

UDC 543.6:546.9

Platinum Metals in the Environment: Content, Determination, Behaviour in Natural Systems

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(Received July 26, 2012)

Abstract

Modern analytical methods of the investigation of platinum-containing objects are considered, including the features and possibilities of the combined methods to determine trace amounts of platinum and palladium in surface water, soil and rocks. The data on metal content, the forms of their occurrence in geochemical systems and in technogenic sources from which they enter the environment are reported. The migration behaviour of different forms of platinum and palladium under the conditions characteristic of natural systems are considered, along with the results of model studies of the sorption behaviour of these elements at geochemical barriers.

Key words: platinum, palladium, content and forms of occurrence in natural systems, determination methods, modelling of behaviour at geochemical barriers

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INTRODUCTION

Chemistry, geochemistry, methods of determination of platinum group elements (PGE) traditionally attract increased attention of Russian researchers. This is connected first of all with enormous resources of these metals, with the urgency of search and evaluation of new deposits, and with the importance of investigations of alternative sources of raw material. Much attention is paid to the fundamental stud-

ies of geochemical processes for which the siderophile elements including those of platinum group serve as indicators. During the recent years, the significance of the studies of technogenic environmental pollution with platinum and other PGE in the zones of development of ore deposits and in large cities is increasing. This defines the necessity to develop research methods and the means to obtain new data on the content and migration behaviour of PGE in natural ecosystems.

TABLE 1

Palladium and platinum content in the environment [4, 7, 8]

Environmental objects	Palladium	Platinum
Earth's crust	0.4 ng/g	0.4 ng/g
Chondrite	1 µg/g	0.5 µg/g
Ores	up to 10n µg/g	up to 10n µg/g
Surface water	0.4–40 ng/L	0.1–75 ng/L
Bottom sediments	0.1–61 ng/g	0.2–100 ng/g
Urban aerosol	0.1–280 pg/m ³	0.02–2700 pg/m ³
Road dust	1–500 ng/g	0.3–680 ng/g
Soil	0.9–1760 ng/g	0.03–500 ng/g

The information concerning natural and technogenic content of platinum and palladium, the sources of these elements in the environment, the forms of occurrence and migration ability, as well as the methods of investigation of the behaviour of PGE under natural conditions is presented in the review.

NATURAL PALLADIUM AND PLATINUM CONTENT, SOURCES AND FORMS OF THEIR ARRIVAL INTO NATURAL ECOSYSTEMS

In spite of the existence of large and superlarge deposits of PGE, these metals occur rarely in nature (Table 1) and are characterized by low migration ability [1]. At the same time, progress in extensive mining and processing of PGE inevitably cause the arrival of enormous amounts of these metals into the environment. The major technogenic sources from which these elements enter the ecosystems include automobile and industrial catalysts, as well as the wastes of mining industry, metallurgical and radiochemical plants [2–4]. In addition, definite contributions into the propagation of platinum and palladium over natural systems

are made by the electronic industry and jewelry production, wastes from medical centres. As a consequence, the background levels of PGE in soil, bottom sediments and surface water have increased substantially during the recent years [5, 6]. At the same time, the data on the behaviour of technogenic PGE under natural conditions and their effect on ecosystems are extremely scarce.

The migration ability of the elements is determined both by the forms in which they enter the environment and by the oxidation-reduction and acid-base properties of natural media, their salt composition, the presence of natural complex-forming agents, coagulation and sorption of the elements on suspended matter and bottom sediments, hydrodynamic characteristics of aqueous systems and many other factors.

The data on the major forms in which palladium and platinum enter the atmosphere, water ecosystems and soil are presented in Table 2. The transformations of PGE under natural conditions, transport and accumulation of these elements and the methods of investigation of these processes are considered below.

TABLE 2

Forms and sources of palladium and platinum entering the environment

Forms of arrival	Sources
Fine metal particles (micro- and nanometer-sized)	Ores, rocks, industrial emissions, automobile catalysts
Oxides, chlorides, organometallic compounds	Catalysts, wastes from medical centres
Partially dissolved and hydrolyzed forms	Accessway rocks, industrial wastes, medicine

METHODS OF INVESTIGATION OF THE TRACE AMOUNTS OF PLATINUM GROUP ELEMENTS

The possibility to investigate the behaviour of PGE and their role in geochemical and ecological processes is directly connected with the possibilities of the analytical methods to determine the trace amounts of these elements in natural objects.

