressure. Further work of Staniewski et al. on the use of PTV injectors for large volume sample introduction in GC in-

cluded the application of large volume injection in environmental analysis [43], the development of a multi-dimensional GC technique for the introduction of large volumes of dichloromethane in capillary GC with electron-capture detection (ECD) [44] and the construction of a two-dimensional set-up for large volume sampling [45]. With the latter system solvent vapours are discharged via a precolumn instead of via the split exit. This system provided an elegant way of eliminating losses of volatiles in PTV-based large volume sampling. Components as volatile as nonane could be quantitatively retained from a 100- μl test sample containing over 90 priority pollutants in hexane.

In their pioneering work on large volume sampling using PTV techniques both Herraiz et al. and Staniewski et al. applied speed-controlled sample introduction. Once fully optimized the use of this technique in principle enables the introduction of unlimited sample volumes. The only parameter that restricts the volume to be injected to a certain upper value is the maximum allowable sampling rate or, directly related to this, the total time required to introduce the sample. With these systems micropollutants were determined at the sub- $\mu\text{g/l}$ level after miniaturized LLE, as was shown for polycyclic aromatic hydrocarbons and several nitrogen-containing pesticides [46]. With a slightly modified system for PTV large volume sampling Trisciani et al. [47] were able to determine organophosphorus pesticides and barbiturates at the low $\mu\text{g/l}$ level in extracts of various samples.

Recently, Mol et al. proposed an alternative method for PTV-based large volume sampling in capillary GC [48,49]. By applying liners with a much larger inner diameter (3.5 mm instead of the usual 1 mm) the volume of liquid sample that can be retained in a packed insert was increased to ca. 150 μl , i.e., sample volumes up to ca. 150 μl can be introduced rapidly without flooding the liner. This means that for sample volumes smaller than 150 μl there is no need to optimize and control the speed of sample introduction. This, in turn, greatly simplifies method development and the need for costly speed-programmable (auto)samplers. Preliminary results indicate that

with this approach losses of volatiles can be reduced significantly [50].

3. On-line water analysis based on large volume injection

In the introduction to the present paper two basic approaches for water analysis were distinguished. With the direct methods the aqueous sample is directly introduced into the GC system; with the indirect methods the water is eliminated prior to transfer of the analytes of interest to the GC column. In the next sections various direct and indirect methods will be discussed.

3.1. Direct injection

At first sight, direct aqueous injection seems to be a very straightforward way of analysing water samples by means of GC. There is no possibility of errors associated with, e.g., poor extraction efficiency and losses of analytes by evaporation. Since the sample is directly injected into the GC, the procedure is rapid and reliable. However, as outlined in the introduction, water is a very unfavourable solvent for injection into GC. Another inherent disadvantage of direct aqueous injection is that salts and involatile matrix constituents are introduced into the GC system which will lead to deterioration of the system's performance. For these reasons, there are few applications only; most of these deal with the analysis of volatiles in clean water samples. In the next sections three different methods for direct water sampling will be discussed.

3.1.1. On-column injection

Using highly sensitive detection systems, such as ECD and ion trap MS, injection of a few microlitres of sample is sufficient for obtaining the desired detection limits. Gurka et al. [51] injected 0.2–5 μl of water samples containing polar volatile organics (alcohols, nitriles). Most of these compounds are not easily extracted from water and are often not amenable to gas strip-

ping methods. In their study Gurka et al. used ion trap mass spectrometry for detection. Although detection limits at the $\mu\text{g/l}$ level were obtained, precision was hampered by severe tailing of some of the peaks. This indicates insufficient inertness of the liner of the injector and the column upon water injection.

Middleditch et al. [52] also applied direct aqueous injection for the analysis of polar volatile organics in water. The use of several detectors was evaluated. As most of the analytes did not contain halogen atoms, sensitive detection could not be achieved by using ECD. With flame ionization detection (FID) low detection limits could be achieved but the flame had to be reignited after elution of the solvent peak.

A typical example of direct introduction of the water samples is in the determination of volatile halocarbons (dichloroethylene, chloroform) in water using GC–ECD [53,54] (Fig. 5). The analytes are readily soluble in water, which renders their extraction from water critical. In addition, some of the halocarbons elute close to solvents such as pentane and carbon disulphide. Alternative methods, such as purge and trap methods, are generally more critical in terms of quantification. Hence direct water sampling is a

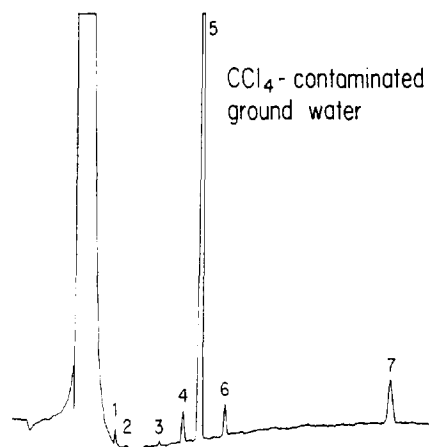


Fig. 5. Analysis of CCl_4 -contaminated ground water. Peak assignment: 1 = 1,1-dichloroethylene, 0.7 $\mu\text{g/l}$; 2 = dichloromethane, 0.2 $\mu\text{g/l}$; 3 = 1,1,1-trichloroethane, 0.02 $\mu\text{g/l}$; 4 = trichloromethane, 0.12 $\mu\text{g/l}$; 5 = tetrachloromethane, 2.8 $\mu\text{g/l}$; 6 = trichloroethylene, 0.16 $\mu\text{g/l}$; 7 = tetrachloroethylene, 0.18 $\mu\text{g/l}$. Reprinted from Ref. [53].

good choice for this particular application. The most important requirement in direct aqueous injection GC-ECD is that water should elute as rapidly and completely as possible ahead of the analytes. The water peak should be well separated from the peaks of the target compounds because water can significantly reduce the sensitivity of ECD. For this reason non-polar columns are used at initial oven temperatures slightly above the boiling point of water. In order to maintain sufficient separation between the halocarbons and water, on-column injections of sample volumes not exceeding 2–3 μl have to be performed using thick film columns. Under optimal conditions detection limits down to 0.02 $\mu\text{g/l}$ can be achieved [53]. In the quoted study long-term operation was seriously hampered by increased retention of water caused by a slowly increasing column activity and the deposition of salts in the column. This led to tailing of the water peak and a reduced ECD sensitivity.

On-column injection of large volumes of aqueous samples has achieved considerable attention in the field of on-line reversed-phase LC-GC where deactivated uncoated precolumns [6] are used. Although the work done so far does not deal with real-life water samples, interesting results have been obtained which are worth mentioning here. The key problems in direct water introduction using uncoated precolumns are the poor wettability of deactivated glass surfaces by water, and the destruction of the deactivation layer of the retention gap by water. The wettability problem was solved by the addition of a (water-miscible) organic solvent to the water sample. This greatly improves the wetting characteristics of the solvent in uncoated precolumns, thus enabling the application of retention gap techniques through the on-column interface [55]. The requirement is that water must evaporate more rapidly than the organic solvent. This is achieved by adding an organic solvent with a boiling point higher than water or by adding an organic solvent with which water evaporates azeotropically [55,56]. In the latter case, the water content after addition of the organic solvent should be below that of the azeotropic mixture, e.g., below 16 wt.% for

acetonitrile and 28 wt.% for 1-propanol. With addition of propanol to water (final concentration 75% propanol) methyl esters of fatty acids down to C_8 were successfully reconcentrated after a 50- μl on-column injection.

