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Evaluation of solid-phase extraction sorbent with ketoimine groups for the preconcentration of benzene and phenolic compounds in water

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The applicability of silica gel, modified with ketoimine groups, to solid phase extraction (SPE) was tested. Basic characteristics of the modified silica were determined using elemental analysis, and ²⁹Si CP MAS NMR spectroscopy, as well as measurement of specific surface area.

Some applications of the sorbent studied to preconcentration and further determination of organic compounds, such as benzene, phenol, and o-chlorophenol, by means of solid-phase extraction (SPE) and gas chromatography are presented. The determined recovery rates were about 95%-98%.

Key Words: Modified silica, solid-phase extraction SPE, sorbents, hydrocarbon analysis.

Introduction

Many organic pollutants, such as phenol, o-chlorophenol, and benzene, are present in the environment in trace amounts. Due to their high toxicity¹ and capability of accumulating in the environment, these pollutants are hazardous to living organisms.² Due to their toxicity, persistence, and unpleasant organoleptic properties, both the US Environmental Protection Agency (EPA) and the European Union (EU) have classified several phenols and chlorophenols as priority pollutants.^{3,4}

Phenol is a pollutant widely occurring in surface waters, in which it originates mainly from sewage effluents of chemical, pharmaceutical, and dye industries.⁵ Phenol derivatives,^{5,6} including chlorophenols, show genotoxic, mutagenic, and carcinogenic properties,⁷ and are characterized by high stability.⁸

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Benzene can naturally occur in crude oil; therefore it can be found in refinery products.^{9,10} Since it has been classified as a first class carcinogenic factor,¹¹ targeting bone marrow, more and more limits are being placed on its use.

The above-mentioned pollutants are commonly present in surface waters. Since surface waters, after their treatment, are used by humans and in animal breeding,¹² it is necessary to control the levels of organic pollutants,⁷ particularly those that are present in trace amounts and show toxic and carcinogenic activities. Therefore, research on efficient methods for purification and preconcentration of analytes before their determination by means of an appropriate analytical technique is of great importance.¹³

Among the many techniques developed for the isolation and preconcentration of different organic compounds⁸ and metal ions, solid phase extraction (SPE) is the most frequently used.^{14–17} The extraction process to the solid phase is based on the retention of an analyte on a sorbent.^{18–20} Originally, the SPE application area was usually restricted to preconcentration of analytes showing strongly hydrophobic properties, whereas the recovery rates for polar compounds were not satisfactory.²¹ In our previous papers, a successful application of silica modified with ketoimine to the determination of trace amounts of bisphenol-A (BPA) in mineral water and powdered milk samples was reported.^{22,23} We also studied the packing of ketoimine groups bonded with complexes of transition metals.²⁴

The present study was devoted to the application of silica sorbents modified by ketoimine groups to the preconcentration of aromatic compounds of different nature, i.e. polar ones, such as phenol and o-chlorophenol, and non-polar ones, such as benzene. The main goal of the paper is to propose a new, efficient method for the analysis of water samples containing trace amounts of aromatic compounds, generic enough to be applied for both the compounds of hydrophobic and polar nature. The proposed method was used in real environmental analysis, namely for analyzing surface waters (lake water).

Experimental

Apparatus

- Elemental analysis was performed on a 2400 CHN Elemental Analyzer (Perkin-Elmer, Norwalk, CT, USA).
- ²⁹Si CP MAS NMR spectra of solid phases were obtained using a spectrometer 300 MSL (Bruker, Rhenstetten, Germany).
- Specific surface areas were measured using the Brunauer, Emmett, Teller (BET) method on an ASAP 2010 sorptometer (Micromeritics, GA, USA).
- Gas chromatograph CP-3380 (Varian, CA, USA) equipped with a flame ionization detector (FID) and a DB-WAX (30 m × 0.251 mm × 0.25 μm) capillary column was used in the study. A Bakerbond SPE vacuum manifold was used for the elution of SPE columns.
- Water was purified in a Milli-Q apparatus (Millipore S.A., 67120 Molsheim, France).

