Synthesis and investigation of silver-coated monolithic solid phase microextraction silica sorbent

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Monolithic solid phase microextraction silica sorbent coated with silver nanoparticles (Ag NPs) was successfully synthesized in a small quartz capillary. The sorbent was tested in a headspace microextraction mode using various aromatic compounds followed by gas chromatography analysis. Due to the π-π electronic interaction between analytes aromatic systems and silver particles immobilized on the sorbent surface, the analytes were successfully extracted from a sample headspace and determined by gas chromatographic analysis.

Keywords: solid phase microextraction, silver nanoparticles, monolithic sorbent

INTRODUCTION

Today the safety of our environment and products that we consume plays an import role in scientific research. Environmental and food analysis is a rather difficult process compared to the analysis of other matrixes: the samples are very diverse, usually non homogenous and have a huge range of chemical compounds that makes it hard to isolate and determine analytes of interest [1]. Due to this, the sample preparation prior the analysis is usually needed, that may include chemical or non-chemical processes, such as filtration, distillation and solid/liquid phase extraction [2]. It was calculated that sample preparation can take up to 80% of the total time of complete separation-based analytical process [2] so it is important to develop new sample preparation methods that can make sample preparation more efficient than traditional methods.

In 1989, J. Pawliszyn and his colleagues developed a new type of sorbent, that could extract various analytes from a solution that can later be directly injected in a gas chromatographic (GC) system [3]. It was a start of solid phase microextraction or SPME. SPME can be used in direct immersion (DI-SPME) or sample headspace (HS-SPME)

modes, with the HS-SPME mode having a problem when extracting less volatile analytes but having an advantage when extracting analytes from solid samples [4]. It should be noted that due to the miniature sorbent size, SPME relies on a partition of the analyte between the sample matrix and the fiber (or the sample matrix, sample headspace and fiber in HS-SPME), so the temperature, the sample pH (for acidic and basic analytes) and the time of the extraction should be carefully controlled for the optimal and reproductible results of the analysis [4]. SPME, compared to traditional methods, can shorten the overall time of the analysis by combining sampling, pretreatment, enrichment, and a sample introduction in a single, solvent-free step by utilizing a miniature extraction phase [5]. There is a broad range of geometries of SPME devices, ranging from a needle coated with an extraction phase to a stirring bar [6] and their coating materials, that can achieve very selective extractions from various matrixes [7].

Silica is one of the most used materials in sorbent synthesis [8]. Unmodified silica with its silanol groups is polar [9], but by varying staring materials or modifying it after synthesis by reacting various reagents with silanol groups on the silica surface, different properties can be achieved: 4-vinylphenylboronic acid modified silica sorbent can be used

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for biomolecules separation [10], sulfonic acid groups modified silica sorbent was used for extraction of anesthetics from urine [11], by modifying silica beads with molecularly imprinted nanoparticles, and a chiral stationary phase for liquid chromatography was created [12].

It is known that due to the weak and reversible charge transfer complex between silver ions and π electrons of the double bonds of unsaturated compounds, the separation of compounds like unsaturated trans fatty acids can be achieved [13]. In the case of Ag NPs, in the presence of an electron acceptor, Ag NPs could be partially charged making it possible to form a complex with electron-donating groups or double bonds [14, 15]. This enables separation of mixtures containing trans fatty acids esters [13], benzo[a]pyrene extraction (from petroleum) [16], benzene, naphthalene, anthracene and phenanthrene [14]. Such type of monolithic sorbent can also be used in high-performance liquid chromatography to separate mixtures of benzene, naphthalene, anthracene and pyrene or a mixture of cis-trans stilbenes [15]. In this study, we decided to synthesize an Ag NPs embedded silica monolith in a small diameter quartz capillary and test its extraction capabilities in a headspace microextraction mode using various aromatic compounds as analytes.

EXPERIMENTAL

Reagents and solutions
All reagents were of analytical grade. Urea, pluronic P123 (99.7%), formaldehyde solution in water (37°C) and 4-methyl styrene were purchased from Sigma Aldrich (Germany), acetic acid (99.7%), tetramethoxysilane (TMOS) (98%), toluene and (3-aminoproyl) triethoxysilane (APTES) (98%) were purchased from Alfa Aesar (USA), silver nitrate was obtained from Girochem (Slovenia), polyimide resin was purchased from Supelco (Germany), ethanol (96.3%) was obtained from Vilniaus Degtinė (Lithuania), naphthalene and anthracene were purchased from Dr. Ehrenstorfer (Germany), sodium hydroxide and hydrochloric acid were obtained from Eurochemicals (Lithuania).