3.1.2. Loop-type injection

Originally developed for on-line LC-GC, the loop-type interface is also used for direct injection of aqueous samples. Direct water introduction into the GC column is possible because with FCSE there is no need for good wettability characteristics of the solvent [57]. However, due to the high temperatures needed for FCSE of water (110–140°C) and the very large volume of vapour formed, even fairly high boiling analytes are lost (if an early vapour exit is installed) or appear as severely broadened peaks. Therefore, this method can only be used for compounds with elution temperatures of 230–260°C or higher. As an illustration the determination of atrazine in tap water is shown in Fig. 6. The applicability for more volatile analytes can be extended by the addition of an organic co-solvent with a higher boiling point than water [58]. During transfer of the mixture to the GC under FCSE conditions, a layer of organic solvent remains in the retention gap in which the analytes are trapped. For the injection of 1 ml of water containing 20% of butoxyethanol analyte losses through the vapour exit could be prevented for methyl esters of alkanolic acids down

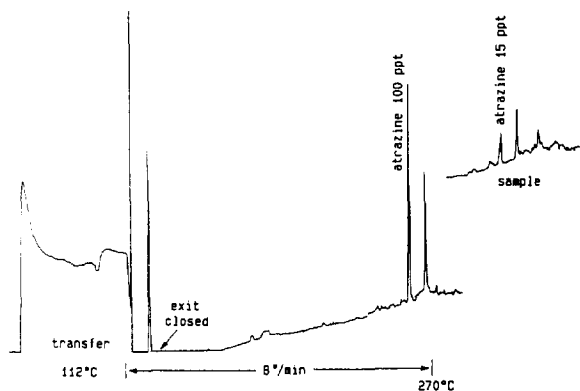


Fig. 6. Chromatogram of tap water spiked with 100 ng/l of atrazine. The insert shows part of a chromatogram of a tap water spiked at the 15 ng/l level. Reprinted from Ref. [57].

to C₁₄. Without co-solvent trapping methyl esters as high as C₂₀ were (partly) lost. So far direct injection of real-life water samples by applying FCSE has not been reported.

3.1.3. Multi-dimensional GC

Most of the problems associated with direct introduction of water samples can be solved by using two-dimensional GC systems, as was already shown several years ago [59]. Up to 200 μ l of water sample could be injected onto a Tenax-packed GC column at a temperature above the solvent boiling point, the water being eluted while the analytes (cresols/alcohols) were retained. With the two-oven system, the analytes were transferred in the split mode from the Tenax-packed precolumn (in the first oven) to a capillary GC column (located in the second oven) by heating the first oven with a steep gradient. This interesting approach has not resulted in the development of systems for routine water analysis. Recently, as a result of the developments in large volume injection using PTV injectors, there has been a renewed interest in this approach. Here the first dimension, i.e. the packed precolumn, is incorporated in the liner of the PTV injector (see section 3.2.2.3).

Despite the inherent advantages of methods for direct water analysis, the unfavourable properties of water with regard to large volume sampling as well as the aggressive nature of water restricts the application of direct sampling

to a narrow range of compounds. An overview of the characteristics and application areas of the different methods for direct water analysis is presented in Table 3.

3.2. Indirect injection

As stated above, indirect methods involve elimination of water prior to transfer of the compounds of interest to the GC column. In this section different techniques are considered that use phase-switching methods or sorption-thermal desorption for the isolation of the analytes from the water matrix.

3.2.1. Techniques based on extraction-liquid desorption

In extraction-based methods for water analysis the compounds of interest are transferred from the aqueous sample to an organic solvent which is more favourable for GC sample introduction. These techniques are often referred to as phase-switching methods. The most simple phase-switching method is LLE. Here the compounds are directly transferred from the water phase to a water-immiscible organic phase. In SPE and open tubular trap (OTT) phase switching occurs via intermediate trapping of the compounds onto/into a solid phase or an immobilized liquid, respectively. These three methods are discussed below.

Table 3
Summary of applications for water analysis based on direct introduction of the sample into the GC system

Analytes	Matrix	Injection technique	Detector	Limit of detection	Reference
<i>Direct aqueous injection</i>					
Water soluble alcohols low M_r	Ground water (hazardous waste)	On-column (2 μ l)	FTIR ITD	5–100 ng 8–400 pg	[51]
Volatile polar organics (acetone, MEK, THF)	Drinking water	On-column (4 μ l)	FID	5 μ g/l	[52]
Volatile halocarbons	Drinking water	On-column (2 μ l)	ECD	0.02 μ g/l	[53]
Volatile halocarbons	Drinking water	On-column (3–5 μ l)	ECD	0.017 μ g/l	[54]

FTIR = fourier transform infrared detection; ITD = ion trap detector.

3.2.1.1. Liquid–liquid extraction

LLE is basically an equilibrium distribution technique where the solutes of interest partition between the aqueous phase and an organic phase. The extraction efficiency, θ , can be written as:

$$\theta = 1 - \frac{1}{1 + K \left(\frac{V_{\text{org}}}{V_{\text{aq}}} \right)} \quad (1)$$

where K is the distribution constant, and V_{org} and V_{aq} are the volumes of the organic and the water phase, respectively. Eq. 1 shows that extraction yields are higher the larger is the phase ratio ($=V_{\text{org}}/V_{\text{aq}}$) and the higher is the distribution constant.

On-line LLE can be performed by periodically injecting the aqueous sample into a stream of organic solvent. Because it takes some time

before the extraction reaches equilibrium, several meters of PTFE or fused-silica tubing are used, in which a segmented flow is formed. After extraction, phase separation is achieved using a semi-permeable membrane [60] or a sandwich-type phase separator [61]. The GC amenable phase is directed to an interface for large volume sampling and a portion in the order of 100–500 μl is transferred into the GC system. The total on-line set-up has successfully been used for, e.g., the LLE–GC analysis of halocarbons in seawater [60], hydrocarbons in municipal sewage water (Fig. 7) [62] and organochlorine pesticides in ground water [63].

Recently, Goosens et al. [64] introduced on-line LLE–GC with simultaneous derivatization for the determination of organic acids and chlorinated anilines in aqueous samples. The organic acids and chlorinated anilines were alkylated and acylated, respectively, in a two-phase reaction. In the two-phase derivatization of acids, the

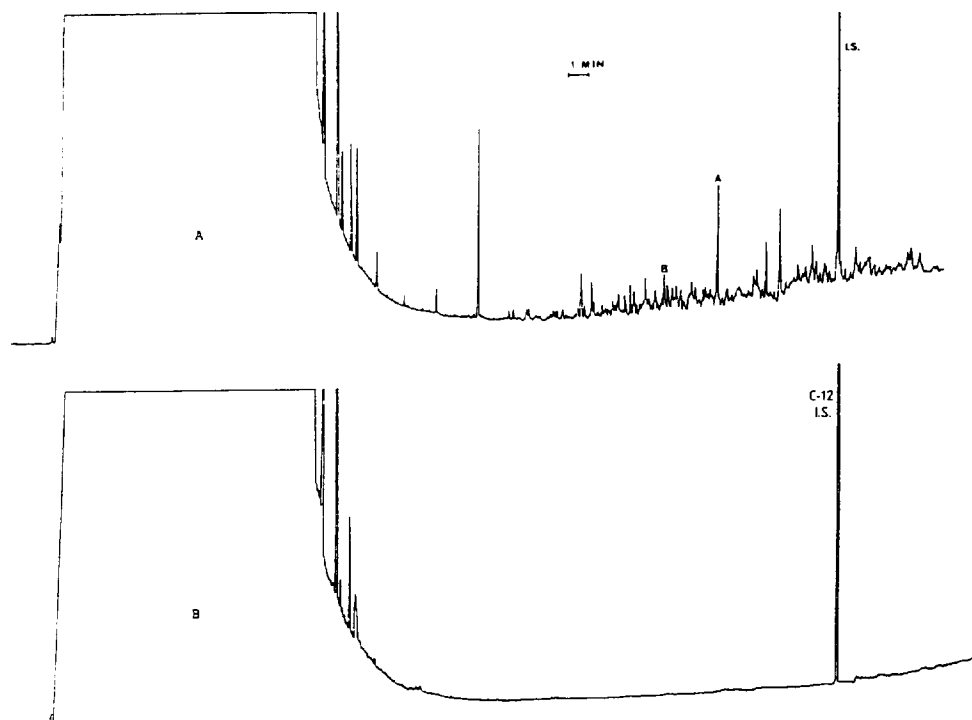


Fig. 7. GC–FID chromatogram of (A) a concentrated sample of Stockholm municipal sewage waste-water, obtained by continuous LLE–GC and (B) the solvent blank (*n*-pentane with 30 $\mu\text{g/l}$ of dodecane as internal standard). Peaks A and B in chromatogram (A) represent a level of ca. 200 and 50 ng/l , respectively. Reprinted from [62].

analyte is associated with a tetraalkylammonium ion in the water phase. The ion-pair is extracted into the organic phase, where alkylation takes place. Acylation of the anilines occurs at the boundary between the phases. With this on-line LLE derivatization set-up the authors were able to enhance the extraction yield and to improve the chromatographic behaviour of the polar solutes. A disadvantage of the on-line system is the excess of reagent present in the organic solvent, which results in a large and broad peak in the GC chromatogram.

