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Silicas Chemically Modified with Sulfur-Containing Groups for Separation and Preconcentration of Precious Metals Followed by Spectrometric Determination

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Abstract: Silicas chemically modified with a number of sulfur-containing groups (mercaptopropyl, mercaptophenyl, dipropyl disulfide, thiadiazole thiol, dithiocarbamate and thiourea derivatives) were proposed for the separation and preconcentration of precious metals. These adsorbents quantitatively extracted precious metals from 0.5 to 4 M solutions of hydrochloric acid. It allowed their separation from high concentrations of non-ferrous, alkaline earth, alkali and some other related metals. The selectivity of separation of kinetically labile precious metal ions in ligand substitution reactions from kinetically inert ones depended on the nature of sulfur atom within the functional group of adsorbents and increased when passing from thione to thiol sulfur. Approaches for the preconcentration of precious metals using silicas chemically modified with sulfur-containing groups prior to their AAS, ICP-OES, and ICP-MS determination in ores, concentrates and their processing products were proposed. The correctness of the developed methods was confirmed by the analysis of certified reference materials.

Keywords: chemically modified silicas; sulfur-containing groups; precious metals; separation; preconcentration; determination; AAS; ICP-OES; ICP-MS

Citation: Losev, V.; Elzuf'ev, E.; Borodina, E.; Buyko, O.; Maznyak, N.; Trofimchuk, A. Silicas Chemically Modified with Sulfur-Containing Groups for Separation and Preconcentration of Precious Metals Followed by Spectrometric Determination. *Minerals* **2021**, *11*, 481. <https://doi.org/10.3390/min11050481>

Academic Editor: Francisco Franco

Received: 8 March 2021

Accepted: 26 April 2021

Published: 30 April 2021

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1. Introduction

Due to their unique properties, the platinum metals are widely used in various fields of science and technology. In the environment, the platinum metals are found in low concentrations in the presence of high concentrations of accompanying elements. Spectrometric methods of analysis are mainly used to determine trace components in objects of various composition.

Direct analysis of the solutions obtained after the decomposition of geological materials for the content of the platinum group metals is difficult due to the overlapping of spectral lines of elements in atomic absorption (AAS) and optical emission spectrometry (OES). The easily ionized alkali and alkaline earth metals present in the solution reduce the intensity of the spectral lines of the analytes. The results of the determination of precious metals by inductively coupled plasma mass spectrometry (ICP-MS) are distorted due to polyatomic interferences of non-ferrous metals [1–3].

The use of preconcentration methods makes it possible to separate analytes from the predominant amounts of accompanying and interfering elements and to increase the selectivity of spectrometric methods. As a result of preconcentration and desorption, the

analyzed solutions have a simple matrix of a known composition, which allows us to reduce the number of calibration standards.

The solid-phase extraction (SPE) method makes it possible to isolate a trace component on a relatively small mass of adsorbent from a large volume of solution, providing good separation efficiency and high preconcentration coefficients.

A number of adsorbents have been proposed for solid-phase extraction of precious metals; they are characterized by high capacity, good kinetics and exceptional selectivity. Adsorbents differ in matrices, nature of functional groups, capacities, particle size, and other ways. Adsorbents, depending on the nature of the functional groups, are divided into ion-exchange (cation exchangers, anion exchangers) and complexing (including chelating) adsorbents.

There are two possible options for using cation exchangers for separating platinum metals from accompanying ones. The first option is based on the separation of the matrix (ions of non-ferrous, alkali and alkaline earth metals from precious metals) from solutions of hydrochloric acid in which platinum metals are present in the form of negatively charged chloro complexes and are not extracted by cation exchangers [4]. The second option is based on the ability of some platinum metals to form cationic complexes (aqua complexes, complexes with ammonia, pyridine, etc.) and, accordingly, they can be extracted by cation exchangers [5,6]. The use of cation exchangers is ineffective, since to remove the predominant amounts of cations of non-ferrous and other accompanying metals, it is necessary to use a lot of cation exchanger, and the separation of cationic complexes of precious metals from cations of accompanying metals is a complex task.

It is most advisable to use adsorbents that allow the separation of trace amounts of precious metals from solutions with a high content of accompanying elements.

The use of anion exchangers for the separation of precious metals from base metals in hydrochloric acid solutions is based on the ability of chloride complexes of precious metals to be retained by strongly basic anion exchangers with groups of quaternary ammonium, phosphonium, pyridinium bases [7–9]. Adsorbents with primary, secondary and tertiary amines, depending on the acidity of the medium, can act both as anion exchangers and as complexing adsorbents [10–13].

The use of N, S- and N-containing adsorbents of various natures for the preconcentration and separation of platinum metals was considered in [14–18]. When considering the adsorbents proposed for the preconcentration of precious metals, there is a tendency to create adsorbents with the highest possible selectivity, which was the reason for the passing from nitrogen- to nitrogen- and sulfur-, and further to sulfur-containing adsorbents.

Sulfur-containing functional groups of adsorbents, in contrast to nitrogen-containing groups, are less sensitive to the anionic composition of solutions and bind a narrow range of metal ions. Precious metals in acidic solutions form much stronger complexes with sulfur-containing groups than non-ferrous and other accompanying metals. Non-ferrous metal ions forming insoluble sulfides are bound by sulfur-containing groups in weakly acidic, neutral or weakly alkaline media, which makes it possible to effectively separate platinum metals from them by solid-phase extraction in acidic media [19–21]. It should be noted that the sulfur-containing groups of adsorbents are also less sensitive to the composition of the inner coordination sphere of the complexes of precious metals than nitrogen-containing ones. They extract precious metals with equal efficiency both from 2 to 4 M solutions of hydrochloric acid, in which precious metals exist in the form of chloride complexes, and from dilute solutions of hydrochloric acid (0.1–1 M), in which precious metals exist in the form of aquachloride complexes of various composition.

In this regard, adsorbents based on silicas chemically modified with sulfur-containing groups are of particular interest. Due to silicon oxide matrix these adsorbents do not swell in aqueous solutions, and possess enough mechanical strength and hydrolytic stability in acidic and slightly alkaline media. Due to the surface arrangement of functional groups chemically modified silicas (CMS) are characterized by good kinetics and adsorbed elements are easy to elute.

