= REVIEWS =

## Sorption-Mass Spectrometry Determination of Platinum Metals in Basic Rocs and Ores

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Abstract—The results of a systematic study of sorption systems for the reversible group extraction of Ru, Rh, Pd, Ir, and Pt and their subsequent determination by inductively coupled plasma mass spectrometry are presented. The sorption system includes an sorbent, a reagent, and a desorbing solution. Purolite MN-200, HP, and Styrosorb hypercrosslinked polystyrene sorbents and Strata sorbents with immobilized nitrogen atoms were studied. Various aliphatic and aromatic amines were used as ion-pair amine reagents for the sorption extraction of PGMs. A possibility of the desorption of Ru, Rh, Pd, Ir, and Pt complexes with reagents of different nature was studied. Sorption systems were selected for the preconcentration of PGMs from solutions obtained after the decomposition of rocks. A flow-injection method for introducing high-salt and organic solutions into a mass spectrometer was proposed. Possible spectral and nonspectral effects were investigated, and the conditions for quantifying Ru, Rh, Pd, Ir, and Pt in the obtained preconcentrates were selected.

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Continuously developing technologies cause that the consumption of platinum group metals (PGMs) is continuously increasing because of their unique properties. In recent decades, geological exploration in the search for new deposits of PGMs has been intensified in various regions of the world. PGMs are found in nature in a dispersed state. Geochemically, they are associated with ultrabasic and basic rocks, in which their concentration is somewhat elevated. The deposits of PGMs are associated with these types of rocks. and, as a result, it is necessary to determine PGMs in the silicate component of the rocks. In addition to searching for new sources of PGMs, one of the most critical problems of today is the analysis of so-called "technogenic deposits," that is, dumps, mill tailings, and other mining waste. The efficiency of the extraction of PGMs from primary and secondary mining raw materials is rather high only with the availability of modern highly sensitive and precision methods for their determination. Thus, the simultaneous determination of Ru, Rh, Pd, Ir, and Pt at the level of their abundance in Earth's crust is an important analytical task. Osmium is usually determined separately because of its peculiar properties; namely, it is readily oxidized to volatile tetraoxide and requires the use of specialized sample preparation methods.

The abundance of platinum group metals in rocks varies from  $10^{-11}$  to  $10^{-8}$  wt % but does not exceed 5 ng/g on the average. For the simultaneous determination of elements at such low concentrations, the most convenient method is inductively coupled plasma-mass spectrometry (ICP-MS). Direct analysis methods (instrumental neutron activation, X-ray fluorescence, and laser ablation ICP-MS) are characterized by low accuracy and have poor detection sensitivity. In ICP–MS measurements, it is necessary to completely transfer a solid rock sample into a solution. To use the main advantages of ICP-MS, it is necessary to combine the procedures of analysis and preconcentration of PGMs because when a solid sample weighing 10–20 g is transferred into a solution of 100-500 mL, the concentration of metals decreases to 1-10 ng/L against the background of high concentrations of matrix components. Preconcentration is also necessary because, in analyzing industry-related raw materials, the matrix composition of the sample varies greatly depending on the technology of primary processing. In this regard, a solution with different qualitative and quantitative composition can be obtained in every single case, which makes difficult the use of the external calibration method for ICP-MS detection of PGMs.

In recent decades, dynamic sorption preconcentration has been used most frequently [1] because it is a highly efficient, technologically advanced, simple to perform, environmentally safe, and inexpensive method. Its dynamic version is rapid, enables the extraction of PGMs from solutions of different volumes, and excludes substantial loss of the detected components [2]. It is essential that the sorption preconcentration stage vields a liquid concentrate of a unified composition.

A wide range of functional groups and the propensity of PGMs to form stable complexes and/or ion pairs with such donor atoms as nitrogen, sulfur and oxygen, ensures the implementation of various mechanisms for the extraction of these metals. There are three main options [3]: sorption of hydrophobic ion associates or complex compounds on the nonpolar sorbent surface (reversed-phase systems), ion exchange and complex formation; these processes often coincide.

Reversed-phase sorption systems for the preconcentration of PGMs. PGMs are usually extracted on the surface of sorbents from hydrochloric acid solutions (most often 0.1-3 M HCl) because in this medium, PGMs occur as sorption-active chlorocomplexes and aquachlorocomplexes [4]. Chlorine complexes of PGMs form stable ion pairs (associates) or complex compounds with protonated nitrogen atoms of various nitrogen-containing reagents, which, in addition to ion-exchange or donor functional groups, also have hydrophobic substituents (aliphatic or aromatic) [4]. The degree of hydrophobicity of the compounds depends on the composition and structure of the reagents used. The sorption of the resulting hydrophobic compounds is due to their partition between the aqueous phase and the nonpolar sorbent. Compounds of PGMs can be desorbed by decreasing the polarity of the solvent using alcohols or ketones. The use of such systems for preconcentrating PGMs ensures rapid sorption and desorption in the dynamic mode, reusable sorbent, and automation of the entire cycle of determination by creating flow-injection systems of on-line injection of the analyte into the device.