A continuous extraction system with and without two-phase derivatization was developed by Ballesteros et al. and was used for the determination of phenols [65] and carbamate pesticides [66]. Phenolic compounds in water were extracted by mixing the water with ethyl acetate and with *n*-hexane plus 8 vol.% of acetic anhydride for simultaneous extraction and derivatization. After extraction, and derivatization, the extract was stored in a loop and introduced into the GC injector by the carrier gas via a heated transfer line. Because of the use of FID and, more importantly, of low injection volumes of only 4 μ l detection limits were fairly high (mg/l range). The R.S.D. values were satisfactory. The same set-up was used for the determination of carbamate pesticides. Using a basic sodium hydroxide solution as aqueous phase, aryl *N*-methylcarbamates were hydrolysed to the corresponding phenols. The FID responses obtained for six pesticides were linear in the 0.1–160 mg/l range with R.S.D. values of 1.9–3.9%. In a further study, the use of ECD and pentafluoropropionic anhydride as derivatization reagent improved the detection limits to the low μ g/l level [67]. This method was applied to the determination of *N*-methylcarbamates in cow milk. Similar R.S.D. values were obtained.

3.2.1.2. Solid-phase extraction–liquid desorption

In SPE, the aqueous sample is loaded onto a porous packed bed. The trace-level analytes of interest, but also some less desirable sample constituents, accumulate on the particles while the water is flushed out. After washing with,

usually, HPLC-grade water the analytes are desorbed by an organic solvent and collected in a vial. Next, the extract is injected into the GC system and separation proceeds. In most instances, the extraction cartridges are packed with a hydrophobic material such as a C_{18} - or C_8 -bonded silica or a polystyrene–divinylbenzene copolymer. With these packing materials, sensitivity can be increased dramatically (high analyte retention), but selectivity is only slightly improved (non-selective hydrophobic interaction). Improved selectivity can be obtained by introducing proper flushing steps during desorption where undesirable compounds are eluted prior to or after the analytes of interest. The use of more selective sorbents containing, e.g., immobilized antibodies [68] is a good alternative.

If on-line SPE trace enrichment techniques are used, the extraction cartridges are usually called precolumns. In this approach, a small column with dimensions of, typically, 1–4.6 mm I.D. and 2–10 mm length, replaces the conventional injection loop of a six- or ten-port valve. Using a second pump, a large sample volume of 10–100 ml is loaded onto the precolumn at a flow-rate of 1–10 ml/min. Before desorption/transfer to the GC column can take place the water remaining in the precolumn has to be removed. The main reason for this is that the introduction of even small amounts of water destroys the deactivation layer of the retention gap.

Noroozian et al. [69] were the first to use SPE–GC for the analysis of a series of chlorinated pesticides and PCBs in surface water samples. They used a four-valve system and a 4 mm \times 1 mm I.D. micro-precursor which was built-in in a six-port valve. After sample loading and drying by means of a nitrogen purge, the analytes were desorbed with *n*-hexane using the PCSE technique. Recoveries of more than 95% were observed for the majority of the analytes. The method was applied to the SPE–GC–ECD analysis of 1 ml of river water samples. Detection limits of the chlorinated compounds were in the order of 1 ng/l in Amstel river water. With a somewhat modified loop-type interface for the final introduction of the extract, and using 12 ml instead of 1 ml of sample, Noy et al. obtained

similar detection limits for the same group of compounds [70].

In subsequent studies it proved to be beneficial to use more polar solvents than *n*-hexane for the desorption of more polar analytes. When using *n*-propanol the desorption of compounds such as nitrobenzene and *m*-cresol could be carried out with only 50 μ l of solvent [71]. However, the desorption of apolar compounds such as 2-methylnaphthalene and acenaphthene needed 150 μ l of solvent. Such a large volume could not be introduced in one fraction, because this would result in flooding of the GC column. Ethyl acetate was found to be a good compromise between the apolar *n*-hexane and the polar *n*-propanol. Vreuls et al. [72] showed that 30–50 μ l of this solvent were sufficient to desorb seven test solutes of varying polarity from 10 \times 2 mm I.D. precolumns, and to transfer them to the GC system. In actual practice, 75 μ l were used to prevent problems regarding memory effects and to create a safety margin. With SPE–GC–FID several rather polar test compounds could be detected and quantified in 1 ml of river water sample at the 0.1–0.4 μ g/l level. More than 140 analyses were carried out without exchanging any part of the system.

In a subsequent paper, the selectivity of the trace-enrichment procedure was improved by using an antibody-loaded precolumn; 19-norsteroids were used as test compounds [73]. Desorption from the immunoaffinity precolumn was carried out with about 2 ml of methanol–water (95:5, v/v), which obviously could not be transferred directly to the retention gap. The eluate was therefore mixed with HPLC-grade water and the dilute solution was loaded on a conventional C₁₈-bonded silica precolumn. Because the gain in retention caused by the decrease of the modifier percentage distinctly outweighs the volume increase, the analytes were quantitatively trapped on this second precolumn. Desorption and transfer to the GC system were done as described above. The method was applied to the determination of steroid hormones in 5–25 ml human urine. The detection limit for 19- β -nortestosterone was about 0.1 μ g/l with an R.S.D. of 6%.

With the above set-ups, careful optimization of the desorption and transfer procedure was necessary. An early start of the transfer would result in injection of water into the deactivated retention gap, while a late start would result in loss of analytes. Although the system could be used for the automated analysis of aqueous samples, peak tailing of high-boiling analytes due to adsorption in the retention gap was sometimes observed. The active sites responsible for the adsorption are created by the repeated introduction of small amounts of water still present in the first few droplets of ethyl acetate which are introduced into the retention gap. The water evaporates azeotropically with ethyl acetate, but its very presence suffices to partly destroy the retention gap by hydrolysis. In order to overcome the possible introduction of even traces of water, the precolumn–GC system was made more robust by inserting a drying step, which quantitatively removes the residual water. Two systems were described by Vreuls et al. [74]. Either water is removed from the precolumn by means of a nitrogen purge (at ambient temperature; 15–30 min), or the traces of water are retained by physical/chemical interaction during desorption (cf. below).

With the former alternative, the use of so-called membrane extraction disks — which typically contain ca. 90 wt.% of a polymeric or alkyl-bonded silica packing enmeshed in a PTFE matrix (10 wt.%) [75] — instead of conventional packed precolumns appeared to be beneficial [76]. This is because the formation of channels during drying with a gas, which may occur with conventional packed cartridges, is highly unlikely with membrane-disk precolumns. After loading the sample onto a cartridge containing three 0.5-mm thick, 4.2-mm diameter polymer-containing extraction disks, drying was performed by 10–15 min purging with a stream of nitrogen at ambient temperature. SPE–GC–nitrogen phosphorus detection (NPD) was used for the determination of organophosphorus pesticides (OPPs) in tap water and water from several European rivers. With only 2.5 ml of sample, detection limits were 10–30 ng/l in tap water and ca. 50–100 ng/l in river water with R.S.D. values

of 2–4%. The total procedure was linear over the concentration range of 0.06–3 $\mu\text{g/l}$.

Physical/chemical removal of water was achieved using the set-up of Fig. 8. The eluate containing the desorbed analyte is led through a cartridge containing silica or sodium sulphate, which is incorporated in the transfer line to the retention gap. After each transfer the cartridge is regenerated by heating under a small helium purge flow. The device was successfully tested with 10-ml aqueous solutions containing 2–0.3 $\mu\text{g/l}$ of *s*-triazine herbicides. Because of its higher capacity for water, sodium sulphate was preferably used. The drying cartridge option was further evaluated by Picó et al. [77,78] who used silica, sodium sulphate and copper sulphate as drying agents. All drying agents had rather wide application ranges. Several limitations, however, were also reported. Silica interacted with some highly chlorinated phenols, and copper sulphate with all triazine herbicides. When sodium sulphate is used, it is recommended to exchange the cartridge every 20 analyses to prevent disintegrated particles to be transferred into the retention gap. The SPE–drying cartridge–GC system was used to determine OPPs, triazines and organosulphur pesticides at sub- $\mu\text{g/l}$ levels using detectors such as the NPD and FPD (phosphorus and sulphur mode). Louter et al. [79] successfully tested the drying agent set-up for more volatile solvents such as methyl acetate. The method

can now also be used for volatile compounds such as toluene and methylated benzenes.

