ANALYSIS OF CHLORINATED PHENOLS IN WATER

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Abstract: *Glass capillary gas chromatography was used for the examination of solvents (benzene, toluene, dichloromethane, trichloromethane, diethyl ether and ethyl acetate) for the extraction of chlorinated phenols (18 compounds) from water at different pH values (2.0; 4.3 and 7.3). The concentration of the individual chlorophenols in the model sample was 10 μg.l^{-1} of water. The recoveries of the studied compounds were evaluated relative to internal standard (1-Cl-n-octadecane). The highest recoveries were obtained for diethyl ether and ethyl acetate. In this case the recoveries are slight influenced by the change of pH of water. The lowest recoveries were obtained for phenol. Recovery of the other chlorophenols was above 60 %. The results of the recoveries showed that this method is possible to use for routine analysis of chlorophenols in water.*

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

1. Introduction

Phenols are one of the most important and widely found compounds in water. They have an acidic nature and are easily extracted from water, especially from water in plants. Phenols are compounds of a natural as well as an artificial origin, which are extracted with difficulties. Their content decreases, particularly during vegetative periods. They get into water from waste produced by tanneries or woodworking industry.

The need to monitor phenols in water arises because of their toxicity. A few mg.l^{-1} of phenol in industrial wastewater can poison percolating filters with activated cultures. Phenols, which penetrate groundwater through infiltration from various sources, negatively affect the organoleptic properties of water in trace concentrations, especially after chloration [1]. The presence of phenols also increases the effect of polyaromatic hydrocarbons on live organisms and affects biological proportions in rivers [2].

Owing to these facts, the monitoring of phenols in water is important and, at present, attracts attention (phenol and its derivates belong to a class of high priority pollutants).

A photometric method based on the coloured reaction of phenols and 4-aminoantipyrine [3] is used in the determining the presence of phenols in drinking and surface waters. This method is also recommended for the standard methods of water analyses in our country [4]. During its reaction with antipyrine the total phenol content is evaluated, although some substituted phenols in o-, m-, and p-positions (carboxyl, metoxyl, sulfonate or halogenide groups) can react. Other phenols with a substituent in the para position do not react sufficiently. The coloured complex is measured at 460 nm (after extraction using chloroform) or 510 nm (upon direct determination).

A spectrophotometric method with p-nitroaniline [4] is often used.

The constantly expanding spectrum of phenol-like agents in water creates the need to identify its separate components. There are various chromatographic methods, which are suitable for the analyses of trace concentrations of these components. The study [5] provides a survey of chromatographic methods applied in phenol analyses. Considering velocity, sensitivity, effectiveness and multi-component character, various types of gas and liquid chromatography are applied in phenol analyses.

First and foremost, the development of highly effective insulating methods and separating systems is a fundamental step in successful analyses of phenols in water through gas chromatography.

The advantages of direct water dosing into the injector of a gas chromatograph are in the simplicity of the analysis, velocity, quantification and the lack of problems relating to the purification of the solvents and the pretreatment extract. On the other hand, there are problems with the rest of the salts deposited in the injector after the water evaporates, which causes impairment of the column and a low degree of sensitivity.

In the direct injection of water samples, filling columns with a stationary phase or columns filled with rigid sorbent (for example, Tenax GC), which withstand water vapour [6], are applied. In spite of this fact, the process of determining the presence of phenols results in peak tailing and shadow effects. During the application of the stationary phase on Tenax (for example, 5% of OS-138) [7], the suppression of sorptive effects, good peak symmetries, a high response by the FID detector and the sensitivity of the analysis were achieved.

In standard water test methods with the direct injection of a water sample [3] are recommended in analysing phenols in water, the concentration of which exceed 1 $mg.l^{-1}$. This method is recommended in determining phenol, o-, m-, and p-cresol, o-, m-, and p-chlorophenol, 2.3-, 2.4, 2.5, and 3.4-dichlorophenol. Carbowax 20M-TPA in the amount of 20% per Chromosorb W or 5% of FFAP per Chromosorb W are used to fill the chromatographic columns. Since the shadow effect is to be eliminated (false phenol peaks), multiple clean water injection between separate analyses of the water samples is necessary.

Classical separating methods, particularly various types of extractions (for example, extraction by non-ionic sorbents, annexes, thermal desorption or dissolvents), are used in removing phenols from water samples.