Chemicals and materials

Silica gel (Baker Analyzed[®]) was purchased from J.T. Baker Inc, and 3-pentane-2,4-dione derivatives, used for the modification of silica surface, were obtained from the Department of Organometallic Chemistry, Adam Mickiewicz University, Pozna, Poland. Solvents used for modification reactions (xylene and hexane - analytical grade) were purchased either from POCh (Gliwice, Poland), or Fluka (Buchs, Switzerland). Phenol, o-chlorophenol, and benzene were obtained from Fluka (Buchs, Switzerland). All standard stock solutions were prepared in methanol and used after appropriate dilution with the same solvent.

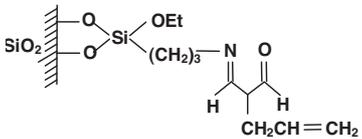
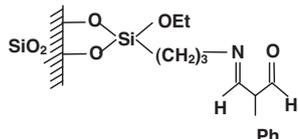
Modification procedure

Five grams of dry silica was immersed in a mixture of anhydrous xylene and 3-aminopropyltriethoxysilane. The mixture was boiled for 12 h in a vessel equipped with a reflux condenser. The contents were continuously stirred and carefully protected against moisture. Unreacted silane was extracted with xylene and hexane in a Soxhlet apparatus. After that, the whole system was dried under vacuum and finally subjected to the so-called end-capping reaction,²⁵ performed according to the standard procedure using hexamethyldisilazane in order to deactivate free silanol groups remaining on the silica surface.

The second step consisted of bonding amino groups using an appropriate derivative of 3-pentane-2,4-dione, namely 3-allyl-2,4-pentadione, and 3-phenyl-2,4-pentadione. As done previously, the reaction was performed under continuous stirring in anhydrous xylene for 12 h at room temperature. The system was protected against moisture. The final product was subsequently extracted with xylene and hexane in a Soxhlet apparatus. Finally, the modified silica was dried under vacuum.

The structure of chemically bonded sorbents is presented in Table 1.

Table 1. Physico-chemical properties of sorbents studied.

Sorbent	Elemental analysis, %			①	②	③	④
	C	H	N	m ² g ⁻¹	μmol m ⁻²	nm	mL g ⁻¹
Silica gel	0.05	0.99	-	552	-	6.18	0.88
	13.44	3.34	1.96	326	4.37	4.87	0.41
	16.36	3.67	1.86	310	4.54	4.60	0.40

① Surface area ② Surface concentration of silane ③ Pore diameter ④ Specific pore volume

Solid phase extraction

Enrichment preconcentration of an analyte from water samples was performed on small columns with a solid sorbent (0.5 g). The columns were conditioned before the introduction of samples by passing through them either 5 mL of acetonitrile followed by 15 mL of deionized water (in the case of phenol and o-chlorophenol) or 6 mL of 2-propanol followed by 6 mL of deionized water (in the case of benzene).

A portion of analyzed water, spiked with a certain amount of the compounds investigated, was injected into columns prepared in the way described above. Once the whole amount of a sample was injected, the sorbent was dried for 10 min under vacuum, and preconcentrated compounds were washed away by the use of 5 mL of acetonitrile (for phenol and o-chlorophenol) or 5 mL of dichloromethane (for benzene). The extract was dried and then dissolved in 1 mL of a solvent previously used for the elution. The obtained samples were analyzed by GC/FID. The temperature program applied was as follows: initial temperature 60 °C, followed by heating at 20 °C min⁻¹ to 230 °C (15 min). Helium was the carrier gas. The measurement was carried out in a constant flow mode set at 1.5 mL min⁻¹.

Results and discussion

Properties of the modified silica

In order to characterize the physico-chemical properties of the packings under study, they were subjected to elemental analysis aimed at determining the contents of carbon, hydrogen, and nitrogen, and to low-temperature nitrogen adsorption to determine BET surface areas. The surface concentration of bonded siloxane (denoted as α) in $\mu\text{mol m}^{-2}$ was calculated from the carbon content according to the following equation:

$$\alpha = \frac{C\% \cdot 10^6}{(100 \cdot n \cdot 12 - C\% \cdot M) \cdot S_{BET}}, \quad (1)$$

where $C\%$ denotes percentage of carbon, n – number of carbon atoms in a molecule of bonded silane, M – molecular mass of the siloxane, and S_{BET} – BET specific surface area [$\text{m}^2 \text{g}^{-1}$]. The results are presented in Table 1.