Coupling MS detection to the SPE–GC system yields a hyphenated system that combines the automation potential of the SPE–GC system and the selectivity and sensitivity of MS detection [80,81]. The connection between the GC column and the ion source of the mass spectrometer was made via a 2 m \times 150 μm I.D. deactivated fused-silica restriction capillary which was permanently mounted in the transfer line to the mass spectrometer. This ensures that during transfer, i.e., when the solvent vapours are released via the solvent vapour exit, less solvent enters the ion source than under standard GC–MS operating conditions. The left hand side of Fig. 9 illustrates the use of the system for the low ng/l level target analysis of atrazine and simazine in 1 ml river water samples using multiple ion detection [80,81]. The right hand side shows that 10 ml suffices to identify the analytes (at the same concentration level) under full scan acquisition conditions [81].

The SPE–GC–MS system was further improved by fully integrating and automating the SPE and GC–MS system. The benchtop instrument used a PROgrammable On-line SOLID-Phase E(K)straction Technique (PROSPEKT) for trace enrichment, and a GC–MS system for separation and detection/identification [82]. Analysis of 10 ml of river Rhine water under

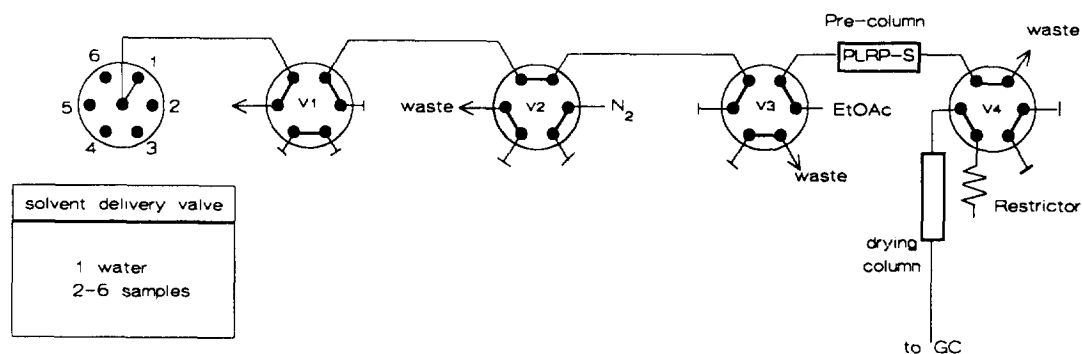


Fig. 8. Schematic diagram of a system for on-line SPE–GC. A PLRP-S packed precolumn is used for trace enrichment; a solvent selection valve for choosing the appropriate solvent, viz. water for conditioning, the sample and water for some clean-up. Four switching valves are used for subsequent functions in the procedure: flushing of the SPE system, drying of the PLRP-S cartridge, desorption of the analytes and transfer of the desorption solvent into the GC system. Reprinted from Ref. [74].

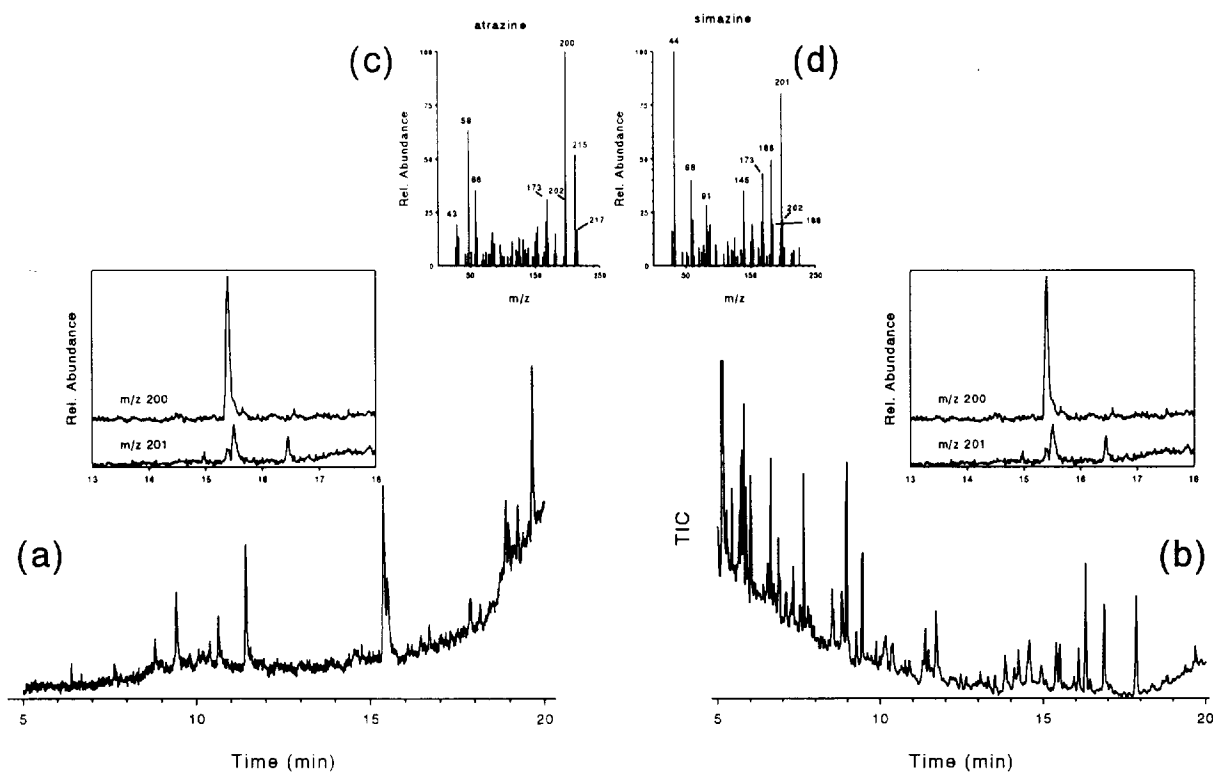


Fig. 9. Chromatograms obtained after on-line SPE-GC-MS of (a) 1 ml of river Meuse water using selected ion recording of eight ions and (b) 10 ml of the same sample using full-scan acquisition. The inserts show the ion traces of m/z 200 and 201 for target analysis of atrazine and simazine, respectively. Mass spectra recorded for (c) atrazine and (d) simazine. Reprinted from Ref. [81].

full-scan conditions enabled the detection of OPPs at the $0.1 \mu\text{g/l}$ level. Next to the target compounds, an unknown analyte was identified, viz. triphenylphosphine oxide. The system was also used for the rapid identification of benzothiale in a river water at a level of $1 \mu\text{g/l}$ [27]. The result was confirmed by analysing an SPE extract of the sample off-line by means of large volume injection GC-AED.

AED detection, which in principle allows the selective detection of any element except helium, is a relative newcomer in the field of GC detectors. Using AED coupled to SPE-GC, Rinkema et al. [26,83] used OPPs as test compounds and were able to obtain good recovery, precision and linearity data in spiked surface water samples. Detection limits as low as 5–20 ng/l for the analysis of 10-ml sample were obtained using the P-channel. The potential of the technique was further demonstrated by analysing waste water

samples. Fig. 10 shows the comparison of chromatograms obtained from influent and effluent samples of a municipal sewage waste water treatment plant.

