

DETERMINATION OF CHLORINATED ETHENES IN WATER USING HEADSPACE SOLID PHASE MICROCOLUMN EXTRACTION COMBINED WITH THERMAL DESORPTION IN GC INJECTION PORT

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Abstract

A solvent-free sample preparation method is presented in which volatilized organic substances are extracted via solid phase microcolumn from an appropriate volume of headspace (tens of millilitres) withdrawn above the sample matrix with the aid of gas-tight syringe. The headspace aliquot is passed through the glass microcolumn packed with an adsorbent, which is then transferred into a modified GC injection port for thermal desorption and analysis of trapped analytes. The method was applied for the determination of chlorinated ethenes in water samples. A linear working range of 0.1-2.0 µg/l for vinyl chloride and of 0.5-15.0 µg/L for other chlorinated ethenes was established with correlation coefficients (r^2) within the range, 0.9917-0.9996. Limits of detection ranged from 0.01 µg/l for vinyl chloride to 0.1 µg/l for *cis*-1,2-dichloroethene. Good chromatographic resolution without need of cryogenic focusing was obtained for all chlorinated ethenes with use of PLOT capillary column (with porous layer of Al₂O₃).

Keywords: *chlorinated ethenes; vinyl chloride; headspace; solid phase microcolumn extraction; thermal desorption; water analysis*

Introduction

Chlorinated ethenes are among the ubiquitous chlorinated compounds found in groundwater contamination. They represent a serious health hazard because of their toxic and carcinogenic properties. Where pollution by tetrachloroethylene or trichloroethylene occurs, in many cases lesser-chlorinated ethenes (dichloroethene isomers, vinyl chloride) can also be found [8, 4]. All chlorinated ethenes have been included in both, the US Environmental Protection Agency (US EPA) and the European Community priority

pollutants lists and their environmental monitoring is mandatory [9].

At present, the determination of chlorinated ethenes and as of other volatile organic compounds (VOCs) in water commonly utilizes liquid-gas extraction methods for sample preparation in combination with capillary gas chromatography. Liquid-gas extraction is generally performed by using static headspace sampling or dynamic – purge-and-trap sampling.

The static headspace method is based on achieving thermodynamic equilibrium of organic compounds between the water and

gas phase in a closed thermostated vessel. For the analysis, a reproducible aliquot of the headspace is delivered to the gas chromatograph injection port. In the case of purge-and-trap sampling, the water sample is placed in a purge vessel. The sample is then sparged with carrier gas for several minutes to remove VOC's, which are trapped on a solid adsorbent. Ballistic heating of the trap desorbs the volatiles, which are carried to the gas chromatograph in the carrier gas stream.

As every sample preparation method has its advantages and disadvantages, so is static headspace versus purge-and-trap sampling^[10]. According to the principle it is obvious that the static headspace is inherently less sensitive than purge-and-trap method because the former procedure samples only an aliquot of gas phase, whereas the latter samples all (or most) of the volatile fraction to the gas chromatograph. Due to its excellent sensitivity the purge-and-trap sampling is routinely used for the determination of volatile priority pollutants and it is the technique recommended by the US EPA^[6]. However, it requires the purchase or fabrication of specialized apparatus, which may be beyond the scope of smaller laboratories. Headspace sampling can be realized in a less expensive way and it is also more easily automated. Great advantage of static headspace is that it can be used for the determination of VOC's in virtually any matrix, including samples of water, soil, sludge, or waste drum contents. Headspace glassware is all disposable, whereas expensive and fragile glassware which must be washed unless very clean samples are being analysed, is used for purge-and-trap sampling. A significant drawback of purge-and-trap sampler performance is that the plumbing and trap are easily contaminated by "dirty" samples (those with a very high content of some volatile components), and samples that foam are a particular problem. In the case of headspace, there is no chance of contamination from foaming or high concentrations of analytes^[10].

Considering the principles and advantages of the two above summarized sample introduction methods, a simple and fast method for the determination of VOC's was developed. In this method, the water sample is equilibrated with the gas phase from which a larger volume aliquot (tens of millilitres) is taken via injection syringe for solid phase extraction of VOC's on glass microcolumn packed with an appropriate adsorbent. The microcolumn is then transferred to a modified

GC injection port for thermal desorption and analysis of trapped analytes^[3].

The present study demonstrates the application of the developed method for the determination of chlorinated ethenes in water samples.

Experimental

Reagents

Standards of 1,1-dichloroethene, trichloroethene and tetrachloroethene in neat form and vinyl chloride as solution at 0.2 mg/ml methanol were obtained from Supelco (Bellefonte, PA, USA).

