Preconcentration of middle oxyethylated nonylphenols from water samples on magnetic solid phase

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Abstract

Magnetic solid phase extraction (MSPE) is proposed as a simple and fast method for the preconcentration of free middle oxyethylated nonylphenols (NPs) from water. Middle oxyethylated NPs were extracted by MSPE from different water samples (10 and 500 ml samples of distilled, potable, well, river and pond water in concentrations of 30 and 0.6 $\mu$g ml$^{-1}$) using magnetically modified polyphenyleneoxide, Tenax TA and Tenax GR as magnetic adsorbents. Recoveries were 80–100% and relative standard deviations were less than 10%.

Keywords: Magnetic solid-phase extraction; Magnetic polyphenyleneoxide; Oxyethylated nonylphenol; Tergitol; Tenax; Nonionic surfactant

1. Introduction

Recently, there has been a significant increase in the consumption of industrially produced chemicals with surface-active properties. These substances are used in processes where there is a need for increased surface activity, and provide excellent all-purpose detergency and wetting, as well as solubilization and emulsification. The main source of tensides are washing and cleaning agents, which could be found in every household and in some branches of industry. While cationic surfactants represent only a minor part of the total amount of detergents, anionic and nonionic ones belong to usual parameters identified during monitoring water quality/contamination. The toxicity and the environmental acceptability of the two most important nonionic groups of surfactants, alcohol polyethoxylates (LAEO) and alkylphenol polyethoxylates (APnEO) have been discussed [1–3]. Although surfactants are relatively nontoxic to mammals, they can be very toxic to aquatic organisms [4–6]. 4-nonylphenols (NPs), which are common products of biodegradation of NP ethoxylates (NPEs), are known to be toxic and estrogen active [7]. There has been a worldwide scientific debate with reference to the potential consequences of human long term dietary exposure to such endocrine disrupters. Surfactants are not only used in industrial applications but also in the home, and hence, surfactants and their residues can be found throughout our environment. The monitoring of these substances, especially in water, is of great environmental significance. The isolation and preconcentration of these substances prior to determination poses several challenges, especially when they are present in low initial concentrations. A number of analytical methods have been successfully employed for the isolation and preconcentration of these substances, including liquid–liquid extraction, column chromatography, solid-phase extraction (SPE) or solid phase microextraction (SPME). Different adsorbents, such as C18 or activated carbon [8,9] have also been applied. Problems such as column clogging, which are commonly encountered with these methods, can be overcome by employing batch, magnetic solid phase extraction (MSPE) [10]. This technique enables adsorption of a target analyte on a magnetic adsorbent and subsequent direct separation of the magnetic complex from the solution or the suspension.

Oxyethylated NPs, for example, Tergitol, i.e. NP-9EO, belong to a group of nonionic tensides with a wide variety of applications, including cleaning product formulations, paints and coatings, emulsion polymerization, and many...
406


others. Tergitol was, therefore, used in our work as a typical nonionic surfactant with a middle oxyethylation level.

2. Materials and methods

Poly(oxy-2,6-dimethyl-1,4-phenylene) (PODMP), ε-caprolactam and powdered iron(II, III) oxide were from Aldrich. Tenax TA and Tenax GR were from Scientific Instrument Services, USA. Nonionic surfactant Tergitol (oxyethylated nonylphenol NP-9EO) was from Aldrich. Water was obtained locally. A vortex mixer, Heidolph Reax Top and Reax 2 (Heidolph Instruments, Germany), the Dynal sample mixer (Dynal, Norway), a flat magnetic separator (SVUM Praha, Czech Republic) and a flow-through dipole magnetic separator (Clemente Associates, USA) were used for the adsorption of an analyte and extraction of magnetic particles. Concentrations of Tergitol were determined using UV–VIS spectrophotometer Cintra 20 (GBC, Australia).

Magnetic adsorbents were prepared as follows. Magnetic PODMP was melted with ε-caprolactam and powdered iron (II, III) oxide, milled and washed [11]. Tenax TA and Tenax GR were post-magnetized with magnetic fluid stabilized with perchloric acid (prepared according to Ref. [12]).

For the extraction of Tergitol, a solution of Tergitol was added to 8 ml of distilled water containing 50 μl of settled magnetic adsorbent and made up to 10.0 ml with water. The sample was rotated on Dynal sample mixer (28 rpm) for 5 min. Magnetic particles were separated from the suspension using a magnetic separator or a strong permanent magnet. Water samples (500 ml) containing Tergitol were mixed with 0.8 ml suspension of adsorbent (settled volume 200 μl) in PET flasks. The suspension was then stirred on Heidolph Reax 2 mixer (22 rpm) for 1 h. The magnetic adsorbent was then recovered on a strong flat permanent magnet or flow-through dipole magnetic separator (flow rate 200 ml min⁻¹ for PODMP and 50 ml min⁻¹ for Tenax) and transferred to a test tube. The adsorbed tenside was eluted with 1 ml methanol under thorough stirring on a vortex mixer (shaking frequency 2400 min⁻¹). The time for maximum adsorption and elution was determined from time dependence curves. Efficiency of elution was determined from the amount of adsorbed and subsequently released Tergitol. Relative standard deviation (RSD) was calculated from 5 to 10 measurements.