Noy and Van der Kooi [84] used a loop-type interface rather than an on-column interface for automated pesticide analysis involving SPE-GC-NPD. The loop-type interface was preferred over the on-column interface because it is more rugged. 28 polar OPPs and organonitrogen pesticides were selected as test compounds. The SPE module and the procedure for trace enrichment were identical to the one described above. Desorption of the analytes was now carried out into one of the two loops of the interface using $500 \mu\text{l}$ of solvent. When *tert.*-butyl methyl ether was used for desorption the application range included compounds less volatile than ethoprophos. OPPs such as dichlorvos, mevinphos and methamidphos were (partly) lost. The on-line

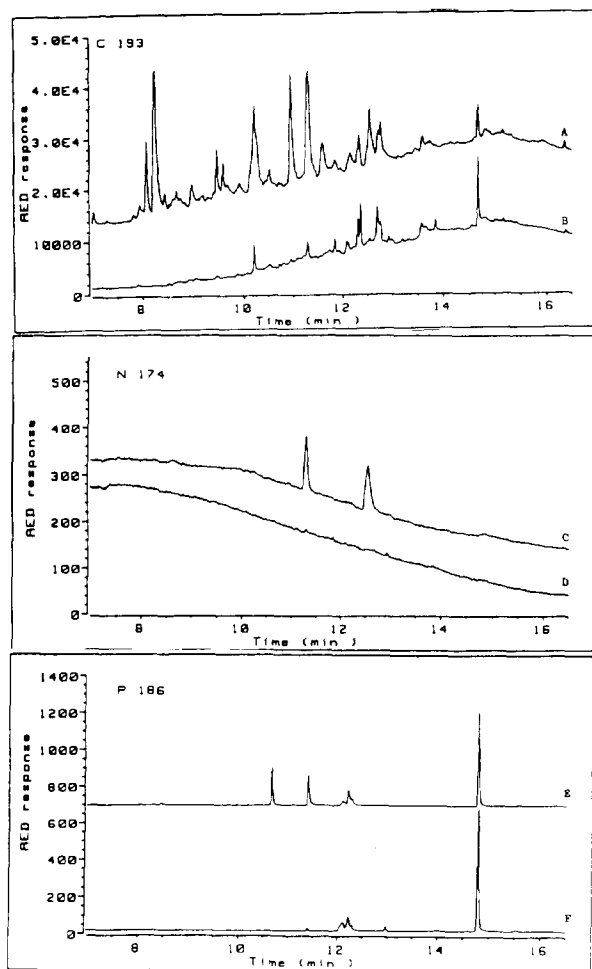


Fig. 10. On-line SPE-GC-AED of 10-ml municipal waste water samples using (A, B) the carbon 193 nm, (C, D) the nitrogen 174 nm, and (E, F) the phosphorus 186 nm channels, respectively. Chromatograms A, C and E show the influent, while B, D and F show the effluent water samples. Reprinted from Ref. [83].

procedure gave better recoveries for the more polar solutes in the test set than an approach where SPE was carried out in an off-line fashion. This is due to a better sorbent:sample volume ratio, viz. 0.015 and 0.002 for the on-line and off-line approach, respectively.

Recently, an ASPEC automated sample preparation module was coupled on-line with an SPE-GC-NPD system using an approach similar to that described for SPE-GC [85]. The system was optimized for the determination of the

antidepressant drug trazodone in plasma. The clean-up of untreated plasma was carried out with disposable C_{18} cartridges, using several washing steps to enhance the selectivity. The analyte was desorbed with methanol, and the extract was diluted with buffer and reinjected in the cartridge of the SPE-GC system. With a volume of only 1 ml of plasma, the analyte could be detected at the $3 \mu\text{g/l}$ level. The method showed good linearity and repeatability in the range of 0.01–1 mg/l.

In conclusion, SPE-GC is a highly interesting approach for the rapid trace-level detection and quantification of the wide range of GC-amenable compounds that have to be monitored in, e.g., surface, ground and drinking water.

3.2.1.3. Open tubular trap-liquid desorption

An alternative to trapping analytes by means of SPE is trapping in the coating of a short piece of capillary GC column. Compared to the use of packed SPE cartridges, the main advantage of applying OTT columns is that complete removal of water remaining in the trap after sampling can be obtained by simply purging a short plug of gas through the capillary. The main disadvantage of OTTs is that their retention power is much lower than that of SPE cartridges. Furthermore, the flow-rate during the sorption step is rather critical. OTTs were used by Zlatkis et al. [86] for the off-line extraction of large volumes of water samples. On-line systems for water analysis based on OTTs were described by Mol et al. [87,88]. In their system the analytes are trapped in a $2 \text{ m} \times 0.32 \text{ mm}$ I.D. OTT coated with a $5\text{-}\mu\text{m}$ dimethylsiloxane stationary phase. Water was removed by brief purging with a low flow of nitrogen. Next, desorption into the GC system was carried out with an organic solvent. Transfer to the GC system was done using a PTV injector as the interface.

It can be derived theoretically that breakthrough of an analyte through an OTT will occur when [88]:

$$V_b = KV_s \left(1 - 0.9 \sqrt{\frac{F}{D_m L}} \right) \quad (2)$$

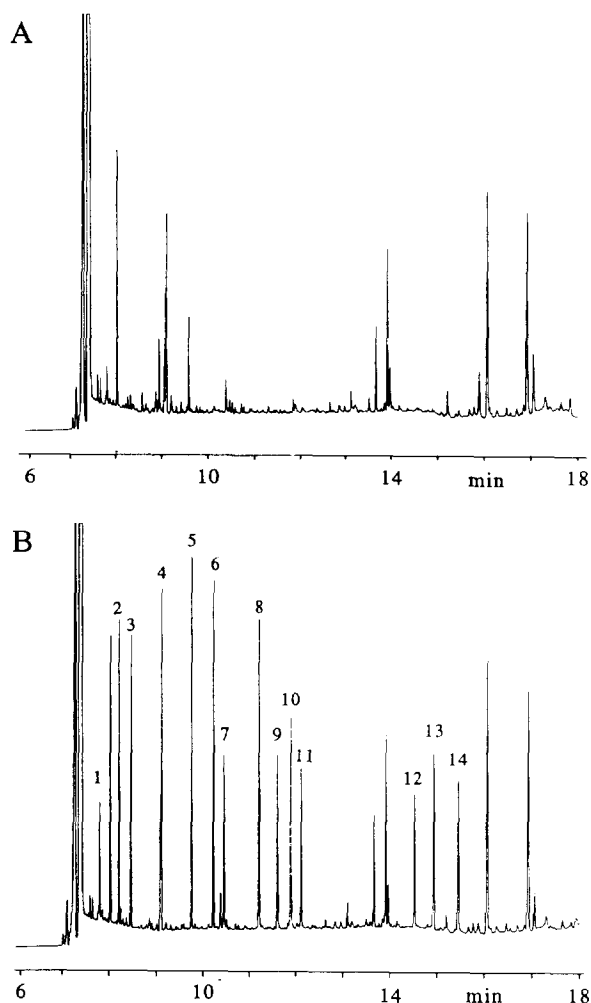


Fig. 11. On-line OTT-GC of water from River Dommel. (A) 2.25 ml river water. (B) 2.25 ml river water spiked at $5 \mu\text{g/l}$ of various organic compounds. Swelling agent: chloroform. Peak assignment: 1 = toluene; 2 = ethylbenzene; 3 = methoxybenzene; 4 = *p*-dichlorobenzene; 5 = dimethylphenol; 6 = dimethylaniline; 7 = chloroaniline; 8 = indole; 9 = dichlorobenzonitrile; 10 = trichlorophenol; 11 = dinitrobenzene; 12 = trifluralin; 13 = atrazine; and 14 = phenanthrene. Reprinted from Ref. [88].

eliminates the need for prolonged drying steps and/or the necessity to incorporate drying columns in the set-up.

3.2.2. Sorption–thermal desorption techniques

In contrast to the situation in phase-switching-based extraction procedures, no organic solvents

are needed for desorption in sorption–thermal desorption (TD) methods. In the latter case the analytes are again sorbed onto/into a solid phase or an immobilized liquid. After drying of the sorbent, the solutes are desorbed thermally and transferred to the GC column in the gaseous phase. Sorption into a liquid phase occurs in SPME and in the OTT approach. A solid sorbent is used in techniques based on SPE–TD and vapour overflow. Each of these methods will be outlined in more detail below.

3.2.2.1. Solid-phase micro-extraction

In solid-phase micro-extraction (SPME), which is a relatively new technique for sorption–thermal desorption [89], a small-diameter fibre coated with a polymeric phase is placed in an aqueous sample. The analytes partition into the stationary phase and are then thermally desorbed in the injector of the gas chromatograph. The 1-cm fibre is glued to the stainless-steel plunger of the syringe in such a way that the fibre is drawn into the syringe needle when the plunger is retracted. This facilitates introduction of the fibre through the septum of a sample vial or the GC injector. After extraction the syringe is transferred to the GC injector for thermal desorption of the analytes. For volatile analytes cryofocusing prior to GC separation may be necessary in order to eliminate band broadening caused by a relatively slow desorption. The technique can be automated by mounting the SPME modified syringe in an autosampler.