The current determination of eleven priority pollutants in waste water (a US EPA method) is based on the application of the acidification of a sample to pH 2, the extraction of dichloromethane (3 x 60 ml), drying by waterless sodium sulfate, devaporation and direct GC determination using FID detection in glass columns with a liquid SE-54 phase or filling columns (1% of SP–1240 DA on Supelcoport). Some interfering components can be removed by water extraction at pH 12, but only at the expense of partial losses of some phenols, mainly 2.4-dimethyl phenol. The limit of this method for detecting phenol ranges from 0.1 $\mu g.l^{-1}$ to 7.4 $\mu g.l^{-1}$ for pentachlorophenol [8].

Phenols, which belong among a class of priority pollutants, may be separated and analyzed in subnanogram amounts on a capillary column coated by SE-30 [9]. For chromatographic identification of separate phenols in complex mixtures, the eluting characteristics of over 50 compounds on a capillary column with Superox 20 M [10] or OV-1701 [11] can be applied.

Phenols can be analyzed by micro-extraction in a glass syringe [12]. A water sample of 20 ml saturated by NaCl (6

mol.l^{-1}) at pH 2 is extracted for 15 minutes by a 0.5 ml mixture of butylacetate and hexanol. As far as phenols, cresols and xylenols are concerned, 90 % - 98 % of the recovery at 5 µg.l^{-1} to 50 µg.l^{-1} of the concentration is achieved.

In the study in [13] chlorophenols were extracted from an acidified water sample (0.5 mol.l^{-1} of H_2SO_4) at pH 5 using three doses of toluene (50, 25, 25 ml) in a separating funnel. After thickening in a revolving vacuum evaporator, the mixed toluene extracts were analyzed through gas chromatography directly or after derivatization.

In the study in [14] the recovery of 25 alkylphenols through extraction by various solvents (pentane, tetrachloromethane, trichloromethane, dichloromethane, benzene, diethyl ether) was observed. The extracts were analyzed directly by capillary GC using FID detection. A glass capillary column (50 m x 0.25 mm) with tri-2,4-xylenyl phosphate liquid stationary phase were used in separating the individual components.

The results indicated that the increase in dissolvent polarity resulted in an increase in the recovery of extracted alkylphenol. The best results were achieved by using diethyl ether, and the lowest for phenol and its lower alkyl derivates.

In paper [15] were achieved the similar results at the extraction of chlorinated phenols by using diethyl ether.

Analysis acidified fraction after extracting samples of priority pollutants is describe in paper [16]. A water sample of pH 11 was extracted using dichloromethane, and the neutral and basic fractions were separated. After pH treatment to the value of 2, an acidic fracture, containing phenol, 2,4-dimethyl phenol, chlorine and phenol nitroderivates, was separated.

The study in [17] deals with the extraction of phenols by means of the continual distillation using water vapor or extraction. If a sample is acidified to pH 1 and salt displacement by NaCl is used, this distillation method achieves about 10 % effectiveness from 0.1 to 30 mg.l^{-1}. The whole system reaches a stable state after two hours. The phenols are extracted in a small amount of diethyl ether so another thickening for chromatographic determination is not necessary. In this method the double separation of phenols from water, extraction and distillation are applied. The limit of determination in splitless injection and using capillary columns is about 10 µg.l^{-1}.

In GC analyses of phenols and chlorinated phenols, enrichment by distillation methods is often used. Even very simple distillation by means of common laboratory devices is an efficient technique in the treatment of phenols and chlorinated phenols. For example, in study [18], 50 ml of a water sample were distilled at the same time with NaCl until a saturated solution was created. After distilling the first 5 ml of water, the recovery of phenols exceeding 80% were identified. There was 1 mg.l^{-1} of concentrated phenol in the water sample.

Distillation methods are applied when a spectrophotometric terminal is used for determining. Recently, the most common method has been the extraction by diethyl ether or dichloromethane from an acidified solution.

In the study in [19] sorption in a macroporous polymer sorbent Separon SE combined with thermal desorption were applied.

Likewise in study [20] its authors used Amberlit XAD and activated carbon to achieve a recovery exceeding 83% for 17 phenolic compounds to separate the phenols from the water.

The above stated Amberlit XAD 2 and XAD 4 macroreticular styrene divinyl-benzene copolymers were used to separate various model samples of organic additives, including phenols, from drinking and waste water [21]. After the expulsion

of the absorbed substances by diethyl ether and the drying and evaporation of part of the diethyl ether, the extract was injected into a gas chromatograph. The recovery of phenols (after pH treatment) exceeded 80 %.