The concentration of Tergitol was determined after reaction with a complex forming reagent (30 g Co(NO₃)₂·6H₂O and 200 g NH₄SCN in 1000 ml distilled water). Tergitol present in the eluent (1–3 ml methanol) was pipetted into a flask with 15 ml methanol and evaporated using a rotary evaporator. 10 ml 1,2-dichloroethane was added to the evaporation residue, mixed and transferred into 150 ml separatory funnel with 5 ml of the complex forming reagent. After agitating for 60 s, the bottom 1,2-dichloroethane fraction containing the dyed complex was filtered through porous glass and measured spectrophotometrically at 620 nm. Unbound Tergitol was determined in the same way after extraction of the supernatant with 1,2-dichloroethane [13]. Alternatively Tergitol concentration was directly determined spectrophotometrically at 276 nm.

For the construction of adsorption isotherms, a solution of Tergitol was added to 8 ml of distilled water containing 50 μl of settled adsorbent and the total volume was made up to 10.0 ml with water. The suspension was mixed for 4 h at room temperature. Adsorption time was determined from a time dependence curve. After magnetic separation the concentration of free analyte (C_{eq}) was determined spectrophotometrically, and the amount of tenside bound to the unit volume of the adsorbent (q_{eq}) was calculated. Maximum adsorption capacity Q (mg g⁻¹) was calculated from a linearized form of Langmuir isotherm.

3. Results

Recently several nonionic surfactants have been pre-concentrated from water by MSPE, using magnetically modified materials, such as activated carbon, hydrophobic polymer PODMP, polyamide DPA-6S or Al₂O₃ [14]. The work presented here explores the use of MSPE to extract Tergitol, a model surfactant of middle oxyethylated NPs from volumes up to 500 ml from real water samples. Linear hydrophobic polymer PODMP, Tenax TA (poly(oxy-2,6-diphenyl-1,4-phenylene)) and Tenax GR (containing 30% graphite) were magnetically modified and used as magnetic adsorbents. Particle size of PODMP was ca. 100 μm, the diameter of Tenax TA and GR particles was ca. 200 μm (60/80 mesh). The dry weight of settled suspension was 191.5 mg ml⁻¹ (PODMP), 137.6 mg ml⁻¹ (Tenax GR) and 148.8 mg ml⁻¹ (Tenax TA).

Different types of water samples, such as distilled, potable, well, river (Vltava) and pond (stagnant water) were used. Water was analyzed in the Central Military Institute of Health, Ceske Budejovice (Table 1). All necessary parameters affecting the extraction of Tergitol were studied, and according to these experiments the amount of adsorbent, extraction and elution time, number of elution steps and conditions for flow-through magnetic separation, were determined. Spectrophotometry was chosen for the determination of Tergitol due to the high volume of samples analyzed. In cases where the water samples are more contaminated with interfering compounds, spectrophotometric determination can be replaced by another technique, such as HPLC.

The equilibrium adsorption isotherms of Tergitol (Fig. 1) show a big difference between a maximum adsorption capacity of PODMP (111.7 mg g⁻¹) and Tenax (29.6 mg g⁻¹) for Tenax TA and 47.2 mg g⁻¹ for Tenax GR). Isotherms follow Langmuir adsorption patterns, and were found to belong to the Class L2 as per the classification system of Giles et al. [15]. Despite this disparity in adsorption
Table 1
Selected characteristics of water samples (Provided by Central Military Institute of Health, Ceske Budejovice, Czech Republic.)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Water source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>River, Vltava, Pond, Well</td>
</tr>
<tr>
<td>Conductivity (mS m⁻¹)</td>
<td>7.3, 7.7, 5.5</td>
</tr>
<tr>
<td>COD₃⁻ (mg l⁻¹)</td>
<td>13.6, 12.9, 71.6</td>
</tr>
<tr>
<td>Total Fe (mg l⁻¹)</td>
<td>0.22, 0.07, 0</td>
</tr>
<tr>
<td>Total (NH₄)⁺ (mg l⁻¹)</td>
<td>0.01, 0.05, 0</td>
</tr>
<tr>
<td>Total Cl⁻ (mg l⁻¹)</td>
<td>8.9, 10.3, 100.4</td>
</tr>
<tr>
<td>Total (NO₃)⁻ (mg l⁻¹)</td>
<td>4.85, 2.91, 0</td>
</tr>
<tr>
<td>Total (SO₄)²⁻ (mg l⁻¹)</td>
<td>15.2, 16.5, 53.4</td>
</tr>
<tr>
<td>Total NEL (mg l⁻¹)</td>
<td>0.021, 0.016, 0</td>
</tr>
<tr>
<td>Total surfactant (mg l⁻¹)</td>
<td>0.03, 0.05, 0</td>
</tr>
</tbody>
</table>

NEL—non-polar extractable compounds, COD—chemical oxygen demand.

