A VISION to On-Line SPE–PTV–GC–MS Determination of Organic Micro Pollutants in Surface Water

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Summary

The trace-level analysis of unknown pollutants in water requires the use of fast and sensitive methods which also provide structural information. In the present preliminary study, solid phase extraction (SPE), programmed temperature vaporisation (PTV) and gas chromatography (GC) with mass spectrometric (MS) detection are combined. A fully automated SPE system was connected to a GC via a PTV injector. The PTV injector was selected because of its robustness (over 100 analyses) when analysing real-life samples. The mass spectrometer was used in the full-scan mode to allow compound identification.

The technique is applied to the determination of a series of priority pollutants in water from the river Rhine and Meuse. In this way tributhylphosphate and caffeine were detected. The results of this analysis were confirmed by RIZA both qualitative as well as quantitative.

1 Introduction

The monitoring of water samples for the presence of organic micro pollutants at trace levels requires sensitive and selective analytical methods. Because European surface water legislation is becoming more stringent every year, new methods have to be developed. To meet the sensitivity and selectivity demands, the determination of organic substances in water commonly involves selective isolation of the compounds of interest, separation by means of a chromatographic technique and detection using a sensitive and selective detector.

In recent years, much attention has been paid to the development of on-line techniques, that combine sample preparation and separation plus detection in one fully automated analytical set-up. For such on-line systems, Solid Phase Extraction (SPE) is generally preferred over liquid-liquid extraction as the isolation technique, because it is less laborious, uses smaller amounts of organic solvent, yields better analyte enrichment and is easier to couple on-line to the chromatographic technique to be used [1,2]. Because of its superior separation efficiency, capillary gas chromatography (GC) should be the method of choice as the separation technique. For selective and sensitive detection, the mass spectrometer is the most suitable detector.

A weak point in analyses by means of GC is the sample introduction step. The main problem being that until recently, and in many instances even today, the injection volumes are limited to some 1 to 5 µL. Since, after suitable sample pre-treatment, the volume of the final SPE extract typically is between 50 and 500 µL, this implies that in the last step prior to the GC analysis, some 95-99% of the analytes collected is discarded. For the successful performance of trace analysis it is advantageous to inject a much larger proportion of the sample. Much work in on-line sample preparation with GC analysis for the analysis of water samples was carried out by Öllers et al. [3] and Louter et al. [4]. In these systems large volume injection techniques hold a key position [5].

Louter [4] describes the use of the on-column large volume injection technique after solid phase extraction. A main problem of this approach is the limited life time of the retention gap. In the analysis of real-life samples the retention gap has to be replaced frequently.

This preliminary contribution reports on the development of a fully automated SPE–GC–MS system using a Programmable Temperature Vaporisation injector (PTV) as the injection interface to the GC column. First, the SPE cartridge is activated and conditioned using methanol and water. Then, the analytes from the sample are enriched. Finally, after drying the cartridge, the analytes are desorbed and directly injected into the PTV-liner after which the GC–MS analysis starts. The surface and drinking water samples under investigation are analysed for the presence of a wide range of priority pollutants. The quantitative performance of the system is evaluated with special attention to the detection limits, repeatability and linearity of the method. Various water samples are analysed.

2 Experimental

2.1 Chemicals

A test mixture containing 42 priority pollutants in ethyl acetate was prepared by RIZA (Lelystad, The Netherlands) at a concentration level of 1 g/L. This test solution was used to prepare diluted mixtures in ethyl acetate and HPLC water. Ethyl acetate was obtained from Merck (Darmstadt, Germany). HPLC water and Methanol were purchased from Biosolve (Valkenswaard, The Netherlands). Ethyl acetate was glass-distilled prior to use.

2.2. SPE System

Trace enrichment was performed on a PROSPEKT sample preparation system combined with a MIDAS autosampler both from Spark Holland (Emmen, The Netherlands). The PROSPEKT system consists of three pneumatic six-port valves, an automated cartridge exchanger and a Solvent Delivery Unit (SDU) which is equipped with three six-port solvent delivery valves and a single-piston pump.