Phenols and chlorine phenols can be analyzed without the treatment of a sample or through derivatization, as a result of which molecular polarity and the boiling temperature increase and the parameters of gas-chromatographic separation (peak tailing, creation of hydrogen bridges, detection sensitivity) and also the separation and concentration of these substances from water improve [5, 22].

One of the methods for increasing the sensitivity of the ECD detector is the direct bromation of phenols in a water sample, the extraction of tribromine phenols and a chromatographic analysis using ECD [23]. A water sample of 300 ml is acted upon by an acidified solution of potassium bromide (10 $g.l^{-1}$) for 10 minutes. After removing the excess bromine by sodium thio-sulphate, the water is extracted from 10 ml of hexane, the hexane layer is dried using 2 g of waterless sodium sulfate, and the hexane extract is analyzed by gas chromatography with ECD. The injection of 5 µl (without thickening the extract), the detection limit for the phenol is 0.1 $\mu g.l^{-1}$.

Phenols and chlorine phenols can be derivated directly in an alkaline water solution. Acetyl phenols or acetyl-chlorinated phenols are created during acetylation. The acetyl derivates obtained are extracted from the water more easily than from the original substances.

The study in [24, 25] describes a method, according to which 10 g of $NaHCO_3$ and 0.5 ml of acetanhydride are added to 250 ml of water. The solution is shaken until the carbon dioxide starts to escape. Then the created acetates are separated from the water through extraction by dichloro-methane (10 to 30 ml of CH_2Cl_2 two or three times) [24, 25] or through sorption on Chromosorb 102 polymer sorbent with the following elution using carbon disulfide [26] or sorption on modified silicagel C_{18} and elution using benzene [25].

Such methods are used deriving phenol, according to which the deriving reaction is carried out after the extraction and concentration of the phenols from the water into the extract. For example, [28] states that 3 ml of potassium carbonate solution (0.1 $mol.l^{-1}$), 1 ml benzene or hexane and 50 µl acetanhydride are added to an organic extract in a test tube. After shaking, the phenols turn into acetates, and the derivates are converted to an organic phase. In the case of chlorinated phenols, chromatographic analysis of the extract is carried out by means of ECD. There are numerous variations of this method [30], and the recovery of chlorine phenol acetylation and its subsequent extraction exceeds 90%.

With the exception of acetylation, the derivation of phenols and chlorinated phenols during routine analyses to ethers by means of pentafluoro benzyl bromide is recommended. The derivate obtained can be effectively analyzed by an electron capture detector. The derivation is carried out so that 100 µl of a 10% solution of sodium carbonate and 100 µl of 5% pentafluoro benzyl bromide in acetone are added to 8 ml of an acetone solution of phenols. The reactive mixture in a corked test tube is heated to 60°C for an hour. When the reaction is complete, the mixture is evaporated to 0.5 ml, 3 ml of hexane are added, and the mixture is evaporated to 0.5 ml again. After clarifying the reaction mixture in the column using silicagel or fluorisil (chlorphenol derivates eluate in the first 8 ml of the toluene-hexane mobile phase in a proportion of 25:75), the solution is injected into a chromatographic column. Chlorine phenols (22 derivates) were determined by such a method [29].

A similar method of derivation is also stated in a standard method [30], which is,

except for phenols and chlorine phenols, focused on the determination of nitrophenols, too.
The experimental part of this study involves the results of the observation of the recovery of sixteen chlorinated phenols by micro-extraction of water in benzene, toluene, chlorophorm, dichlorine methane, diethyl ether and ethyl acetate.

2. Experimental

2.1 Instrumentation

The analysis was performed with the Carlo Erba (VEGA 6000) gas chromatograph (modified for usage with capillary columns) equipped with a flame ionization detector (FID) and split/ splitless capillary injector. The chromatograph was fitted with glass capillary column (50 m x 0.25 mm i.d.) coated with tri-2,4-xylenyl phosphate liquid stationary phase. The gas chromatographic conditions were as follows: the column temperature during injection 160 ^{o}C, than programmed linearly at 3 ^{o}C/min to a final temperature of 220 ^{o}C. The injection port and detector temperature were 225 ^{o}C, carrier gas hydrogen, 1.5 µl samples were injected using split/splitless. Chromatograms were integrated with HP 3392A (Hewlett-Packard) integrator.