In addition to low concentrations and diversity of mineral forms of PGE, these objects are characterized by the complicated matrix composition affecting the instrumental determination. Besides, precious metals are characterized by the diversity of chemical forms in solution and kinetic inertness. As a result, even the most up-to-date and sensitive instrumental methods of elemental analysis (mass spectrometry with inductively coupled plasma, MS-ICP), electrothermal atomic absorption spectrometry (ETAAS) that were considered in detail in [9–11] do not provide the possibility of the direct determination of total content of PGE in rocks, soil, dust, water and other natural objects. It is possible to solve these problems only using combined methods.

The efficiency of analytical schemes for the determination of elements at the trace level is determined by preliminary sample preparation including sample dissolution and analyte concentrating (separation of the matrix), as well as by a combination of concentrating and determination. At the stage of concentrating, numerous matrix effects are removed to one extent or another, which, in combination with the use of instrumental possibilities of elimination [12] and account [13] of the influence, provides the reliability of results.

In the majority of cases, the schemes of determination of PGE traces in complex objects are based on the analysis of dissolved matter. On the one hand, this simplifies the introduction of the substance under study into the analyzer; on the other hand, this ensures the representative character and homogeneity of the sample to be introduced, and simplifies calibration.

Evaluating the technogenic pollution of ecological objects (soil urban dust) by platinum metals, one usually uses acidic treatment which does not affect the silicate matrix of the samples. To solve geochemical problems, the deter-

mination of PGE includes complete treatment of the sample through acidic dissolution, additional melting of the residue and separation of previous metals from matrix components using various concentrating methods.

Sample decomposition with acids (hydrochloric, hydrobromic, hydrofluoric, perchloric and nitric) is often carried out under increased pressure and temperature [12, 14–19]. In some cases the samples are treated preliminarily with a mixture of acids; non-dissolved residue is then fused [20]. Microwave heating is often used to leach analytes from soil, road dust *etc.* [21–23]. Acid decomposition profitably differs from other procedures by the minimal salt background, the possibility to achieve extremely low detection limits [24] and sufficiently high productivity. These advantages become determinative when solving ecological problems. Acid decomposition goes well together with various concentrating methods: extraction, sorption, co-precipitation with tellurium.

Preparation of geological objects for analyses often involves sample fusion; in particular fusion on nickel sulphide is used. This approach allows one to take a better account of non-homogeneity of element distribution but generates problems connected with high salt content of the resulting solutions and worsening of the correction of reference (blank) experiment.

Simple and technologically sound sorption methods dominate in combined analysis schemes as the methods to concentrate precious metals [8]. The major requirements to sorbents for concentrating PGE traces are selectivity, efficiency of use under dynamic conditions, possibility of metal elution and repeated use of the sorbent. In addition, the possibility to use acid media and to obtain concentrates free of admixtures that would affect subsequent instrumental determination is essential. The dynamic mode of concentrating is very attractive; this mode involves operation in a closed cycle, which provides the low level of solution contamination and a decrease in detection limit. Analysis schemes based on sorption concentrating of PGE in combination with spectrometric methods were considered in reviews [25, 26].

To extract PGE with ion exchange resins, direct passing of the solution under analysis through columns filled with resins is used, or

TABLE 3
Examples of the determination of trace amounts of platinum, palladium and gold in natural objects using combined methods