Cis-1,2-dichloroethene and *trans*-1,2-dichloroethene were purchased as methanol solutions with concentration of 2.0 mg/ml and 0.2 mg/ml, respectively, from AccuStandard (New Haven, CT, USA). From the neat standard materials were prepared stock standards solutions of individual analytes in methanol (SupraSolv, Merck, Darmstadt, Germany) with concentration of 1.0 mg/ml. Stock standard solutions were stored at -18°C, and protected from light. Aliquots of stock standard solutions were added to tap water (pH ranged from 7.2 to 7.6) to give fresh test samples and calibration solutions. Tap water was preferred over distilled or ultrapure water to obtain realistic conditions in aqueous matrix with a low organic load.

Apparatus

Analyses were conducted using a Hewlett-Packard Model 5890 Series II gas chromatograph (Palo Alto, CA, USA) equipped with a modified split-splitless inlet (see Fig. 1) and flame ionization detector. The split-splitless inlet was modified so that it was possible to put a glass microcolumn in and out of the chamber, where a liner was previously placed. The microcolumn with internal diameter of 2.0 mm and length of 105 mm (length of filling 55 mm) was packed with 35 mg of 60-80 mesh Tenax-TA (Alltech, Deerfield, IL, USA). The inside of the exit end of the microcolumn was conically broadened (similarly as in glass press-fit connectors) to make a gas-tight connection when it was put on the end of a capillary column inserted into the inlet chamber. Carrier gas line system including gas regulator with pressure gauge was rebuilt so that the carrier gas was passing through the microcolumn connected to the capillary column and it was possible to manually regulate the gas pressure in the inlet.

The fused-silica capillary column Rt-Alumina PLOT (Porous Layer Open Tubular), 50 m x 0.53 mm I.D. (Restek, Bellefonte, PA, USA),

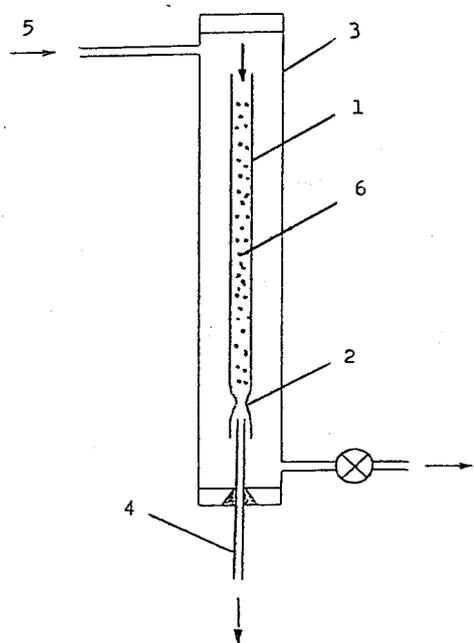


Figure 1. Schematic diagram of the modified GC inlet with inserted microcolumn (1 – microcolumn, 2 – gas-tight connection, 3 – GC injection port, 4 – capillary column, 5 – carrier gas, 6 – adsorbent)

Nitrogen (purity: for ECD, Linde, Bratislava, Slovak Republic) was used as the carrier and make-up gas. The FID operating conditions were as follows: carrier gas at 10 ml/min, make-up gas at 16 ml/min, hydrogen at 32 ml/min and air at 520 ml/min. The detector and inlet were both held at 200°C. The GC column was temperature programmed from 35 °C to 150°C (5 min) at 10 °C/min.

Procedure

Test and calibration water solutions of chlorinated ethenes were prepared in 2000 ml and 500 ml volumetric flasks, respectively, and brought to room temperature ($21 \pm 1^\circ\text{C}$). For the analysis, 250 ml aliquots of prepared solutions were quickly transferred (by means of graduated cylinder) into a 500 ml volumetric flask, which was capped with aluminium foil.

with porous layer of Al_2O_3 was used for the separation of analytes.

The flask was vigorously shaken by hand for 20 seconds. Then the foil was pierced with narrow glass tube mounted on the gas-tight syringe (with the aid of short piece of flexible tubing) and an appropriate volume of headspace was withdrawn. For the sampling 20 and 30-ml all-glass syringes with glass luer were used (Poulten & Graf, Wertheim, Germany). The headspace content of the syringe was passed through the microcolumn packed with adsorbent at a flow rate of 20 ml/min. The loaded microcolumn was transferred into a GC injection port, in which the gas pressure was decreased to 10 kPa. The trapped analytes were desorbed by heating of the microcolumn for 60 seconds, then the carrier gas pressure was increased to 60 kPa and the temperature programme was started. A computer equipped with GC ChemStation (A.08.03, Agilent Technologies, 1990-2000) was used for data acquisition.