The success of using organic reagents with thionic or thiol sulfur in liquid extraction [22,23] and solid-phase extraction of precious metals using polymer adsorbents with sulfur-containing groups [24–26] was the reason for the synthesis and study of adsorbents based on silica chemically modified with sulfur-containing functional groups.

In this work, we investigated CMS with sulfur-containing functional groups (mercaptopropyl, dipropyldisulfide, dithiocarbamate, thiodiazoethiol, mercaptophenyl and thiourea derivatives groups) to separate and preconcentrate precious metals and to study the effect of the nature of sulfur in the functional groups fixed on the silica surface.

These functional groups fixed on the silica surface were chosen because thiourea and its derivatives, as well as dithiocarbamates, are widely used in liquid extraction of precious metals [27–30]. Reagents containing thiol sulfur are more selective than reagents containing thionic or sulfide sulfur [31,32].

Sulfur-containing groups, in particular mercaptopropyl, can be oxidized [33] to dipropyldisulfide groups. Therefore, we studied the solid-phase extraction of elements with adsorbents containing on the silica surface the oxidized form of the ligand—dipropyldisulfide groups.

2. Materials and Methods

2.1. Reagents

Stock solutions of Au^{3+} , Pd^{2+} , Pt^{2+} , Pt^{4+} , Rh^{3+} , Ir^{4+} , Ru^{4+} , Os^{4+} ($1.0 \text{ mg} \cdot \text{mL}^{-1}$) were prepared by dissolving commercially available $\text{H}[\text{AuCl}_4] \cdot 4\text{H}_2\text{O}$, PdCl_2 , $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$, $\text{H}_2[\text{PtCl}_4] \cdot 2\text{H}_2\text{O}$, $\text{H}_3[\text{RhCl}_6]$, $\text{Na}_3[\text{IrCl}_6]$, RuCl_3 , $\text{H}_2[\text{OsCl}_6] \cdot \text{JSC}$ “Aurat”, Russia) in 2.0 M HCl. Solutions of Ru^{4+} were prepared immediately before the experiment by oxidizing Ru^{3+} with hydrogen peroxide in 6 M HCl. In order to prepare stock solution of Ag^+ with a concentration of $0.5 \text{ mg} \cdot \text{mL}^{-1}$ in 6 M HCl, an exact weighed portion of metallic silver (99.9% grade) was dissolved in nitric acid, followed by conversion into 6 M HCl.

Solutions of alkali, alkaline earth metals, Fe^{3+} , Al^{3+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , and Fe^{2+} were prepared by dissolving the corresponding salts (Reachim, Ufa, Russia) in 0.1 M HCl. Solutions with a lower concentration of metal ions were prepared by diluting the stock solutions.

ICP Multi-element standard USP-III (Ir, Os, Pd, Pt, Rh, Ru) purchased from Merck KGaA (Merck, Darmstadt, Germany), 10-51-1 (Ag), 10-70-2 (Os) purchased from high-purity standards (High-Purity Standards, North Charleston, SC, USA) were used as a calibration standards for determination of precious metals. ICP-MCS-1 (As, Be, B, Cd, Pb, Mn, Se, Zn), ICP-MCS-8 (Al, Ca, Cr, Li, Ni, K, Na, and Sr), ICP-MCS-10 (Al, Ba, Be, Co, Cu, Fe, V) were used as calibration standards for ICP-OES and ICP-MS determination of accompanying metals. The standards were purchased from high-purity standards (High-Purity Standards, North Charleston, SC, USA).

Analytical grade reagents HF, HClO_4 , HCl, HNO_3 , NaOH, thiourea (Reachim, Ufa, Russia) were used. Hydrochloric and nitric acids of reagent grade were purified by distillation using distillacidTM BSB-939-IR (Berghof, Eningen, Germany). Solutions of lower concentrations were prepared by dilution of concentrated acids with deionized water. Deionized water ($18.3 \text{ M}\Omega \cdot \text{cm}^{-1}$) was prepared using E-pure D4642-33 (Barnstead International, Dubuque, IA, USA).

The required pH was adjusted by adding of 1 M solutions of NaOH or HCl dropwise.

The eluent (5% or 10% (*w/w*) thiourea solution in 1.0 M HCl) was prepared by dissolving a weighed portion of thiourea in 1.0 M HCl.

Silica gel 60 (particle size of 0.10–0.16 mm, specific surface area of $270 \text{ m}^2 \cdot \text{g}^{-1}$, an average pore size of ~12 nm) purchased from Merck (Germany) was used as a matrix for the adsorbents synthesis.

γ -aminopropyltriethoxysilane, allyl isothiocyanate, ethyl isothiocyanate, benzoyl isothiocyanate, phenyl isothiocyanate, γ -mercaptopropyltrimethoxysilane, γ -(triethoxysilane)-propyl isocyanate, 4-aminothiophenol, 2-aminothiocyanate, carbon disulfide purchased from Aldrich and 2-amino-1,3,4-thiodiazole-2-thiol purchased from Fluka were used as silica surface modifiers.

2.2. Instrumentation

Metal content in the solutions was determined by ICP-OES, ICP-MS, flame atomic absorption spectrometry (FAAS), and graphite furnace atomic absorption spectrometry (GFAAS) analyses of an aqueous phase using iCAP 6500 Duo, Xseries II and Solaar 6M by Thermo Scientific (Waltham, MA, USA). The instruments' operational conditions are represented in Tables S1–S3.

The pH measurements were carried out with a SevenEasy pH Meter S20 (Mettler-Toledo, Greifensee, Switzerland) equipped with combined electrode InLabExpertPro. A Masterflex L/S peristaltic pump (Cole-Parmer Instruments Company, East Bunker Ct Vernon Hills, IL, USA) was used for pumping fluids through the mini-column packed with an adsorbent. Glass mini-column or thermostated glass minicolumn (i.d. of 3 mm, height of 10 cm) was used for preconcentration of metal ions in dynamic mode. Muffle furnace SNOL 6/10-V (TECHNOTHERM, Istra, Russia) was used for the geological samples firing.

The solutions were heated in glass thermostated columns connected to a UTU-2 thermostat (Horyzont, Krakow, Poland). The solutions were mixed using a WU-4 shaker (Horyzont, Krakow, Poland).