In contrast to packed SPE or OTT procedures, the extraction process in SPME is not exhaustive. The amount of analyte that will be extracted can be calculated from:

$$n_s = KV_s C_{\text{aq}} \quad (3)$$

where n_s is the number of moles of analyte sorbed in the stationary phase, K the distribution constant of the analyte, V_s the volume of the stationary phase, and C_{aq} the analyte concentration in the aqueous sample. From Eq. 3 it is obvious that the lowest detection limits are obtained for analytes with high distribution constants [90] using fibres coated with thick stationary phase films. Eq. 3 is only valid when an

Table 5
Summary of applications for analysis of aqueous samples based on on-line phase switching

Analyte	Matrix	Interface	Detector	Limit of detection	Ref.
<i>LLE-GC</i>					
Halocarbons	Seawater	LTI	ECD	0.5 ng/l	[60]
Nafta	Municipal sewage water	LTI	FID	0.1 µg/l	[62]
Hexachlorcyclohexanes	Ground water	LTI	ECD	0.1 µg/l	[63]
Carboxylic acids	Standard water	LTI	FID	0.1 µg/l	[64]
Chlorinated anilines	Standard water	LTI	ECD	0.01 µg/l	[64]
Phenolic compounds	Standard water	Splitless inj.	FID	0.2–0.3 mg/l	[65]
Carbamates	Standard water	Splitless inj.	FID	0.2–0.3 mg/l	[66]
	Milk	Splitless inj.	ECD	2–20 ng/l	[67]
<i>SPE-liquid desorption</i>					
OCPs	River water	OCI	ECD	1 ng/l	[69]
OCPs	Standard water	modified LTI	ECD	1 ng/l	[70]
Medium polar analytes	Standard water	OCI	FID	0.1 µg/l	[71]
	River water				[72]
19-Norsteroids	Urine	OCI	FID	0.1 µg/l	[73]
Triazines	Standard water	OCI	FID	0.02–0.03 µg/l	[74]
OPPs	River water	OCI	NPD	0.01–0.05 µg/l	[76]
OPPs, OSPs	River water	OCI	FID/NPD/	0.02–0.1 µg/l	[77]
Triazines, OPPs, OSPs	Tap water	OCI	FID/NPD/	0.001–0.03 µg/l	[78]
			FPD		
Atrazine, simazine	River water	OCI	MS (SIR)	3 ng/l	[80]
			MS (FS)	0.03 µg/l	
Various pesticides, organic contaminants	River water	OCI	MS (SIR)	3 ng/l	[81]
			MS (FS)	0.03 µg/l	
OPPs	River water	OCI	MS	0.02–0.05 µg/l	[82]
OPPs	River water	OCI	AED	0.005–0.002 µg/l	[83]
Priority pesticides	River water	LTI	NPD	0.01–0.2 µg/l	[84]
Diazepines, trazodone	Plasma	OCI	FID	3 µg/l	[85]
<i>OTT-liquid desorption</i>					
BTEX	Drinking water	Splitless inj.	FID	Not reported	[86]
PAHs	Water/MeOH standards	PTV	FID	0.3 µg/l	[87]
BTEX, priority pollutants	River water, drinking water, urine, serum	PTV	FID	0.1–1 µg/l	[88]

LTI = loop-type interface; OCI = on-column interface.

equilibrium is reached for the target analytes. The time needed for reaching the equilibrium is affected by the film thickness of the coating, the distribution constant, the vial diameter, and the degree of agitation of the sample solution. For a detailed discussion of the kinetics of the SPME process, the reader is referred to Ref. [91]. Equilibrium times can vary from less than 2 min to over 60 min. High distribution constants and

thick coatings, optimal for obtaining low detection limits, lead to longer extraction times. Stirring of the sample solution considerably reduces the extraction time by decreasing the thickness of the static aqueous layer at the fibre-solution interface. Slow mass transfer through this layer limits the extraction process. Although short extraction times were obtained by stirring the solution in an off-line method [91], mixing

was less efficient with the automated procedure where a micro-stirrer was incorporated in the autosampler [92]. Sonication should provide more efficient mixing, but this can cause a substantial increase in temperature and is therefore less suited for small sample volumes [93], i.e. autosampler vials. When extractions are carefully timed and experimental conditions remain constant, extraction times shorter than needed for reaching equilibrium can be used although this may adversely affect repeatability.

Several interesting applications of SPME–GC have been reported in the literature. These include the determination of BTEX (benzene, toluene, ethylbenzene and xylene isomers) in ground water at the 30–80 ng/l level using ion-trap detection [94,95], the analysis of the EPA 624 components (volatile halocarbons) [96], and rather volatile nitroaromatic compounds [97]. The application range of SPME was extended towards more polar analytes (phenols) by using a fibre coated with a polyacrylate [98]. Using this fibre, detection limits at the sub- $\mu\text{g/l}$ level were achieved, but exact quantification was still a problem as the extraction efficiency was found to be matrix dependent. Another interesting application of SPME was the on-line monitoring of flowing samples [93]. More recently, SPME has been applied for the determination of chlorinated and organophosphorus pesticides in water [99,100]. Fig. 12 shows the analysis of some chlorinated pesticides (concentration level, 200 ng/l) in waste water. The combination of ECD and the high extraction efficiencies obtained for these non-polar solutes resulted in low detection limits. For some more polar pesticides [101,102] the unfavourable distribution coefficients made analysis at the sub- $\mu\text{g/l}$ almost impossible even with a rather sensitive detection system such as NPD. With the highly sensitive ion trap detector [103] it was possible to detect polar pesticides at the 200 ng/l level. Experimental difficulties were encountered in the determination of derivatized butyl-, phenyl- and cyclohexyltin compounds in water [104]. Extraction times of 30 min or more were necessary to obtain equilibrium conditions. R.S.D. values were in the range of 20–70%. Moreover, up to 20% carry over was observed.

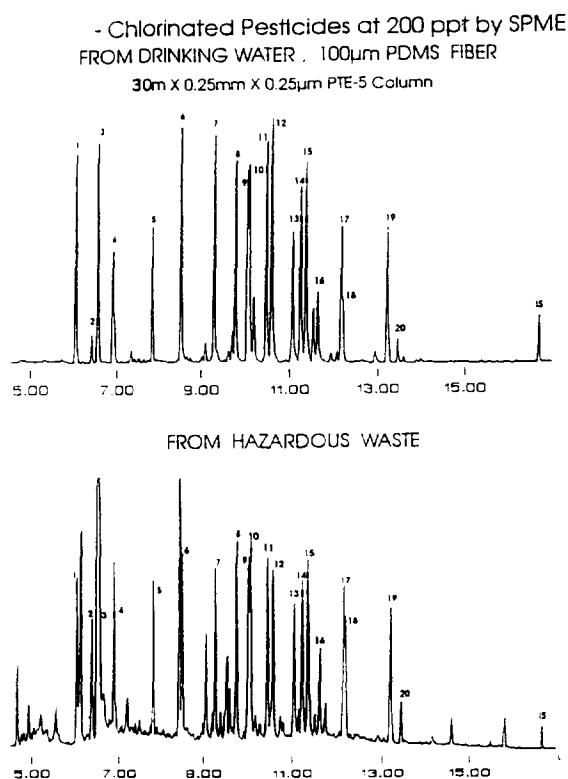


Fig. 12. SPME–GC–ECD of chlorinated pesticides from 1.8 ml of (top) drinking water and (bottom) hazardous waste water. Injection temperature 260°C. Peaks: 1 = α -HCH; 2 = β -HCH; 3 = δ -HCH; 4 = γ -HCH; 5 = heptachlor; 6 = aldrin; 7 = heptachlor epoxide; 8 = γ -chlordane; 9 = endosulfan I; 10 = α -chlordane; 11 = 4,4'-DDE; 12 = dieldrin; 13 = endrin; 14 = endosulfan II; 15 = 4,4'-DDD; 16 = endrin aldehyde; 17 = endosulfan sulfate; 18 = 4,4'-DDT; 19 = endrin ketone; 20 = methoxychlor; IS = decachlorobiphenyl. Reprinted from Ref. [99].

Although the experience with SPME–GC at this moment still is somewhat limited, it is clear that it is an interesting technique for the screening of water samples. It has also been used to detect methadone in urine [105].

3.2.2.2. Vapour overflow technique

The vapour overflow technique was initially described for PTV splitless injection [106]. More recently, it was applied to conventional (hot) splitless injection of large sample volumes [107,108]. In the vapour overflow method the entire sample is injected rapidly at high temperatures into a large-bore liner packed with Tenax.

