

Short communication

Comparison of three derivatization ways in the separation of phenol and hydroquinone from water samples

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Abstract

Hydroquinone and phenol were analysed in aqueous alkaline model samples using chromatographic techniques. The compounds were isolated by solid-phase extraction and determined quantitatively by capillary gas chromatography after derivatization. The effectivity of derivatization was tested in three phases of sample handling: (i) before extraction; (ii) in the extraction bed; and (iii) during elution.

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1. Introduction

Phenols are important starting- and by-products of various industrial processes [1]. Consequently, they are constituents of industrial wastewaters, which are hazardous, e.g. to aquatic life [2].

Phenols caused serious problems in the environmental protection because of their good solubility in water, high reactivity, and poor biodegradation. One of the methods used in the removal or neutralization of phenol in water is its oxidation [3], and phenol can be oxidised in the environment as well. The final oxidation products of phenol are carbon dioxide and water but often the oxidation process does not lead to the final products and some by-products can remain in the environment.

In the first oxidation step, phenol (C_6H_5OH) may be transformed to 1,4-hydroquinone ($C_6H_4(OH)_2$), which is further oxidised to 1,4-benzoquinone ($C_6H_4O_2$) [4].

In this work, we examined the products of the first oxidation step and the possibility of the determination of phenol and hydroquinone in water samples. The oxidation process

starts easier if phenol is present in its dissociated form. It is known from literature that the equilibrium between dissociated and non-dissociated phenol is a function of pH. In basic pH ($pH > 12$), the content of dissociated phenol is close to 100%. Some authors [5] state that under alkaline conditions, phenol can be oxidised into quinones at room temperature.

Solid-phase extraction (SPE) is very often used in the sample preparation step of the chromatographic analysis of phenols [6–24]. The extraction on solid phase is useful for the isolation, concentration, and purification of the analytes.

There are several difficulties in the analysis of phenols by using chromatographic methods: phenols' properties (especially their polarity) cause problems during their isolation from the matrix (water, ground, urine, food) as well as determination in the chromatographic column.

This is true also for the various chromatographic techniques (GC, HPLC, and TLC), which are used in the analytical step of phenols' determination. In GC, phenols tend to give broad, tailed peaks, leading to relatively low efficiency of chromatographic columns. Therefore, derivatization of phenols, transformation to less polar compounds, is required [25]. Derivatization can be carried out before extraction in the matrix (for example, in the water sample). The derivatives are subsequently isolated from the sample solution [1,25,26,32,33].

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The derivatization can also be carried out after extraction of compounds before GC analysis. In such a case, derivatization is performed in the eluate [33]. A different way of derivatization can be realised on the sorbent bed, after sorption of the analytes. The derivatization agent is retained on the solid phase before or after retention of analytes. Then, derivatives are eluted after their formation in the SPE bed. This kind of derivatization is called solid phase analytical derivatization (SPAD). It is useful for the analysis of polar compounds such as alcohols, phenols, carboxylic acids, and carbonyls [26,32,33].¹

There are many derivatization methods: esterification, acylation, silylation, alkylation, and others [24,28,32,33]. However, phenols' acetylation seems to be the most appropriate derivatisation method [1,25,26,29,30,31].

The aim of our research was to propose the most sufficient analytical procedure for determination of phenol and hydroquinone in water samples using chromatographic methods. We worked with model mixtures.

2. Experimental

2.1. Chemicals

Samples were obtained: hydroquinone (pure for analysis) from Aldrich (Steinheim, Germany), organic solvents: methanol, dichloromethane, trichloromethane, acetonitrile (p.a.) from Merck (Darmstadt, Germany), ethyl acetate (p.a.) from Chempur[®] (Piekary Śląskie, Poland), acetic anhydride and potassium carbonate (p.a.) from POCh (Gliwice, Poland); phenol (p.a.) from Sigma–Aldrich (Steinheim, Germany).

2.2. Derivatization procedures

We have used and examined three ways of derivatization and compared their efficiency:

1. Derivatization during elution from SPE sorbents (C8, CN, Ph, SDB-1): pure derivatization agent was used as eluent, 2 ml and 5 ml of acetic anhydride was used;
2. Derivatization on SPE sorbents: compounds were isolated from water solution onto the sorbent (C8, CN, Ph, SDB-1), then the sorbent was dried, and then 1 ml of acetic anhydride as derivatization agent was added and derivatives were eluted with dichloromethane (3 ml or 5 ml);
3. Derivatization in water sample: compounds were dissolved in 50 ml of water, then 0.5 g of potassium carbonate (pH 11), and afterwards, 1 cm³ of acetic anhydride was

added to the water sample and then the acetates were extracted with SPE on C8, CN, Ph, SDB-1 sorbents. Finally, they were eluted with different solvents: dichloromethane, trichloromethane, acetonitrile, and ethyl acetate (3 ml or 5 ml).

We worked under alkaline conditions because then phenol and hydroquinone are present in their dissociated forms, and the acetylation process is easier and faster than under neutral conditions.