Instrumentation
Chromatographic analysis was performed on a PerkinElmer Clarus 580 gas chromatograph equipped with a PerkinElmer Clarus 560S mass spectrometric detector. The GC system was equipped with a PerkinElmer (5% diphenyl – 95% dimethyl siloxane) capillary column (30 m × 0.25 mm, 0.25 μm).

GC conditions
Helium was employed as carrier gas with a flow rate of 1 ml/min. The injector temperature was held at 200°C. Injection was performed on a split mode. The split ratio was 10:1. The oven temperature was programmed as follows: from 20 to 200°C at 20°C/min and held at 200 for 4 min. The mass spectrometry was performed on a SIR mode with a positive electron ionization in a sequence as follows: 3 to 3.40 min – 91 m/z ion, from 5.20 to 5.40 min – 118 m/z ion, from 6.80 to 7.00 min – 128 m/z ion and from 11.50 to 11.80 min – 178 m/z ion.

Quartz capillary preparation
0.32 mm diameter quartz capillary before the synthesis of monolithic silica was firstly cut into 4.5–5 cm length pieces. Then, the quartz capillaries were activated according to the procedure E3, provided in Ref. [17]. Briefly, the capillaries were first immersed into a 0.2 M NaOH solution for 30 min, followed by the immersion into a 0.2 M HCl solution for 30 min, and lastly the capillaries were washed with a stream of distilled water and acetone.

Synthesis of monolithic silica
Silica monolith was synthesized according to the procedure provided in Ref. [13]. In brief, 0.35 g of P123 was dissolved into 4 ml of 0.01 M acetic acid. After the complete dissolution of P123, the mixture was kept stirring for 5 min in an ice bath, followed by the addition of 0.25 g of urea. Then, 0.625 ml of TMOS was added under vigorous stirring until a clear solution was obtained. The resultant solution was then transferred to previously prepared capillaries with airtight lids at both ends and kept at 60°C for 3 days. The synthesized monoliths were washed 2 times with distilled water and 1 time with a water/ethanol solution (2:1) for 12 h per each time. After the washing, the capillaries with monoliths were dried at 40°C for 5 days. The capillaries with monoliths, after the drying step, were calcified using a temperature ramp rate of 1°C/min up to 800°C and kept at the same temperature for 5 h.

Modification of monolithic silica with aminopropyl groups

Modification of the silica monolith with aminopropyl groups was accomplished according to the procedure provided in Ref. [13]. In brief, capillaries with monolithic silica were immersed into an APTES/toluene (4% v/v) solution in a sealed amber test tube which was then left under 80°C for 24 h. Then, the capillaries were washed extensively with ethanol three times for at least 12 h per each time.

Introduction of Ag NPs into aminopropyl groups modified silica monolith

Introduction of Ag NPs into aminopropyl groups modified silica monolith was accomplished according to Ref. [13] with some modifications. In brief, capillaries with aminopropyl groups modified silica were immersed in a 0.1 M ethanol solution of silver nitrate for 48 h at room temperature. Then, the capillaries were immersed into a 37% formaldehyde solution for 24 h, after that, the capillaries were washed 3 times with ethanol solution for at least 12 h each time and dried for 72 h in 40°C in the oven.

Characterization of the sorbent

The SEM analysis on a synthesized monolith was performed on a Hitachi SU-70 microscope, and the thermogravimetric analysis was carried out using a PerkinElmer Pyris 1 instrument in a heating rate of 10°C/min from room temperature to 800°C.

RESULTS AND DISCUSSION

Synthesis and characterization of the sorbent

Monolithic silica has been synthesized by a sol-gel method that includes hydrolysis, condensation and polycondensation of silica precursors. Firstly, the TMOS (silica precursor) is hydrolyzed by acetic acid, then, the condensation reaction occurs and the siloxane chains are formed [11]. Lastly, urea hydrolysis products (carbon dioxide and ammonia) lead to the base catalyzed polycondensation of TMOS and result in silica monolith formation [13]. The synthesized monoliths were calcified, without removing them from the quartz capillaries, at 800°C. After the calcification, the monolith kept its cylinder shape and was not detached from a quartz capillary wall. It should be noted that a good sorbent-capillary wall bond is very important for practical reasons which include sorbent splitting prevention after the calcination step and ensuring that the sorbent does not fall out from the capillary during the microextraction procedure. In this study, with the primary capillary wall preparation method, E3, no preparation and E1 preparation method, provided in Ref. [17], were also tested. The results showed that the E3 method was the best suited for future synthesis – the sorbent, after the calcination, was not fractured and detached from the capillary wall. In no preparation and E1 method case, the sorbent was fractured and detached for the capillary walls – such sorbents cannot be used for microextraction. Figure 1 shows a morphology of the calcified silica monolith in a quartz capillary.