Objects of analysis	Method of sample decomposition	Concentrating method	Determination method	Content, ng/g			Ref.
				Pt	Pd	Au	
Pyroxenite	Assay melting for lead	-	MS-ICP	90-284	150-192	60-104	[52]
Komatiite, diorite, gabbro, silicate rocks	Melting for nickel stein	Co-precipitation with Te	MS-ICP	6-100	5-940	1.5-150	[53, 54]
Peridotite, soil	Melting for nickel stein	Co-precipitation with Te	MS-ICP	0.2-14	0.2-15	-	[55]
Soil	Acid treatment	Extraction of palladium by 1-pentanol in the form of Pd(II)-SnCl ₃ -N-butylacetamide complexes	ETAAS	-	7-59	-	[56]
Chromites, basalts, gabbro	Acid treatment in Carius tubes	Sorption with anion exchange resin Dowex 1-X8	MS-ICP	4.7-30	12-56	-	[21]
Gabbro, tailing ultramafic rocks, peridotite	Acid treatment in teflon bombs	Co-precipitation with Te, sorption with a mixture of cation-exchange resin Dowex 50 WX 8 and P507 resin	MS-ICP	4-1741	4-1185	-	[57]
Sand, waste rock, cobalt-copper-nickel ore	Acid treatment under microwave heating	Sorption with cation-exchange resin AG 50W-X8	MS-ICP	43-1400	300-470	19-370	[20]
Silicate rocks, oceanic basalts	Acid treatment in Parr bombs	Sorption with cation-exchange resin Dowex AG 50WX-8	MS-ICP	12-130	5.5-106	30-60	[33]
Peridotite, gabbro, road dust	Acid treatment under pressure or under microwave heating	Sorption with anion-exchange resin AG 1-X8	MS-ICP	6-87	3-226	-	[12, 28]
Spinel lherzollite, serpentinite	Acid treatment in teflon autoclaves at high temperature and pressure	Sorption with cation-exchange resin AG 50WX8	MS-ICP	up to 9	up to 8	-	[58]
Iron-manganese scum, sedimentary rocks	Acid treatment under microwave heating	Sorption with complex-forming sorbent POLIORGS IV	ETAAS	1-890	1-20	7-100	[37, 38]
Ores, olivinite, meladiorite, iron-manganese scum	Acid treatment	Solid-phase extraction (super-crosslinked, highly crosslinked polystyrene/1-hexadecyl-3-methylimidazolium bromide)	ETAAS	40-3520	6-6490	2-230	[50]

Road dust	Acid treatment under microwave heating	Micellar extraction under microwave heating (chelating agent: 2-mercaptobenzothiazol, surfactant: Triton X-100)	MS-ICP	62-97	3-184	-	[13]
Urban aerosol	Acid treatment at high temperature and pressure	Co-precipitation with Te or Hg	MS-ICP	-	(0.06-7.4) ^a	-	[12]
Road dust, coke	Acid treatment under microwave heating	Micellar extraction under microwave heating (complexing agent: 2-mercaptobenzothiazol, surfactant: Triton X-100)	MS-ICP	1.2-75	-	-	[3]
Road dust	Acid treatment under microwave heating	Solid-phase extraction (silica gel C19/N,N-diethyl-N-benzylthiourea)	ETAAS	(20-30) ^b	(4-16) ^b	-	[46, 47]
Urban aerosol	Acid treatment under microwave heating	Solid-phase extraction (silica gel/3-(1-thioureydo)propyl)	MS-ICP	(1-3) ^c	(8-13) ^c	-	[44]
Mineral water, soil	Acid treatment of soil	Dispersing liquid - liquid microextraction of palladium complexes with 2-amino-1-cyclohexene-1-dithiocarboxylic acid (dispersing reagent - acetone, extragent - carbon tetrachloride)	ETAAS	-	(100-400) ^d	-	[59]
River sediments, road dust	Acid treatment under microwave heating	Extraction of platinum and palladium complexes in the form of iodides with diethyldithiocarbamate in chloroform	MS-ICP	15-280	21-650	-	[60]

^a in ng/mL.^b in pg/m³.^c in pg/L.^d in pg/mL.

the solution obtained by dissolving tellurium or thioacetamide collector in used [25, 27–30]. Anion exchange resins have won the broadest application in concentrating PGE. Precious metals readily form anion complexes, especially chloride ones, which are well extracted by strongly basic anion exchange resins. However, the necessity of concentrated acid solutions for elution may cause depression of the analytical signal and worsening of reproducibility of the results [31, 32]. With the use of cation-exchange resins [20, 21, 33, 34], in view of their low selectivity, it is often necessary to use additional methods for matrix removal [17] or other methods to take into account the influence of the matrix, for example isotopic dilution [12, 14, 16–19, 24, 28, 33, 34] and reaction cells [12]. In general, the use of ion-exchange resins allows one not only to automatize the sorption process but also to combine it efficiently with subsequent instrumental determination in the on-line mode [12, 28, 30]. However, the reasonableness of this approach is not evident for the reason of large differences in the times of sorption (including elution) and measurement.

The highest selectivity with respect to platinum, palladium and gold in the presence of copper, iron, nickel and other metals is exhibited by complex-forming sorbing materials, for example the sorbents of POLIORGS series [35–38] but metal desorption from their surface is hindered; as a rule, the concentrate for subsequent determination is subjected to acid decomposition or combustion in a muffle [39–41]. Using ETAAS determination, it is possible to analyze the concentrate introducing it into the atomizer in the form of suspension [35, 36]; however, in order to automatize dosing, it is necessary to add stabilizing agents and use special dosing devices.

