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ANALYSIS TRICHLORO- AND TETRACHLORO-ETHYLENE IN WATER

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Abstract: *The method for determination of trichloroethylene (TCE) and tetrachloroethylene (TTCE), also known as perchloroethylene (PCE), in water at 1 – 30 μg.l^{-1} concentrations was elaborated. Water (1000 ml) is extracted by manual shaking (5 minutes) at 5-7 °C with n-pentane (0,5 ml) in the presence of internal standard (1-Cl-n-hexane, 1-Cl-n-octane) and the extract chromatographed using split-splitless injection technique. The recoveries of 28 chlorinated hydrocarbons in water at 5 μg.l^{-1} concentrations for each compound relative to internal standard (R=100%) are also introduced. The FID and ECD detectors (in the case of ECD detector without of internal standard) were used in final stage of determination.*

Keywords: *capillary gas chromatography, microextraction, water analysis, chlorinated hydrocarbons*

1. Introduction

Organic Compounds of chlorine and other halogens present in water predominantly come from human activities or are influenced by them.

It is mainly chemical industry (production of synthetic polymers, fibers, organic solvents, etc.) engineering (degreasing and surface treatment of metals), metallurgical and electrical industry (microelectronics), agriculture (pesticides), communal undertaking (chemical cleaning of clothes) and others that are responsible for abrupt increase in contamination of all kinds of water including rain water. Moreover, the organohalogen compounds are formed in the course of water disinfection itself as undersirable products of chlorination of different hydrocarbons of biogenic or synthetic origine.

On the basic of present knowledge, these substances are considered to by very dangerous for environment as well as for human being itself. Many organohalogen compounds are very resistent to oxidative, photolytic and other physicochemical degradation processes and therefore they stay in aqueous medium for a long time. The half-times of decay of some chlorinated hydrocarbons in aqueous medium are given in **Table 1** [1,2].

Table 1

Half-times of decay of some chlorinated hydrocarbons in aqueous medium [1,2]

Compound	Half-time of decay
tetrachloroethylene	6 years
trichloroethylene	9 months
chloroethylenes	6 – 12 weeks
chloromethanes	10 – 33 weeks
chloroethanes	10 – 33 weeks

As organohalogens belong among substances detrimental to aqueous medium and biological life, they should not be present in water. However, the requirement of absolute zero concentration of these substances even in drinking water is hardly realizable for the present.

The concentration ranges of some chlorinated hydrocarbons in different kinds of water statistically processed according to literary resources [3] are given in **Table 2**.

Table 2
Concentration ranges of trichloro-ethylene (TCE) and tetrachloroethylene (TTCE) in different kinds of water [3]

Water	TCE [µg/l]	TTCE [µg/l]
Surface water	0.01 - 11	0.1 - 1300
Drinking water	0.1 - 15	0.1 - 200
Ground water	0.1 - 150	0.1 - 1000
Rain water	0.1 - 13	0.1 - 50
Waste water	up to 2000	0.1 - 6000

The International Agency for Research on Cancer has classified trichloroethylene and tetrachloroethylene as a Group 2A carcinogen, which means that it is probably carcinogenic to humans [4]. Maximum contaminant level (USEPA) for TCE and TTCE in drinking water is 0,005 mg/l (according to the requirements of the Regulation of the Government of the Slovak Republic No. 496/2010 on drinking water, the contaminant level is 0,01 mg/l). The granular activated carbon in combination with packed tower aeration are required for effective removing TCE and TTCE from water [5].

The analysis of volatile organohalogene compounds (VOC) in water samples requires a several steps:

a) isolation and preconcentration of the pollutants from water,
b) trace organic analysis by capillary gas chromatography (GC),
c) identification and quantitative determination individual compounds.

Sample preparation methods include static headspace, dynamic headspace (purge and trap), solvent extraction and solid-phase microextraction techniques, or direct injection of water into gas gromatograph. The advantages and disadvantages of these methods are presented and discussed [6].

The chlorinated hydrocarbons in water can by analyzed by injection water directly into a gas chromatograph [7-14]. This method is profitable because of simplicity. The rests of salts deposited in the injector after evaporation of water bringcauses the problems. However, such problems can be solved by simple exchange of glass tube of the injector after 50 – 100 analyses (according to quantity of the dosed volume of sample). The sensitivity of this method reaches 0,1 µg/l H_2O.