Timed events such as valve switching, solvent selection and switching auxiliary on/off, e.g. start of the MIDAS and GC–MS analysis, could be programmed using the PROSPEKT controller unit. The MIDAS consists of a syringe pump, a six-port injection valve and a sample tray. Also this unit is programmed from its own controller unit. Samples were preconcentrated on a 10 mm x 2.0 mm i.d. cartridge containing 15-25 µm PLRP-S copolymer (Spark Holland) that was placed in a loop on the left side valve (Figure 1) of the PROSPEKT. A 0.60 m x 320 µm i.d. fused silica capillary was used to interface this valve with the PTV-injector, installed in the GC–MS system.

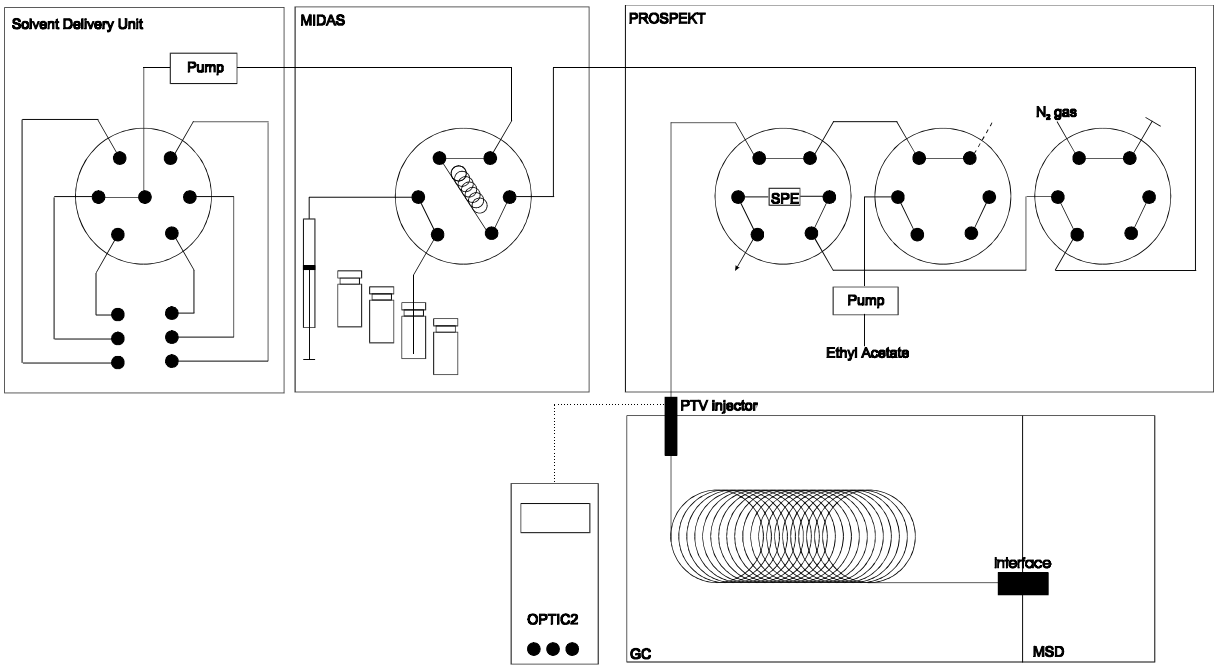

Figure 1. Set-up for on-line SPE–PTV–GC–MS.

2.3 GC System

A Shimadzu GC-17A gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a QP-5000 mass spectrometric detector was used for GC analysis. Injections were done by an Electronic Pressure Controlled (EPC) PTV injector OPTIC2 (ATAS, Veldhoven, The Netherlands). The PTV was connected to a 50 m x 0.25 mm i.d. CP-SIL 5 CB FS capillary GC column coated with a film thickness of 0.4 µm (Chrompack, Middelburg, The Netherlands). Helium was used as the carrier gas.

2.4. SPE Procedure

The SPE procedure is outlined in Table 1 and is largely analogous to the procedure described by Louter et al. [6]. First, the SPE cartridge is activated and conditioned by flushing it with methanol and

HPLC water. Next, the sample is loaded into the loop of the MIDAS autosampler and then flushed onto the SPE cartridge with HPLC water delivered by the SDU. After loading, the cartridge is dried by N_2 gas. Finally, the analytes of interest are desorbed by ethyl acetate. The desorption fluid is directly transferred into the GC–MS system. Solvent elimination is performed inside the PTV injector.

