

## Reextraction of Pt, Rh, Ir, Ru from Organic Sulphides Using Ultra-Violet Light Treatment

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### Abstract

Results of investigations into reextraction of Pt, Ir, Rh and Ru from organic sulphides by water solutions of a number of reagents by the action of the ultra-violet (UV) light have been presented. It has been demonstrated that the UV light has a pronounced effect upon the reextraction of platinum metals. Separating of Rh and Ru from Pt and Ir by a muriatic acid solution of sodium and ammonium nitrates and rongalite has been performed. The UV light irradiation of a system of an extract of organic sulphides and muriatic acid makes it possible to separate iridium from the other platinoids and to reextract rhodium selectively by a sodium hypochlorite solution. The activation mechanism of the reextraction process upon irradiation by the UV light is discussed, which consists in a labilization of the complexes and in the reduction of a central atom to lower oxidation states.

### INTRODUCTION

Organic sulphides (OS) are used to extract the Pt(II, IV) chlorocomplexes at a temperature of 100 °C, Rh(III) at 150 °C, Ru(III) at more than 150 °C and Ir at 130 °C. It is impossible to isolate platinum metals (PM) selectively, except for palladium, upon an extraction with the use of OS. Extraction of Pt (II) by sulphides at 80 °C is characterized by a low degree of a recovery into the extract (up to 78 %) and by coextraction of ruthenium (up to 10 %) and rhodium (up to 5 %). If a deep Pt (II) extraction is performed at a temperature of 100 °C, then its satellites will also pass in the extract: Rh(III), by 20 %, Ru(III), by 30 % and Ir(III), approximately by 3 %. As a consequence of this, a collective extract of platinum with its satellites can be obtained without separation effects [1].

In this connection, selective extraction of each platinoid with the use of OS is related either with its underextraction, or with a co-extractibility of all platinoids. Therefore, the

extract of the sum of Pt, Rh, Ru and Ir has been selected as a subject of the research, this extract being later separated at the reextraction stages.

Work [1] discusses reextraction of platinum metals (PM) from OS extracts by ammonia and by water solutions of alkali metal sulphides. The authors highlight that the process is characterized by low separation factors and by high reextraction temperatures. Accordingly, reextraction of Pt, Rh and Ru by solutions of alkali metal sulphides is possible only at a temperature of 90–110 °C and upon a long-term contact of the phases, while Ir is completely reextracted only at 130–140 °C. This reagent allows to obtain concentrate of the sum of PM sulphides without a separation into the individual metals.

Metal zinc can be also applied as a collective reextractant. Cementation of all PM by zinc from their extracts proceeds successfully to obtain a concentrate of the precious metals; however, the separation factors are lacking.

In connection with the fact that a deep separation of platinum metals is impossible at the extraction stage, we have solved the problem of their separation during a reextraction by various reagents using the UV-light to labilize the complexes.

Photochemistry of complexes of platinum metals may be of scientific and practical interest. Previously, amino complexes of the first row transition metals along with similar compounds of rhodium and platinum have been investigated in sufficient detail. Several works [2–5] point out at the significant acceleration of double replacement reactions and reactions of hydrolysis in Pt(IV) complexes under an effect of the UV light.

The features of photochemistry of Pt and Rh amino complexes have been studied in work [6]. Authors have recognized that only replacement reactions proceed in Rh(III) complexes irrespective of the excitation energy.

Transformation type of the platinum (IV) complexes depends on the energy of light, structure of the complex and composition of the coordination sphere.

Photochemistry of the mixed acido-, amino-complexes of platinum (IV) is characterized by two basic types of the reactions: oxidation-reduction and replacement reactions.

Photoreduction rate of the central atom increases with an increase in the energy of light. The replacement rate of acido ligands depends on the energy of light in the same way, too. It has been found that a structure of the complex, the nature of an amino ligand and of an acid group has an influence on the rate of oxidation-reduction reactions and of the reactions of photoreplacement of the ligands. A conclusion has been drawn that homolytic decomposition of a metal-ligand bond represents the primary act that is responsible for the types of the observed photochemical transformations of platinum (IV) complexes.

Work [7] is devoted to the study into photochemical reactions and isotope exchange reactions of certain nitroso complexes. This work presents the results that bear evidence that the complexes such as  $[\text{Ru}(\text{NO})\text{Cl}_5]^{2-}$  are capable to attach  $\text{OH}^-$  and  $\text{SH}^-$  ions in the presence of the UV light with formation of  $[\text{Ru}(\text{NO}_2\text{H})\text{Cl}_5]^{3-}$  and  $[\text{Ru}(\text{NOSH})\text{Cl}_5]^{3-}$ . However, it was assumed

previously [8] that they do not enter the similar reactions.

We have conducted the investigations into the effect of the UV irradiation on the reextraction of platinum metals from OS solutions. The UV irradiation is being applied to reextraction processes for the first time. This work considers a fundamental potential to use the UV light to accelerate passing of the reactions under study and to recover the metal directly from the extract.

