



# Synthesis and application of thiolated mesoporous silicas for sorption, preconcentration and determination of platinum



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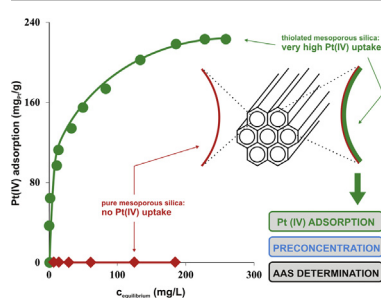
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## HIGHLIGHTS

- A thiol-functionalized organosilica sorbents were synthesized and characterized.
- The sorbents were used in the sorption process of Pt(IV) ions.
- Excellent adsorption capacity with respect to Pt(IV) ions was achieved.
- Pt(IV) preconcentration and AAS determination using the sorbents was validated.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Thiol-functionalized mesoporous silicas were synthesized by co-condensation of tetraethoxysilane (TEOS) and mercaptopropyltriethoxysilane (MPTES). All materials exhibit high values of specific surface area (456–857 m<sup>2</sup>/g), pore volume (0.5–1.3 cm<sup>3</sup>), and pore sizes (2.5–5.3 nm). These values gradually decrease with the increasing amount of MPTES. The obtained thiolated mesoporous silicas were used as sorbents of Pt(IV) species from water solution. The obtained materials exhibit an extremely good ability to remove Pt(IV) ions in the pH range 1–4. The highest adsorption capacity of platinum ions onto the thiolated mesoporous silica reached the value of 222 mg/g (1.14 mmol/g). The analytical applicability of the synthesized sorbents for Pt(IV) preconcentration was investigated and validated using the platinum reference materials. High accuracy of platinum determination was achieved which makes the obtained silicas very promising materials for the above mentioned application.

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## 1. Introduction

The use of platinum group metals (PGMs) in many areas, such as technology, medicine, jewellery production and industry is

constantly increasing. The high cost of noble metals and their wide application as catalysts (e.g. petroleum reforming, nitric acid production) make their effective recycling from industrial wastes and concentration control in industrial and environmental samples absolutely necessary. Although chemical, glass and electronic industries emit large amounts of PGMs, their main source are undoubtedly catalytic converters used in vehicles to control the emission of exhaust gases [1,2].

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In motor converters three PGMs are used: platinum, palladium and rhodium. The first two are responsible for oxidation of unburnt hydrocarbons and carbon monoxide, whereas the last one - for reduction of nitrogen oxides [3]. Convertors slowly undergo destruction, due to the mechanical wearing off and operating at very high working temperature, which results in the reduction of their efficiency and release of those metals from the supporting matrix to the environment [4–6]. Such emitted PGM (and particularly platinum, due to its highest content in the converter among three metals used) can be accumulated in tissues of living organisms, including humans [7]. Due to the observed negative impact of many platinum compounds on human health [8,9], it is absolutely necessary to monitor the platinum content in the environment. This is, however, not an easy task due to its low content in solid or plant samples collected from the roadside areas [10–12].

Another reason for determination of trace amounts of platinum is connected with its presence in biological samples coming from oncology patients treated by platinum-based chemotherapeutic agents (e.g. cisplatin, oxaliplatin, carboplatin [13]). Such samples are characterized by complex matrix and low levels of platinum concentration below the limits of detection of most analytical techniques.

Therefore selective and very sensitive methods are required for PGMs determination. Common analytical techniques, such as neutron activation analysis NAA [14], ICP-MS and inductively coupled plasma-mass spectrometry (ICP-MS) [15–22] or graphite furnace atomic absorption spectrometry GF AAS [23,24] are not suitable for their determination in many samples due to the too low platinum content and matrix interferences. In this case it is necessary to introduce the separation/preconcentration step to the analytical procedure – owing to that, matrix interferences can be minimized and the detection limit can be improved [25].

In the literature, there are a few approaches proposed for the preconcentration of PGMs from water samples, including ion-exchange, liquid-liquid extraction, membrane sorption and adsorption [26]. Among them, adsorption seems to be the most promising method of enrichment due to its high efficiency, low cost and simplicity [27–29]. Unfortunately, the popular adsorbents such as  $\text{Fe}_3\text{O}_4$  [30] or activated carbon [31,32] have relatively low sorption capacity and poor affinity for noble metal ions. Thus, new types of sorbents should be searched for to solve the above problem. Ordered mesoporous silica materials functionalized with proper groups seem to be perfectly suited for this application, due to high thermal stability, high pore volumes, large mesopores, and relatively thick pore walls [33,34]. Particularly, mesoporous silica modified with thiol ligands can exhibit high loading capacities for the removal of heavy metal ions [35].