In order to modify silica monoliths with Ag NPs, the previously calcified silica monoliths were modified with amino groups via the silanization reaction between the APTES and silanol groups of the monoliths [18]. The successful modification with aminopropyl groups was proved by the thermogravimetric analysis of the APTES and Ag NP
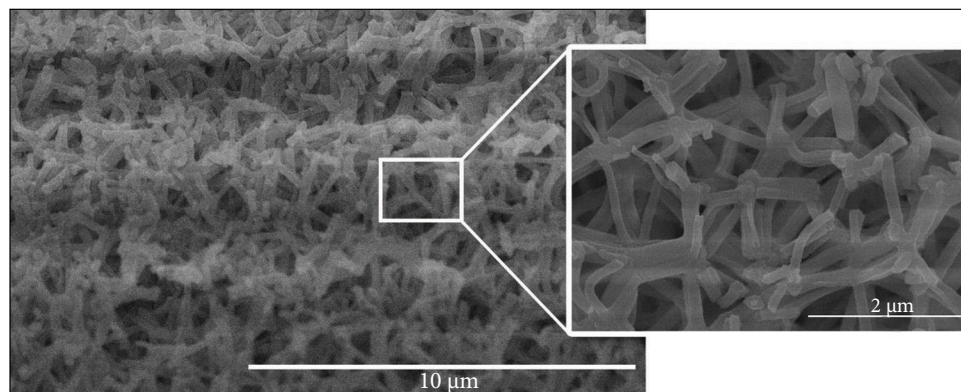

Fig. 1. The SEM picture of a silica sorbent in a small quartz capillary after calcination in 800°C for 4 h

modified silica monolith, removed from a capillary after its synthesis (Fig. 2). An exothermic peak between 270 and 330°C together with the weight loss in the same temperature region was observed due to the pyrolysis of aminopropyl groups grafted on the surface of silica, as seen in Fig. 2. Other weight loss peak between 330 and 600°C can be attributed to the elimination of silanol groups [14].

To obtain the Ag NP modified silica monolith, capillaries with the previously modified silica monoliths were further treaded with the 0.1 M $AgNO_3$ solution in ethanol. Then the Ag^+ ions were reduced using a 37% formaldehyde solution. There are several methods in the scientific studies that describe the Ag^+ ions reduction into Ag NP and reducing agents, that typically are citric acid and its salts, $NaBH_4$, formaldehyde and ascorbic acid [14, 9–21]. In our case, only the bonded silver ions have to be reduced and non-bonded ones should be washed off: it is known that the reduction potential for the $Ag(NH_3)^+_2$/Ag pair is lower (+0.373) than the reduction potential for the Ag^+/Ag redox pair (+0.799) so the reducing agent needs to be strong enough to reduce silver ions bonded to the aminopropyl groups but not too strong to reduce free silver ions. Other studies

and our previous work [13, 14] showed that an aqueous formaldehyde solution can successfully be applied as a reducing agent to reduce silver ions bonded to the aminopropyl groups modified monolithic silica sorbent. Based on this, in this work we have also applied formaldehyde to reduce silver ions bonded to the sorbent surface. Figure 3 shows a SEM image of the Ag NPs modified silica monolith, that was removed from a silica capillary and crushed prior to the analysis.