2.3. Synthesis of the Adsorbents

There are several approaches to the synthesis of sulfur-containing CMS. The first approach is based on the interaction of organosilicon modifiers with silica in an organic solvent, such as toluene [34,35]. It was used for the synthesis of the MPS adsorbent [36].

The second approach is based on the chemical “assembly” of the functional group on the silica surface and was used in the synthesis of an adsorbent with dithiocarbamate groups (DTCS): the previously synthesized aminopropyl silica gel was treated with carbon disulfide [37].

The third approach is based on the synthesis of a modifier in an organic solvent by the interaction of a reagent containing the required functional group with triethoxysilanes and subsequent fixation of the resulting modifier on the silica surface. For example, the preparation of chemically modified silicas with groups of thiourea derivatives (ATUS, ETUS, BTUS, PhTUS) is based on the fixation on the silica surface of a modifier previously synthesized in an organic solvent by the interaction of γ -aminopropyltriethoxysilane with the corresponding isothiocyanates $RN=C=S$ (where R is allyl, ethyl, benzoyl, phenyl). An adsorbent with thiodiazoethiol groups (TDTS) was synthesized by fixing on the surface of silica gel a modifier previously prepared in an organic solvent by the interaction of γ -(triethoxysilane)-propyl isocyanate with 2-amino-1,3,4-thiodiazole-2-thiol. The preparation of silicas with mercaptophenyl and aminobenzothiazole groups (MPhS, ABTS) was carried out in a similar manner, but for the reaction with γ -(triethoxysilane)propyl isocyanate, 4-aminothiophenol and 2-aminothiophenol were used, respectively.

The fourth approach for obtaining sulfur-containing CMS is the chemical transformation of fixed sulfur-containing groups. For example, the DSS adsorbent was prepared by oxidizing the mercapropyl groups fixed on the silica surface to dipropyldisulfide groups with iodine. The characteristics of the synthesized adsorbents are represented in Table 1.

Table 1. Silicas chemically modified with sulfur-containing groups.

Adsorbent	Structure of Functional Group	Concentration of Fixed Groups, mmol·g ^{−1}
<i>N</i> -allyl- <i>N'</i> -propyl thiourea silica (ATUS)		0.55
<i>N</i> -ethyl- <i>N'</i> -propyl thiourea silica (ETUS)		0.45
<i>N</i> -benzoyl- <i>N'</i> -propyl thiourea silica (BTUS)		0.35
<i>N</i> -phenyl- <i>N'</i> -propyl thiourea silica (PhTUS)		0.39
Mercaptopropyl silica (MPS)		0.87
Dipropyldisulfide silica (DSS)		0.43
Dithiocarbamate silica (DTCS)		0.16
<i>N</i> -(1,3,4-thiodiazol-2-thiol)- <i>N'</i> -propyl urea silica (TDTS)		0.13
Mercaptophenylpropyl urea silica (MPhS)		0.11
Aminobenzothiazolepropyl silica (ABTS)		0.11

2.4. Batch Procedure

In the batch experiment 10.0 µg of metal ion as a solution in 0.5–4.0 M HCl was placed into a thermostated test tube; HCl or NaOH was added to adjust required acidity; and deionized water was added to a total volume of 10.0 mL. The adsorbent mass of 0.100 g was added; the tube was stopped and stirred for 1–60 min at 20 °C or 95 °C. In the study of adsorption of kinetically inert platinum metals at 95 °C, 1.0 mL of a 0.025 M SnCl₂ solution was added. The solution was separated from the adsorbent by decantation. For desorption of precious metals, 10.0 mL of a 10% (*w/w*) solution of thiourea in 1.0 M HCl was added to the adsorbent and stirred for 1 min–60 min at 20 °C or 95 °C. The distribution of the metal was monitored by the analysis of aqueous phase by ICP-OES.

2.5. Column Procedure

The study of adsorption of precious metals in the dynamic mode was carried out at 20 °C by passing of 10.0 mL of a solution containing 10.0 µg·mL^{−1} of a precious metal ion through a column (height of 5 cm, i.d. of 3 mm) containing 0.1 g of adsorbent with a flow rate

of 1.0 mL min^{−1}. To elute retained precious metals, 10.0 mL of a 10% (*w/w*) thiourea solution in 1 M HCl at 20 °C was passed through the column at a flow rate of 1.0 mL min^{−1}.

The study of adsorption of Rh³⁺, Ir⁴⁺, Ru⁴⁺, and Os⁴⁺ in the dynamic mode was carried out at 95 °C by passing of 10.0 mL of a solution containing 10.0 µg·mL^{−1} of a precious metal ion and 0.0025 M SnCl₂ through a thermostated column containing 0.1 g of adsorbent with a flow rate of 1.0 mL·min^{−1}. To desorb these precious metals, 10.0 mL of a 10% (*w/w*) thiourea solution in 1.0 M HCl at 95 °C was passed through the column at a flow rate of 1.0 mL·min^{−1}.

The separation of kinetically labile chloride complexes of precious metals from kinetically inert ones and their preconcentration was carried out using a system of two sequentially connected mini-columns containing 0.1 g of adsorbent in each. On the first column at 20 °C, the kinetically labile chlorocomplexes Au³⁺, Pd²⁺, Pt⁴⁺ were retained. SnCl₂ solution was added in the stream after the first column. Then, the solution was passed through the second thermostated column at 95 °C. On the second column, adsorption of kinetically inert complexes of Rh³⁺, Ir⁴⁺, Ru⁴⁺, Os⁴⁺ occurred. The desorption of retained precious metals was carried out by passing of 10.0 mL 10% (*w/w*) thiourea solution in 1.0 M HCl through each column with the flow rate of 1.0 mL·min^{−1}: at 20 °C through the first column and 95 °C through the second one.

2.6. Sample Preparation

We have developed a method for digestion of geological samples and their processing products, which made it possible to use a general approach for the digestion of materials of various composition containing precious metals.