The chlorinated hydrocarbons in water can be determined by using the "headspace" method. This method is either static, i.e. carried out in closed system [15-17] or dynamic, the so-called stripping or purge and trap, with adsorption, i.e. on Tenax [18-20]. The dynamic method is more sensitive and if we use a detector ECD, we can analyze these componds even when they are present in concentrations under 0,01 µg/l H_2O.

The static headspace method is an attractive method regarding its rapid times and simplicity, i.e., no sample workup is required outside the vial [21]. In static headspace method a sample of water is placed into a vial, sealed, and heated to a specific temperature. All of the components volatile at or below the pre-set temperature escape from the sample to form a gaseous "headspace" above the sample. After a certain period of time, the headspace gas is extracted from the vial and injected into a gas chromatograph with selective detector. The sensitivity for static headspace is typically in the sub microgram range. However, it depends on the volatility of the compounds.

In dynamic headspace method the sample is purged with ultra pure nitrogen while being heated in a Teflon vessel. As the nitrogen stream exits the vessel it passes through the thermal desorption tube filled with an adsorbent material. The outgassed products are collected onto the adsorbent material. Following the predetermined collection time, the tubes are transferred to a thermal desorption unit which is inline with the gas chromatograph and selective detector (GC/MS or GC/ECD).

The thermal desorption unit heats the individual tubes while a flow of gas is applied through the tube. The collected analytes are flushed from the sorbent and collected onto a cold trap within the thermal desorption unit. The cold trap is heated rapidly after purging the entire sample from the sample tube and collected in the cold trap. The collected analytes are then swept from the cold trap into the GC/MS for analysis as a volatile sample.

The static headspace method is less expensive than the purge-and-trap since no expensive purging equipment is used here. With the headspace method, multiple runs can be performed on a single sample vial, whereas the purge-and trap method is essentially destructive; the sample may only be purged and analysed once [21]. The disadvantage of the purge-and-trap method is associated with the problems related to the use of adsorbents, such as overloading, carryover, and breakdown with repeated heating and purging cycles.

Solid-phase microextraction (SPME) is a relatively new technique, first published in 1989 [22]. A thin fused silica fiber coated with a layer of polymeric adsorbent material is introduced directly into the aqueous sample, whereupon the analytes diffuse into the fibre coating until equilibrium is established, thus being extracted in amounts determined by their distribution coefficients and concentrations. Subsequently, the analytes are desorbed thermally in GC injector. The method is effective, sensitive to wide range of compounds (detection limits are typically from 20 ng/l to 200 ng/l, except for the very light VOCs), less expensive and easier to use then well-established methods such as purge and trap and traditional head-space analysis techniques. Solid-phase microextraction has been applied to quantitative analysis of organohalogens in drinking water [23-29]. The temperature has a very direct influence on extraction. A higher temperature reduces the time to reach equilibrium because of faster diffusion in the water. However, it lowers the total amount absorbed on the fibre as the distribution coefficients decrease. For this reason the SPME method requires examination of the extraction time, fibre coating-water distribution coefficient, equilibration curves for VOCs compound, adsorption heat and analytes volatility.

The extraction methods are frequently used for determining the chlorinated hydrocarbons present in water. In literature issued in our country as well as abroad many methods of extraction of the halogenated organic compounds from water have been described. They differ from each other by kind and amount of the used extractant (ratio water : solvent) as well as by the recovery of extraction.

n-Pentane [30-38], n-hexane [31,33,39,40], methylcyklohexane [31,33,42], isooctane [31-33], petroleum ether [43], mixture of n-hexane + diisopropylether [39,41], etc are used for extraction. By comparing the efficiencies of extraction methods with each other, it has been found that no significant differences appear if different extractants are used [44].

The effectiveness of extraction mainly depends on affinity of dissolved substance to extractant (the measure of which is distribution coefficient, i.e. the ratio of concentration of organohalogen in extractant to its concentration in water) and phase ratio (the ratio of extractant volume to sample volume) as well as on number of extraction steps. The extraction can be carried out either in one step or in several steps in series (the extraction is performed either with successive addition extractant or in countercurrent of water and solvent).

The efficiency of extraction is affected by extent of the interface contact, solubility of the investigated substances in both phases, ionic strenght and pH of the medium.

A comparison of extraction methods with the headspace or stripping methods is presented in papers [45,46]. For instance, the stripping method is about ten times more sensitive method then micro-extraction for compounds with boiling points up to 200 °C. On the other hand, the stripping method necessitates special apparatus and is slow and therefore it is less convenient for routine analysis of organohalogens in water when compared with microextraction.