Table 1. SPE Procedure.

Conditioning	5 ml methanol (2.5 ml/min)
	5 ml HPLC water (2.5 ml/min)
Sample loading	7.5 ml sample
	1 ml HPLC water (1 ml/min)
Drying	15 min N_2-gas (5 bar)
Desorption	50 µL ethyl acetate (100 µL/min)

2.5. OPTIC2 Procedure

Table 2 summarises the parameters of the OPTIC2 program, controlling the PTV injection interface for manual large volume injections. The parameters used in the on-line SPE–PTV–GC–MS approach were slightly adjusted to minimise losses of volatile sample constituents.

Table 2. OPTIC2 program for LVI.

Vent flow	140 ml/min	P_{purge}	170 kPa
Split flow	70 ml/min	$P_{transfer}$	170 kPa
$T_{initial}$	40 °C	$t_{transfer}$	3:00 m:s
Ramp rate	5 °C/s	$P_{initial}$	170 kPa
T_{final}	325 °C	P_{final}	360 kPa
t_{end}	62:00 m:s	t_{vent}	0:40 m:s
$t_{split\ open}$	3:00 m:s		

2.6. GC–MS Procedure

Table 3 outlines the relevant GC–MS parameters. Quantification of the detected compounds is performed by analysing calibration samples of spiked HPLC water (range, 0.1-10 µg/L; 7 data points in duplicate) based on peak areas using the full SPE–GC–MS procedure.

Table 3. relevant GC–MS parameters.

Initial temperature	40 °C	Final temperature	300 °C
Initial hold time	2 min	Final hold time	10 min
Rate 1	4 °C/min	MS interface temperature	275 °C
Temperature 1	200 °C	Mass range	40-350
Rate 2	10 °C/min	Scans/sec	2

3 Results and Discussion

The present study was intended to demonstrate the possibility of automated on-line SPE–GC–MS using a PTV injector as the solvent elimination interface. First, the GC–MS method was developed by the injection of 1 µL of a 10 ng/µL standard solution using a glass-fritted empty PTV liner (8 cm x 0.32 cm) and packed PTV liners. Second, 50 µL of a 50 times diluted standard mixture (200 pg/µL) was injected to optimise the PTV large volume method and to verify the inertness of the packing of the PTV. Third, the SPE procedure was optimised by extraction of 1 µg/L-spikes of all compounds of interest in HPLC water. In the last step, the SPE–GC interface was optimised. The ruggedness of the PTV large volume method is illustrated by the fact that we are still using our first PTV liner. The number of injections performed is already significantly above 100.

3.1 Application range

The application range of the PTV–GC–MS system in terms of analyte volatility was studied by analysing 50 µL of an ethyl acetate standard mixture at the level of 200 pg/µL containing solutes ranging from trichloroethylene (most volatile) to squalene (least volatile). Figure 2 shows the GC–MS chromatogram of this analysis. The first analyte detected (peak 8) is pyridine and the last one (peak 51) is triphenylphosphate.