2.2 Reagents and Solutions

The chlorinated phenols examined were obtained from different manufactures and were generally of 98 % purity. Standard mixture of this compounds were diluted in acetone (concentration of each component of 1 mg.ml^{-1}).
The purity of the internal standard (1-Cl-n-dodecane) was 99% (Supelco, Bellefonte, Pa., USA).
The extraction solvents (benzene, toluene, dichloromethane, trichloromethane, diethyl ether and ethyl acetate) were highly purified and checked chromatographically.

2.3 Microextraction

For the microextraction a simple glass extraction (volumetric) flask (1) equipped with the conical stopper (5) was used. For n-pentane and toluene separation a separator of the thin solvent layer (2) was connected to the flask, and through the side arm, 3, pure water is added until the solvent is transferred into the dry capillary, 4, to the height required. (**Fig. 1**) [31].

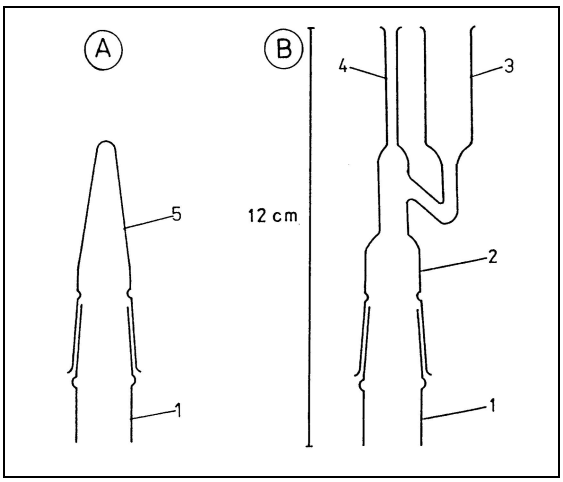

Figure 1

A: The glass extraction (volumetric) flask, equipped with a male joint (1) and conical stopper (5), prepared to microextraction.
B: The solvent thin layer separator (2) containing side arm for water (3), capillary for extract (4) connected to the flask (1) after extraction.

If dichloromethane and chloroform is used as solvent (as a heavier liquid than water) conical stopper was used for trapping the solvent (up side down). The water layer over the solvent one prevents its evaporation (or some volatile components). The extracts are easily accessible and can be injected immediately by means of a syringe into a gas chromatograph for both cases.
Model water samples of 0.1 litre with known contents of studied chlorophenols were acidified to pH 4.3 or 2 with concentrated hydrochloric acid, cooled to 5 ^{o}C, extracted in the presence of internal standard (1-Cl-n-dodecane) by vigorous mechanical shaking for 5 minutes and

allowed to stand until the layer separator. The volumes of the organic phase added (depending on solubility) were 0,1 ml of toluene, 0,3 ml of benzene, 0,6 ml of chloroform, 2 ml of dichloromethane, 10 ml of diethyl ether and ethyl acetate. For extraction glass extraction flask equipped with the conical stopper was used. For separation of solvent (as a lighter liquid than water) a separator of the thin solvent layer was used.

The extracts were injected directly by capillary gas chromatography.

3. Results and discussion

Figure 2 shows a chromatogram of a chloroform extract of the model water sample. The concentration of the individual chlorophenols in the model samples was 10 $\mu g.l^{-1}$ of water. The extraction recoveries relative to 1-Cl-n-octadecane (recovery = 100 %) are shown in Table 1 – 3 (the values represent arithmetic means of tree measurements).