Capillary holder construction
In order to test our Ag NPs embedded monolithic silica sorbent, the proper sorbent holder must be constructed. In Fig. 4, we provide a photo with our constructed microextraction sorbent holder and a commercially available microextraction sorbent holder. Our capillary holder (Fig. 4a) is constructed using a double surgical needle: outer needle (G25, numbered 2 in Fig. 4) serves as a puncturing tool and protective casing, an inner needle (G20) (Fig. 4, 6) was glued in a capillary with a sorbent (Fig. 4 1) using polyimide resin and serves as a plunger for regulating a capillary position inside an outer needle. Such capillary movement is needed because extraction/desorption procedures rely on the principle
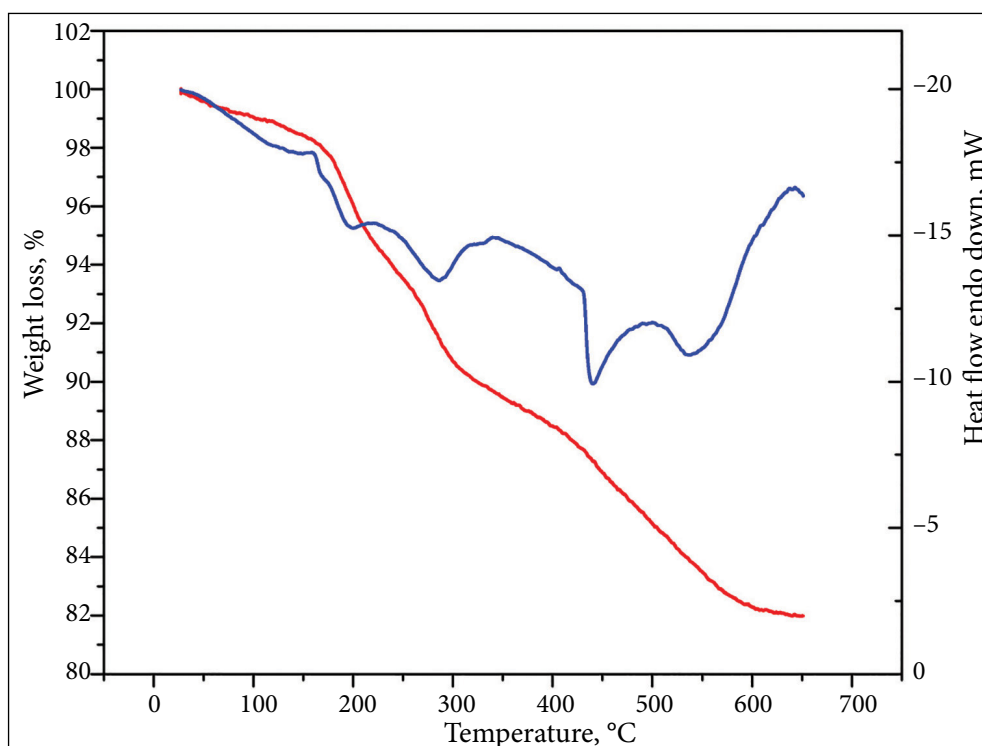

Fig. 2. The thermogravimetric (TG) and differential scanning colorimetry (DSC) analysis graphs of the silica sorbent, removed from a quartz capillary, after modification with amino propyl groups and Ag NPs
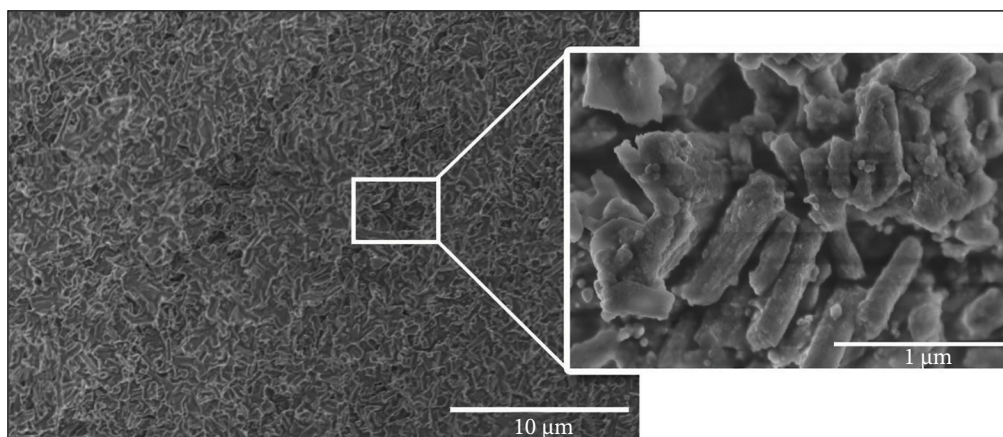
Fig. 3. The SEM picture of a silica sorbent, after the modification with amino propyl groups and Ag NPs, that was removed from a quartz capillary and crushed prior to the analysis

that when the extraction/desorption is taking place, the capillary's front is outside the outer needle; in other cases, the capillary is inside the outer needle to protect it from breaking. Rubber septa (Fig. 4, 3) with a plastic tube (Fig. 4, 4) ensure that the sorbent in extraction/desorption steps is in the similar position, compared to the commercial sorbent holder (Fig. 4b).

