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A stir-bar sorptive extraction coating based on chemically bonded silica for the analysis of polar organic compounds and heavy metal ions

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The new stir-bar coating based on silica gel modified with ketoimine groups was applied to the preconcentration of phenolic endocrine disruptors and heavy metal ions such as Cu^{II}, Cr^{III} and Ni^{II} in water samples followed by determination using LD-GC/MS and ICP-OES, respectively.

Stir bar sorptive extraction (SBSE) is a solid phase extraction technique in which the sorbent is a coating of a solid magnetic stir bar.[1] Polydimethylsiloxane (PDMS) is a typical coating material in commercial stir bars. Due to the nonpolar character of PDMS, SBSE cannot be applied to the extraction of strongly polar compounds without derivatization.[2,3] However, it is important to develop extraction phases that have better affinities to polar compounds. Among the components to be determined by SBSE, attention should be focused on estrogens (steroid sexual hormones), phytoestrogens (plant hormones) and xenoestrogens (endocrine disruptors) – industrially produced chemical compounds, which are further disposed to the water environment (such as alkyl phenols and bisphenol A). These components are responsible for a so called estrogenic effect, which leads to the feminization and hermaphroditism of aquatic organisms and further humans.[4–6]

Here, we proposed a new SBSE coating based on chemically bonded silica for the analysis of phenolic endocrine disruptors. We applied this coating to the preconcentration and further determination of 4-nonylphenol (4NP), 4-*tert*-octylphenol (4tOP), and 2,2-bis(4-hydroxyphenyl)propane (BPA) using SBSE and liquid desorption gas chromatography/mass spectrometry (LD-GC/MS). An iron bar (10 mm × 1.2 mm o.d.) was placed in a flat bottom glass tube (15 mm × 1.2 mm i.d.). The bared glass bars were cleaned with acetone and then sequentially treated with 1 M NaOH for 1 h and with 0.1 M HCl for 0.5 h; finally, they were rinsed with deionized water for 1 h and dried at room temperature.

To cover a bar with modified silica,[7] the bar was immersed in a 3% OV1 solution to obtain a thin layer. Subsequently, the bar was coated with ketoimino-modified silica gel to obtain a sorbent monolayer and heated in an oven at 180 °C. The formation of the sorbent monolayer on the stir bar was inspected using scanning electron microscopy (SEM). Figure 1 shows the SEM images of the SBSE surface structures.

A thin monolayer of modified silica was created on the stir bar over the surface of an OV1 layer, which was fully covered by silica, and this compound could not react with the analytes.

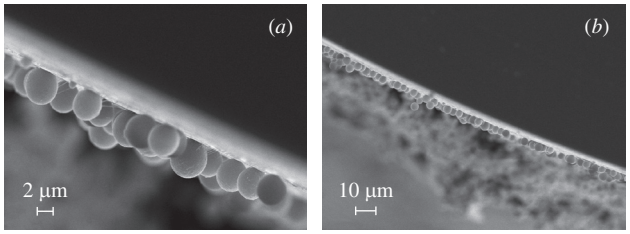

Figure 1 SEM images of SBSE surfaces.

The extraction of phenolic endocrine disruptors by means of the modified stir bar was performed according to the following procedure: a water sample (25 ml, pH 7) was placed in a 30 ml glass vial. The stir bar was stirred in the sample for 120 min at room temperature. Next, the stir bar was placed in a 3 ml glass vial with 1 ml of MeOH for liquid desorption under ultrasonic treatment for 60 min (25 °C). After back extraction, the stir bar was removed by means of a magnetic rod, the extract was evaporated and followed by the reconstitution with 250 μl of MeOH. The samples were analyzed by GC/MS.

GC/MS was performed using a Thermo Scientific Focus instrument equipped with a mass spectrometric detector (MS). A TG-SQC GC (15 m × 0.25 mm × 0.25 μm) capillary column was used. Helium was a carrier gas with a constant flow rate of 1 ml min^{-1}. The oven temperature was programmed from 80 to 270 °C (held for 2 min) at a rate of 15 K min^{-1}. The transfer line to the mass spectrometer was set at 300 °C. The dwell time was set at 80 ms and the multiplier potential was 450 V. Full-scan mass spectra between *m*/*z* 35 and 200 were acquired once every second. For selected ion monitoring (SIM), *m*/*z* 135, 107 and 177 were monitored for 4tOP and 4NP, and *m*/*z* 213, 270 for BPA.

The new coating and commercial PDMS coating were compared before the analysis. Stir bars coated with a 0.5 mm layer of PDMS (twister: a magnetic stirring rod placed in a glass jacket and coated with PDMS) were obtained from Gerstel (Germany). The recovery rates of the analytes for water samples from sewage plants spiked with standards at 50 ng cm^{-3} ranged from 70.2 ± 2.31% (4tOP), 62.5 ± 1.50% (BPA) and 61.5 ± 3.21% (4NP).

Next, recovery tests were performed for the new stir-bar coating based on modified silica gel with ketoimine groups using SBSE-LD-GC/MS SBSE. The recovery rates of the same analytes for water samples from sewage plants spiked with standards at 50 ng cm^{-3} ranged from 81.3 ± 3.31% (4tOP), 74.1 ± 2.50% (BPA) and 80.9 ± 3.00% (4NP). Thus, the recovery rates for the new stir-bar coating are significantly better than those for commercial PDMS coating.