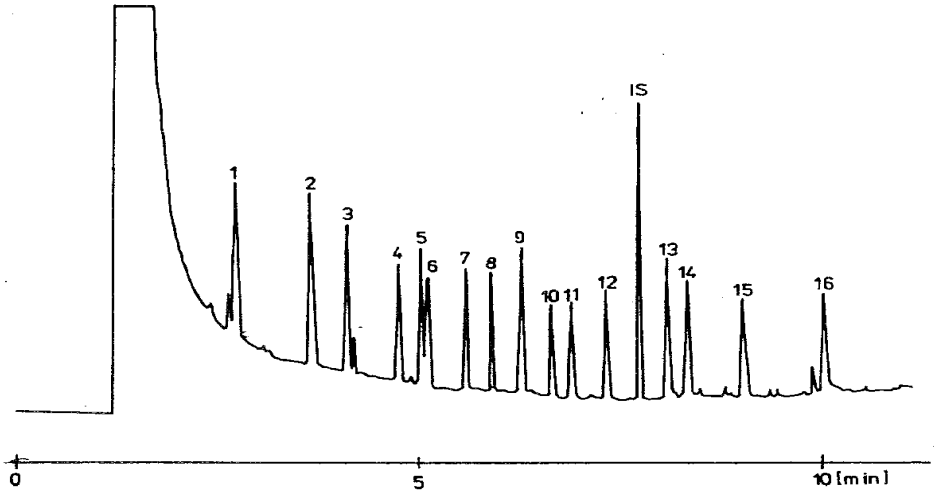

Figure 2. Chromatogram of model mixture of this chlorinated phenols (at concentration of each component of 10 $\mu g.l^{-1}$ of water) in chloroform before extraction. For identification of peaks, see Table 1-3. IS = 1-Cl-n-octadecane.

Table 1

Extraction recoveries of chlorophenols from water (at pH 2) relative to 1-Cl-n-octadecane

Peak No.	Compound	Recovery (%)					
		C_6H_6	C_7H_8	$CHCl_3$	CH_2Cl_2	$C_4H_{10}O$	$C_4H_8O_2$
1	2-chlor	2.2	0	1.8	19.6	59.3	76.2
2	phenol	0	0	0	2.5	33.2	49.0
3	2,6-dichloro	16.7	6.3	21.1	63.2	93.6	96.7
4	hexachlorobenzene	85.4	98.0	94.6	98.2	97.8	98.5
A	2,5-dichloro	13.2	8.5	18.3	46.4	91.7	92.8
5	2,4-dichloro	11.6	4.6	16.7	47.4	89.1	91.3

6	2,3-dichloro	11.7	4.6	15.7	51.6	90.8	92.6
7	2,4,6-trichloro	50.3	30.7	55.9	88.7	97.6	95.0
8	2,3,6-trichloro	51.2	27.2	53.0	91.3	98.1	95.9
9	3-chlor	1.8	2.9	0.9	8.3	83.6	90.5
10	2,3,5-trichloro	42.1	29.1	49.0	72.6	96.5	95.0
B	2,3,4-trichloro	44.4	35.4	42.7	75.0	92.9	93.8
11	2,4,5-trichloro	37.0	25.8	41.1	74.1	90.3	94.5
12	2,3,5,6-tetrachloro	84.8	74.6	87.6	82.5	92.6	93.2
13	3,5-dichloro	7.3	6.1	5.4	28.3	83.6	85.6
14	3,4-dichloro	5.7	6.8	4.8	32.7	82.9	83.7
15	pentachloro	92.4	96.0	90.5	98.8	91.6	85.5
16	3,4,5-trichloro	26.8	18.5	21.7	61.0	83.0	79.8

Table 2

Extraction recoveries of chlorophenols from water (pH 4.3) relative to 1-Cl-n-octadecane

Peak No.	Compound	Recovery (%)					
		C_6H_6	C_7H_8	$CHCl_3$	CH_2Cl_2	$C_4H_{10}O$	$C_4H_8O_2$
1	2-chlor	2.3	0	2.0	15.5	61.0	69.6
2	phenol	0	0	0	1.8	30.2	44.4
3	2,6-dichloro	17.8	6.5	21.2	50.1	87.7	93.0
4	hexachlorobenzene	86.4	96.1	93.5	92.3	94.4	95.6
A	2,5-dichloro	13.9	9.3	15.8	33.4	85.5	91.0
5	2,4-dichloro	12.4	5.2	13.4	38.7	86.2	85.1
6	2,3-dichloro	12.4	4.9	13.0	42.4	84.5	87.3
7	2,4,6-trichloro	57.0	33.9	51.1	73.4	95.9	92.8
8	2,3,6-trichloro	56.6	29.8	51.7	84.1	94. 8	92.4
9	3-chlor	1.4	3.7	1.2	6.5	80.8	86.4
10	2,3,5-trichloro	48.5	36.1	45.5	65.2	86.9	91.3
B	2,3,4-trichloro	49.8	28.8	40.3	64.1	85.3	90.0
11	2,4,5-trichloro	41.1	30.0	41.6	67.0	81.4	93.6
12	2,3,5,6-tetrachloro	89.6	73.9	88.7	79.3	87.0	90.4
13	3,5-dichloro	7.8	4.8	4.9	27.0	80.6	83.0
14	3,4-dichloro	6.0	5.6	4.5	27.5	81.1	81.9
15	pentachloro	93.7	96.7	91.2	93.4	90.3	84.5
16	3,4,5-trichloro	31.3	20.1	22.3	44.5	81.4	78.5