To examine the surface of sorbents obtained, we used solid-state NMR (²⁹Si CP MAS NMR). The NMR technique is widely used in chromatographic research, for example to determine the presence of functional groups on a sorbent surface.^{26–29} The ²⁹Si CP MAS NMR spectrum makes it possible to discriminate between different silanol groups on the silica surface.

²⁹Si CP MAS NMR spectra of the unmodified silica are presented in Figure 1a, with the spectra of the sorbents under study in Figures 1b and 1c.

Analysis of the spectra confirms that the synthesis reaction took place on the silica surface. During this reaction, geminal silanol groups were blocked. The distinct signal at –90 ppm in the spectrum of the unmodified silica is, in the case of modified silica, definitely weaker. At the same time, the signal at –100 ppm was changed, and this fact proves that the isolated silanol groups were blocked as well. A clear signal at +12 ppm, accompanied by signals at –46 ppm (T1), –50 ppm (T2), and –64 to –70 ppm (T4 + T4'), indicates

the occurrence of the modification of silica by trifunctional silane and the end-capping process by the use of hexamethyldisilazane.

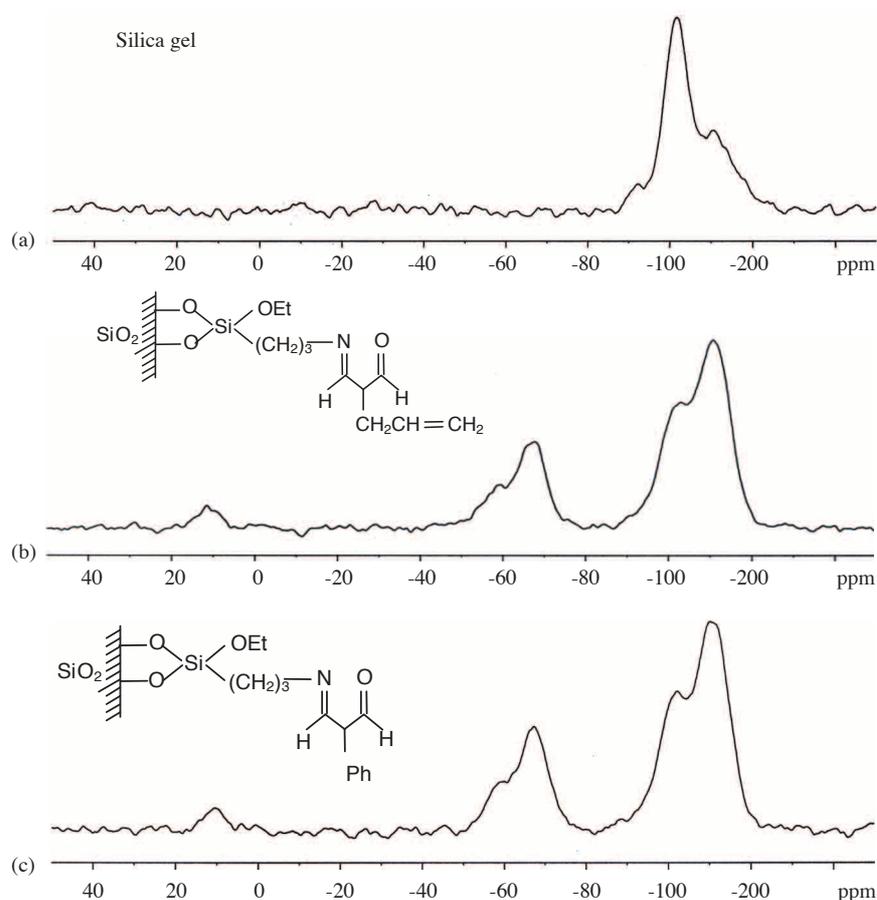


Figure 1. ^{29}Si CP MAS NMR spectra of a) the unmodified silica, b) sorbent with chemically bonded 3-allyl-pentane-2,4-dione, and c) sorbent with chemically bonded 3-phenyl-pentane-2,4-dione.