Geological samples and products of their processing were placed in a glassy carbon crucible and pre-dried at 105 °C. Then, sample portions of 1.0000 g were roasted in a muffle furnace for 2 h at 500 °C. After cooling, the roasted sample was moistened with deionized water, then 25.0 mL conc. HF and 2.0 mL H₂SO₄ (diluted 1:1) were added. The digestion was carried out under slow heating until sulfuric anhydride vapors appeared. Then, 30.0 mL mixture of acids HF:HClO₄:HCl:HNO₃ (2:2:3:3) was added; the digestion was carried out under heating, and mixture of acids was evaporated to dryness. Then, 30.0 mL mixture of acids HCl:HNO₃ (3:1) was added to sample and evaporated to wet salts. We added 10.0 mL of concentrated HCl to the residue and evaporated to wet salts; the procedure was repeated twice. Afterwards, 20.0 mL of concentrated HCl and 20.0 mL of deionized water was added, and salts were dissolved under heating (50 °C). If an insoluble precipitate was present, which contains ruthenium, osmium, iridium, and rhodium, it was filtered through a paper filter, the filter with the precipitate was placed in a corundum crucible and turned to ash. A fivefold excess of sodium peroxide was added to the ash residue, the mixture was stirred and fused at 650 °C for 20 min. The melt was leached with 20 mL of 2 M HCl. The solutions were joined together, transferred into a 100 mL volumetric flask and diluted with 2.0 M HCl to the mark.

3. Results and Discussion

3.1. Solid-Phase Extraction of Platinum Group Metals, Ag⁺ and Au³⁺, and Non-Ferrous Metals Using Silicas Chemically Modified with Sulfur-Containing Groups

The efficiency of using CMS with sulfur-containing groups for the preconcentration of precious metals, first of all, depends on the conditions of the extraction of the non-ferrous and other accompanying metals. This determines the conditions for their separate extraction. Silicas, chemically modified with sulfur-containing groups, extracted non-ferrous metals from weakly acidic, neutral and weakly alkaline solutions (Figure S1); the time of the attainment of adsorption equilibrium did not exceed 5 min. Calcium(II), magnesium(II), strontium(II), aluminum(III) and alkali metals were not extracted by sulfur-containing silicas in a wide pH range from 1 to 9.

DSS adsorbent extracted non-ferrous metal ions at higher pH values than MPS adsorbent (Figure S1); in addition, the extraction of some metals was not quantitative.

Chloride complexes of precious metals are divided into kinetically labile (Ag^+ , Au^{3+} , Pd^{2+} , Pt^{2+} , Pt^{4+}) and kinetically inert complexes (Rh^{3+} , Ir^{4+} , Ru^{4+} and Os^{4+}) in reactions of ligand substitution.

Most of the studies are devoted to the SPE of Au^{3+} , Pd^{2+} , Pt^{2+} , and Pt^{4+} , which are kinetically labile in the reactions of ligand substitution; the adsorption of kinetically inert Rh^{3+} , Ir^{4+} , Ru^{4+} , Os^{4+} remains without attention as a rule.

Solid-phase extraction of precious metals should be carried out from dilute solutions of hydrochloric acid (0.5–4 M), since accompanying non-ferrous and other metals are extracted from weakly acidic and weakly alkaline solutions; their noticeable extraction was observed at $\text{pH} > 3$ (Figure S1). In addition, in weakly acidic and neutral solutions, aquation and hydrolysis of chloro complexes of platinum group metals occurs. In hydrochloric acid solutions (after liquid-phase oxidative decomposition of natural and industrial samples) precious metals are represented by chloride complexes in the following oxidation states: Ag^+ , Au^{3+} , Pd^{2+} , Pt^{4+} , Rh^{3+} , Ir^{4+} , Ru^{4+} , Os^{4+} .

When preconcentrating platinum group metals, it is also necessary to take into account the extraction of Ag^+ and Au^{3+} , which interact with sulfur-containing groups of adsorbents under similar conditions as kinetically labile chloro complexes of platinum group metals. All studied adsorbents quantitatively extracted Au^{3+} from 0.5 to 4 M HCl at room temperature. The DTCS and DSS adsorbents did not extract Ag^+ from hydrochloric acid solutions, which can be used to separate Au^{3+} and other platinum group metals from it.

The conditions for the quantitative extraction of platinum metals from hydrochloric acid solutions by silicas chemically modified with sulfur-containing groups are given in Table 2. As can be seen from the table, all the studied adsorbents (except ABTS) extracted Pd^{2+} in a wide range of hydrochloric acid concentrations at room temperature with a time of attainment of adsorption equilibrium from 2 min to 5 min. For the quantitative extraction of Pd^{2+} with the ABTS adsorbent, heating to 95 °C and the phase contact time of 30 min were required.

Table 2. Conditions for the quantitative extraction of platinum group metals ions from hydrochloric acid solutions by silicas chemically modified with sulfur-containing groups.

Adsorbent	T, °C	Pd^{2+}	Pt^{4+}	Rh^{3+}	Ir^{4+}	Ru^{4+}	Os^{4+}
ATUS	25	0.5–6 M 5 min	0.5–4 M 10 min	-	-	-	-
	95	0.5–6 M 5 min	0.5–4 M 10 min	0.5–5 M 10 min	0.5–4 M 10 min	2–4 M 10 min	0.5–4 M 30 min SnCl_2
DTCS	25	0.5–6 M 5 min	0.5–4 M 5 min	-	-	-	-
	95	0.5–6 M 5 min	0.5–2 M 5 min	1–4 M 5 min SnCl_2	0.5–4 M 30 min	0.5–1 M 40 min SnCl_2	2–4 M 60 min SnCl_2
MPS	25	0.5–6 M 2 min	-	-	-	-	-
	95	0.5–6 M 2 min	0.5–5 M 5 min	0.5–5 M 10 min	0.5–4 M 10 min	2–6 M 5 min	0.5–4 M 30 min SnCl_2
DSS	25	0.2–2 M 15 min	-	-	-	-	-
	95	0.5–2 M 15 min	0.5–4 M 20 min	0.5–4 M 20 min	0.5–4 M 30 min	4–6 M 20 min	0.5–4 M 60 min SnCl_2

Table 2. Cont.