Table 2
Adsorption of Tergitol on magnetic adsorbents in 10 ml distilled water

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>PODMP</th>
<th>Tenax TA</th>
<th>Tenax GR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elution (ml)</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Unbound (%)</td>
<td>0</td>
<td>44</td>
<td>52</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>92.6</td>
<td>99.8</td>
<td>99.7</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>3.6</td>
<td>3.3</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Concentration of Tergitol: 30 µg ml⁻¹, sorption time: 5 min (PODMP) and 30 min (Tenax), desorption time: 3 min.

Table 3
Extraction of Tergitol from 10 ml and 500 ml water samples on magnetic PODMP

<table>
<thead>
<tr>
<th>Water</th>
<th>Distilled</th>
<th>Potable</th>
<th>Vltava river</th>
<th>Pond</th>
<th>Well</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml</td>
<td>Recovery (%)</td>
<td>92.6</td>
<td>96.8</td>
<td>87.6</td>
<td>90.5</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>3.6</td>
<td>2.3</td>
<td>5.2</td>
<td>8.0</td>
<td>6.5</td>
</tr>
<tr>
<td>500 ml</td>
<td>Recovery (%)</td>
<td>95.4</td>
<td>93.8</td>
<td>84.3</td>
<td>87.1</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>1.3</td>
<td>2.0</td>
<td>7.6</td>
<td>9.5</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Concentration of Tergitol: 30 µg ml⁻¹ (0.6 µg ml⁻¹), sorption time: 5 min (60 min), elution time: 3 min, elution with 1 ml methanol. The entire initial amount of Tergitol was adsorbed.

Fig. 1. Equilibrium sorption isotherms of Tergitol on magnetic PODMP (■), Tenax TA (○) and Tenax GR (▲). Cₑq—equilibrium liquid-phase concentration of the nonadsorbed Tergitol (mg dm⁻³); qₑq—equilibrium solid-phase concentration of the adsorbed Tergitol (mg cm⁻³).

capacities the recoveries of Tergitol (calculated from the amount of adsorbed and subsequently released tenside) were comparable for all tested adsorbents.

Adsorption of Tergitol was first tested on three selected magnetic adsorbents in 10 ml distilled water, with very similar results (Table 2). The recoveries were above 90%, and therefore, all these materials were used for further experiments. Although similar results were achieved, POMDP was used for the detailed study due to its lower price. Table 3 shows results of extraction of Tergitol from 10 ml of different water samples by magnetic PODMP. In all cases, the entire initial amount of Tergitol (concentration 30 µg ml⁻¹) was adsorbed, and with an exception of river water, all recoveries were above 90%.

The extraction of low concentration of Tergitol from larger sample volumes was also investigated. Adsorption time was extended to 60 min and the recovery was calculated from the initial amount of Tergitol (concentration 0.6 µg ml⁻¹) while other parameters remained unchanged. Results of extraction from 500 ml samples are also presented in Table 3 and show that while recoveries from distilled, potable and well water all exceeded 90%, recoveries from pond and river water were slightly lower.

In all cases, RSDs were less than 10%.

The possibility of regeneration of adsorbents was also tested. After elution the adsorbent was washed 5 times with 1 ml methanol and 3 times with 1 ml distilled water and reused. After 3 repeated regenerations of PODMP, the amount of adsorbed Tergitol decreased to 90%, nevertheless the recovery was not affected (Fig. 2).

4. Discussion

MSPE is an environmentally friendly technique, which enables the extraction of free analytes under mild conditions, avoiding organic solvents. This technique, therefore, does not afford the extraction of an analyte adsorbed onto solid impurities. In order to be able to calculate the recovery from pond and river water, the water was first filtered to remove solids prior to the addition of Tergitol. Nevertheless some fine impurities may remain in water causing a decrease of recoveries. Pond and river water samples were collected from May to October and similar results were obtained. At that time the amount of surface-active agents and nonpolar extractable compounds contained in the water were relatively low and did not significantly affect the results.

Column SPE was used several times for the preconcentration of nonionic tensides from water samples with similar recoveries [16]. MSPE can be an equivalent
alternative of SPE, especially when the analysis is performed in samples containing particulate matter.

5. Conclusion

Surfactants and their residues can be found throughout our environment. The monitoring of these substances, especially in water, is of great environmental significance. Magnetic solid phase extraction is a suitable method for the extraction of middle oxyethylated nonylphenols and other nonionic tensides from different water samples. Magnetic derivatives of PODMP and Tenax exhibit good adsorption and desorption characteristics. The selection of the optimal parameters (such as amount of adsorbent, extraction and elution time and number of elution steps) depends on the type of adsorbent and tenside.

Acknowledgments

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References