During the recent years, solid-phase extracting agents (SPE) became very popular as sorption materials [42]. The selectivity of SPE with respect to the elements under determination is regulated within a broad range by choosing a proper impregnating reagent. This type of sorption materials allows concentrating in the dynamic mode and, as a consequence, it allows one to automatize the sample preparation stage. Solid-phase extraction is distinguished by the high rate of extraction of the components un-

der determination and the possibility to obtain small volumes of liquid concentrates, which is convenient for subsequent instrumental analysis. In this respect, it is promising to perform elution under the conditions of microwave heating, which enables not only a substantial decrease in process temperature but also its intensification and automation [43, 44].

Solid-phase extraction is rather frequently used to extract the trace amounts of PGE during the analysis of ecological objects. However, along with evident advantages, this method has limitations which are especially substantial for the analysis of the objects with complicated matrix composition. This is so because the majority of SPE are used in neutral or weakly acid media (with exclusions described in [45–49]) and are insufficiently selective (the admissible excess of interfering elements with respect to PGE is usually not more than 10^3). Separate SPE [50] are rather selective to platinum, palladium and gold, and stable in strongly acid media, which allows using them in the analysis of geochemical objects.

Some examples of the combined methods to determine the trace amounts of platinum, palladium and gold are presented in Table 3. One can see that instrumental determination of precious metals at a level of ppb is achieved using different concentrating methods. In spite of the diversity of methods and means considered in academic works, applied studies most frequently involve assay melting on nickel sulphide followed by co-precipitation with tellurium, as well as ion exchange (multistage and/or in combination with complexing with organic reagents) [51–53]. A new trend is increased attention to sorption materials of the type of solid-phase extracting agents. MS-ICP and ETAAS are most widely used for element determination.

INVESTIGATION OF THE FORMS OF OCCURRENCE AND MIGRATION BEHAVIOUR OF PLATINUM GROUP ELEMENTS IN GEOCHEMICAL SYSTEMS

As it follows from the above-described information, the possibilities of the experimental investigation of the forms of occurrence and migration of PGE under real conditions are limited. The most reasonable approach to the in-

investigation of the behaviour of these elements under natural settings implies a combination of analytical studies (determination of the content) of PGE in environmental objects with the experimental modelling of the effect of separate factors on the behaviour of elements. In addition, the use of thermodynamic calculations allows taking into account the action of several factors at the same time and evaluating their total effect. The examples describing the application of this approach are presented below.

Dissolved forms of platinum and palladium in aqueous media

The majority of technogenic PGE enter the environment in the form of nanometer-sized metal particles that undergo a number of transformations when they are in contact with water, oxygen and organic substances. The rate of these transformations is determined, among other factors, also by pH value, the presence and nature of microorganisms and the organic matter. In acid media and in the presence of complex-forming agents the solubility of PGE increases substantially [61, 62]. Dissolved forms of PGE along with pseudo-colloids formed as a result of sorption of these forms on natural suspensions are the major migration form of platinum group metals.

The data on the forms of PGE occurrence under the conditions characteristic of natural water are rather contradictory [63, 64]. Palladium can exist in these solutions in the form of aquated and hydrolyzed chloro complexes [65], while in chloride systems like sea water it may exist mainly as $\text{PdCl}_3(\text{OH})^{2-}$ [66]. Both palladium chlorides and hydroxides with the composition $\text{Pd}(\text{OH})_2 \cdot m\text{H}_2\text{O}$ in nearly neutral media in the absence of organic ligands have minimal solubility. The major inorganic forms of platinum in water are considered to be chloride complexes with composition $[\text{PtCl}_6]^{2-}$ [67, 68] and $[\text{PtCl}_4]^{2-}$, disproportionating to form Pt(IV) and Pt(0) [69], as well as $\text{Pt}(\text{OH})_4^{2-}$ [70]. At the same time, according to the results of solubility studies of platinum (II) and (IV) states within pH range of natural water [62, 70] and in the solutions of different compositions [70], the dissolved

form of platinum under these conditions is represented mainly by hydroxo or hydroxo/chloro complexes of Pt(IV) with the composition $[\text{Pt}(\text{OH})_n\text{Cl}_{6-n}]^{2-}$. Unlike for palladium and platinum (II), platinum (II) hydroxide $\text{Pt}(\text{OH})_4 \cdot m\text{H}_2\text{O}$ is characterized by high solubility which increases sharply with an increase in pH from 4 to 11 [62]. This points to the prevalence of the contribution from hydroxyl ion into inorganic complexation of platinum in water. Under some natural conditions, essential part in binding and transport of platinum and palladium (by analogy with gold) may be played by thiosulphate ion; however, its role in the migration behaviour of PGE is almost unexplored.