In solutions with a high concentration of hydrochloric acid, sorbents with a developed spatial (threedimensional) structure, the polymer base of which is composed by a hypercrosslinked hydrophobic matrix based on various styrene-divinylbenzene copolymers, are the most stable [5]. Hypercrosslinked polystyrene materials have long been known on the world market of sorbents and are widely used in industrial sorption technologies. They are used to preconcentrate trace amounts of various aliphatic and aromatic organic substances (polycyclic aromatic hydrocarbons, phenols, polyphenols, some steroids, etc.) in environmental, pharmaceutical, and biochemical analysis, and more recently also in HPLC [6, 7]. Varying the degree of crosslinking and the conditions for the synthesis of these polymer materials leads to a variation in a wide range of sizes of internal cavities and the electron donor activity of aromatic fragments of the polymer network [8, 9]. These features make promising the use of this group of sorbents for preconcentrating PGMs as neutral associates or complexes with various aliphatic or aromatic reagents.

Some requirements for reagents used in such systems were given in [10]: (1) high rate of formation of a hydrophobic compound with PGMs, (2) fast and quantitative sorption of ion associates on the sorbent surface, (3) fast and quantitative desorption from the sorbent under mild conditions, and (4) high selectivity to PGMs in the presence of other elements.

It is known [11, 12] that the use of quaternary ammonium salts for the formation of ion associates only due to electrostatic interactions is ineffective for extracting the entire group of PGMs. It is advisable to use nitrogen-containing reagents (amines) with primary, secondary, or tertiary groups capable of reacting with PGMs by a mixed mechanism: the formation of complexes due to a lone electron pair of the nitrogen atom and also ion pairs through the protonation of the nitrogen atom in an acidic medium.

We have studied a wide range of sorption systems consisting of hypercrosslinked polystyrenes of various structures and amine reagents of various chemical nature. The properties of the sorbents are presented in Table 1.

At the early stages of the study, Diasorb  $C_{16}$  modified silica was used as a conventional reversed-phase sorbent [13]. In using tributylamine (TBA) as a reagent, it was found that Diasorb C<sub>16</sub> quantitatively sorbs only Pd (by 98%), while Rh and Ir are virtually not sorbed. For desorption, "acidic alcohol" (1 M solution of HCl in ethyl alcohol) was used, while Pd was desorbed only by 77%. Poor results of the extraction of rhodium and iridium in such an sorption system may be related to the fact that the silica matrix itself is polar, and even the introduction of  $C_{16}$  groups does not offer the full implementation of hydrophobic interactions of the resulting ion associates with the sorbent surface.

To increase the degree of sorption of platinum metal compounds with TBA, the hydrophobicity of the sorbent was varied. The extraction of metals on various polystyrenes was investigated: Merrifield Resin, Amberlite XAD-2, and Purolite MN-200 [13, 14]. In this series of sorbents, the strength of hydrophobic interactions with the surface increases. Merrifield Resin, which is *p*-(chloromethyl)polystyrene resin, has the worst performance. In the case of Purolite MN-200, quantitative extraction of Pd and Pt is achieved only in the presence of TBA. The maximum extraction of Ru on this sorbent was 40%; for Ir, it was 20%; Rh was virtually not extracted.

It was suggested [15] that, in the system of hypercrosslinked polystyrene-high-molecular-weight

Table 1. Main characteristics	of the studied sorbents
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Sorbent	Particle size, µm	$S_{\rm sp},{\rm m^2/g}$	Degree of crosslinking, %
Diasorb C <sub>16</sub>	60-100	300	_
Amberlite XAD-2	250-850	300	55
Merrifield Resin	160-210	_	6-60
Purolite MN-200	75-125	860	100
HP-500/6	10-50	1200	500
HP-300/6	10-50	1200	300
HP-100/6	10-50	1100	100
Styrosorb-2	30-40	1500	200
Styrosorb-514	10-50	1000	200
Styrosorb-584	10-50	1300	200