Results and discussion

The optimization of the method for determination of chlorinated ethenes in water resulted in setting chromatographic conditions and development of the procedure described in the previous section. To obtain a sample phase equilibration a vigorous hand shaking for 20 seconds was sufficient. This corresponds with the results of Dietz and Singley^[2] who were studying effects of agitation and equilibration time on the headspace gas chromatographic responses of chlorinated hydrocarbons. Fig. 2 shows chromatograms from the analyses performed with a non-loaded microcolumn (a), with a microcolumn through which 20 ml of headspace from tap water blank was passed (b) and a microcolumn loaded with analytes from 20 ml of headspace from tap water sample spiked with chlorinated ethenes at 1.0 µg/l each (c). From these chromatograms, it can be seen that there is a negligible peak contribution of the non-loaded microcolumn and that the peaks from tap water blank do not interfere with those of chlorinated ethenes. The third chromatogram (c) shows a baseline resolution of symmetrical peaks for all studied analytes with the best sensitivity obtained for vinyl chloride.

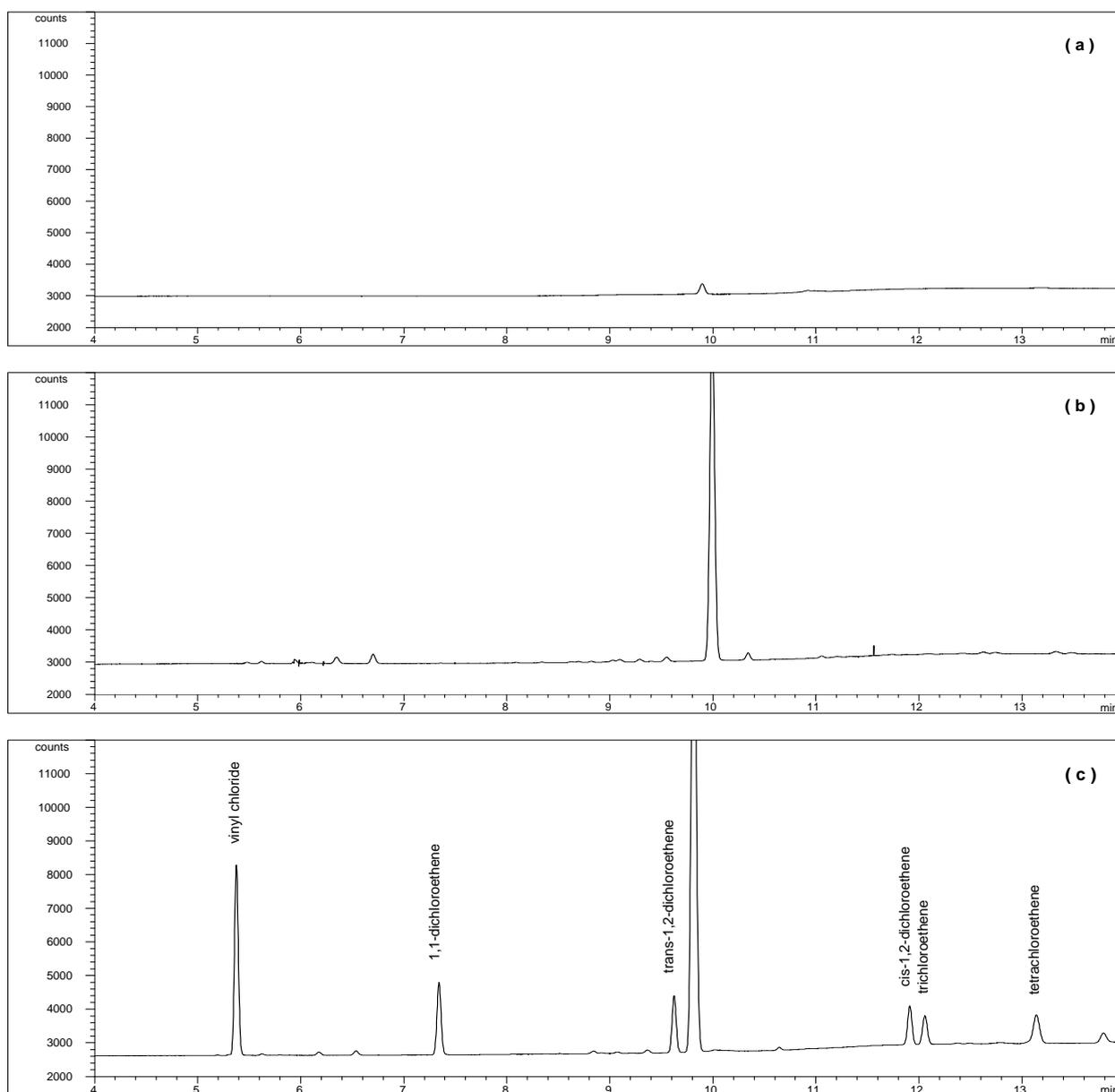


Figure 2. Chromatograms obtained with: (a) a non-loaded microcolumn; (b) a microcolumn loaded with a content of volatiles from 20 ml of headspace from tap water blank; (c) a microcolumn loaded with analytes from 20 ml of headspace from tap water sample spiked with chlorinated ethenes at 1.0 $\mu\text{g/l}$ each.

In order to investigate the possibility of increasing the sensitivity of the method, the effect of headspace volume passed through the microcolumn on the gas chromatographic response of chlorinated ethenes was evaluated. The results obtained from headspace analyses of multiple-component aqueous solutions of 0.5 and 5.0 $\mu\text{g/l}$ (in case of vinyl chloride 2.0 $\mu\text{g/l}$), respectively, indicate a unique position of vinyl chloride among the