In the presence of organic substances in surface water, the majority of trace elements including palladium and platinum are likely to exist in the form of strong complex compounds with organic ligands [71]. This is confirmed by the data of experimental studies of the interaction of platinum in solutions with model organic compounds (acetates and EDTA as the fragments of acyl polysaccharides), as well as humic acids extracted from highly coloured water [62, 72]. The interaction of platinum and palladium with natural complex-forming substances substantially increases (by several orders of magnitude) the migration ability of these elements.

Thermodynamic calculations carried out on the basis of the data on the stability constants of hydroxo and fulvato complexes showed that hydroxosulphate complexes are most characteristic of palladium within the broad pH range, while in the case of platinum hydroxo complexes dominate in weakly alkaline region ($\text{pH} > 7.5$), while hydroxofulvates dominate in weakly acidic region ($\text{pH} < 7.5$) [73]. The ratio of inorganic and organic platinum forms is strongly dependent on the concentration of humic substances in solution: the contribution from organic complex forms even for relatively high ($>10^{-5}$ mol/L) concentration of fulvic acids is essential only for $\text{pH} < 6$.

Another form in which PGE and gold participate in transport and accumulation processes is nanometer-sized forms stabilized with organic substances. However, this question is only weakly studied and requires separate consideration.

Interaction of dissolved platinum group elements forms with the components of natural geochemical barriers

Inorganic forms of PGE entering water systems may interact with the components of water forming new dissolved compounds with organic substances or precipitate on colloid particles or bottom sediments. To evaluate the efficiency of element concentrating on various geochemical barriers and element migration with suspended matter in natural water, it is necessary to know the data on the sorption ability of separate components of these systems: humic acids, iron oxides with different compositions (ferryhydrite, hematite, magnetite) and luminosilicates – with respect of precious metals within a broad pH range. The listed components are typical for natural settings and thus they are of interest for studying various sources of the technogenic pollution of environment with platinum group metals. The reasons of this pollution, as it was mentioned above, are industrial emissions, the use of catalysts, drainage of accessway rocks by atmospheric precipitation and surface water flows, *etc.*

Figure 1 shows the results of investigation of platinum and palladium sorption on humic acids (HA) – the major organic component of soil and bottom sediments – under the conditions close to equilibrium. A specific feature of HA as sorbent is its ability to partially dissolve in neutral and alkaline media (pH ~ 5.0). As a consequence, starting from pH 5 and above, two competing processes take place in the system under investigation during the interaction of metal ions with HA: the formation of well soluble metal complexes with relatively low molecular mass fraction of HA – fulvic acids (FA) – and sorption on HA precipitate. As a consequence of the formation of soluble fulvato complexes in media with pH > 5.0 palladium sorption on HA decreases sharply. For platinum, the contribution from the interaction with deposited HA is more substantial: at pH 8.0 a half of its initial content is sorbed. So, in highly coloured water palladium will be present most probably in the form of well soluble organic complexes with FA, while platinum will get distributed over the solution and suspended matter.

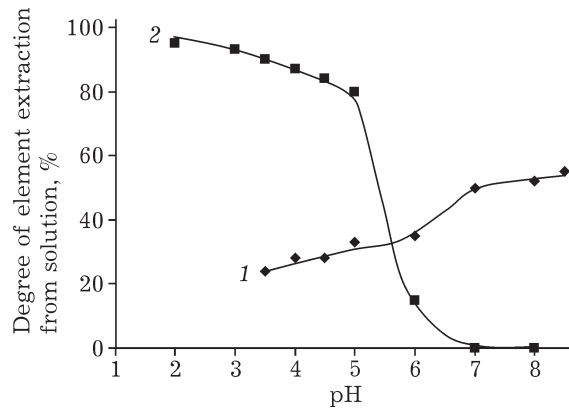


Fig. 1. Dependence of the sorption of inorganic complex forms of platinum (1) and palladium (2) on the sediment of humic acids on pH. Duration of experiment: 21 days.