In most cases the cappilary gas chromatography with an ECD detector or the GC/MS combination is used in final stage of determination. If a FID detector appropriate for the chlorinated hydrocarbons containing 1 or 2 chlorine atoms in a molecule is used, we must choose a volitale solvent (or a column with more polar phase) so that the solvent should not interfere with waves of the analyzed substances.

In view of the above – mentioned facts, we have paid attention to the possibility of using microextraction for the analysis of the chlorinated hydrocarbons in water. The experimental part of this paper comprises the results of investigation represented by the recovery of 28 chlorinated hydrocarbons obtained by microextraction with n-pentane.

2. Experimental

2.1 Instrumentation

Gas chromatograph Carlo Erba (VEGA 6000) equipped with an ECD or FID detectors and split-splitless injector system was used.

For the chromatographic separation (in the case of FID detector) a glass capillary columns with stationary phase PEG 400, TRITON TX-305 and UCON LB550+ IGEPAL CO 880 (4:1) were used. For the chromatographic separation (in the case of ECD detector) a silica capillary column DB-5 wet with silicone stationary phase SE-54 was used.

Chromatograms were integrated with DP 700 (Carlo Erba) integrators.

2.2 Microextraction

One litre of water containing defined content of chlorinated hydrocarbons was subjected to microextraction (at + 5-7 °C) with 0,5 ml of n-pentane containing internarnal standard (in the case when a FID detector was used) by intense manual shaking 5 minutes. The glass extraction flask, equipped with a male joint (1) and conical stopper (5) was used to extraction (A). After extraction (B) the solvent thin layer separator (2) containing side arm for water (3), capillary for extract (4) was connected to the extraction flask (**Figure 1**) [47]. In this case the n-pentane extracts are easily accessible and can be injected immediately by means of a syringe into a gas chromatograph.

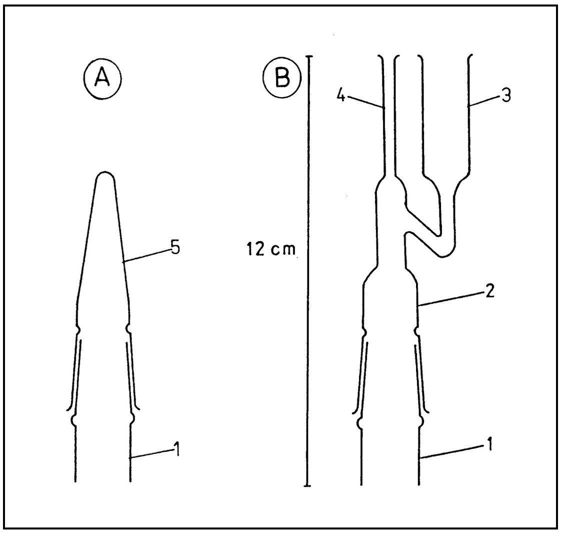

Fig.1 Solvent thin layer separator for microextraction of water

2.3 Chemicals

For the analysis of the chlorinated hydrocarbons certified standards from Slovak Metrology Institute and standards from Supelco (purity at least 98 %) were used. As the internal standards 1-Cl-n-hexane, 1-Cl-n-octane or 1-Cl-n-dodecane were used (purity at least 98% - Supelco, Bellefonte, USA). Solvent (n-pentane) was highly purified and checked chromatographically (E. Merck, Darmstadt, Germany).

3. Results and discussion

It results from literature review that n-pentane is most frequently used as extractant in extraction methods. Because of volatility of lower chlorinated hydrocarbons and boiling point of n-pentane we may expect lower losses of the analyzed components for this solvent than for extractants with higher boiling point. For this reason, it is serviceable to add into extractant an internal standard exhibiting similar volatility as analyzed compounds. The recoveries (average of five analysis) of some chlorinated hydrocarbons with respect to 1-Cl-n-hexane as internal standard (R=100%) for equal concentration of each component (5 µg/l of water) are given in **Table 3.**

Table 3
The recoveries of volatile chlorinated hydrocarbons from water by microextraction with n-pentane