In our previous papers we investigated the amino-functionalized SBA-15 materials as sorbents of platinum species [36,37]. In this work thiol-functionalized mesoporous silicas were synthesized by the sol-gel method and applied for Pt(IV) ions adsorption. In order to check the possibility of the application of synthesized sorbents for separation and enrichment of Pt(IV) ions from digested solutions, the parameters affecting adsorption process were studied in detail. Taking into account potential analytical applications of such mesoporous silicas, the removal of platinum species from loaded sorbents was studied. The selected sorbent was used for Pt(IV) preconcentration and subsequent determination in the mineralized geological samples using slurry sampling atomic absorption spectrometry with electrothermal atomization (SS GF AAS).

## 2. Materials and methods

### 2.1. Materials

In the present study the following chemicals were used:

tetraethoxysilane (TEOS, 96%, ABCR, Germany), 3-mercaptopropyltriethoxysilane (MPTES, 95%, Sigma-Aldrich, Poland), Pluronic P123 (P123, Sigma-Aldrich, Poland), ethanol (99.8%, POCH, Poland), standard solution of Pt(IV) ( $1000 \text{ mg L}^{-1}$ ) (Merck, Germany), hydrochloric acid Suprapure (36%) (Merck, Germany),  $\text{HNO}_3$  Suprapure (65%) (Merck, Germany), thiourea (POCH, Poland), NaOH (Merck, Germany), HCl Suprapure (Merck, Germany), HF (40%, pure p.a., POCH, Poland). All chemicals were used as received, without further purification. The platinum ore certified reference material (SARM 7) was obtained from SA Bureau of Standards (Republic of South Africa). The samples of oxidized Kupferschiefer shales designated POLK I and POLK II from the West Polkowice mine were delivered by the Polish Geological Institute (Poland). Deionized water (DW; resistivity  $< 17.5 \text{ MV cm}$ ) was obtained using the millipore ion-exchange purification system. Stock solutions were stored in the glass vessels previously soaked in a 10%  $\text{HNO}_3$  acid solution overnight.

### 2.2. Sorbent preparation

One-pot syntheses of mesoporous SBA-15 organosilicas were carried out via co-condensation of MPTES and TEOS; the detailed description can be found elsewhere [38,39]. Briefly, 3 g of P123 was dissolved in 11 mL of deionized water and 60 mL of 2 M HCl with vigorous stirring at 40 °C. After 8 h of stirring TEOS was added dropwise into this solution. After 15 min a co-monomer (MPTES) was added dropwise. Then the mixture was stirred at 40 °C for 24 h and aged at 100 °C for next 48 h. The resulting white solid was washed with deionized water, filtered and dried at 70 °C. The template was removed by four-time extraction with the acidified ethanol (99.8% EtOH with the addition of 5% v/v of the conc. HCl) at 70 °C. The numeration of the samples and the initial ratio of monomers used in the synthesis were as follows: **A1** (TEOS), **A2** (TEOS/MPTES=19), **A3** (TEOS/MPTES=9), **A4** (TEOS/MPTES=3).

### 2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded by using a Seifert RTG DRON-3 diffractometer ( $\text{CuK}\alpha$  radiation) with 0.02° size step and 10 s time step covering a range of  $0.5^\circ < 2\theta < 5.0^\circ$  at RT. Nitrogen adsorption isotherms were measured at  $-196^\circ\text{C}$  using an ASAP 2405 N adsorption analyzer (Micromeritics). Prior to adsorption measurements each sample was degassed (at 110 °C). The content of the sulfur in the obtained samples was determined quantitatively by elemental analysis using the Perkin-Elmer CHN 2400 analyzer. The scanning electron microscope Carl Zeiss Ultra Plus (Germany) was used for the inspection of the surface of thiol functionalized SBA-15. The microscope was also equipped with a secondary electron and backscattered electron detectors. All experiments were carried out under the required conditions (20-kV acceleration voltage and 5-nA probe current). XPS spectra were obtained by using a Multi-Chamber Analytical System (Prevac, Poland) with monochromated  $\text{K}\alpha\text{-Al}$  radiation (1486.6 eV) (Gammatada Scienta, Sweden) and the X-ray power of 450 W. The binding energy (BE) scale was referenced against  $\text{C1s} = 284.7 \text{ eV}$  line. The vacuum in the analysis chamber was better than  $1.5 \times 10^{-7} \text{ Pa}$ .

The platinum concentrations were measured with the aid of AAS-3 (Carl Zeiss, Jena, Germany) atomic absorption spectrometer before and after the contact with SBA-15 to determine the Pt uptake. This instrument is featured with a deuterium-lamp background corrector, an EA-3 electrothermal atomizer and a MPE autosampler. Pyrolytically coated graphite tubes were acquired from Perkin Elmer. Measurements were made using the Pt hollow cathode lamp (Varian) at a wavelength of 265.9 nm; 0.2 nm slit

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