chlorinated ethenes. While for other studied analytes the headspace volume dependence of the peak area in the investigated headspace volume range was linear, the breakthrough curves were obtained for vinyl chloride. To indicate general features, in Fig. 3 are presented plots for vinyl chloride and 1,1-dichloroethene as a representative of other chlorinated ethenes. The relatively small breakthrough volume of vinyl chloride (about 20 ml) can be explained by the fact that, in

contrast to other chlorinated ethenes, it is a gas with boiling point of $-13.4\text{ }^{\circ}\text{C}$ and it has the highest mobility in the solid phase extraction microcolumn. For all of the studied analytes, with the exception of vinyl chloride, the sensitivity of the method can be increased, however, by simply increasing the analysed headspace volume. In the case of vinyl chloride, to increase the sensitivity is primarily

necessary to enlarge the amount of adsorbent in the microcolumn. In the following studies with the prepared microcolumn, 20 ml headspace volume aliquots were taken for the analysis.

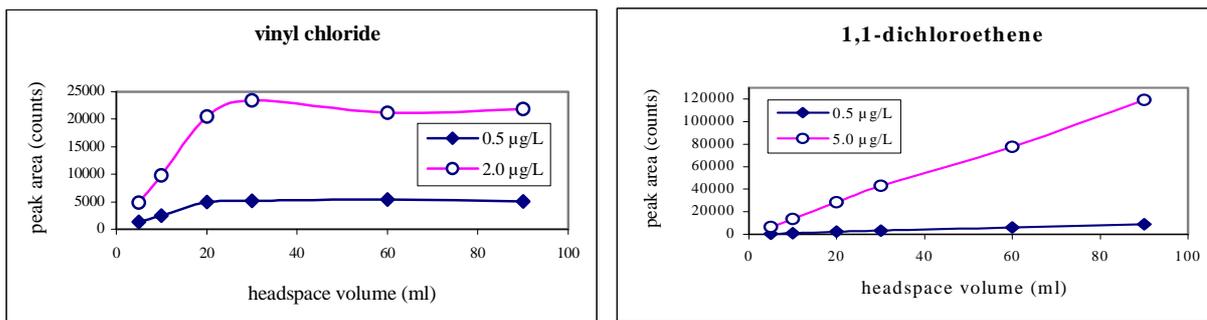


Figure 3. Headspace volume dependence of chromatographic peak area of selected chlorinated ethenes at two concentration levels.

When linearity range of the analytical method was evaluated the requirements of Directive 98/83/EC on the quality of water intended for human consumption were taken into account (regulatory limit for vinyl chloride $0.5\text{ }\mu\text{g/l}$, for tetrachloroethene and trichloroethene $10.0\text{ }\mu\text{g/l}$) (Official Journal of EC, 1998). Standard calibration curves of the area versus the concentration of each analyte

were plotted for concentrations of vinyl chloride ranging from 0.1 to $2.0\text{ }\mu\text{g/l}$ and for other chlorinated ethenes for concentrations ranging from 0.5 to $15.0\text{ }\mu\text{g/L}$ ($n = 7$). For the selected concentration ranges good linearity was achieved and the obtained correlation coefficients (r^2) were 0.9917 - 0.9996 (Table 1).