amine-MeCl<sup>n-</sup>, the resulting ion associates are extracted not only by the reversed-phase mechanism in the form of hydrophobic compounds. Probably, to extract "difficult" elements from the point of view of their chemistry, such as Ru, Rh, and Ir, it is necessary that additional chemical or specific interactions with the surface of the sorbent exist in the sorption system. We systematically studied the sorption of PGMs on neutral hypercrosslinked polystyrenes HP and Styrosorb in the presence of TBA and several aromatic amines, that is, N-methylbenzylamine (MBA), N,Ndimethylbenzylamine (DMBA), and N,N-dibenzylmethylamine (DBMA) [15]. The studied sorbents were first used for the preconcentration of PGMs. They are characterized by various physicochemical parameters (Table 1). This is due to the use of different procedures for the synthesis of copolymers, which can lead to a difference in their sorption properties [16, 17]. Styrene fragments of the polymer matrix of the sorbent can also be considered as an electron-donating reagent. It was found that the highest degree of sorption of PGMs was achieved for Styrosorb-514: Pd and Pt were sorbed quantitatively, and Ru was sorbed reproducibly by 60%. The sorption efficiency of PGMs on this sorbent is almost the same in using TBA and DBMA. In using MBA and DMBA, PGMs are virtually not extracted. It is suggested [15] that the observed difference in the sorption efficiency of the ion associates of Ru, Pd, and Pt on different polystyrene materials is because the sorbents significantly differ in the degree of crosslinking of the polymer network and the structure of the pore space. In the case of Styrosorb polystyrenes, the approaching of the degree of crosslinking to ~200% leads to an increase in the degree of sorption of Ru, Pd, and Pt. The likely reason for the increase in the degree of sorption of PGMs is the presence of a more significant number of pores in such sorbents, available for the resulting ion associates. The ability of benzylamine radicals to enter  $\pi - \pi$ interactions with styrene fragments of the polymer matrix, combined with favorable steric factors, probably explains the sorption characteristics of the reagents themselves: DBMA has two benzyl radicals, while MBA and DMBA each have only one; therefore, DBMA exhibits a higher affinity for the polymer. Thus, in the proposed Styrosorb-514–TBA and Styrosorb-514–DBMA systems [15], Ru, Pd, and Pt can be sorbed simultaneously. The degree of sorption does not depend on the nature of the amine. Rh is not extracted in any combinations of polystyrene–amine; the degree of Ir sorption does not exceed 5–10%, as is the case with TBA. Thus, the use of aromatic amines also does not increase the degree of sorption of Rh and Ir.

An advantage of reversible sorption preconcentration is a possibility of obtaining a liquid preconcentrate of PGMs after desorption. To use this advantage, it is necessary to select the composition of the solution, which is suitable for the quantitative desorption of PGMs compounds. It was previously shown [13, 14] that the most suitable desorbing solution in an sorption system based on Purolite MN-200 hypercrosslinked polystyrene is a 1 M HCl solution in ethanol. Ethanol has a lower dielectric constant compared to water, and hydrochloric acid is necessary to increase the solubility of the ion associates of PGMs in an alcohol medium. This desorbing solution was used to extract PGMs in sorption systems based on Styrosorb-514 and TBA or DBMA. Countercurrent desorption was carried out in at a flow rate of the solution of 1 mL/min [18]. Under these conditions, Pd and Pt are quantitatively desorbed in the Styrosorb-514-TBA sorption system. Also, all sorbed ruthenium (60%) is quantitatively and reproducibly desorbed. In the sorption system of Styrosorb-514-DBMA, desorption is not quantitative. It is likely that the flow rate of the solution at the desorption stage is quite high. After decreasing the flow rate of the desorbing solution through the column to 0.3 mL/min, Pd and Pt are quantitatively desorbed (Fig. 1). Ruthenium is also extracted quantitatively: the degree of sorption is 60%, and all adsorbed ruthenium is desorbed quantitatively.



**Fig. 1.** Dependence of the recovery of PGMs on the flow rate of the solution at the desorption stage in the DBMA–Styrosorb-514 sorption system. Solution flow rate, mL/min: (I) 1, (II) 0.5, and (III) 0.3;  $c_{\text{DBMA}} = 0.02 \text{ M}$ ;  $c_{\text{HCI}} = 1 \text{ M}$ ;  $c_{\text{Ru}} = 10 \text{ µg/L}$ ;  $c_{\text{PGMs}} = 25 \text{ µg/L}$ ; desorbing solution: 1 M HCl in ethanol; n = 3; P = 0.95.

Thus, at the flow rate of the solution at the desorption stage 0.3 mL/min, the sorption systems of Styrosorb-514–TBA and Styrosorb-514–DBMA are equivalent in their characteristics and offer the simultaneous extraction of Ru, Pd, and Pt.

The reason for the low degree of sorption of the Ru, Rh, and Ir chlorocomplexes in the presence of TBA and aromatic amines is likely to be steric hindrances that arise when an associate formed in an acidic medium. The resulting charged ion associates of the composition  $(MCl_6)^{n-} \cdot (n-x)RH^+$  cannot be quantitatively adsorbed on the hydrophobic surface of the hypercrosslinked polystyrene. In this regard, sorbents with their own nitrogen atoms were investigated.

Sorbents with immobilized nitrogen atoms for the preconcentration of PGMs. Nitrogen-containing sorbents (N-sorbents) are a group of sorbents most widely used for preconcentrating platinum and many other metals. The functional groups of N-sorbents contain nitrogen atoms in both the polymer chain (heterochain sorbents) and in the composition of immobilized aliphatic and aromatic radicals. The presence of amine groups causes sorption by both the formation of ion pairs and the formation of platinum metal complexes with nitrogen atoms [5].