The concentration of examined compounds in water (in all samples) was equal to 0.1 g/l, the model water samples contained individual compounds (hydroquinone or phenol) or these two compounds together, the volume of extracted solution was 50 ml, the volumes of eluents were 2 ml or 5 ml when the derivatization agent served as eluent, and 3 ml or 5 ml for other solvents.

2.3. Solid-phase extraction

We have used various sorbents (in normal-phase and reversed-phase systems) and various solvents to choose the best arrangement for the analysis of phenol and hydroquinone.

All sorbents were placed in polypropylene cartridges, produced by J.T. Baker (Deventer, Holland, supplied by Witko, Łódź, Poland). C8 sorbent–silica bonded with octadecyl (reversed-phase), cartridge volume: 6 ml, sorbent mass: 500 mg; CN sorbent–silica bonded with cyanopropyl (normal-phase), cartridge volume: 6 ml, sorbent mass: 500 mg; Ph sorbent–silica bonded with phenyl (normal-phase), cartridge volume: 3 ml, sorbent mass: 200 mg; SDB-1 sorbent–copolymer polystyrene-divinylbenzene (normal-phase), cartridge volume: 6 ml, sorbent mass: 200 mg.

Methanol and water were used as the conditioning solvents in each extraction.

2.4. GC analysis

GC analyses were made on a HP 5890II gas chromatograph (supplied by Hewlett Packard–Poland, Warsaw, Poland) on capillary column dimethyl-diphenyl polysiloxane with a film thickness of 0.25 μm, 30 m × 0.28 mm i.d. MXT-5 (Resteck, supplied by AnaSerwis, Baranowo, Poland). Helium was used as the carrier gas at a flow-rate of 2.5 ml/min and a head pressure of 90 kPa. The column temperature was held at 120 °C for 1 min, then ramped at 10 °C/min to 125 °C, then at 25 °C/min to 250 °C where it was held for 2 min. For the analysis of phenol acetates, the initial temperature was 100 °C.

3. Results and discussion

Recovery in different extraction systems as well as the efficiency of derivatization methods show considerable vari-

¹ Nawrocki et al. [27] extracted aldehydes from water samples with C18 SPE sorbents impregnated with derivatization agent *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBOA), and the derivatization process occurred in the sorbent. Oximes (derivatives of aldehydes) were eluted from SPE bed with *n*-hexane. Derivatization on solid supports was also described by Molins-Legua et al. [33].

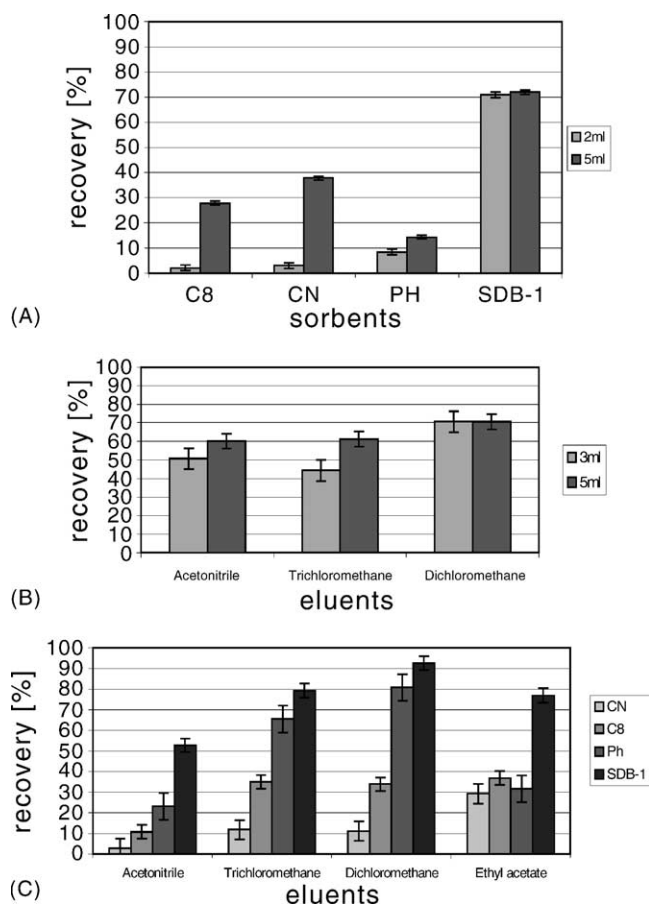


Fig. 1. The recovery of hydroquinone in SPE. (A) First kind of derivatization, different SPE sorbents, two eluent's volumes; (B) third kind of derivatization, SDB-1 sorbent, different eluents, two eluents' volumes; (C) third kind of derivatization, different sorbent/eluent systems (the volume of eluents: 3 ml).

ation. The best recovery was achieved on SDB-1 sorbent (approximately 70%) for both eluent's volumes (2 ml and 5 ml) when using *the first way of derivatization* (Fig. 1A). The recovery is lower than 40% when other, i.e. silica sorbents were used. The volume of 2 ml of acetic anhydride is too low to complete elution of analyte from silica sorbents. The recovery increased when 5 ml of eluent was used, but was not exceeding 38% (for CN sorbent). The recovery for extraction on SDB-1 sorbent increased to approximately 70%, and it is similar both for 2 ml and 5 ml of eluent.