Table 3

Extraction recoveries of chlorophenols from water (pH 7.3) relative to 1-Cl-n-octadecane

Peak No.	Compound	Recovery (%)					
		C_6H_6	C_7H_8	$CHCl_3$	CH_2Cl_2	$C_4H_{10}O$	$C_4H_8O_2$
1	2-chlor	2.0	0	1.2	13.3	51.8	61.1
2	phenol	0	0	0	1.8	30.1	35.6
3	2,6-dichloro	0	0	3.6	23.6	84.3	80.0
4	hexachlorobenzene	98.3	96.7	94.2	94.6	98.8	96.9
A	2,5-dichloro	6.5	7.6	4.5	25.9	79.3	82.8
5	2,4-dichloro	6.8	3.9	4.4	29.1	78.0	79.6
6	2,3-dichloro	5.6	2.7	5.2	31.5	78.6	80.4
7	2,4,6-trichloro	2.8	8.6	3.7	28.2	84.9	83.5
8	2,3,6-trichloro	3.1	7.2	3.5	34.7	86.1	84.3
9	3-chlor	1.0	1.0	0.4	6.8	72.2	70.9
10	2,3,5-trichloro	6.8	8.8	5.7	30.9	87.0	84.9
B	2,3,4-trichloro	6.6	8.2	6.3	35.8	83.1	87.3
11	2,4,5-trichloro	7.9	9.1	7.4	30.8	82.3	88.7
12	2,3,5,6-tetrachloro	1.9	6.3	6.7	37.1	85.6	85.9
13	3,5-dichloro	4.7	3.8	4.2	22.9	76.3	76.4
14	3,4-dichloro	4.8	6.0	6.3	27.3	75.8	75.8
15	pentachloro	5.3	7.2	13.9	39.8	86.7	76.6
16	3,4,5-trichloro	4.6	10.9	7.1	21.8	79.8	73.0

The influence by the change of pH value of water (pH 2.0, 4.3 and 7.3) on the recoveries chlorinated phenols from water is shown in **Fig. 3-8**.