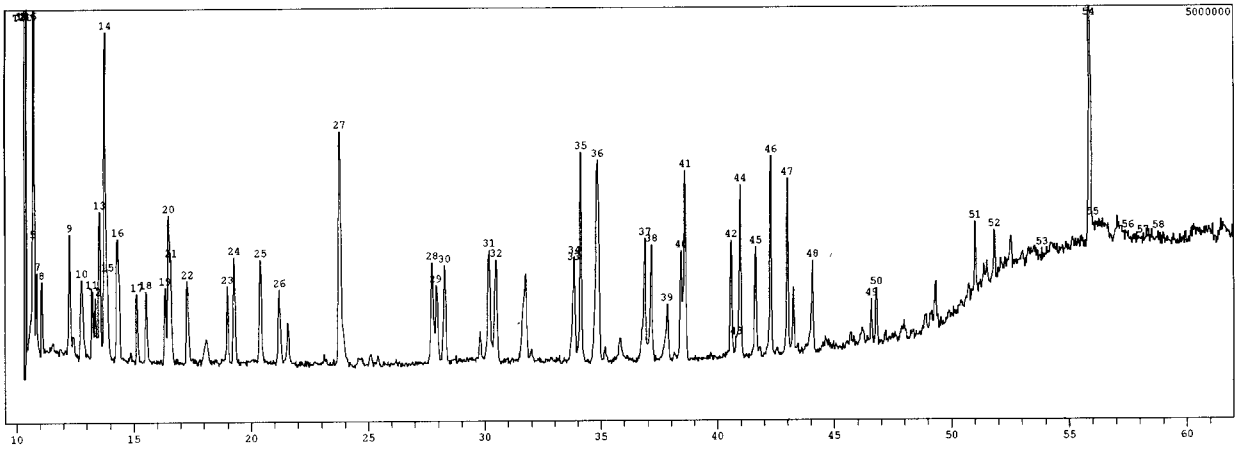

Figure 2. Full scan chromatogram of 50 µl of an ethyl acetate standard mixture at the level of 200 pg/µL.

3.2 Off-line SPE PTV–GC–MS

To facilitate method development, the SPE part was not immediately interfaced on-line to the PTV–GC–MS system. After SPE of the analytes, the desorbate in ethyl acetate was collected in a vial. 50 µL of this solution was injected manually into the PTV–GC–MS system, giving a chromatogram like the upper one shown in Figure 3. To do this, the conditions applied for the OPTIC2 and the GC–MS system were identical to those used for the standard injections. A comparison of the peak areas of the upper and the lower chromatogram given in Figure 3 shows that the recoveries for most of the solutes are around 100%. We also see some impurities, the origin of which is still unclear.

In the optimisation of the desorption flow rate, we did not see any effect of the flow rate on the recovery for flow rates in the range from 100 µL/min to 2400 µL/min. At the higher flow rate, however, gas bubbles occurred in the desorbate stream. To avoid the occurrence of these bubbles a desorption flow rate of 100 µL/min was chosen. The required volume of desorption fluid to obtain maximum recovery was found to be approximately 40 µL. For safety reasons a desorption volume of 50 µL was used.