Headspace microextraction of aromatic compounds using Ag NPs embedded monolithic silica sorbent

The Ag NPs embedded monolithic silica sorbent was tested in a headspace microextraction mode with 4 analytes: toluene, 4-methyl styrene, naphthalene and anthracene. The idea behind the selection of these 4 compounds as analytes was a need to test an extraction limit of our sorbent: interaction difference between different analytes

and our sorbent was achieved due to the different size of the selected compounds aromatic systems. The analytes were firstly dissolved in acetone separately and their solutions were used to make a final solution in distilled water with an analyte concentration of 0.04 mg/ml. The final solution was transferred into a chromatographic vial, the vial was transferred into a water thermostat with water temperature set at 80°C, and the microextraction was carried out for 15 min while the solution was mixed by a magnetic stirrer. After 15 min, the sorbent holder was transferred into a GC-MS system and chromatographic analysis was carried out. Figure 5 shows clear peaks of anthracene (Fig. 5a), naphthalene (Fig. 5b) and 4-methyl styrene (Fig. 5c) after the headspace microextraction and chromatographic analysis with single ion reading (SIR), indicating that the Ag NPs embedded silica monolith has a tendency to extract aromatic
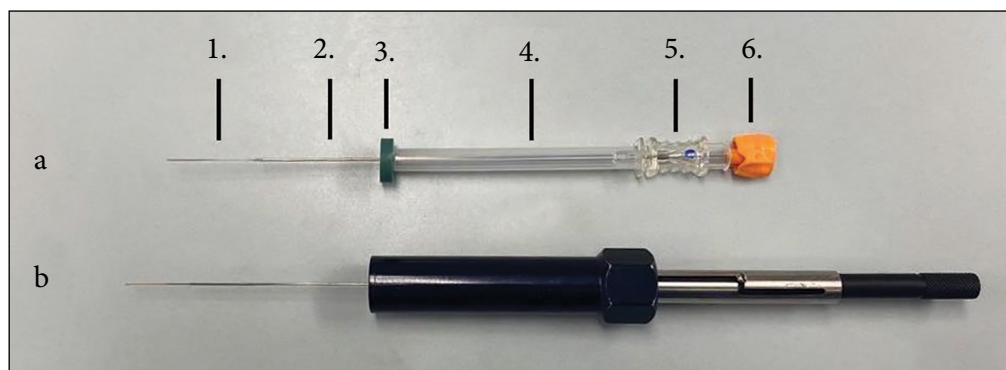

Fig. 4. The comparison between our (a) and commercial (b) microextraction sorbent holders. 1, sorbent in a small quartz capillary; 2, outer needle (G25); 3, rubber septa; 4, plastic tube; 5, inner needle (G20) insertion port; 6, inner needle end
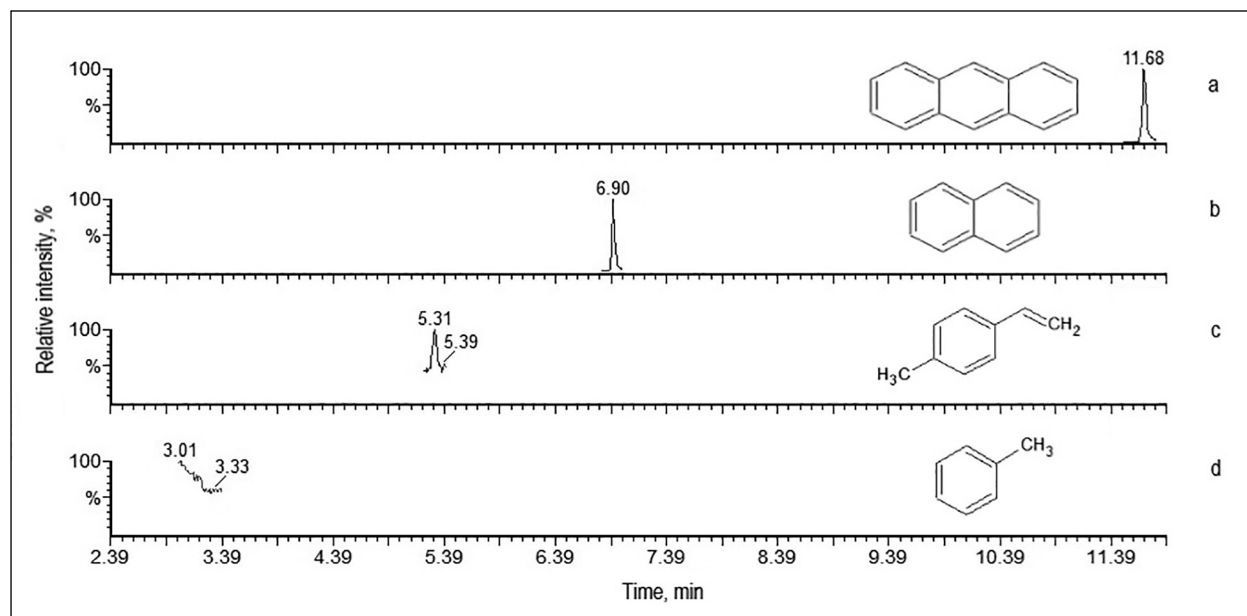
Fig. 5. The chromatogram of anthracene (a), naphthalene (b), 4-methyl styrene (c) and toluene (d) after the headspace mode microextraction with the silica based SPME sorbent synthesized in the quartz capillary, embedded with Ag NPs, measured in the SIR mode