Sorption systems based on Strata sorbents were studied, having nitrogen atoms in the structure: StrataX with pyrrolidone groups and StrataX-AW with ethylenediamine groups [19]. Tributylamine and conformationally mobile 4-(n-octyl)diethylenetriamine (ODETA) were used as ion-pair reagents. The nature

of both the sorbent and the reagent affects the degree of sorption of PGMs. We showed that, in the StrataX– TBA system, iridium was extracted by only 20%. However, the use of ODETA increased the degree of sorption of iridium up to 70%. Iridium is adsorbed quantitatively on StrataX-AW in using both TBA and ODETA. The sorption of Rh and Pt is also increased in the case of Strata sorbents, and the degree of sorption of Ru does not change as compared to hypercrosslinked polystyrenes.

Probably, in the case of sorbents with their own nitrogen atoms, hydrophobic interactions of the ion associate with the uncharged sorbent surface are not primary. Such a noticeable increase in the degree of sorption of iridium, regardless of the nature of the amine, can be explained by the involvement of the functional groups of sorbents into the retention of analyte; namely, the charged ion associate of the iridium chlorocomplex with the amine interacts with the protonated nitrogen atom on the sorbent surface. Obviously, this interaction is quite significant because the desorption of Pd, Ir, and Pt with "acidic alcohol" is difficult.

For the desorption of iridium, aqueous solutions of sodium perchlorate, potassium thiocyanate, sodium nitrite, sodium formate, potassium oxalate, sodium acetate, sodium arsenate, and sodium tetraborate were used in a concentration of 0.05 M. To desorb Pd and Pt, solutions of the same salts, "acid alcohol," and a hydrochloric acid solution of thiourea were used. Quantitative desorption of iridium is achieved using solutions of sodium tetraborate or arsenate. The increase in the degree of iridium extraction can apparently be explained as follows: the basicity constant of the immobilized amino group of StrataX-AW is  $K_{\rm b} \sim 10^{-5}$ . The use of eluents with weakly basic properties enables deprotonation of the nitrogen atom of the sorbent and desorption of the iridium chlorocomplexes. At the same time, Pd and Pt complexes can be desorbed with neither "acidic alcohol," nor thiourea solution, nor reagents with basic properties. It is likely that during the sorption of Pd and Pt on Strata sorbents, the nitrogen atom of the sorbent enters the internal coordination sphere of the metal with the formation of stable inner-sphere complexes. A procedure for dynamic sorption concentration of Ru, Rh, and Ir from hydrochloric acid solutions using StrataX-AW sorbent was proposed [19]. Thus, the use of sorbents with immobilized nitrogen-containing groups did not lead to the extraction of the entire group of PGMs.

Sample preparation of rocks in the determination of **PGMs.** In studying the efficiency of the sorption of PGMs in the Styrosorb-514-TBA system, it was found that the composition of the solution from which sorption is carried out affects the extraction rate of elements [20]. If the extraction is carried out from a model solution, then the recovery of Pd and Pt in this system is 100%. A solution of copper alloy SOMB-6 with a concentration of Ru of 10 µg/L and other PGMs of 25  $\mu$ g/L was used as a model solution. Under these conditions, ruthenium is recovered by 60%. At the same time, in determining ruthenium in the same sorption system in a real rock sample after its fusion into a nickel sulfide matte and dissolving the latter in "aqua regia," it was found that ruthenium is quantitatively extracted from such a solution. Probably, an extractable form of ruthenium chlorocomplex is formed in the solution in this case. It is known that in determining PGMs in rocks, two methods of sample preparation are most common: fusion into matte and acid decomposition. To examine the proposed assumption about the effect of sample preparation on the sorption behavior of analytes, the dependence of the recovery of all PGMs on the sample preparation method was studied [21]. The standard rock sample GPt-6 was dissolved in a mixture of acids, and PGMs were extracted from the resulting solution in the sorption system of Styrosorb-514–TBA. It turned out that the recovery of Ru, Pd, and Pt from solutions obtained after the acid decomposition of rocks decreases by 20-40% compared to solutions obtained after dissolving a matte (Table 2). The fact of a significant increase in the recovery for iridium is rather interesting. The recovery of iridium from solutions after the acid decomposition of GPt-6 increases by a factor of 1.5-2 compared with the model solution and is 25-30%. Thus, in analyzing solutions of rocks obtained by acid decomposition of a solid sample, the recovery of ruthenium does not change, and for iridium, it increases. It is evident that the method of obtaining the solution and its composition significantly affect

**Table 2.** Effect the method of sample preparation of peridotite GPt-6 on the results (ng/g) of the determination of PGMs in a solid sample (recovery after the stage of sorption and desorption are given; Styrosorb-514–TBA–1 M HCl in ethanol; n = 10; P = 0.95)