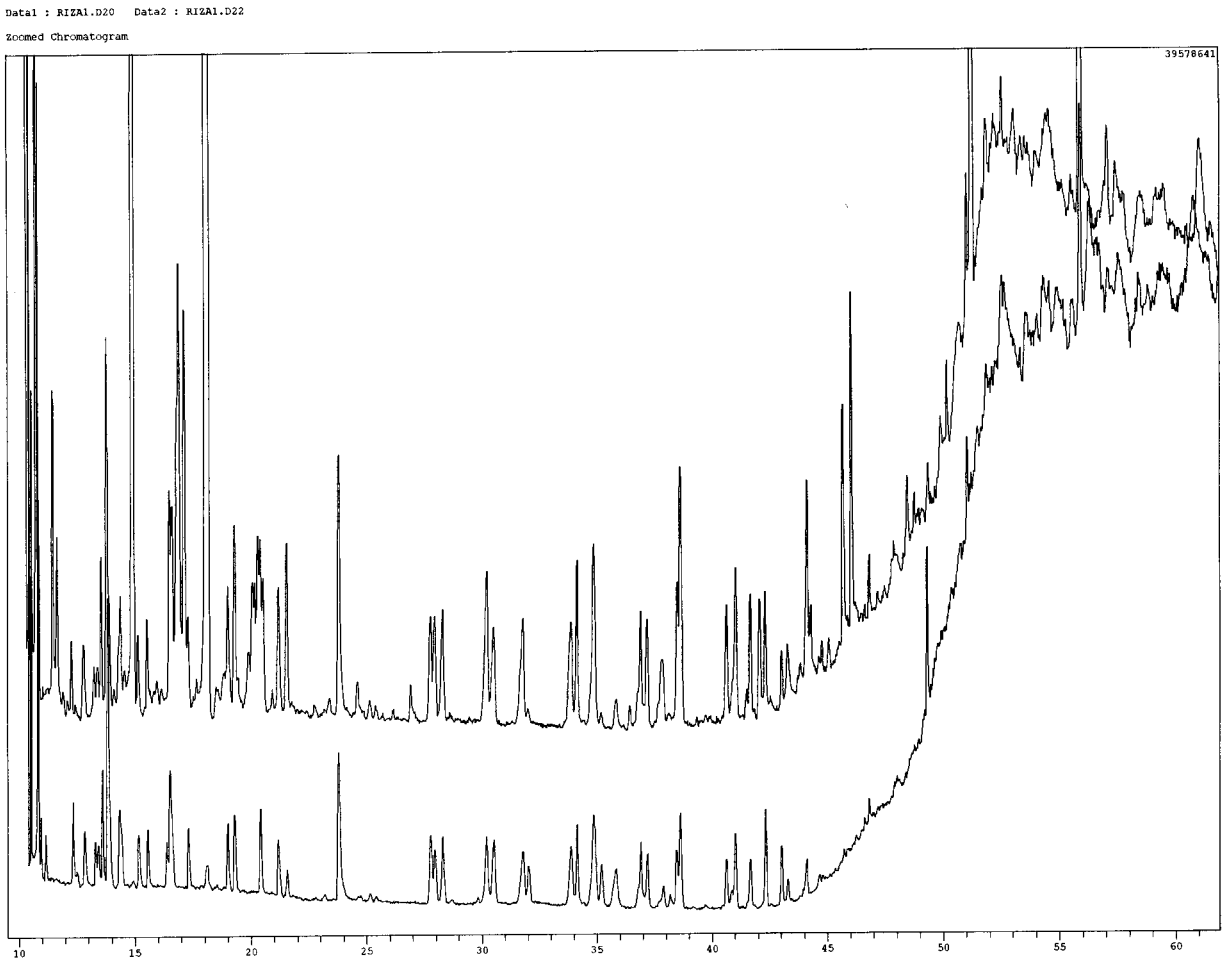

Figure 3. Lower chromatogram, 50 µl of an 200 g/µl standard; Upper chromatogram, Off-line SPE PTV–GC–MS full scan chromatogram of 10 mL spiked Meuse water at the level of 1 µg/l.

3.3 On-line SPE–PTV–GC–MS

In the on-line analyses the parameters for the SPE part of method are identical to those used in the off-line procedures. The main parameters of interest at this point of the research work are the PTV sample introduction parameters. First, we used the conditions specified in Table 2. This however, resulted in losses of the most volatile compounds. Most likely this is a result of the rapid evaporation of the first droplets of desorbate, which contain the main fraction of the volatiles, immediately after their introduction in the liner. A solution to this problem is introduction of the sample at ambient liner pressure. In this way there is no flow through the liner, eliminating losses by evaporation. In this way it is possible to introduce a part, or the full desorbate, prior to starting evaporation of the ethyl acetate. Hence, the analytes are no longer lost from the packing material in the liner.

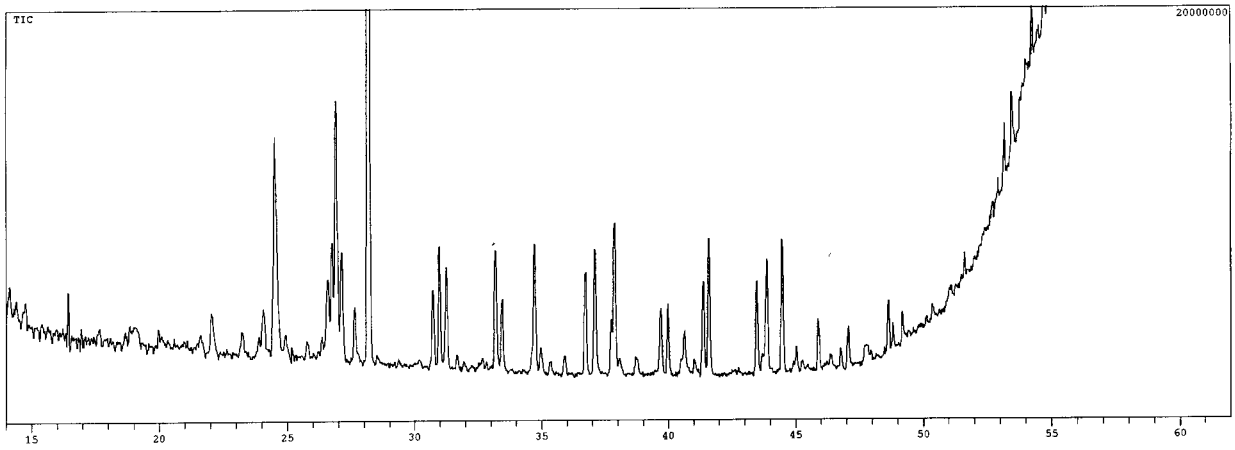

Figure 4: On-line SPE–PTV–GC–MS chromatogram of 10 mL of Eindhoven tap water spiked at the level of 1 µg/L using a too long solvent vent time.

