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# Investigation of the new sorption preconcentration systems for determination of noble metals in rocks by inductively coupled plasma–mass spectrometry

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## ABSTRACT

The reversible sorption preconcentration of noble metals (NMs) prior to their determination by inductively coupled plasma–mass spectrometry (ICP-MS) was investigated. Six new hypercrosslinked polystyrene sorbents were tested. The dependence of the degree of NMs sorption on the average degree of polymer network crosslinking and pore diameters was investigated. It was found that sorbents HP-100/6, HP-300/6 and HP-500/6 have low efficiency of NMs chlorocomplexes extraction. Among Stirosorb sorbents (Stirosorb-2, Stirosorb-514 and Stirosorb-584) the highest efficiency of the extraction of NMs' chlorocomplexes has Stirosorb-514. Tributylamine (TBA), *N*-methylbenzylamine (MBA), *N,N*-dimethylbenzylamine (DMBA), *N,N*-dibenzylmethylamine (DBMA) were studied as the reagents for extraction of Ru, Rh, Pd, Ir, Pt and Au chlorocomplexes from hydrochloric acid solutions in the form of ion associates by reversed-phase mechanism. The reversible quantitative extraction of Ru, Pd, Pt and Au in system Stirosorb-514 – TBA – 1 M HCl in ethanol as eluent was achieved. It was found that resulting eluates do not contain matrix components which may cause spectral interferences on the stage of NMs determination by ICP-MS. The found scheme of NMs reversible sorption was validated by the analysis of certified reference materials of basic and ultrabasic rocks GPt-5, GPt-6 and SARM-7. Good agreement between the measured NMs concentrations and the certified values was demonstrated. The achieved limits of detection for Ru, Pd, Pt and Au vary within  $10^{-8}$ – $10^{-7}$  wt% range.

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## 1. Introduction

Noble metals (NMs) are widely used in science and technology. NMs-based alloys are applied as catalysts in petrochemical and automobile industry [1]. A large amount of NMs are consumed by electrical and radio engineering, telemecaniques [2,3], as well as medicine and pharmaceutical industry [4].

NMs are rare elements. According to various sources, their average concentration in the Earth's crust is 1–10 ng g<sup>-1</sup> for Pt, Pd and less than 0.1 ng g<sup>-1</sup> for Rh, Ru, Os, Ir [5]. The content of NMs is increased in ultrabasic and basic igneous rocks the origin of which is associated with deep magmatic processes. The deposits of NMs are attached to these rocks [6]. That is why the problem of determining low concentrations of NMs (clarke content) in rocks is

very relevant.

The non-destructive methods of analysis (neutron activation, atomic emission and mass spectrometry with spark or laser sampling) are not adequate for the determination of NMs in rocks because of insufficient sensitivity [7]. Moreover, NMs are irregularly distributed in geological objects. It causes problems with selection of the standard reference materials to be used for calibration. Therefore, it is necessary to solubilize solid samples for the determination of NMs in rocks. However, the direct measurement of NMs' low concentrations ( $10^{-9}$ – $10^{-7}$  wt%) is impossible even with highly sensitive inductively coupled plasma–mass spectrometry (ICP-MS). The reason is complex composition of the resulting solutions with high content of matrix elements and acids [8]. The step of target NMs preconcentration is needed for increasing the sensitivity of determination.

Reversible dynamic preconcentration systems providing quantitative sorption and quantitative desorption of elements are promising for this purpose. Repeated use of sorbent and on-line determination of NMs directly in the solution after desorption

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become possible in that case.

Extraction of only individual components but not the whole group of NMs can generally be achieved by application of the systems based on ion exchange and complexing sorbents [9]. Non-polar sorbents which allow extracting neutral ion associates or chelates of NMs by reversed-phase mechanism are of greater interest. Desorption may be achieved by a simple change of solvent polarity in this case. Currently, there are only a small number of systems that use non-polar sorbents for NMs' preconcentration. Modified silica gels (C8, C16, C18) [10–14], polytetrafluoroethylene [15,16] in most cases and less often copolymers of styrene and divinylbenzene (hypercrosslinked polystyrene, XAD-2, XAD-4, XAD-8) [17,18] are used as sorbents. Only individual NMs (Pd, Pt, Rh or Au) are reversibly and quantitatively extracted from the same solution under dynamic conditions in the presence of high concentrations of matrix elements using these systems. The system for sorption preconcentration of all NMs from the same solution is still not found. Thus, the search for reversible systems based on non-polar sorbents aimed at extraction of the whole group of NMs remains the task of current interest.

It was shown in our previous studies [19] that Ru, Rh and Ir are extracted in the form of ion associates with protonated aliphatic amines (tributylamine TBA and 4-(*n*-octyl)-diethylenetriamine ODETA) on the non-polar polystyrene MN-200 by 30–50%. Such low sorption efficiency may be related to a hybrid mechanism of sorption. Apparently, the quantitative extraction of the formed NMs' compounds with amines requires not only hydrophobic but also additional specific interactions of amine with the sorbent surface. Obviously, the aliphatic TBA and ODETA slightly interact with non-polar surface of the sorbent MN-200.