Calibration graph and recovery

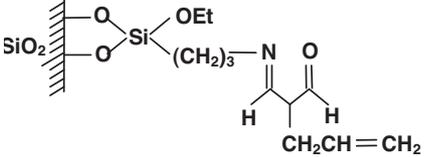
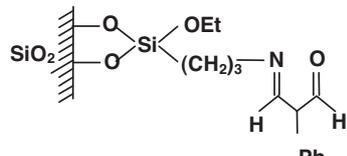
Relationships between peak area and compound concentration were determined by chromatographic analysis of water samples with added phenol, o-chlorophenol, and benzene, respectively. Based on these relationships, calibration curves were plotted. For this purpose, standard solutions were used with the concentration level of compounds studied ranging from 0.5 to 50 $\mu\text{g mL}^{-1}$. The final peak area was taken as an average of 3 subsequent experiments. The calibration plot is described by the general equation: $y = ax + b$, where y is the peak area, and x – the amount of compound determined in $\mu\text{g mL}^{-1}$. In the concentration range studied, the plot is linear for calibration coefficients greater than 0.9998.

The detection limits were defined as the amount of compound producing a peak 3 times higher than the noise level recorded for a matrix without the component determined. The obtained parameters of calibration curves for the analyzed compounds are the following:

- phenol: $a = 22.69$; $b = 40.64$; $r^2 = 0.9998$; $0.2 \text{ LOD } \mu\text{g L}^{-1}$,
- o-chlorophenol: $a = 18.62$; $b = -19.55$; $r^2 = 0.9999$; $1 \text{ LOD } \mu\text{g L}^{-1}$,
- benzene: $a = 171.86$; $b = -421.15$; $r^2 = 0.9998$; $0.5 \text{ LOD } \mu\text{g L}^{-1}$.

Recovery tests were performed for deionized water with known amounts of phenol, o-chlorophenol, and benzene added (1 and $10 \mu\text{g L}^{-1}$). These tests were carried out using the method described above. The results obtained are presented in Table 2. It is worth adding that the calibration curves show a very good linearity. The method is characterized by good recovery rates, as well as by low detection limits.

Table 2. Results of fortification experiments for phenol, o-chlorophenol, and benzene solution in 500 mL of water ($n = 5$).

Sorbent	Recovery rate \pm SD, %		
	Phenol	o-Chlorophenol	Benzene
	$96.2 \pm 1.2^*$ $97.0 \pm 1.0^{**}$	$95.6 \pm 0.5^{**}$	$98.2 \pm 0.2^{**}$
	$94.6 \pm 1.7^*$ $97.4 \pm 1.5^{**}$	$97.1 \pm 1.9^{**}$	$98.7 \pm 1.0^{**}$

* $1 \mu\text{g L}^{-1}$ sample, ** $10 \mu\text{g L}^{-1}$ sample

While comparing the obtained recovery rates with results reported earlier, a significant improvement is clearly seen in the case of sorbents modified with ketoimine groups. For instance, Chi Wan Jeon et al.³⁰ described the application of C_{18} and polystyrene-divinylbenzene adsorbents to the separation of phenols and chlorophenols, and reported recovery rates of 28%-65% for the former and 25%-33% for the latter adsorbent. Moreover, Min Woo Jung investigated several modified polymeric adsorbents³¹ and obtained recovery rates 24%-92% for phenol and 53%-101% for o-chlorophenol. These results are significantly worse compared to the recovery rates determined for the sorbents obtained in the present study (95%-98%).