The new stir-bar coating was applied to the extraction of trace phenolic compounds from aqueous samples. The optimized parameters for the extraction of phenolic endocrine disruptors from water were the following: extraction and desorption times, 2.0 and 2.0 h, respectively; pH 8.0. The detection limits ranged from 1.0 to 3.0 ng cm^{-3}.

Phenolic endocrine disruptors were determined in two water samples (fresh and cleaned effluents) collected from sewage plants by SBSE-LD-GC/MS SBSE using the standard addition method (Figure 2, Table 1).

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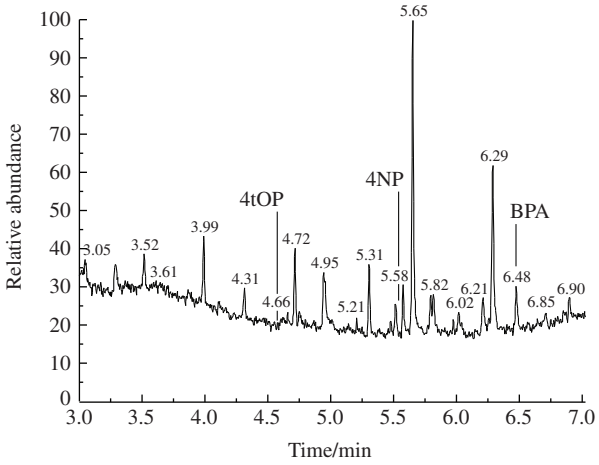

Figure 2 Chromatogram obtained by the analysis of fresh water samples.

Table 1 Concentrations of phenolic endocrine disruptors in water samples.

Water sample	Concentration/μg dm^{-3}		
	4tOP	4NP	BPA
Fresh water	0.076 ± 0.026	2.47 ± 1.40	10.04 ± 1.65
Cleaned effluent	0.064 ± 0.024	0.38 ± 0.10	4.65 ± 1.12

In addition to the adsorption of organic compounds, the new SBSE coating material can be used to extract heavy metal ions such as Cu^{II}, Cr^{III} and Ni^{II}. These elements were determined by ICP-OES.

Ketoimines used for the silica modification are bidentate chelating ligands. Figure 3 shows complex structures at the modified silica surface.

For the extraction of Cu^{II}, Cr^{III} and Ni^{II} with the modified stir bar, water samples were prepared with deionized water (25 ml) to contain 0.1 μg of Cu^{II}, Cr^{III} and Ni^{II}. The pH of the test solution was adjusted at 4–8 with 0.1 M KNO_3 and 30% NH_4OH solutions. The stir bars were stirred for 2 h for the extraction; then, the stir

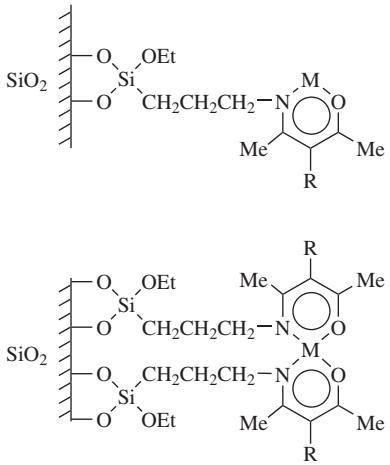

Figure 3 Surface structures of the ketoimino complexes.

Table 2 Effect of the elution solutions on the recovery of Cu^{II}, Cr^{III} and Ni^{II}.

Element	Eluent	Recovery[a] (%)	
		0.5 mol dm^{-3} [b]	1 mol dm^{-3} [b]
Cu^{II}	HCl	53 ± 4	65 ± 2
	HNO_3	96 ± 3	91 ± 3
Cr^{III}	HCl	60 ± 2	74 ± 4
	HNO_3	95 ± 1	90 ± 3
Ni^{II}	HCl	59 ± 2	72 ± 3
	HNO_3	92 ± 2	89 ± 4

[a] $\bar{x} \pm s$ (n = 3), $\bar{x}$ is the average value for three determinations, and s is the standard deviation. [b] Concentration of the elution solution.

bars were removed and immersed in 10 ml of a 0.5 M HNO_3 solution, where they were stirred for 1 h to release the extracted analytes at room temperature.

We also examined the effect of the concentration and type of eluting acids (0.5 and 1 M HNO_3 and 0.5 and 1 M HCl) on recovery at pH 5 (Table 2). As it can be seen, HNO_3 was a better eluent, which was chosen for the analysis.

The concentration levels of Cu^{II}, Cr^{III} and Ni^{II} in water samples were the following: 5, 2 and 20 μg dm^{-3} for fresh water samples and 2 μg dm^{-3}, below detection limits, and 10 μg dm^{-3} for the cleaned effluent, respectively.

Despite a lower sensitivity in comparison with that of a thermal desorption method,[8] the proposed method can be applied to environmental analysis.

Note that the proposed stir bars may be fully reused more than 50 times with no special treatment. After each experiment, the stir bars were only washed with methanol and then distilled water for about 1 h.

Thus, the new stir bar coating with ketoimine groups can be used for the preconcentration of trace phenolic endocrine disruptors and heavy metals.

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