Very similar relationships between the recovery and the kind of sorbent were achieved in *the second way of derivatization* (Table 1). Recoveries for silica sorbents were very

Table 1
The recovery of hydroquinone on different sorbents, second derivatization method, and dichloromethane as eluent

Sorbent	C8	CN	Ph	SDB-1
\bar{X} [%]	1.40	2.00	6.80	74.3
s	0.46	0.65	1.70	4.40
S_x	0.19	0.27	0.70	1.80

s , standard deviation; S_x , precision; $\alpha = 0.05$.

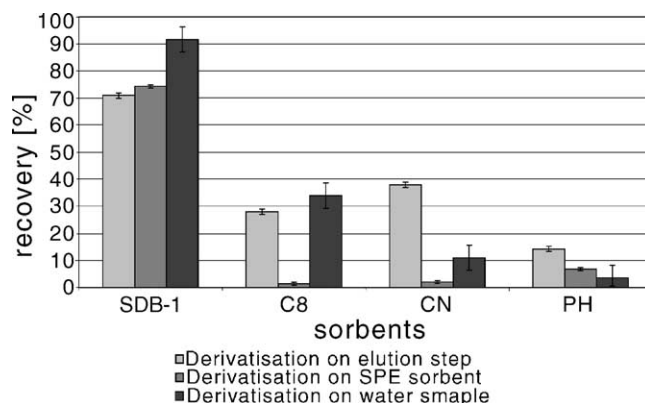


Fig. 2. Comparison of the efficiency of three kinds of derivatization of hydroquinone.

low, near 7% for Ph sorbent, while those for polymeric sorbent (SDB-1) exceeded 70%.

Values of recovery for *the third way of derivatization* (Fig. 1C) are highest when the polymeric sorbent was used for the extraction of acetyl derivatives. The level of recovery is also influenced by the use of solvent in the SPE step. The lowest recovery was achieved for acetonitrile and all examined sorbents (highest values for SDB-1 sorbent were close to 50%). Chloromethanes (dichloromethane and trichloromethane) seem to be most efficient eluents. However, for extraction from the CN sorbent, the use of ethyl acetate gave the best result, but the recovery was not higher than 30%. We found that the use of SDB-1 sorbent and dichloromethane as eluent was most effective sorbent/eluent system. It allowed to achieve a recovery close to 90%.

For SDB-1, the influence of eluent's volume for different eluents was examined (Fig. 1B). The increase of eluent's volume caused increase of recovery for acetonitrile and trichloromethane, i.e. a volume of 3 ml is too low to elute all derivatives completely. This effect was not observed for dichloromethane (values of recovery were similar for 3 ml and 5 ml) what means that here a volume of 3 ml is sufficient.

Regardless of the kind of derivatization, the best results (highest recovery) were achieved on polymeric sorbents with dichloromethane as eluent. Values of recovery on SDB-1 sorbent in different derivatization methods are compared in Fig. 2. In the second and third derivatization methods, dichloromethane was used as eluent. The recovery achieved with *the third way of derivatization* was nearly 20% higher than for other derivatization procedures. It means that the third procedure is the most effective method of derivatization (in water samples).

In summary, the best results for the extraction of hydroquinone from water samples were achieved when derivatization in water sample before the extraction, a polymeric sorbent (SDB-1) and dichloromethane (3 ml) as eluent were selected. *The third way of derivatization* yielded the highest recovery; the isolated acetates gave narrow, non-tailing peaks on GC chromatograms. The reaction of acetylation proceeds

well under alkaline conditions, and that appropriate basic pH was achieved by using potassium carbonate.

Similar experiments were carried out for phenol. Due to similarity of their structure, we chose *the third way of derivatization* also for phenol. Phenol acetates were extracted from the water sample on SDB-1 sorbent and further eluted by using different solvents. Results of earlier experiments induced us to select the same sorbent/eluent system as for hydroquinone. The highest recovery (90%) was achieved when the volume of eluent (dichloromethane) was equal to 5 ml.

We examined also the determination of phenol and hydroquinone dissolved together into the same water sample. In this case, the third kind of derivatization was used and SDB-1 sorbent and dichloromethane (5 ml) were used as extraction system. The recovery of these compounds was 98.4% ($s = 3.8$) for phenol and 54.4% ($s = 1.9$) for hydroquinone.

The LOD and LOQ values for this analytical method were calculated. For hydroquinone determination, LOD = 0.86 μg and LOQ = 1.28 μg . For phenol determination, LOD = 0.14 μg and LOQ = 0.21 μg .

4. Conclusion

Application of SPE–GC procedures allow the analysis of aqueous model samples containing phenol and hydroquinone. The derivatization of these species, necessary before GC analysis, can effectively be accomplished directly in the alkaline water solutions. The derivatives (acetates) are most satisfactorily extracted on polymeric SPE sorbents (SDB-1) and afterwards eluted therefrom with dichloromethane.

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