Current analytical methods, such as EPA 604 and 625, based on liquid-liquid extraction, are difficult to apply for the analysis of several phenols in water, mainly due to their high solubility. Moreover, it is reported that one may observe substantial analyte loss at the stepwise concentration and clean up procedure.³²

The proposed sorbents were applied to pre-concentrated analytes in order to determine their content in lake water. Analyses were performed using the method of standard addition. Sample chromatograms obtained as a result of analyses are presented in Figure 2. Among the 3 compounds investigated, only o-chlorophenol was detected at the level of $2 \mu\text{g L}^{-1}$.

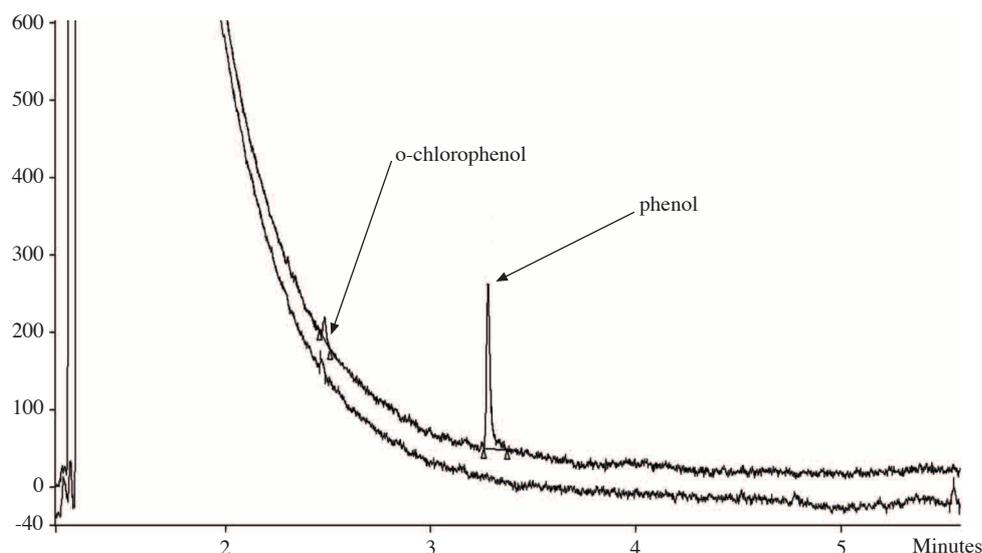


Figure 2. Sample chromatograms of a sample of lake-water extract (lower curve), and sample with added known amount of compounds studied (upper curve, $2 \mu\text{g L}^{-1}$ of *o*-chlorophenol, and $5 \mu\text{g L}^{-1}$ of phenol, respectively).

Conclusions

In this paper we propose a new application of sorbents with chemically bonded ketoimine groups for the SPE method. The way of the preparation, as well as physico-chemical properties of these sorbents, is presented and discussed. Some examples of the application of these sorbents to preconcentration and further determination of phenol, *o*-chlorophenol, and benzene by means of solid-phase extraction (SPE) and GC-FID methods are given. On the basis of the results obtained, we proved that the studied sorbents with ketoimine groups can be used for efficient preconcentration of trace amounts of these compounds with the determined recovery rates at the level of 95%-98%, which are considerably better than those reported in similar studies. Although many authors reported the results of concentration of phenol and its derivatives, it is very difficult to unambiguously include which of these results is the most useful, as different authors have obtained very different results. For example, the sorption ratios found for C_{18} sorbent were in the limits from 3% to 96%.³³

The obtained results prove that the studied sorbents may be effectively applied for the analysis of non-polar benzene, as well as polar phenol and *o*-chlorophenol. It is caused by a generic influence of π -electrons of the aromatic ring to adsorbent-adsorbent interactions. Similar conclusions were drawn by Biernat and Makuch.³³

It is worth noting that we have proved again that preconcentration of phenols with the use of chemically modified sorbents is generally possible. In the case of analysis of phenols and chlorophenols, the chemically modified sorbents showed higher recovery rates compared to non-derivatized sorbents, due to the increase in $\pi-\pi$ interactions between phenol and adsorbent molecules. Concluding, the sorbents studied can be effectively applied to the solid phase extraction of phenolic compounds at lower concentration levels, as well as to SPE of some other organic compounds with π -electrons.

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