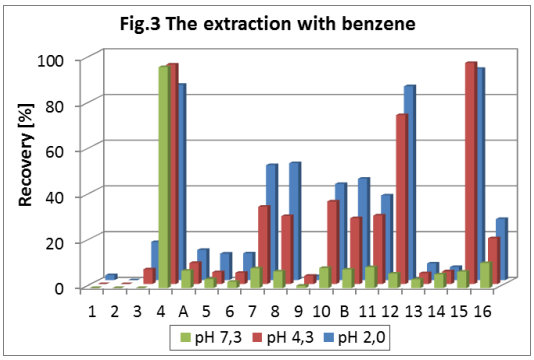

Figure 3. The extraction with benzene

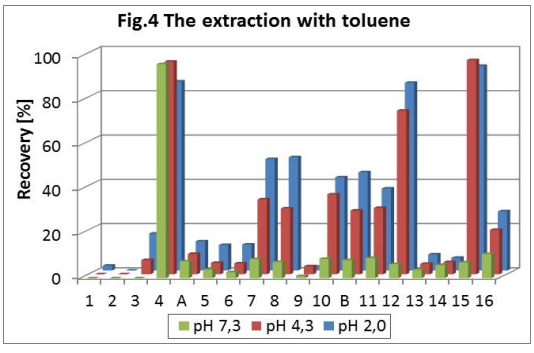

Figure 4. The extraction with toluene

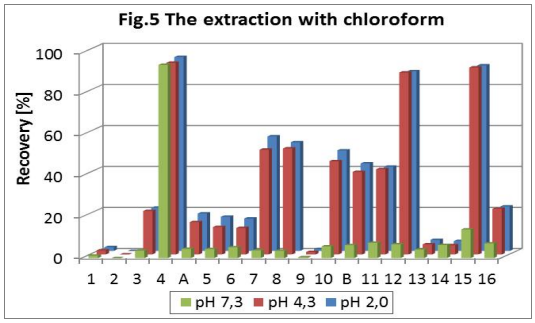

Figure 5. The extraction with chloroform

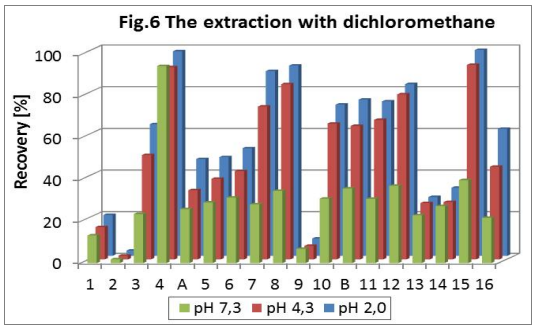

Figure 6. The extraction with dichloromethane

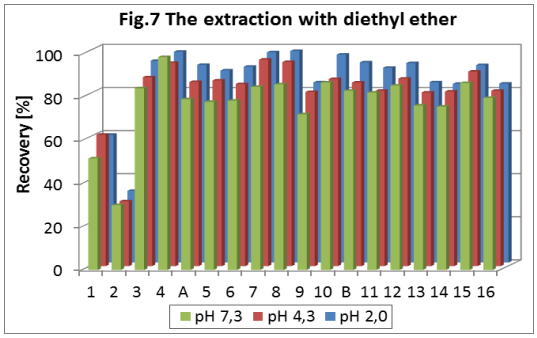

Figure 7. The extraction with diethyl ether

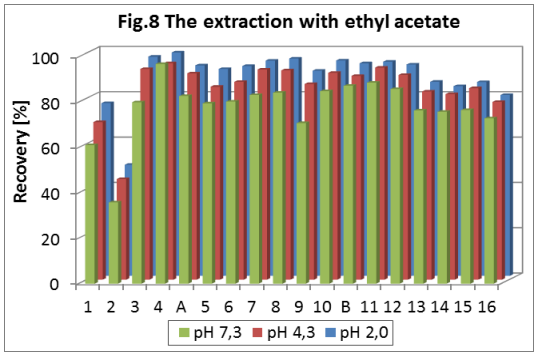

Figure 8. The extraction with ethyl acetate

Table 1-3 shows that with increasing solvent polarity the extraction recoveries of chlorinated phenols increase, particularly with phenol and its lower chlorine derivatives. The recoveries of chlorinated phenols are influenced by the structure of the phenol, the length of the alkyl chain and the number of chlorine on the ring. The lowest recovery was given by phenol itself, at it shows the highest solvation of the phenols studied. On the other hand, the best recovery was obtained for pentachloro-phenols and hexachloro-benzene.

The highest recovery was given by diethyl ether and ethyl acetate (recovery was above 60 %), which are thus the most suitable solvent, especially when the determination of phenol and its lower chlorine derivatives is required. They are readily available, volatile, but often require additional purification. Disadvantage of this solvents are as follows: its water solubility, and its therefore not recommended for micro-extraction.

The recoveries chlorinated phenols with diethyl ether and ethyl acetate are slight influenced by the change of pH value of water. The best results are given by acidified water samples (at pH value 2). In the case the next solvents, pH value of water has effect on the recoveries chlorinated phenols.

Table 1 may be useful for selecting extractants for the isolation of microgram amount of organic substances from water when the determination of chlorinated phenols is required. For instance, for the extraction of higher chlorinated phenols from water it is possible to use a less polar solvent (dichlormethane, toluene).

The results of the recoveries showed that this method is possible to use for routine analysis of chlorinated phenols in water.

4. Conclusions

It result from the above considerations that the microextraction method of chlorinated phenols isolation is very rapid, simple, and economically profitable. The

results of this study give data important for analysis of these compounds in waters which may be used for their routine quantitative analysis involving micro-extraction and capillary gas chromatography.

The recovery of sixteen chlorinated phenols from water (at different pH of water) in benzene, toluene, chloroform, dichloromethane, diethyl ether and ethyl acetate was determined. The recoveries of the studied compounds were evaluated relative to internal standard. The highest recoveries were obtained for diethyl ether and ethyl acetate. In this case the recoveries are slight influenced by the change of pH of water. The lowest recoveries were obtained for phenol. Recovery of the other chlorinated phenols was above 60 %.

5. References

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