The importance of using correct solvent vent conditions is illustrated in Figure 4 and Figure 5. Too long solvent venting times (Figure 4) result in chromatograms containing only the analytes with a higher boiling point. Too short solvent vent times (Figure 5) result in a chromatogram containing all analytes, but in the later part of the chromatogram the peaks are very small and broadened because of too large amount of solvent transferred to the analytical column [7]. The chromatogram obtained at a correct vent time is shown in Figure 6. As can be seen from this chromatogram good peak shapes are obtained throughout the entire chromatogram if using the appropriate solvent vent time.

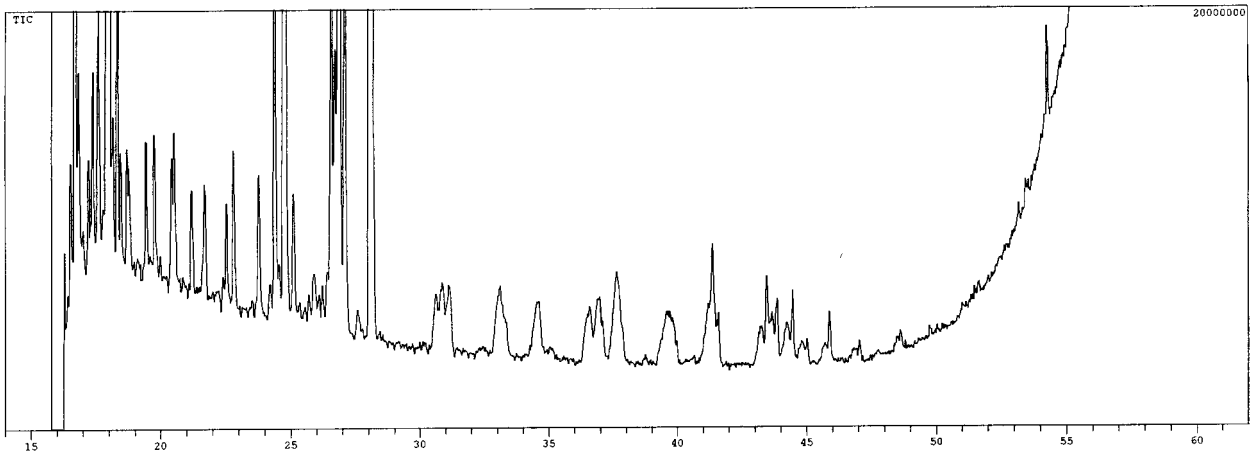

Figure 5. On-line SPE–PTV–GC–MS chromatogram of 10 mL of Eindhoven tap water spiked at the level of 1 µg/L using a too short solvent vent time.