Adsorbent	T, °C	Pd ²⁺	Pt ⁴⁺	Rh ³⁺	Ir ⁴⁺	Ru ⁴⁺	Os ⁴⁺
TDTS	25	0.2–6 M 5 min	-	-	-	-	-
	95	0.5–4 M 5 min	0.5–4 M 10 min	0.5–4 M 5 min SnCl ₂	0.5–4 M 30 min SnCl ₂	0.5–2 M 40 min SnCl ₂	1–4 M 60 min SnCl ₂
MPhS	25	0.5–4 M 5 min	-	-	-	-	-
	95	0.5–4 M 5 min	0.5–4 M 5 min SnCl ₂	0.5–4 M 5 min SnCl ₂	-	0.5–4 M 10 min SnCl ₂	-
ABTS	25	-	-	-	-	-	-
	95	0.5–4 M 5 min SnCl ₂	0.5–4 M 5 min SnCl ₂	0.5–4 M 15 min SnCl ₂	-	-	-

At room temperature, Pt⁴⁺ was extracted only by adsorbents containing thionic sulfur (ATUS, DTCS). At 95 °C, Pt⁴⁺ was quantitatively recovered by all adsorbents, with the exception of DSS. A long phase contact time up to 30 min was required to attain the adsorption equilibrium when using MPhS and ABTS adsorbents. The ABTS adsorbent, the sulfur atom of which is in the heterocycle, is the least effective for the extraction of precious metal ions.

For the labilization of kinetically inert chlorocomplexes of platinum metals, tin(II) chloride was used as a labilizing agent. During the interaction of Rh³⁺, Ir⁴⁺, Ru⁴⁺, Os⁴⁺, as well as Pd²⁺ and Pt⁴⁺ with tin (II) chloride in solutions of hydrochloric acid, chloride–tin chloride complexes of various composition were formed, in which the central ion can be in various oxidation states, including the zero-valent state. The composition of the complexes depends on the concentration of acid and tin(II) chloride. The ligands SnCl₃[−] have a strong trans-effect, which determines the kinetic lability of tinchloride complexes of precious metals in ligand substitution reactions. Thus, the addition of SnCl₂ led to a decrease in the time of the attainment of the adsorption equilibrium during the extraction of Pd²⁺ and Pt⁴⁺ with MPhS and ABTS adsorbents for 5 min.

For the quantitative extraction of kinetically inert chloro complexes of platinum metals (Rh³⁺, Ir⁴⁺, Ru⁴⁺, Os⁴⁺) from hydrochloric acid solutions using the proposed adsorbents, it was necessary to increase the temperature to 95 °C and/or add a labilizing agent—tin(II) chloride (Table 2).

Without the addition of a labilizing agent, Rh³⁺ was quantitatively extracted from hydrochloric acid solutions at 95 °C with ATUS, MPS, DSS adsorbents; time of attainment of adsorption equilibrium was 20 min or less. The addition of tin(II) chloride made it possible to achieve a quantitative extraction of Rh³⁺ also with DTCS, TDTS, MPhS and ABTS adsorbents.

The quantitative extraction of Ir⁴⁺ with ATUS, DTCS, MPS, DSS adsorbents was observed at 95 °C. For the quantitative extraction of Ir⁴⁺ by the TDTS adsorbent, it was necessary to add a labilizing agent.

ATUS, MPS, DSS adsorbents extracted Ru⁴⁺ from hydrochloric acid solutions at 95 °C without the addition of SnCl₂. The quantitative extraction of Ru⁴⁺ with DTCS, TDTS, MPhS adsorbents and Os⁴⁺ with ATUS, DTCS, MPS, DSS, TDTS adsorbents was observed at 95 °C and after adding a labilizing agent; the time of attainment of adsorption equilibrium was 30–60 min.

The quantitative extraction of Ir⁴⁺, Ru⁴⁺, Os⁴⁺ with the ABTS adsorbent was not achieved upon heating in the presence of SnCl₂ even at a phase contact time of 60 min.

A comparison of the extraction of Ag⁺, Au³⁺, and platinum group metals by silicas chemically modified with various sulfur-containing groups from 2 M HCl at room temper-

ature is shown in Figure 1. Since solutions with a concentration of hydrochloric acid of 2 M in most cases are final after digestion of natural and industrial samples; in these solutions precious metals are represented by chloride complexes of Ag^+ , Au^{3+} , Pd^{2+} , Pt^{4+} , Rh^{3+} , Ir^{4+} , Ru^{4+} , Os^{4+} .

Figure 1. Extraction of platinum group metals, Ag^+ and Au^{3+} from 2 M HCl using silicas chemically modified with sulfur-containing groups at room temperature ($C_{Me} = 5 \mu\text{g}\cdot\text{mL}^{-1}$, 25°C , 0.1 g of adsorbent, phase contact time of 10 min).

As can be seen from Figure 1, CMS with thiourea derivative, along with the quantitative extraction of Ag^+ , Au^{3+} , Pd^{2+} and Pt^{4+} , also partially extracted Rh^{3+} and Ir^{4+} ; their extraction was 75% and 60%, respectively. When using adsorbents containing thiol sulfur in the functional group (MPS, TDTS, MPhS), a similar dependence was observed: quantitative extraction from hydrochloric acid solutions at room temperature was attained only for Ag^+ , Au^{3+} , Pd^{2+} , and there was practically no adsorption of Pt^{4+} and other kinetically inert platinum group metals (Rh^{3+} , Ir^{4+} , Ru^{4+} , Os^{4+}). The adsorbent with dipropyldisulfide groups exhibited the best selectivity and extracted only Pd^{2+} and Au^{3+} from 2 M HCl. Thus, the selectivity of adsorbents for intragroup separation of platinum group metals increased from adsorbents with functional groups containing thionic sulfur to adsorbents with groups containing thiol sulfur, and further to adsorbents with disulfide groups.

When passing from 4 M HCl to more dilute solutions of hydrochloric acid (0.5–2 M), chloride complexes of precious metals are aquated with the formation of aquachloride complexes of various composition and charge. The quantitative extraction of precious metals in a wide range of hydrochloric acid concentrations (0.5–4 M) indicates the absence of a noticeable effect of the composition of the inner coordination sphere of precious metal complexes on their interaction with sulfur-containing groups of adsorbents. The main effect on the extraction of precious metals was exerted by the nature of the sulfur-containing functional group, covalently attached to the silica surface, and the nature of the precious metal.