The major inorganic component of natural geochemical barriers is iron oxides and oxyhydroxides. They are present in soil, bottom sediments, suspended matter of water; the formation of colloid oxyhydroxides is also observed during the oxidation of sulphide minerals of ores interacting with oxygen and atmospheric precipitation in mined platinum metal and other deposits. It was established that all the studied kinds of iron oxides characteristic of natural conditions may serve in nearly neutral and weakly alkaline media as collectors of the inorganic forms of precious metals. The data shown in Fig. 2 illustrate the sorption capacity of freshly formed iron oxyhydroxide (FeOOH) with respect to platinum (IV) and palladium (II)

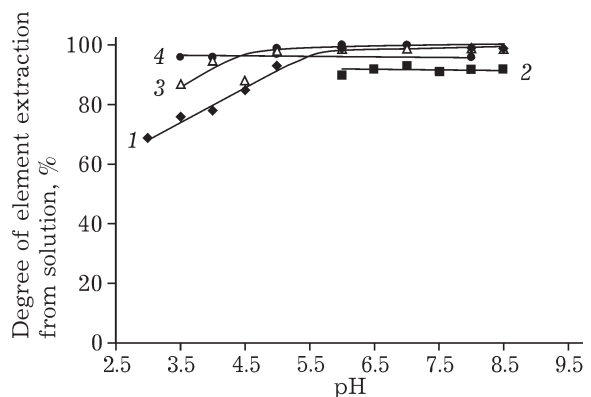


Fig. 2. Dependence of the sorption of inorganic complex forms of platinum and palladium on FeOOH precipitates (1, 2, respectively) and FeOOH modified with fulvic acids (3, 4, respectively) on pH. Duration of experiment: 21 days.

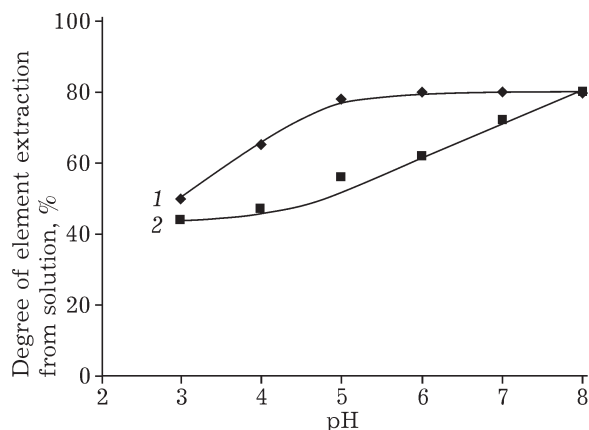


Fig. 3. Dependence of the sorption of inorganic complex forms of platinum (1) and palladium (2) on clay slate. Duration of experiment: 21 days.

present in solution with pH 3.0–9.0 in the form of chlorides and hydroxides. Sorption curves provide evidence of the high efficiency of the interaction of elements under study with the sorbent under these conditions: extraction extent is 85–95 %. The presence of HA in solution causes the modification of the developed surface of iron oxyhydroxide and an increase (after removal of the solution containing HA) in the sorption properties of iron oxyhydroxide: the kinetics and extraction degree of all the considered metal ions increase noticeably within a broad pH range (see Fig. 2). It is likely that the sorbents of this kind may be considered as a prototype of natural mineral and organomineral colloids based on goethite providing the transport of many microelements.

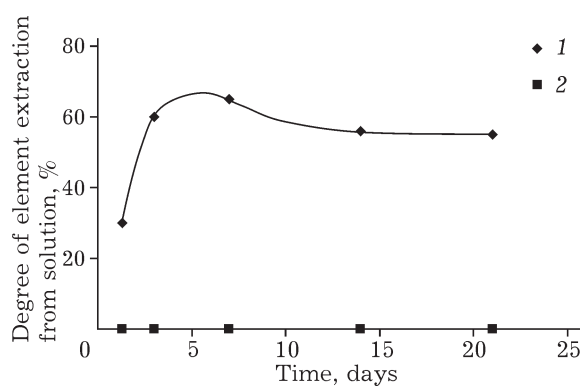


Fig. 4. Dependence of the degree of extraction of hydroxochloride complexes of Pt(IV) (1) and Pd(II) (2) on the time of contact with the suspension isolated from river water.