Compound	Recovery [%]	
	FID detector	
	5 µg/l	% RSD
dichloromethane	1.74	5.63
trichloromethane	3.79	5.42
dichlorobromomethane	4.27	5.86
chlorodibromomethane	3.05[1]	6.31
tribromomethane	6.92[1]	6.58
tetrachloromethane	57.20	5.12
1,1-dichloroethane	4.32	4.39
1,2-dichloroethane	1.05	6.92
1,1,1-trichloroethane	-	-
1,1,2-trichloroethane	2.71	5.38
1,1,2,2-tetrachloroethane	7.14[1]	4.92
1,2-dichloropropane	6.12	5.14
1,1-dichloroethylene	-	-
1,2-dichloroethylene (trans)	4.71	4.95
trichloroethylene	34.75	3.82
tetrachloroethylene	85.98	3.73
1,3-dichloropropene (trans)	1.16	6.38
1,3-dichloropropene (cis)	3.44	4.78
2-chloroethylvinylether	4.62	5.41
chlorobenzene	1.68	5.17
1,3-dichlorobenzene	58.17[1]	3.32
1,4-dichlorobenzene	54.86[1]	3.60
1,2-dichlorobenzene	53.23[1]	3.98
1,3,5-trichlorobenzene	77.62[2]	4.09
1,2,4-trichlorobenzene	77.10[2]	4.18
1,2,3-trichlorobenzene	76.97[2]	4.37
1,2,3,5-tetrachlorobenzene	85.77[2]	3.89
1,2,4,5-tetrachlorobenzene	85.86[2]	3.54
pentachlorobenzene	94.85[2]	3.84
hexachlorobenzene	97.71[2]	3.32

Compound	Recovery [%]	
	ECD detector	
	5 µg/l	% RSD
dichloromethane	8.12	7.58
trichloromethane	9.75	7.21
dichlorobromomethane	11.62	6.89
chlorodibromomethane	12.20	6.45
tribromomethane	14.68	6.14
tetrachloromethane	76.20	6.06
1,1-dichloroethane	8.65	6.37
1,2-dichloroethane	9.84	6.18
1,1,1-trichloroethane	27.92	6.52
1,1,2-trichloroethane	14.58	6.20
1,1,2,2-tetrachloroethane	15.32	6.36
1,2-dichloropropane	11.26	6.78
1,1-dichloroethylene	9.41	7.15
trichloroethylene	41.92	5.89
tetrachloroethylene	86.56	5.22
1,3-dichloropropene (trans)	7.68	7.34
1,3-dichloropropene (cis)	7.82	7.21
chlorobenzene	-	-
1,3-dichlorobenzene	39.72	5.76
1,4-dichlorobenzene	38.98	5.92
1,2-dichlorobenzene	38.58	4.89
1,3,5-trichlorobenzene	-	-
1,2,4-trichlorobenzene	-	-
1,2,3,5-tetrachlorobenzene	-	-
1,2,4,5-tetrachlorobenzene	-	-
pentachlorobenzene	-	-
hexachlorobenzene	-	-

[1] the recovery with respect 1-Cl-n-octane (IS)

[2] the recovery with respect 1-Cl-n-dodecane

The values obtained for the investigated compounds show that microextraction into n-pentane is convenient for tetrachloromethane, trichloroethylene, tetrachloroethylene, dichlorobenzene and other higher chlorinated benzenes. The recovery of other chlorinated hydrocarbons are relatively low which is due to stronger hydrogen bonds between the OH groups of water and the chlorine atoms in a molecule of hydrocarbon.

The efficiency of isolation is significantly affected by polarity of the extracted compounds (its solubility in water).

Therefore the solubilities of some chlorinated hydrocarbons in water taken from literature are given in **Table 4**.

The values of recovery given in Table 3 were obtained by reverse extraction of 0,5 ml of n-pentane containing 5 µg of eachcomponent (including 1-Cl-n-hexane as internal standard) with water (1 litre). The extraction was performed by intense manual shaking for 5 minutes.

Table 4 The solubilities of some chlorinated hydrocarbons in water [48,49,50]

Compound	Solubility [g/l at 20 °C]
chloromethane	7.25
dichloromethane	19.80
trichloromethane	8.20
tetrachloromethane	0.78
chloroethane	4.1
1,1-dichloroethane	5.5
1,2-dichloroethane	8.7
1,1,1-trichloroethane	0.48-4.4
1,1,2-trichloroethane	1.1-4.6
1,1,2,2-tetrachloroethane	2.87
pentachloroethane	0.5
hexachloroethane	0.05
1,2-dichloropropane	2.8
1,3-dichloropropane	2.7
1,2,3-trichloropropane	1.9
tribromomethane	3.1
chloroethylene	0.40-2.66
1,1-dichloroethylene	0.4
1,2-dichloroethylene (trans)	8.8
1,2-dichloroethylene (cis)	3.5
trichloroethylene	1.1
tetrachloroethylene	0.149
chlorobenzene	0.502
1,3-dichlorobenzene	0.143
1,4-dichlorobenzene	0.065
1,2-dichlorobenzene	0.137
1,3,5-trichlorobenzene	0.006
1,2,4-trichlorobenzene	0.031
1,2,3-trichlorobenzene	0.018
1,2,3,5-tetrachlorobenzene	0.0051
1,2,4,5-tetrachlorobenzene	0.00046
1,2,3,4-tetrachlorobenzene	0.00592