PGM	c <sub>min</sub>	Certified value	Found	
			NiS	acid decomposition
Ru	0.3	$13 \pm 1$	$14 \pm 3$	$7\pm 2$
Rh	—	$22\pm3$	—	_
Pd	3.3	$568\pm50$	$570 \pm 40$	$455\pm25$
Ir	0.3	$28\pm7$	—	$6\pm 2$
Pt	1.4	$440\pm40$	$400 \pm 30$	$390\pm30$

the efficiency of extraction of PGMs. The effect of the main rock-forming elements (Na, Ca, Mg, Al, and Fe) on the efficiency of the sorption separation of PGMs was studied in detail [21]. It is found that the effect of individual elements on the degree of sorption of all PGMs, with an exception of iridium, is insignificant. The desorption of these elements with a 1 M HCl solution in ethanol decreases. It is interesting that the degree of sorption of iridium from a solution containing 5 g/L of iron(III) increases abnormally (up to 90%). It was suggested that this may be due to the formation of new mixed outer-sphere iridium complexes, which are quantitatively sorbed on hypercrosslinked polystyrene. Thus, it was found that a combination of a procedure of fusing a rock into a NiS matte and adding iron(III) ions at a concentration of 2 g/L to the final solution leads to 100% sorption of four PGMs in the Styrosorb 514–TBA sorption system [21]. However, only Ru, Pd, and Pt are quantitatively desorbed with 1 M HCl solution in ethanol.

Selection of conditions for the mass spectrometric determination of PGMs in the resulting concentrates. Analysis of alcohol solutions of PGMs. The selected sorption systems were used to determine PGMs in ultrabasic rocks using ICP-MS. A known disadvantage of this method is a significant matrix effect when the main components of the test solution affect the magnitude of the analytical signal. The most significant effect is exerted by a high concentration of acid and mineral salts and by the presence of organic compounds [22]. It was noted above that, as a result of sorption preconcentration, alcohol solutions are obtained that cannot be directly introduced into the mass spectrometer in the mode of continuous sample injection; therefore, a possibility of injecting small volumes of solutions in 96% ethanol was studied. For this purpose, a combination of a mass spectrometer and a flow-injection system consisting of a manual injector, metering loops, and a programmable HPLC pump was used. With this method of sample injection, the profile of the analytical signal was changed. In the



**Fig. 2.** Shape and position of In, Rh and Ir peaks in various solvents. Volume of the metering loop, 50  $\mu$ L; sample flow rate, 1 mL/min;  $c_{PGMs and In} = 5 \,\mu$ g/L; (1) In, water; (2) In; (3) Ir, water; (4) Ir, alcohol; (5) Rh, water; and (6) Rh.

case of stationary injection of a sample, a version of the ChemStation program was used, resulting in an average signal during the recording of a particular isotope. With the injection of a limited sample volume into the steady-state flow of the carrier, the resulting signal was a bell-shaped (Fig. 2). In this case, another version of the program (Time Resolution) was used, in which the area of the profiles shown in Fig. 2 was considered an analytical signal. In this mode, the concentration of elements was determined by the method of external calibration with a similar injection of reference solutions and the calculation of concentrations. This system was described in detail in [23].

The introduction of alcoholic solutions significantly decreases the sensitivity of the determination of elements. Therefore, two methods were used to eliminate the matrix effect: (1) the calibration solutions of PGMs were also prepared in 96% ethanol, and (2) the method of internal standard (IS) was used to calculate the concentrations [23]. Concentrations were calculated as the ratio of the peak area of the element being determined to the peak area of the internal standard  $S_{\text{Me}}/S_{\text{In}}$ , where Me was platinum metal and In served as an internal standard (Fig. 2). The limits of detection for PGMs in their determination in the mode of nonstationary signals were 15 (Ru), 1 (Rh), 10 (Pd), 2 (Ir), and 7 (Pt) ng/L.

Spectral interference and the selection of isotopes of *PGMs*. Another limitation of ICP–MS is the presence of a spectral interference, which is determined by the proximity (or coincidence) of the mass of the analyte isotope and the mass of ions produced by the components of the matrix. All possible spectral superpositions of polyatomic and doubly charged ions on the masses of PGMs are presented in Table 3.