Thus, the use of CMS with sulfur-containing groups allows us to solve the main problems in the field of analytical chemistry of precious metals:

- Separation of a group of precious metals (Au^{3+} , Pd^{2+} , Pt^{2+} , Pt^{4+} , Rh^{3+} , Ir^{4+} , Ru^{4+} , and Os^{4+}) using ATUS, MPS, MPhS, and DTCS adsorbents at 95°C in the presence of tin(II) chloride from the prevailing amounts of related elements.

- Separation of platinum metal ions that are kinetically labile in the reactions of ligand substitution from kinetically inert ones (for example, the ATUS and DTCS adsorbents at room temperature made possible the quantitative extraction of Ag^+ , Au^{3+} , Pd^{2+} , and Pt^{4+} , while the TDTS and MPS adsorbents-extraction of Ag^+ , Au^{3+} , Pd^{2+} separated them from Rh^{3+} , Ir^{4+} , Ru^{4+} and Os^{4+} ; the DPSS adsorbent made it possible to selectively isolate only Au^{3+} and Pd^{2+} from hydrochloric acid solutions).
- Separation of platinum metals with similar chemical properties (for example, the use of TDTS, MPS, and DPSS adsorbents made it possible to separate Pd^{2+} from Pt^{4+}).

3.2. Determination of Platinum Group Metals, Ag^+ , and Au^{3+} in Geological Samples and Their Processing Products

The adsorption of precious metals in the column mode allows them to be preconcentrated from large volumes of solutions and to achieve a greater extraction of elements in comparison with adsorption in the batch mode. By means of SPE of precious metals from acidic solutions, it is possible to effectively separate them from the prevailing amounts of non-ferrous and other accompanying metals, which is important in the analysis of geological materials and the products of their processing.

In addition, it is possible to effectively separate kinetically labile chloro complexes of platinum metals from kinetically inert ones in a dynamic mode, since the latter were not retained by the proposed adsorbents at room temperature.

The platinum group metals, Ag^+ and Au^{3+} , were determined (including to check the correctness of the results obtained) in certified reference materials of sulfide copper-nickel and gold-bearing ores and products of their processing (concentrates, tailings, matte, feinstein, blister and cathode copper). The approximate content of accompanying non-ferrous and other metals in the samples is given in Table S4.

For the simultaneous determination of platinum group metals, gold and silver, it is advisable to use multielement methods of analysis—ICP-OES and ICP-MS. To determine one or two precious metals, for example, gold, silver, palladium or platinum, FAAS or GFAAS (depending on the concentration of the element being determined) can be used.

For the solid-phase extraction of Ag^+ , Au^{3+} , Pd^{2+} and Pt^{4+} and their separation from the ions of non-ferrous and other accompanying metals, as well as kinetically inert platinum metals in a dynamic mode using a single-column method (Figure 2a) an ATUS adsorbent was used for the preconcentration of Ag^+ , Au^{3+} , Pd^{2+} —TDTS adsorbent and for preconcentration of Au^{3+} , Pd^{2+} —MPS adsorbent.

Figure 2. Single-column system for SPE of kinetically labile complexes of platinum group metals (a) and for simultaneous SPE of all precious metals (b).

Although the degree of Cu^{2+} extraction from 1 M HCl by DTCS and MPS adsorbents was 40% and 80%, respectively (Figure S1), it did not interfere with the solid-phase extraction of precious metals. Thus, when solutions containing Pd^{2+} and Cu^{2+} were passed through the column, the upper zone of the adsorbent was colored brown, corresponding to palladium complexes with sulfur-containing groups attached to the silica surface, and the entire surface of the adsorbent in the column became yellow-green, corresponding to

adsorbed copper. After passing 1–2 M HCl, the yellow-green color of the adsorbent disappeared as a result of copper desorption, while the zone corresponding to the palladium complex remained unchanged. This confirms the lower stability of copper complexes with sulfur-containing groups in acidic media. When dilute solutions of hydrochloric acid were passed through the column, adsorbed bismuth and lead ions were also removed from the surface, which were partially adsorbed from slightly acidic solutions.

To determine silver, gold, palladium and platinum in a single-column mode, the solution after decomposition of geological sample (50 mL) was passed through a glass column containing 0.1 g of adsorbent, at a flow rate of 1 mL·min^{−1}, at room temperature. To remove the adsorbed ions of the accompanying elements, 20 mL of 2 M HCl was passed through the column. Desorption of kinetically labile precious metals was carried out at room temperature by passing of 10 mL of a 10% *w/v* thiourea solution in 1 M HCl through the column at a flow rate of 1 mL·min^{−1}.

FAAS and GFAAS were used for determination of silver, gold, palladium, and platinum in eluates. Calibration graphs were constructed against standards prepared using the eluent (thiourea solution) as matrix and blank solution. The results of silver, gold, palladium and platinum determination are given in Table 3.

Table 3. Results of determination of precious metals in geological samples and products of their processing using SPE-FAAS and SPE-GFAAS methods (n = 5, P = 0.95).