If we compare data in Table 3 with Table 4, we can see that the recovery of chlorinated hydrocarbons are consistent with their solubility in water. The highest recovery appear if the solubility falls under 1 g/l of water. The data in Table 4 may serve as orientation for determination of other chlorinated hydrocarbons in water by using microextraction as well.

Furthermore, it results from Table 3 that the recovery increases with number of the chlorine atoms in a molecule of hydrocarbon which manifests itself e.g. in the series di-, tri- and tetrachloromethane or mono-, and as far as hexachlorobenzene.

The recovery of extraction are usually affected by concentration of the analyzed substance in water which is most conspicuous if the concentration is very low. It is very important to taken this fact into consideration, especially if the recovery are low which is usual in the case of microextraction. The errors due to the change in recovery produced by varying concentration may be reduced by drawing the analytical curve for a given concentration range.

The values for analytical curve of trichloroethylene and tetrachloroethylene in the concentration range 1 – 30 μg/l of water were obtained by the use of micro-extraction of model sample of water (1 litre) containing know quantity of the analyzed substances with 0,5 ml of n-pentane containing 5 μg of 1-Cl-n-hexane. The analytical curves are represented in **Figure 2** which shows that it is practically possible to execute linearization of the curve in the investigation concentration region and thus to neglect the variation of recovery with concentration.

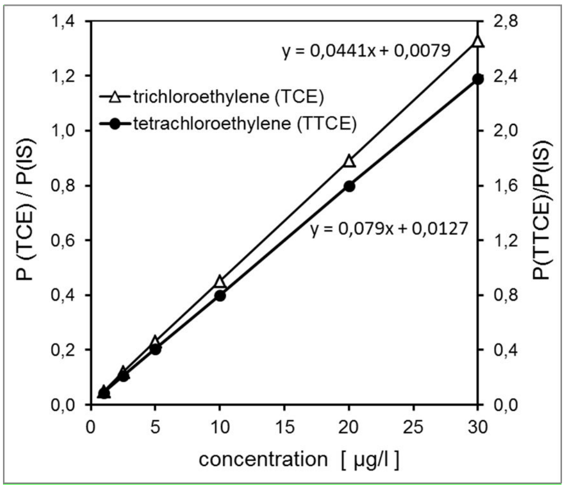

Fig. 2 The analytical curves of trichloroethylene (TCE) and tetrachloroethylene (TTCE) in the concentration range 1 – 30 μg/l of water
P_{TCE} – area of TCE elution peak, P_{TTCE} – area of TTCE elution peak, P_{IS} – area of IS elution peaks

We have also had the reason for paying attention to TCE and TTCE because these two substances belong among the most frequent contaminants of ground waters.

We analyzed real samples of water in the same way as described for determining the analytical curve.

This method was used to determine the areal and vertical distribution of groundwater contaminated by chlorinated hydrocarbons water source, the Red Willows in Piestany. Water source yielding 80 l / s was located 350 m from the plant site, there was used organic solvents based on chlorinated hydrocarbons in manufacturing process. Inadequate provision of storage facilities and handling facilities to the leakage of chlorinated hydrocarbons caused degradation of groundwater and soil in the area of this plant site. The pollution spread to an area 4.2 square kilometers with an average depth range of 15 m.

Within the monitoring we analyzed 164 samples, 88 samples in TCE content and content TTCE 47 was equal to or higher than 0.01 ug/l. From the total number of samples the limit value of 0.01 mg/l for drinking water (GR 496/2010) exceeded for TCE 27 samples and for TTCE 3 samples. Repeated analyzes of groundwater samples in the following years confirmed the existing pollution of groundwater and water resource Red Willow was declared unsuitable for public drinking water supply.