Table 1 Linearity, repeatability and limits of detection for chlorinated ethenes from analysis of fortified tap water

Compound	r^2	RSD % (n=6)			LOD ($\mu\text{g/l}$)
		$0.5\text{ }(\mu\text{g/l})$	$1.0\text{ }(\mu\text{g/l})$	$10.0\text{ }(\mu\text{g/l})^a$	
Vinyl chloride	0.9976	7.7	3.8	6.1	0.01
1,1-Dichloroethene	0.9969	6.2	5.7	7.3	0.02
trans-1,2-Dichloroethene	0.9944	2.1	4.6	2.5	0.02
cis-1,2-Dichloroethene	0.9917	10.2	3.0	10.9	0.10
Trichloroethene	0.9971	6.3	2.8	5.3	0.07
Tetrachloroethene	0.9996	3.7	4.0	2.7	0.04

The repeatability of the method was investigated by analysing tap water solutions at standard concentrations of 0.5 , 1.0 and $10.0\text{ }\mu\text{g/l}$ (in case of vinyl chloride $2.0\text{ }\mu\text{g/l}$), respectively. The relative standard deviations (RSD) ranging from 2.1 to 10.9% (see Table 1) were very satisfactory when comparing with

those that were obtained from the static headspace analysis^[5] of volatile halogenated compounds in drinking water (RSDs ranged from 0.8 to 19.6% ; values for trichloroethene and tetrachloroethene at $1\text{ }\mu\text{g/L}$ were 7.2 and 8.2% , respectively). A good repeatability can be attributed to vinyl chloride (RSDs from 3.8

to 7.7%), which is known as a compound difficult to handle because of its extreme volatility.

The sensitivity of the method was considered in terms of limit of detection (LOD), which depends on the basis of the signal-to-noise ratio ($s/n = 3$). The detection limits were calculated based on the signal generated at the lowest standard concentration of $0.1 \mu\text{g/l}$ for vinyl chloride and $0.5 \mu\text{g/l}$ for other chlorinated ethenes. The LOD values (Table 1) ranged from $0.01 \mu\text{g/l}$ for gaseous vinyl chloride to $0.1 \mu\text{g/L}$ for *cis*-1,2-dichloroethene.

The obtained analytical parameters indicate that the developed method is sufficiently precise and sensitive to measure the regulated chlorinated ethenes below the limits set out in the EU Council Directive. The method has been applied to analysis of samples ranging from pure drinking water to highly contaminated landfill leachate.

Examples of chromatograms from analyses of polluted groundwater and landfill leachate samples are shown in Figs. 4 and 5. Both samples were diluted with tap water; the first one 5-times and the latter 25-times. In the chromatogram from the groundwater analysis, the largest peak belongs to tetrachloroethene; the concentration in non-diluted sample was $42 \text{ ppb } (\mu\text{g/L})$. In this sample also $3.3 \text{ ppb } (\mu\text{g/l})$ of trichloroethene and $5.9 \text{ ppb } (\mu\text{g/l})$ of vinyl chloride, the probable biotransformation products of the previous one, were detected. In Fig. 5 is a chromatogram from the analysis of diluted landfill leachate sample. The results gave $176 \text{ ppb } (\mu\text{g/l})$ of *cis*-1,2-dichloroethene, $803 \text{ ppb } (\mu\text{g/l})$ of trichloroethene and $83 \text{ ppb } (\mu\text{g/l})$ of tetrachloroethene, respectively. For quantification, the calibration curves method was chosen.