To take into account the effect of matrix components, ethanol concentrates of PGMs were analyzed for the concentrations of Ni, Cu, Zn, Co, Sr, Mo, Cd, Ta, Zr, Hf, and Hg after extracting PGMs from solutions of rocks. An analysis of alcohol concentrates showed that only nickel was present in these solutions at ~100  $\mu$ g/L; the concentration of the remaining elements did not exceed 0.5 µg/L. We additionally studied the contribution of polyatomic particles <sup>62</sup>Ni<sup>37</sup>Cl<sup>+</sup> and <sup>64</sup>Ni<sup>35</sup>Cl<sup>+</sup> to the signal intensity on the mass of the <sup>99</sup>Ru isotope because this is the only ruthenium isotope that is free from the interference of ions of other PGMs. It was found that, at a nickel concentration of up to 2000  $\mu$ g/L, the signals from <sup>64</sup>Ni<sup>35</sup>Cl<sup>+</sup> and <sup>62</sup>Ni<sup>37</sup>Cl<sup>+</sup> ions did not make a noticeable contribution to the <sup>99</sup>Ru signal [20]. The contribution of this nickel concentration corresponds to the level of the ruthenium signal in the blank solution (0.02  $\mu$ g/L). Such a weak contribution of nickel is probably because the interfering polyatomic ions formed by less common nickel isotopes (62Ni, 3.59%, and 64Ni, 0.91%). Further measurements of the analytical signal were carried out for the masses of <sup>99</sup>Ru, <sup>103</sup>Rh, <sup>108</sup>Pd, <sup>193</sup>Ir, <sup>195</sup>Pt, and <sup>197</sup>Au since the components of the alcohol preconcentrate do not affect the analytical signal.

## CONCLUSIONS

Thus, problems arising in the dynamic sorption preconcentration of PGMs on sorbents of various nature are discussed. The results of the sorption preconcentration of Ru, Rh, Pd, Ir, and Pt on various hypercrosslinked polystyrenes and on StrataX sorbents with immobilized nitrogen atoms are presented. The nature of the sorbent and its physicochemical