The chromatogram of a model sample of water containing chlorinated hydrocarbons represented in **Figure 3** may serve as an example of the determination of trichloroethylene and tertachloroethylene in water frequent contaminants of ground waters. The developed method was used for analytical determination TCE and TTCE in ground waters of accident regions.

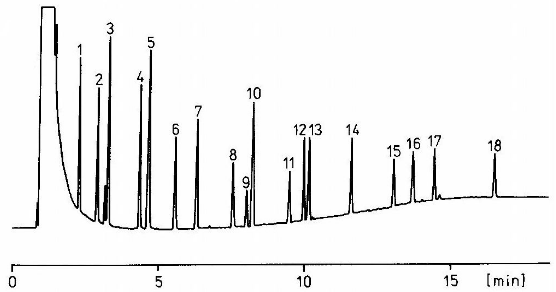

Fig. 3 The gas chromatogram of a model sample of water containing trichloroethylene and tetra-chloroethylene together with aromatic and saturated hydrocarbons

Elution peaks (Fig. 3):
1 - benzene, 2 - octane, 3 – trichloroethylene,
4 - methylbenzene, 5 - tetrachloroethylene,
6 - nonane, 7 - 1-Cl-n-hexane (IS), 8-ethylbenzene,
9 - 1,3-dimethylbenzene, 10 - 1,4-dimethylbenzene,
11-1,2-dimethylbenzene, 12-decane, 13-iso-propylbenzene, 14-n-propylbenzene, 15-sek-buthylbenzene, 16- iso-buthylbenzene, 17- undecane,
18- n-buthylbenzene

Figure 4 shows the gas chromatogram of chlorinated hydrocarbons mixture with identification of individual elution peaks. Identification of components is based on certified standard allowance into n-pentane solvent. For the analysis of chlorinated hydrocarbons in water a microextraction with the following gas capillary chromatography equipped with ECD can be used. ECD detector is more sensitive to amount of chlorine atoms in compound. Therefore, the recoveries of trichloroethylene and tetrachloroethylene (in table 3) are higher when using of ECD detector rather than FID detector.

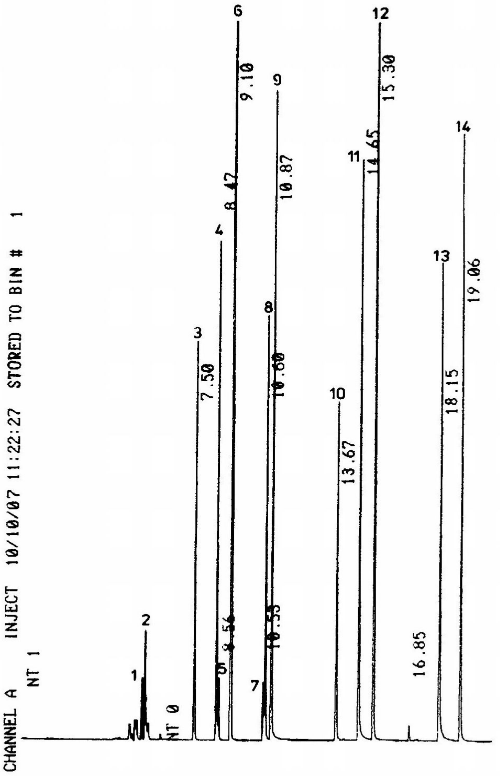

Fig. 4 Gas chromatogram of the model mixture of chlorinated hydrocarbons (concentration of each component of 1 μg) in 0,5 ml of n-pentane before the microextraction

Elution peaks (Fig. 4):
1– 1,1-dichloroethylene, 2– dichloromethane, 3– trichloromethane, 4– 1,1,1-trichlorothane, 5– 1,2-dichloroethane, 6– tetrachloromethane, 7– 1,2-dichloropropane, 8– trichloroethylene, 9–dichlorobromomethane,10–1,1,2-trichloroethane, 11–dibromochloromethane,12– tetrachloroethylene, 13–tribromomethane, 14–1,1,2,2-tetrachloroethane.

4. Conclusions

The above-mentioned considerations indicate that the microextraction methods of trichloroethylene and tetrachloroethylene isolation is very rapid, simple, economically profitable and with low detection limit (0,1 μg/l of water). The recovery of trichloroethylene into n-pentane is above 40% and for tetrachloroethylene it is higher than 85%.
These values are influenced by number of chlorine atoms in molecule and their solubility in water.
The results of this study give provide data important for quantitative analysis of these compounds in water and they can be used for routine quantitative analysis involving microextraction and capillary gas chromatography.

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