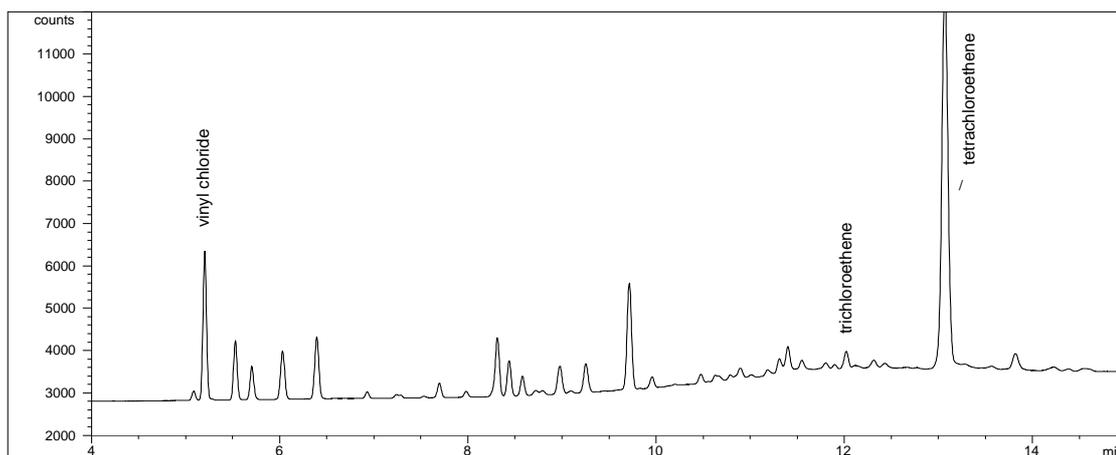


Figure 4. Chromatogram from the analysis of groundwater sample for pollution survey (dilution 1 : 4).

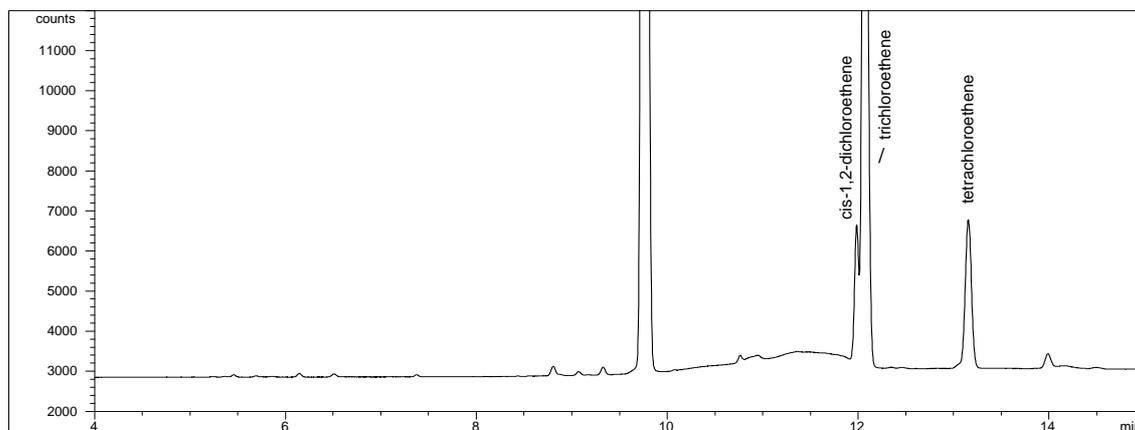


Figure 5. Chromatogram from the analysis of landfill leachate sample (dilution 1 : 24)

Conclusions

Developed sample preparation method combines the extraction and concentration of volatilized organic substances from headspace on solid phase microcolumn, which also facilitates direct transfer of the trapped analytes into GC injection port. This approach enables benefits from a combination of advantages characteristic for both, the static headspace and the purge-and-trap sampling. The obtained sensitivity is comparable to that of purge-and-trap method, while the possibility of analysis of virtually any matrix (e.g. water, sludge, soil) is same as in the case of static headspace. The simplicity of technical solution for the performance of solid phase microcolumn extraction with the following thermal desorption in a modified split-splitless inlet of GC is in contrast to the mechanically complicated design of purge-and-trap concentrator. According to the way of usage, the solid phase microcolumn can be considered as a miniature of conventional traps for purge-and-trap method. This miniaturisation together with desorption of analytes accomplished directly in the GC

injector have a positive effect on the shape of obtained chromatographic peaks (see Figs. 2, 4 and 5) with no problem of elongation of analyte bands introduced into the chromatographic column.

From the above mentioned it can be concluded that the developed method is an inexpensive alternative to the purge-and-trap instrumentation. It also has common features with the sorptive sample preparation techniques such as open tubular trapping (OTT), solid phase microextraction (SPME) or stir bar sorptive extraction (SBSE) which are, in contrast with adsorptive trapping, based on dissolution of the analytes in a liquid polymeric material^[11,1].

The method was successfully applied to the determination of chlorinated ethenes in water samples. The use of PLOT capillary column enables the rapid determination of all chlorinated ethenes with a good chromatographic resolution without need of cryogenic focusing. Obtained sensitivity, linearity and repeatability indicate that the method is reliable and useful for routine analysis.

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