Adsorbent	Sample	Found, g·t ^{−1} (Certified, g·t ^{−1})				Method
		Ag	Au	Pd	Pt	
ATUS	Sulfide copper-nickel ore (VT-1 GSO * no. 929-86)	2.8 ± 0.3 (2.6 ± 0.4)	0.25 ± 0.03 (0.26 ± 0.04)	6.3 ± 0.5 (6.40 ± 0.45)	2.6 ± 0.2 (2.55 ± 0.34)	FAAS
	Matte of ore-thermal smelting (ShT-1 GSO no. 2432-83)	41.6 ± 0.8 (41.45 ± 9.46)	1.66 ± 0.06 (1.62 ± 0.16)	51.4 ± 0.8 (51.5 ± 2.6)	16 ± 1 (16.60 ± 1.56)	
	Copper alloys with precious metals	176 ± 2 (180 ± 10)	29.7 ± 0.06 (29 ± 1)	305 ± 4 (310 ± 10)	97 ± 3 (100 ± 10)	
	GSO no. 933-76	- **	9.6 ± 0.8	97 ± 3	29.6 ± 08	
	GSO no. 934-76	-	(10 ± 1)	(100 ± 10)	(30 ± 1)	
	GSO no. 935-76	28 ± 1 (30 ± 6)	4.7 ± 0.7 (5 ± 1)	50.5 ± 0.5 (49 ± 2)	13 ± 1 (15 ± 2)	
	Copper ore of the Chineysky deposit (Chita Oblast, Russia)	14.2 ± 0.1 (14.0 ± 0.3)	4.7 ± 0.2 (4.9 ± 0.3)	4.0 ± 0.1 (4.1 ± 0.2)	5.0 ± 0.5 (5.4 ± 0.6)	
MPS	Sample 12	21.0 ± 0.1 (21.1 ± 0.3)	3.9 ± 0.1 (3.9 ± 0.2)	6.3 ± 0.3 (6.4 ± 0.5)	-	FAAS
	Sample 13					
	Blister copper	200 ± 5 (213 ± 3)	3.0 ± 0.1 (2.96 ± 0.06)	2.5 ± 0.1 (2.35 ± 0.05)	n.d. ***	
	Cathode copper	13.8 ± 0.8 (14.0 ± 0.5)	2.4 ± 0.2 (2.2 ± 0.2)	-	n.d.	
	Copper concentrate (KM-1 GSO no. 1701-86)	70 ± 1 (-)	3.5 ± 0.4 (3.8 ± 0.3)	37.8 ± 0.8 (37.6 ± 4.2)	n.d.	
	Gold-bearing flotation concentrate SOP **** ZSK-3-99	1.85 ± 0.09 (1.92 ± 0.38)	105 ± 4 (103 ± 6)	-	n.d.	
	Gold ore SOP ZSR-1-99	0.08 ± 0.02 (0.09 ± 0.05)	3.4 ± 0.3 (3.3 ± 0.3)	-	-	
DSS	Concentration tailing (ChO-1 GSO no. 1703-86)	0.50 ± 0.08 (0.58 ± 0.07)	0.10 ± 0.01 (0.07 ± 0.01)	0.82 ± 0.06 (0.84 ± 0.17)	n.d.	GFAAS
	Copper concentrate (KM-1 GSO no. 1701-86)	n.d.	3.7 ± 0.3 (3.8 ± 0.3)	37.2 ± 0.5 (37.6 ± 4.2)	n.d.	FAAS
	Sulfide copper-nickel ore (VT-1 GSO no. 929-86)	n.d.	0.29 ± 0.04 (0.26 ± 0.04)	6.3 ± 0.3 (6.40 ± 0.45)	n.d.	FAAS
	Concentration tailing (ChO-1 GSO no. 1703-86)	n.d.	0.07 ± 0.01 (0.07 ± 0.01)	0.81 ± 0.07 (0.84 ± 0.17)	n.d.	GFAAS

* GSO—national standard sample; ** “-” —not certified; *** n.d.—not detected; **** SOP—factory standard sample.

The single-column mode was used for the simultaneous preconcentration of all precious metals using ATUS and DTCS adsorbents (Figure 2b). Then, 1.0 mL of 0.025 M SnCl_2 was added to the solution prior to SPE, and the resulting solution was passed through the thermostated glass column at 95 °C filled with 0.1 g of the adsorbent with the flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$. The column was rinsed with 20.0 mL of 2 M HCl to remove the adsorbed ions of accompanying elements. The desorption of the precious metals was carried out at 95 °C by passing through the column 10.0 mL of a 10% *w/v* solution of thiourea in 1 M HCl at a solution flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$. The content of precious metals in the eluates was determined by ICP-OES and ICP-MS. Calibration graphs were constructed against standards prepared using the eluent (thiourea solution) as matrix and blank solution. The results of the determination of the precious metals are represented in Table 4.

Table 4. Results of SPE-ICP-OES and SPE-ICP-MS determination of Au and platinum group metals in ore samples and their processing products using silicas chemically modified with sulfur-containing groups ($n = 5$, $P = 0.95$).