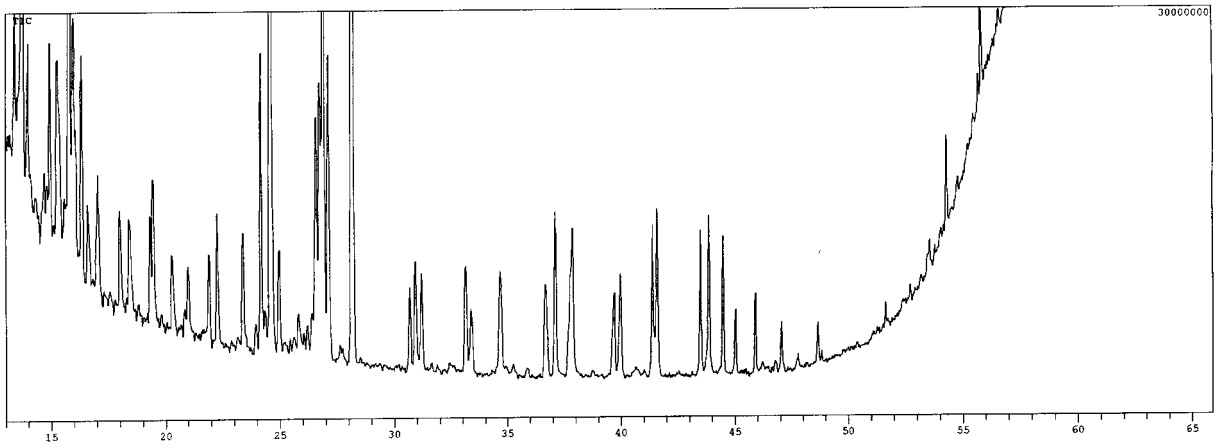

Figure 6. On-line SPE–PTV–GC–MS chromatogram of 10 mL of Eindhoven tap water spiked at the level of 1 µg/L using correct solvent vent time.

3.4 Real water samples

The procedure described above was used to analyse a 10 ml real-life water sample from the river Meuse. The chromatogram obtained in this analysis is shown in Figure 7. In this sample tributylphosphate and caffeine were found at the level of approximately 0.7 µg/L each. This value indeed was confirmed by analyses performed by the RIZA.

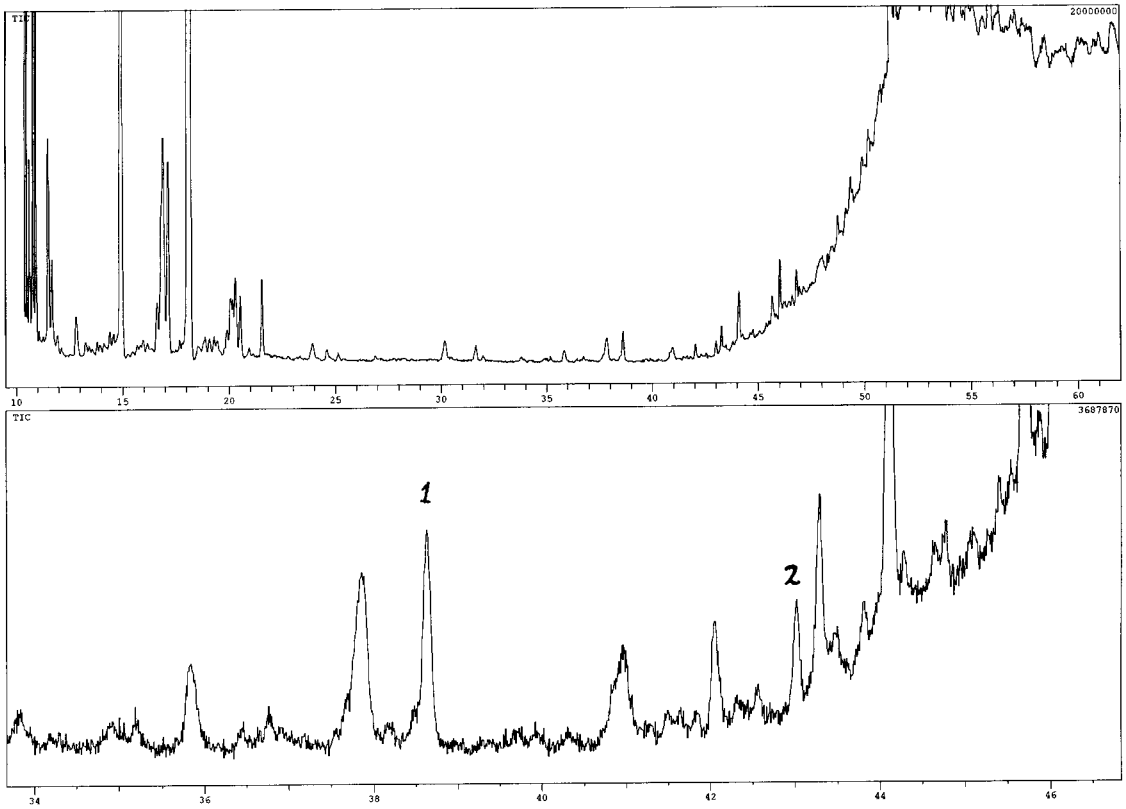

Figure 7. Upper, full scan chromatogram of 10 mL Meuse water. Lower, zoomed part of upper chromatogram. 1, tributhylphosphate; 2, caffeine.

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