compounds from a sample headspace. From Fig. 5 we can also see that the size of the aromatic system also matters – toluene, that has only a benzene ring, was not extracted (Fig. 5d). It is important to state that in our case the microextraction efficiency is limited by the size of capillary's inlet and volatility of the analytes.

In order to better understand the extracted quantities of the compounds, the chromatographic peaks area, that correlates to the quantity of the analyte, has been calculated and corrected using the results of previous measurement of the same analytes in the same chromatographic setup (Table). As we can see from the Table, despite the fact that higher molecular mass analytes, such as anthracene, have a lower volatility, the sorbent extracts more of it compared to lighter molecule, such as 4-metyl styrene. This correlates to the fact that Ag NPs interacts with double bonds and aro-

matic systems – bigger aromatic systems interact stronger than those with less double bonds/aromatic rings.

CONCLUSIONS

The silver nanoparticles embedded monolithic silica sorbent has been successfully synthesized in a small diameter quartz capillary and applied for the extraction of some aromatic compounds in a headspace microextraction mode. Using the Ag NPs embedded solid phase microextraction sorbent, the extraction of 4-methyl styrene, naphthalene and anthracene from the headspace of an aqueous solution was achieved due to the interactions between the Ag NPs embedded on the sorbent surface and the aromatic systems of the compounds. This study showed that it is possible to extract less volatile analytes, such as anthracene,

Ta b l e . **Data of chromatographic analysis**

Analyte 4 – methyl styrene naphthalene anthracene			
Value set in MS SIR, m/z	118	128	178
Correction coefficients	0.47	0.98	1
Chromatographic peak area (a. u.), MS SIR			
Standard solutions c = 0.05 mg/ml	110721	231386	236942
After microextraction with SPME sorbent, c (solution) = 0.04 mg/ml	38	1227	27614
Corrected (after microextraction with SPME sorbent)	81	1256	27614

from a sample headspace using a sorbent, that is placed in a small quartz capillary, and open new possibilities for a new type of sorbent construction that can be used in combination with GC-MS.

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SIDABRU PADENGTO MONOLITINIO KIETAFAZĖS MIKROEKSTRAKCIJOS SORBENTO SINTEZĖ BEI TYRIMAS

S a n t r a u k a

Monolitinis silikatinis kietafazės mikroekstrakcijos sorbentas, padengtas sidabro nanodalelėmis (Ag ND), buvo sėkmingai susintetintas mažo diametro kvarco kapiliare. Sorbentas buvo testuotas viršerdvės mikroekstrakcijos metodu su aromatinėmis analitėmis, kurios po ekstrakcijos buvo nustatinėjamos dujų chromatografinės analizės metodu. Dėl π-π elektroninės sąveikos tarp analičių aromatinių sistemų ir ant sorbento paviršiaus imobilizuotų sidabro nanodalelių tirtos analitės buvo sėkmingai išekstrahuotos iš mėginio viršerdvės bei nustatytos dujų chromatografinės analizės metodu.