Recently, more attention is paid to non-polar hypercrosslinked polystyrene materials [20]. These materials are well known on the world market of sorbents and are widely used in industrial sorption technologies. They are applied for preconcentration of trace amounts of various organic aromatic compounds (polycyclic aromatic hydrocarbons, phenols and polyphenols, some steroids etc.) in environmental, pharmaceutical and biochemical analysis, and recently in high performance liquid chromatography [20,21]. The quantitative extraction of aromatic analytes from aqueous media is related, firstly, to an extended surface of sorbent that allows a reversed-phase sorption mechanism (hydrophobic interaction) to occur; secondly, to a pronounced influence of the styrene polymer fragments on analyte – there is an overlap of their electron density with the electron systems of extracted molecules (so-called  $\pi$ – $\pi$  interaction) [22]. Variation of the degree of crosslinking as well as the conditions of synthesis of these polymeric materials results in alteration of sizes of internal cavities in a wide range and in an electron-donating activity of polymer network aromatic moieties [23,24]. The mentioned peculiarities make application of these types of sorbents promising for preconcentration of NMs in the form of neutral ion associates with different reagents. It is necessary to employ the hydrophobic aromatic amines containing benzyl groups as ion-pair reagents to improve the efficiency of NMs' extraction by the hybrid mechanism (hydrophobic and  $\pi$ – $\pi$  interactions).

The goal of this work is the investigation of new non-polar hypercrosslinked polystyrene sorbents and the search for reversible sorption systems based on them for simultaneous quantitative extraction of Ru(III, IV), Rh(III), Pd(II), Ir(III, IV), Pt(II, IV) and Au(III) from resulting solutions after rock samples digestion.

## 2. Experimental

### 2.1. Solutions, reagents, sorbents and eluents

The following acids were used in the work:

- concentrated nitric acid (65%, «pro analysis» grade, Merck, Germany) for preparation of the calibration solutions and the mobile phase, for digestion of the copper alloy and the certified reference material;
- concentrated hydrochloric acid (37%, «purissimum special» grade, Sigma Tek, Russia) for preparation of the NMs' calibration and model solutions, the solutions of reagents and the eluent, for digestion of the copper alloy and the certified reference material;
- concentrated sulfuric acid (96%, «purissimum» grade, Sigma Tek, Russia) for cleaning the glassware.

The ICP-MS-68A-C multi-element standard solution (High-Purity Standards, USA) containing 10 mg L<sup>-1</sup> Ru, Rh, Pd, Ir, Pt, Os and Au was used for preparation of the calibration solutions. The single-element 1000 mg L<sup>-1</sup> In standard solution (High-Purity Standards, USA) was used for preparation of the internal standard solution. The single-element 1 g L<sup>-1</sup> Cu and Ni standard solutions (High-Purity Standards, USA) were used for preparation of the matrix-type synthetic solutions.

Ethanol (96%, technical grade) was used for preparation of the eluent.

Carbonyl nickel powder (Ni content at least 99.7%, Normetimpex, Russia), sulfur (high purity grade, LabTeh, Russia), sodium carbonate, sodium tetraborate decahydrate (borax) and silicon dioxide (silica) (all reagent grade, ReaHim, Russia) were used for NiS fire assay.

High-purity water for the ICP-MS analysis (18.2 M $\Omega$  cm<sup>-1</sup>) obtained from a Milli-Q purification unit (Millipore Simplicity, France) was used for preparation of all solutions.

Tributylamine (TBA) («for the synthesis» grade, Merck, Germany), *N*-methylbenzylamine (MBA), *N,N*-dimethylbenzylamine (DMBA), *N,N*-dibenzylmethylamine (DBMA) (all are synthesized and purified by distillation and recrystallization of the preliminarily obtained salts of ammonium bases [25] at the Chemistry Department of Lomonosov Moscow State University in the laboratory of organic synthesis of the division of organic chemistry) were used as amine reagents. The structural formulas of the applied reagents are presented in Fig. 1.

The following hypercrosslinked polystyrene sorbents were used for preconcentration of NMs: HP-500/6, HP-300/6, HP-100/6, Stirosorb-2, Stirosorb-514, Stirosorb-584 [26]. The main characteristics of the sorbents are presented in Table 1.

The solution obtained after digestion of the copper alloy SOMB-6 (SRM 7202-95, Russia) was used as the NMs' standard solution.

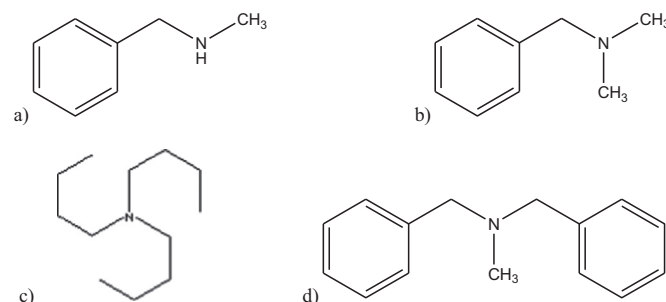


Fig. 1. The structures of the applied amine reagents: (a) MBA, (b) DMBA, (c) TBA, (d) DBMA.

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