The split vent is closed during the solvent evaporation period, whereas the septum purge is opened wide. Driven by its expansion and high vapour pressure, the solvent vapour flows backwards and leaves the system through the septum purge. The Tenax bed is cooled by the rapid evaporation of the solvent. Due to this cooling low to medium volatility solutes are trapped in the Tenax packed liner. More volatile solutes evaporate along with the solvent and are lost. After solvent evaporation is completed, the septum purge is closed, the packed bed regains its high temperature and the trapped analytes are released into the column.

The vapour overflow technique is simple and rugged but for application to water samples the system has to be modified [109]. In order to deal with the very large vapour volumes generated by the injection of aqueous samples a rotary valve has to be incorporated in the gas supply system. By switching this valve the carrier gas supply can be interrupted during solvent evaporation. This prevents vapours from penetrating the gas regulation system and keeps the pressure increase of the injector to a minimum. Additionally, after a short section of the column (coated precolumn), a T-piece has to be installed with a fused-silica tubing leaving the instrument (early vapour exit).

With the modified system, triazines were analyzed in drinking water using direct injection of the sample [110]. The injector temperature was 310°C. During injection the syringe needle, which had a side-port hole, was turned one or two times in order to obtain a homogeneous distribution of the sample in the packed bed inside the liner. Up to 400 μ l of water could be introduced in this way. During injection the flow of carrier gas was interrupted, the vapour exit opened, and the column temperature was maintained at 130°C to prevent condensation of water vapour in the GC column. After 30 s, when most of the water had left the system via the septum purge, the carrier gas was introduced again by switching the rotary valve. The vapour exit was kept open for another 1.5 min to eliminate residual water from the packed bed. During this step triazines which desorb from the Tenax

packing are trapped in the GC precolumn. Recoveries depended on the volume injected and ranged from 17 to 88% (R.S.D. 6–13%) for the different triazines. Using NPD, detection limits of 0.5 μ g/l were achieved. Interestingly, the presence of salts neither affected the peak shapes nor the recoveries. However, after numerous injections, the Tenax bed was found to become more solid. As with FCSE of water, the application range of the method is restricted to compounds eluting above approx. 200°C.

3.2.2.3. Solid-phase extraction–thermal desorption

The concept of on-line SPE on a sorbent held in the liner of a PTV, called SPE–GC using thermal desorption (SPE–TD), was studied by Vreuls et al. [111,112] and in a somewhat modified form, by Mol et al. [113]. The sample is directly percolated through the packed liner of a PTV injector. After removal of the water and drying the packing by purging with a high flow of carrier gas the analytes are thermally desorbed by a rapid increase of the injector temperature and, subsequently, analyzed by GC. The carrier gas supply is modified in order to be able to apply a counterflow from the GC column to the injector. This modification prevents water from entering the GC column during sampling and drying.

Tenax sorbents were found to have the best all-over characteristics, i.e., sufficient retention power for analytes in the liquid phase during sorption, poor interaction with water for optimal drying and good thermal stability during desorption. Other packing materials that had suitable characteristics were carbon phases. The problem encountered with all carbon phases tested [112] was the rather narrow application range due to loss of analytes on both the “volatile” and “non-volatile” end. The loss of volatile compounds was the result of low retention during drying, while incomplete thermal desorption of non-volatile compounds caused low or no recovery for these particular analytes. Fig. 13 shows the analysis of a 10- μ g/l standard solution of chlorinated benzenes and phenols.

If the injection speed with which the water

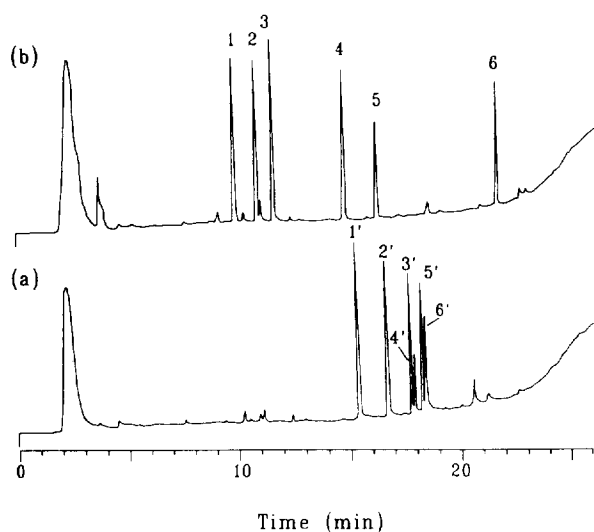


Fig. 13. SPE-TD-GC-FID chromatograms obtained for a 100- μ l water spiked with (a) a chlorophenol and (b) a chlorobenzene mixture at the 10- μ g/l level. Tenax-GR was used as sorbent in the packed liner. Peak assignment: 1 = chlorotoluene; 2 = *m*-dichlorobenzene; 3 = *o*-dichlorobenzene; 4 = 2,3,4-trichlorobenzene; 5 = 2,3,4,5-tetrachlorobenzene; 6 = hexachlorobenzene; 1' = 2,6-dichlorophenol; 2' = 2,4,6-trichlorophenol; 3' = 2,3,5-trichlorophenol; 4' = 2,3,6-trichlorophenol; 5' = 2,3,4-trichlorophenol. For details, see Ref. [112].

sample is injected into the packed liner is below the evaporation rate, sorption of the analytes onto the packing material occurs from the gaseous state [113,114]. Compared to sorption of the analytes from the liquid state the sampling step now is rather long, since the evaporation rate of water is low, viz. 12 μ l/min (at 30°C). The advantage of water injection in the so-called fully evaporative mode, is that the technique can be applied to compounds with high water solubility. In addition, for several packing materials, literature data concerning breakthrough volumes are available. The technique was applied to the determination of pesticides and industrial pollutants in surface water samples. From several packing materials tested, Tenax TA was found to be the best choice. Recoveries of the most volatile analytes and chemically/thermally labile compounds (dimethoate, methamidophos) were below 50%. For most of the other compounds recoveries ranged from 70 to 110% (R.S.D. 2–10%). As deposition of salts and suspended

matter in the insert may lead to discrimination of chemically labile solutes, a frequent change of insert was suggested when injecting real samples [114].

3.2.2.4. Open-tubular trapping–thermal desorption

The use of crosslinked silicone stationary phases held in glass or fused-silica capillaries is an attractive alternative to the use of classical solid adsorbents. The advantages of these materials, as used in capillary GC, are thermal stability, inertness, and well documented retention properties. Moreover, the materials have a homogeneous structure and displacement effects, which are frequently encountered with porous sorbents, are less likely to occur since retention is based on dissolution rather than adsorption. In addition, water removal after sampling is easy. The main disadvantage in comparison with porous adsorbents, however, is the much weaker retention power.

Large, non-polar analytes, such as polycyclic aromatic hydrocarbons, are easily trapped on coated capillaries [115]. In fact, the GC column itself can be used for extracting these compounds from the water sample. It is evident that for such experiments the column has to be removed from the GC or at least disconnected from the detector. After installation of the column, the trapped analytes were analyzed, either directly [116] or after refocusing at the column entrance [117]. The method was used to determine PAHs in up to 5 ml water samples. More polar compounds, like benzaldehyde, *n*-ketones and lindane, were extracted from up to 0.4 ml water samples into the stationary phase of a 50-m GC column. Analytes were cryofocused prior to GC separation. For lindane detection limits were at the ng/l level when using ECD [118].