The role of aluminosilicate component in the migration behaviour of precious metals was studied by us for the example of the sorption of dissolved inorganic forms of platinum and palladium on clay slate (Fig. 3). It is likely that under definite conditions clay slate may serve as a rather efficient sorption barrier for these elements or provide colloidal transport. A similar trend in the behaviour of platinum was observed in [74].

The regularities of platinum and palladium behaviour in model sorption systems were followed in experiments with the samples of coloured river water [75] (pH 6.7) containing 50 $\mu\text{g/mL}$ FA and a suspension with admixture of humus (9.7 % C_{org}) and iron oxides (5.5 %). Investigation of the dynamics of the distribution of platinum (10 $\mu\text{g/L}$) and palladium (1 $\mu\text{g/L}$) in water sample between the solution phase and the suspension confirmed the results of our experiments with individual sorption phases and the data of previously performed thermodynamic calculation [73]: the absence of sorbed forms of palladium and the possibility of platinum accumulation on suspended and/or deposited matter (Fig. 4). Similar results on the distribution of PGE between the phases of solution and suspended matter of natural water were obtained by the author of [76]. Relying on experimental studies and evaluation of the mobility of technogenic PGE (in particular, from road dust) he showed that the highest potential for long-range transport and bioaccumulation in the aqueous medium is characteristic of palladium which remains almost completely in the phase of solution; platinum is distributed between the solution and the suspension in approximately equal portions.

So, on the basis of the data on the composition of water solutions and suspended matter, the forms of occurrence of the metals under study in these systems and the behaviour of their dominant forms in contact with sorption phases of different kinds, it is possible to study the geochemical factors affecting the migration behaviour and transport of platinum, palladium and other platinum group metals entering the environment from secondary sources (accessway and recreation rocks in the zones of mining, road dust near highways etc.) and predict the possibility of the accumu-

lation of these elements and the ecological danger of this technogenic pollution.

CONCLUSIONS

In view of the fact that the concentrations of platinum metals in environmental objects are very small and the metals themselves are characterized by low migration ability in the close-to-neutral media, their migration behaviour in natural systems and the degree of ecological danger remained poorly studied for a long time. During the recent decades, an increase in the extraction of the ores of these metals caused by the broad use of platinum and palladium in automobile catalysts and in medicine results in a substantial increase in the amount of PGE entering the environment. This defined the urgent character of the studies aimed at the development of the methods of determination of ultra-trace amounts of PGE in complicated natural objects and the search for ways to study the transformations and migration behaviour of these elements in various ecosystems.

The most sensitive methods are used to determine the natural concentrations of PGE, first of all MS-ICP. However, as it follows from the analysis of literature data, even in the case of MS-ICP the determination of PGE in the components of ecosystems is possible only if combined analytical schemes are used, including the separation of matrix components, most frequently using the methods based on sorption. These schemes provide determination of PGE in rocks, soil, dust *etc.* at a level of 10^{-7} – 10^{-8} %.

In spite of the new level of instrumental possibilities, the direct experimental investigation of the forms of PGE occurrence under real systems is very limited. Because of this, the most reasonable approach to the studies of the behaviour of these elements in natural settings implies a combination of analytical studies (determination of PGE content) with experimental modelling of the effect of separate factors on the behaviour of elements, in particular on the basis of sorption experiments using model phases – the components of geochemical barriers. The use of calculation methods involving the data on the forms of element occurrence in solution, the stability and

sorption ability with respect to different components of ecosystems allows one to take into account the action of several factors and to evaluate their total effect. This combined approach allows obtaining the data on the behaviour of PGE in natural media, the character of accumulation and migration of the elements, and therefore this allows one to assess the possibility of their interaction with living organisms, that is, the ecological danger.

Using the mentioned approach, for platinum and palladium (the major technogenic pollutants among the PGE) as examples, it was established that their most efficient natural collectors extracting up to 95 % of metals are organomineral phases based on iron oxyhydroxides (ferryhydrite). These phases are present in bottom sediments and natural colloids and provide transport and accumulation of microelements in natural media. The migration behaviour of dissolved forms of palladium and platinum not bound into pseudo-colloids differs substantially: in the presence of organic matter palladium remains in solution phase (but it hardly becomes bioavailable because it is bound in strong complexes with dissolved organic substances), while more toxic platinum demonstrates the ability to accumulate in the substances of natural geochemical barriers.

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