PGM	Interfering ions		
isotope	main	possible	
99Ru	${}^{64}Zn^{35}Cl^+, {}^{64}Ni^{35}Cl^+, {}^{59}Co^{40}Ar^+, {}^{98}Mo^1H^+$	<sup>62</sup> Ni <sup>37</sup> Cl <sup>+</sup> , <sup>198</sup> Pt <sup>2+</sup> , <sup>198</sup> Hg <sup>2+</sup> ,	
<sup>100</sup> Ru	<sup>100</sup> Mo <sup>+</sup> , <sup>99</sup> Ru <sup>1</sup> H <sup>+</sup> , <sup>60</sup> Ni <sup>40</sup> Ar <sup>+</sup> , <sup>65</sup> Cu <sup>35</sup> Cl <sup>+</sup>	$^{84}\mathrm{Sr}^{16}\mathrm{O}^{+},^{200}\mathrm{Hg}^{2+},^{63}\mathrm{Cu}^{37}\mathrm{Cl}^{+},$	
<sup>101</sup> Ru	${}^{66}Zn^{35}Cl^+,  {}^{100}Mo^1H^+,  {}^{100}Ru^1H^+$	${}^{85}\text{Rb}{}^{16}\text{O}^+, {}^{84}\text{Sr}{}^{16}\text{O}{}^{1}\text{H}^+, {}^{61}\text{Ni}{}^{40}\text{Ar}^+, {}^{64}\text{Ni}{}^{37}\text{Cl}^+, {}^{64}\text{Zn}{}^{37}\text{Cl}^+, {}^{202}\text{Hg}{}^{2+}$	
<sup>102</sup> Ru	<sup>86</sup> Sr <sup>16</sup> O <sup>+</sup> , <sup>101</sup> Ru <sup>1</sup> H <sup>+</sup> , <sup>62</sup> Ni <sup>40</sup> Ar <sup>+</sup>	<sup>102</sup> Pd <sup>+</sup> , <sup>204</sup> Pb <sup>2+</sup> , <sup>65</sup> Cu <sup>37</sup> Cl <sup>+</sup> , <sup>65</sup> Zn <sup>37</sup> Cl <sup>+</sup>	
<sup>103</sup> Rh	$^{102}$ Ru <sup>1</sup> H <sup>+</sup> , $^{63}$ Cu <sup>40</sup> Ar <sup>+</sup> , $^{86}$ Sr <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , $^{87}$ Sr <sup>16</sup> O <sup>+</sup>	<sup>87</sup> Rb <sup>16</sup> O <sup>+</sup> , <sup>206</sup> Pb <sup>2+</sup> , <sup>66</sup> Zn <sup>37</sup> Cl <sup>+</sup>	
<sup>104</sup> Ru	<sup>103</sup> Rh <sup>1</sup> H <sup>+</sup> , <sup>88</sup> Sr <sup>16</sup> O <sup>+</sup> , <sup>64</sup> Ni <sup>40</sup> Ar <sup>+</sup>	<sup>104</sup> Pd <sup>+</sup> , <sup>208</sup> Pb <sup>2+</sup> , <sup>67</sup> Zn <sup>37</sup> Cl <sup>+</sup> , <sup>69</sup> Ga <sup>35</sup> Cl <sup>+</sup>	
<sup>105</sup> Pd	<sup>65</sup> Cu <sup>40</sup> Ar <sup>+</sup> , <sup>88</sup> Sr <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>68</sup> Zn <sup>37</sup> Cl <sup>+</sup>	<sup>89</sup> Y <sup>16</sup> O <sup>+</sup> , <sup>70</sup> Ge <sup>35</sup> Cl <sup>+</sup> , <sup>104</sup> Ru <sup>1</sup> H <sup>+</sup> , <sup>104</sup> Pd <sup>1</sup> H <sup>+</sup>	
<sup>106</sup> Pd	$^{106}$ Cd <sup>+</sup> , $^{66}$ Zn <sup>40</sup> Ar <sup>+</sup> , $^{90}$ Zr <sup>16</sup> O <sup>+</sup> , $^{105}$ Pd <sup>1</sup> H <sup>+</sup>	<sup>89</sup> Y <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>69</sup> Ga <sup>37</sup> Cl <sup>+</sup> , <sup>71</sup> Ga <sup>35</sup> Cl <sup>+</sup>	
<sup>108</sup> Pd	$^{108}$ Cd <sup>+</sup> , $^{68}$ Zn <sup>40</sup> Ar <sup>+</sup> , $^{92}$ Zr <sup>16</sup> O <sup>+</sup> , $^{92}$ Mo <sup>16</sup> O <sup>+</sup>	<sup>107</sup> Ag <sup>1</sup> H <sup>+</sup> , <sup>71</sup> Ga <sup>37</sup> Cl <sup>+</sup> , <sup>73</sup> Ge <sup>35</sup> Cl <sup>+</sup>	
<sup>110</sup> Pd	<sup>94</sup> Zr <sup>16</sup> O <sup>+</sup> , <sup>94</sup> Mo <sup>16</sup> O <sup>+</sup> , <sup>110</sup> Cd <sup>+</sup>	$^{109}$ Ag $^{1}$ H <sup>+</sup> , $^{70}$ Zn $^{40}$ Ar <sup>+</sup> , $^{70}$ Ge $^{40}$ Ar <sup>+</sup> , $^{73}$ Ge $^{37}$ Cl <sup>+</sup> , $^{75}$ As $^{35}$ Cl <sup>+</sup>	
<sup>191</sup> Ir	<sup>175</sup> Lu <sup>16</sup> O <sup>+</sup>	<sup>190</sup> Os <sup>1</sup> H <sup>+</sup>	
<sup>193</sup> Ir	<sup>177</sup> Hf <sup>16</sup> O <sup>+</sup>	$^{192}\text{Os}^{1}\text{H}^{+}, ^{192}\text{Pt}^{1}\text{H}^{+}$	
<sup>194</sup> Pt	<sup>178</sup> Hf <sup>16</sup> O <sup>+</sup> , <sup>193</sup> Ir <sup>1</sup> H <sup>+</sup>	-	
<sup>195</sup> Pt	<sup>179</sup> Hf <sup>16</sup> O <sup>+</sup> , <sup>178</sup> Hf <sup>16</sup> O <sup>1</sup> H <sup>+</sup>	$^{194}Pt^{1}H^{+}$	
<sup>196</sup> Pt	<sup>180</sup> Hf <sup>16</sup> O <sup>+</sup> , <sup>195</sup> Pt <sup>1</sup> H <sup>+</sup>	<sup>196</sup> Hg <sup>+</sup> , <sup>180</sup> W <sup>16</sup> O <sup>+</sup>	
<sup>198</sup> Pt	_	$^{198}\text{Hg}^+, ^{182}\text{W}^{16}\text{O}^+$	
<sup>197</sup> Au	$^{180}{\rm Hf^{16}O^{1}H^{+}}$	$^{181}$ Ta $^{16}$ O $^+$	

Table 3. Spectral interference in the determination of PGMs by inductively coupled plasma-mass spectrometry

properties, in particular, pore size and the degree of crosslinking, affect the sorption efficiency. The sorption of PGMs on hypercrosslinked polystyrenes in the presence of aliphatic and aromatic amines was studied. A possibility of the desorption of Ru, Rh, Pd, Ir, and Pt complexes with reagents of different nature was considered. The effect of the main rock-forming elements-Na, Ca, Mg, Al, and Fe-on the efficiency of the sorption preconcentration of the Ru, Pd, Ir, and Pt chlorocomplexes in the Styrosorb-514-TBA sorption system was studied. It was found that a combination of the procedure of fusing a rock into a NiS matte and adding iron(III) ions at a concentration of 2 g/L to the final solution leads to 100% sorption of four PGMs in this sorption system. A flow-injection method for injecting high-salt and organic solutions into a mass spectrometer is proposed. Possible spectral and nonspectral effects are investigated, and the conditions for determining Ru, Rh, Pd, Ir, and Pt in the obtained preconcentrates by ICP-MS are selected.