The use of the same GC column for both extraction and separation of the analytes is rather inconvenient. The use of separate trapping and analytical columns in a two-oven system is a distinct improvement. Such a system, which is shown in Fig. 14a, was described by Blomberg and Roeraade [119]. Here a 95- μ m thick film trap, located in the first oven, was used to

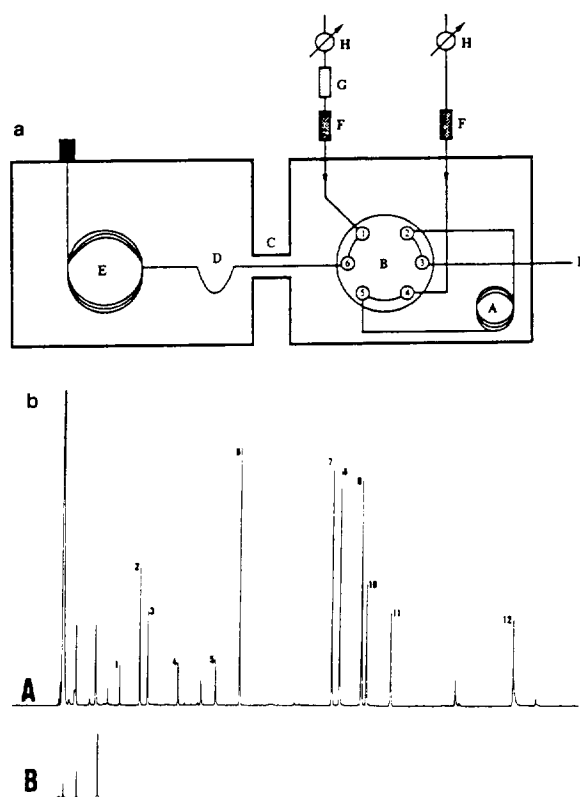


Fig. 14. (a) Schematic diagram of the on-line OTT-GC set-up: (A) thick-film trap, (B) rotary valve, (C) heated tubular aluminium interface, (D) cold trap, (E) GC column, (F) activated charcoal traps, (G) molecular sieve, (H) pressure regulator, (I) outlet vent. (b) (A) Chromatogram obtained after on-line OTT-GC-FID by percolation through a thick-film trap at 0.8 ml/min of 8 ml of a spiked water sample (2–10 μ l/l). Peak assignment: 1 = chloroform; 2 = 1,2-dichloroethane; 3 = cyclohexane; 4 = heptane; 5 = MIBK; 6 = toluene; 7 = ethylbenzene; 8 = *p*-xylene; 9 = *o*-xylene; 10 = nonane; 11 = isopropylbenzene; and 12 = octanol. (B) background from thick film trap (thermal desorption 110°C, 20 min). Reprinted from Ref. [119].

extract volatile (halo)carbons from up to 8 ml water samples. By means of a rotary valve, also located in the first oven, the analytes could be desorbed in the backflush mode. The material released from the first column was refocused in the inlet of the analytical column located in the second oven. As an illustration Fig. 14b shows a chromatogram obtained after extraction of 8 ml of a spiked water sample using an extraction flow-rate of 0.8 ml/min. A chromatogram of a

blank of the procedure without sampling is shown for comparison. A similar application, although not on-line, was described by Burger and Le Roux [120]. Volatile (halo)carbons were determined at the 0.1 μ g/l level using FID. At levels below 1 μ g/l problems were encountered for xylenes, *p*-cymene and less volatile solutes due to interference of artefact peaks produced by decomposition of the polysiloxane trap lining.

Although the application range of sorption-thermal desorption techniques is narrower than that of the sorption-liquid desorption techniques, a large number of solutes can be determined. SPME is a valuable technique for screening aqueous samples. It is, however, less suited for trace analysis of polar pesticides. The use of OTT-thermal desorption is limited to either volatile- or higher boiling non-polar analytes, depending on the film thickness of the OTT. The vapour overflow technique is only applicable to analytes of intermediate volatility (i.e. triazines), more volatile compounds are lost during solvent elimination, less volatile compounds can not be desorbed. The application range of SPE-thermal desorption is larger than that of the vapour overflow technique. Both vapour overflow and SPE-thermal desorption are less suited for chemically/thermally labile analytes. It has to be emphasized here that for all four techniques there has been relatively little experience with real-life samples. An overview of applications of the various methods for sorption-thermal desorption to analytical problems related to water analysis is presented in Table 6.

4. Conclusions

The determination of organic micropollutants in aqueous samples is a true challenge for the analytical chemist. Extremely low concentrations of target compounds have to be determined in a complex matrix. This requires the use of sensitive as well as selective detection devices that—for routine use—are only available in combination with gas chromatographic separation systems. On-line combination of sample preparation and analysis is mandatory in order to be

Table 6
Summary of applications for water analysis using sorption–thermal desorption techniques

Analyte	Matrix	Detector	Limit of detection	Ref.
<i>SPME</i>				
VOCs	Drinking water	FID	1 $\mu\text{g}/\text{l}$	[89]
BTEX	Drinking water	FID	0.3 $\mu\text{g}/\text{l}$	[92]
BTEX	Parking lot runoff water, drinking water	ITD	1–15 $\mu\text{g}/\text{l}$	[94]
Caffeine	Beverages	MS	Not reported	[95]
VOCs	House hold water, landfill leachate	ITD	0.001–3 $\mu\text{g}/\text{l}$	[96]
EPA Method 624, 524.2	Lake water	FID	9–15 $\mu\text{g}/\text{l}$	[97]
Volatile nitro-aromatics	Ground water	FID	Low $\mu\text{g}/\text{l}$ range	[99]
VOCs	Hazardous waste water	ECD	Low ng/l range	[99]
Chlorinated pesticides				
OPPs		AED	0.5–4 $\mu\text{g}/\text{l}$	[100]
(Volatile) PAHs	River water	FID	0.03–2 $\mu\text{g}/\text{l}$	[101]
Organotin compounds	Drinking water	FPD	Low $\mu\text{g}/\text{l}$ range	[104]
Methadon	Urine	MS	Low $\mu\text{g}/\text{l}$	[105]
<i>Vapour overflow</i>				
Triazines	Drinking water	NPD	0.5 $\mu\text{g}/\text{l}$	[110]
<i>SPE–thermal desorption</i>				
Chlorobenzenes, chloro-phenols	Standard water	FID	1 $\mu\text{g}/\text{l}$	[112]
BTEX, priority pollutants	Standard water	FID	0.1 $\mu\text{g}/\text{l}$	[113]
pesticides, nitro-aromatics	Drinking water, surface water	ECD NPD	0.01–0.5 $\mu\text{g}/\text{l}$	[114]
<i>OTT–thermal desorption</i>				
PAHs	Drinking water	FID	Not reported	[116]
High boiling organics (e.g. PAHs)		FID	0.02 $\mu\text{g}/\text{l}$	[118]
BTEX, VOC	Drinking water	FID	0.02 $\mu\text{g}/\text{l}$	[119]
BTEX, heptane, <i>p</i> -cumene, etc.	Drinking water	FID	0.01 $\mu\text{g}/\text{l}$	[120]

able to meet the requirements regarding ease of automation, reliability and sensitivity.

The techniques applied for the analysis of aqueous samples can be classified as either direct or indirect methods. Direct introduction of the aqueous sample is restricted to the determination of low-molecular-mass volatile components. In principle also high-molecular-mass components in water can be determined directly, by using loop-type injection, but no applications of this approach have been reported so far. For the vast majority of components indirect methods, in which the water is eliminated prior to intro-

duction of the analytes onto the GC column, have to be used. Elimination of the water can take place either in the injector of the GC system or before introduction of the sample into the GC injector.

Many indirect on-line methods for water analysis have been described in literature. Liquid–liquid extraction was the first technique that was applied for on-line water analysis in research laboratories. Following the trend in off-line sample preparation, systems for coupled solid-phase extraction–liquid desorption–GC were developed. To circumvent problems associated

with drying of packed cartridges, open-tubular trapping columns were used as an alternative. Problems with the introduction of large volumes of organic solvents gave rise to a renewed interest in sorption–thermal desorption based methods for water elimination. Open-tubular trapping and solid-phase extraction with subsequent thermal desorption, vapour overflow and, the more recently introduced technique SPME, allow the determination of sub-ppb concentrations of pollutants in water without an intermediate liquid desorption step.

In the selection of an analytical method for water analysis both analyte characteristics as well as type and concentration of interfering compounds in the water sample have to be considered. Solute characteristics that are important in this respect are volatility (or molecular mass), polarity and water solubility. At first glance, the diversity of methods available might give the impression that the selection of the proper technique for a given solute- and water type is a difficult task. A closer look reveals, however, that there is a large degree of overlap between the various methods. Components of intermediate volatility and polarity can be addressed by each of the methods described in the present article. It is only in the case of a very low or very high volatility or polarity that a more careful selection of the method is required. Also, if the methods are compared on the basis of analyte detectability and ease of automation, differences exist. Each of the various methods, however, is capable of meeting the detectability requirements specified by regulatory institutions. In the hands of an experienced operator (but not necessarily a true expert), fully automated and on-line analysis of a very wide range of contaminants in water samples from different origins is nowadays possible. This has convincingly been demonstrated by the many references cited in this contribution.

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