Adsorbent	Sample	Found, $\text{g} \cdot \text{t}^{-1}$ (Certified, $\text{g} \cdot \text{t}^{-1}$)							
		Ag	Au	Pd	Pt	Rh	Ir	Ru	Os
ATUS	Nickel concentrate (KN-1 GSO no. 1702-86)	24.3 ± 0.6 (23.4 ± 2.2)	$0.9 \pm 0.1^*$ (0.84 ± 0.09)	29.8 ± 0.3 (30.0 ± 2.2)	8.3 ± 0.3 (8.6 ± 0.3)	$0.95 \pm 0.07^*$ (0.98 ± 0.09)	$0.10 \pm 0.02^*$ (0.11 ± 0.01)	$0.30 \pm 0.05^*$ (0.34 ± 0.06)	$0.06 \pm 0.01^*$ (0.06 ± 0.01)
	Matte of ore-thermal smelting (ShT-1 GSO no. 2432-83)	41.6 ± 0.7 (41.45 ± 9.46)	1.7 ± 0.1 (1.62 ± 0.16)	51.4 ± 0.5 (51.5 ± 2.60)	16.3 ± 0.4 (16.60 ± 1.56)	3.7 ± 0.1 (3.72 ± 0.50)	$0.39 \pm 0.06^*$ (0.43 ± 0.06)	$1.1 \pm 0.1^*$ (1.16 ± 0.15)	$0.14 \pm 0.06^*$ (0.17 ± 0.08)
TDTs	Sulfide copper-nickel ore (VT-1 GSO no. 929-86)	2.8 ± 0.3 (2.6 ± 0.4)	$0.24 \pm 0.05^*$ (0.26 ± 0.04)	6.3 ± 0.3 (6.4 ± 0.5)	2.5 ± 0.2 (2.55 ± 0.34)	$0.31 \pm 0.03^*$ (0.33 ± 0.05)	$0.04 \pm 0.01^*$ (0.041 ± 0.005)	$0.09 \pm 0.01^*$ (0.10 ± 0.01)	$0.02 \pm 0.01^*$ (0.02 ± 0.01)
	Matte of ore-thermal smelting (ShT-1 GSO no. 2432-83)	41.3 ± 0.6 (41.45 ± 9.46)	1.68 ± 0.07 (1.62 ± 0.16)	50.8 ± 0.4 (51.5 ± 2.60)	16.9 ± 0.5 (16.60 ± 1.56)	3.62 ± 0.08 (3.72 ± 0.50)	$0.40 \pm 0.05^*$ (0.43 ± 0.06)	$1.2 \pm 0.1^*$ (1.16 ± 0.15)	$0.16 \pm 0.06^*$ (0.17 ± 0.08)
MPhS	Nickel concentrate (KN-1 GSO no. 1702-86)	24.1 ± 0.8 (23.4 ± 2.2)	$0.8 \pm 0.1^*$ (0.84 ± 0.09)	30.2 ± 0.3 (30.0 ± 2.2)	8.5 ± 0.2 (8.6 ± 0.3)	$1.0 \pm 0.1^*$ (0.98 ± 0.09)	$0.12 \pm 0.02^*$ (0.11 ± 0.01)	$0.31 \pm 0.05^*$ (0.34 ± 0.06)	$0.05 \pm 0.01^*$ (0.06 ± 0.01)
	Copper-nickel feinest (FShT-42 GSO 9315-2009)	105 ± 3 (107 ± 4)	2.56 ± 0.07 (2.55 ± 0.11)	131 ± 1 (130 ± 2)	23.8 ± 0.3 (24.0 ± 0.6)	5.3 ± 0.2 (5.45 ± 0.20)	$0.58 \pm 0.03^*$ (0.6 ± 0.03)	$1.7 \pm 0.1^*$ (1.70 ± 0.09)	$0.21 \pm 0.02^*$ (0.23 ± 0.02)
DTCS	Concentration tailing (ChO-1 GSO no. 1703-86)	-	$0.10 \pm 0.01^*$ (0.07 ± 0.01)	$0.82 \pm 0.06^*$ (0.84 ± 0.17)	$0.5 \pm 0.1^*$ (0.43 ± 0.09)	$0.1 \pm 0.01^*$ (0.096 ± 0.013)	$0.09 \pm 0.01^*$ (0.10 ± 0.01)	$0.025 \pm 0.009^*$ (0.029 ± 0.013)	$0.010 \pm 0.006^*$ (0.011 ± 0.004)
	Copper concentrate (KM-1 GSO no. 1701-86)	-	3.7 ± 0.3 (3.8 ± 0.3)	37.2 ± 0.5 (37.6 ± 4.2)	8.5 ± 0.3 (8.6 ± 0.4)	$0.25 \pm 0.02^*$ (0.27 ± 0.02)	$0.050 \pm 0.005^*$ (0.052 ± 0.004)	$0.11 \pm 0.02^*$ (0.12 ± 0.01)	$0.020 \pm 0.003^*$ (0.022 ± 0.002)

* SPE-ICP-MS.

As can be seen from Tables 3 and 4, the results obtained are characterized by high accuracy and reproducibility.

The two-column procedure (Figure 3) was used for sequential separation and preconcentration of kinetically labile (Au^{3+} , Pd^{2+} , Pt^{2+} , Pt^{4+}) and kinetically inert (Rh^{3+} , Ir^{4+} , Ru^{4+} and Os^{4+}) precious metals using DTCS adsorbent. For this, 50.0 mL of a solution containing precious metal ions in 2 M HCl was passed through a system of two columns with a solution flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$. SnCl_2 solution was added in the stream after the first column (1) at 20 °C by means of tap (2) with the flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$. Then, the solution was passed through the second thermostated column (3) at 95 °C. Then, 20.0 mL of 2.0 M HCl was pumped through two-column system in order to remove retained non-ferrous metals and SnCl_2 . The desorption of retained precious metals was carried out by passing of 10.0 mL 10% (*w/v*) thiourea solution in 1.0 M HCl through each column with

the flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$: at 20°C through the first column and 95°C through the second one.

Figure 3. Two-column system for separation of kinetically labile precious metals from kinetically inert ones.

The results of the determination of precious metals in the tailings obtained by the single-column and two-column methods of preconcentration using DTCS adsorbent are identical (Table 4).

4. Conclusions

Silicas chemically modified with sulfur-containing groups quantitatively extracted precious metals (gold, silver, and platinum group metals) mainly from 0.5 to 4 M solutions of hydrochloric acid and made it possible to efficiently separate them from the accompanying metals. The range of quantitative recovery depended on the nature of the functional group of the adsorbent and the nature of the extracted precious metal ion. Adsorbents with functional groups containing thionic sulfur made it possible to separate kinetically labile chloro complexes of precious metals (Ag^+ , Au^{3+} , Pd^{2+} , Pt^{4+}) in ligand substitution reactions from kinetically inert chloro complexes (Rh^{3+} , Ir^{4+} , Ru^{4+} , Os^{4+}) at room temperature. Solid-phase extraction at 95°C in the presence of a labilizing agent (SnCl_2) made it possible to preconcentrate all precious metals simultaneously. The transition from adsorbents with functional groups containing thionic sulfur to adsorbents with groups containing thiol sulfur and then to disulfide groups leads to an increase in the selectivity of intragroup separation of precious metals. The hyphenated methods of SPE-FAAS, SPE-GFAAS, SPE-ICP-OES and SPE-ICP-MS determination of precious metals in geological materials and products of their processing using silicas with sulfur-containing functional groups were proposed. The analysis of certified reference materials for precious metals shown high accuracy and reproducibility of the results obtained.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11050481/s1>, Table S1. ICP-OES operational conditions; Table S2. ICP-MS operational conditions; Table S3. FAAS and GFAAS operational conditions; Table S4. Average content of accompanying elements in analyzed samples; Figure S1. Extraction of Bi(III) (1); Cu(II) (2); Pb(II) (3); Cd(II) (4); Zn(II) (5); Co(II) (6); Ni(II) (7), Fe(III) (8); Fe(II) (9) with MPS, DSS, DTCS, and TDTs adsorbents vs. pH ($C_{Me} = 10 \mu\text{g} \cdot \text{mL}^{-1}$, $V = 10 \text{ mL}$, 0.1 g of adsorbent).

Author Contributions: Writing—original draft and project administration, V.L.; investigation, E.E.; formal analysis and data curation, E.B.; writing—review, editing and visualization, O.B.; validation, N.M.; methodology, A.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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