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## REFERENCES

- 1. Zolotov, Yu.A., Tsyzin, G.I., Morosanova, E.I., and Dmitrienko, S.G., *Russ. Chem. Rev.*, 2005, vol. 74, no. 1, p. 37.
- 2. Mokhodoeva, O.B., Myasoedova, G.V., and Kubrakova, I.V., J. Anal. Chem., 2007, vol. 62, no. 7, p. 607.
- 3. Bernardis, F.L., Grant, R.A., and Sherrington, D.C., *React. Funct. Polym.*, 2005, vol. 65, p. 205.
- Zolotov, Yu.A., Varshal, G.M., and Ivanov, V.M., *Analiticheskaya khimiya metallov platinovoi gruppy*  (Analytical Chemistry of Platinum Group Metals), Moscow: Editorial URSS, 2003.
- Mladenova, E., Karadjova, I., and Tsalev, D.L., J. Sep. Sci., 2012, vol. 35, p. 1249.
- Sychev, K.N. and Davankov, V.A., Sorbtsionnye Khromatogr. Protsessy, 2004, vol. 4, p. 5.
- 7. Davankov, V.A. and Tsyurupa, M.P., *Hypercrosslinked Polymeric Networks and Adsorbing Materials: Synthesis, Structure, Properties, and Application*, New York: Elsevier, 2010, p. 648.

- 8. Tsuyrupa, M.P. and Davankov, V.A., *React. Funct. Polym.*, 2002, vol. 53, p. 193.
- Tsyurupa, M.P., Blinnikova, Z.K., Borisov, Y.A., Ilyin, M.M., Klimova, T.P., Mitsen, K.V., and Davankov, V.A., *J. Sep. Sci.*, 2014, vol. 37, no. 7, p. 803.
- Bogacheva, L.V., Kovalev, I.A., Tikhomirova, T.I., Formanovsky, A.A., Tsysin, G.I., and Zolotov, Yu.A., *Sep. Purif. Technol.*, 2002, vol. 29, p. 33.
- Vlašánkova, R., Otruba, V., Bendl, J., Fišera, M., and Kanický, V., *Talanta*, 1999, vol. 48, p. 839.
- 12. Yamini, Y., Chaloosi, M., and Ebrahimzadeh, H., Microchim. Acta, 2002, vol. 140, p. 195.
- Fedyunina, N.N., Osipov, K.B., Statkus, M.A., Seregina, I.F., Tsizin, G.I., and Bol'shov, M.A., in *Mater. Vserossiiskoi nauchnoi shkoly po analiticheskoi spektroskopii* (Proc. All-Russian Scientific School on Analytical Spectroscopy), Krasnodar, 2012, p. 271.
- Fedyunina, N.N., Osipov, K.B., Statkus, M.A., Seregina, I.F., Tsizin, G.I., and Bol'shov, M.A., *Analitika Kontrol*<sup>2</sup>, 2012, vol. 16, no. 3, p. 260.
- Dubenskiy, A.S., Seregina, I.F., Blinnikova, Z.K., Tsyurupa, M.P., Pavlova, L.A., Davankov, V.A., and Bolshov, M.A., *Talanta*, 2016, vol. 153, p. 240.
- 16. Tsyurupa, M.P., Borisov, Yu.A., Blinnikova, Z.K., Platonova, N.P., Ul'yanov, A.V., Buryak, A.K., and

Davankov, V.A., Prot. Met. Phys. Chem. Surf., 2014, vol. 50, no. 1, p. 59.

- Tsyurupa, M.P., Blinnikova, Z.K., Proskurina, N.A., Pastukhov, A.V., Pavlova, L.A., and Davankov, V.A., *Nanotechnol. Russ.*, 2009, vol. 4, nos. 9–10, p. 665.
- Dubeskiy, A.S., Iakurnova, E.D., Seregina, I.F., and Bolshov, M.A., in *Proc. XIXth Euroanalysis 2017*, Stockholm, 2017, poster no. 240.
- Fedyunina, N.N., Seregina, I.F., Ossipov, K., Dubenskiy, A.S., Tsysin, G.I., and Bolshov, M.A., *Anal. Chim. Acta*, 2013, vol. 798, p. 109.
- Dubenskiy, A.S., Yakurnova, E.D., Seregina, I.F., Pavlova, L.A., Tsyurupa, M.P., Davankov, V.A., and Bol'shov, M.A., *Zavod. Lab., Diagn. Mater.*, 2017, vol. 83, no. 1, p. 21.
- Dubenskiy, A.S., Shved, A.M., Seregina, I.F., Davankov, V.A., and Bol'shov, M.A., *Zavod. Lab., Diagn. Mater.*, 2017, vol. 83, no. 10, p. 5.
- 22. Ossipov, K., Seregina, I.F., and Bolshov, M.A., *Russ. Chem. Rev.*, 2016, vol. 85, no. 4, p. 335.
- Fedyunina, N.N., Ossipov, K.B., Seregina, I.F., Bolshov, M.A., Statkus, M.A., and Tsyzin, G.I., *Talanta*, 2012, vol. 102, p. 128.

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