## EXPERIMENTAL

In order to perform the research, PRK-2 mercury quartz lamp has been applied as a source of the UV light, the maximum comparative energy of which at the wavelengths of UV spectrum of 365–366.3 nm comprises 100 units. The reagents that do not extract platinum metals under normal conditions were used as reextractants. An extract of metal (DPS in toluene) and the aqueous phase ( $V_o : V_{\text{aq}} = 1 : 1$ ) were put in quartz separating funnels.

Concentration of each platinum metal in an extract comprised  $4 \cdot 10^{-3}$  mol/l. Group extract was obtained by extracting the chlorocomplexes of platinum metals with dipropyl sulphide in toluene at 150 °C in an autoclave. The extracts were mixed with water solutions of the associated reextractants and were shaken up; then the biphasic system was subjected to the UV irradiation. The distance from a source of the UV light to the samples under study was 15–20 cm. The irradiation was conducted to reach a discoloration of the organic layer. Then the reextraction was repeated once again with a fresh portion of the reextractant.

Upon an irradiation over the course of a certain time, organic and aqueous phases were separated and analyzed for the content of platinum metals.

## RESULTS AND DISCUSSION

The results of the investigations (Table 1) demonstrate that UV light has a pronounced effect on the reactions of reextraction.

Without the UV light action, an appreciable transition of a metal into a solution does not

TABLE 1

Reextraction indices of Pt, Rh, Ir, Ru

Reextractant	Reextraction time, min	Concentration of the reextractant	Extraction degree of the metal*, %			
			Pt	Rh	Ir	Ru
NH <sub>4</sub> OH	15	7 M	100/48.0	100/0	100/0	100/13.0
	480	7 M	100/100	100/0	100/0	100/50.0
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	40	1 M	100/0	100/0	100/0	100/0
	120	1 M	100/0	100/0	100/0	100/0
NaOCl	60	1 M	100/0	100/0	100/0	100/80.0
	120	Active Cl <sub>2</sub>	100/0	100/0	100/0	100/98.1
Thio + HCl	6	0.5 M Thio in 2 M HCl	100/74.4	-/0	-/0	-/3.3
	10		100/100	-/0	-/0	100/9.9
	20		100/100	-/0	-/0	100/24.4
	90		100/100	-/0	-/0	100/-
	180		100/100	100/0	100/0	100/-
NaNO <sub>3</sub> or NH <sub>4</sub> NO <sub>3</sub> in HCl	30	8 M in 7 M HCl	0/0	0/65.1	0/0	100/91.0
	60		12/0	100/85.0	0/0	100/100
	120		18.3/0	100/100	0/0	100/100
Rongalite	120	1 M in 2 M HCl	0/0	100/0	100/0	100/0
NaClO <sub>3</sub>	240	0.4 M	0/0	100/0	100/0	100/0
Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , Na <sub>2</sub> SO <sub>3</sub>	60	Saturated solution	0/0	100/0	100/0	100/0
	480		0/0	100/0	100/0	100/0
HCl	20	6-7 M	0/0	0/0	100/0	0/0
	600		11.8/0	100/0	100/0	100/0
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	480	1 M	100/0	100/0	100/0	0/0

\*First value is given for the UV irradiation, second one - without irradiation.

occur in most cases and upon an irradiation with the UV light, the reaction proceeds as fast as upon heating or with the use of oxidation-reduction systems. It has been found that the rate and the depth of reextraction of metals upon the sample irradiation depend on the nature of the reextractant that is in contact with the organic phase. It should be noted that muriatic acid (6-7 mol/dm<sup>3</sup>), which does not interact, with iridium as an example, in solutions of organic monosulphides even under severe conditions (~100 °C) without an irradiation, extracts it rather effectively under the effect of the UV light. Complete transition of iridium into the aqueous phase occurs during 10 min.

If acid solutions of hydroxylamine, ammonium rhodanate and sodium thiosulphate are used as reextractants, reaction does not accelerate. Consequently, by using the UV light in a combination with reextractants of different

nature, it is possible to perform a quantitative recovery of metals from the extracts, both selectively and collectively. For example, use of (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>OH, NaOCl and thiourea in photochemical process allows extracting platinum, rhodium, iridium and ruthenium from an organic phase in a form of water soluble complexes.

Deep reextraction of the sum of rhodium, iridium, ruthenium and their separation from platinum can be performed upon treatment of the extract with Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>SO<sub>3</sub> and NaClO<sub>3</sub> water solutions. To reextract rhodium and ruthenium selectively and to separate them from platinum and iridium during a photochemical reaction, NaNO<sub>3</sub> or NH<sub>4</sub>NO<sub>3</sub> and rongalite solutions in muriatic acid with a concentration of 7 mol/dm<sup>3</sup> can be used. For selective and quantitative iridium recovery from an extract that contains other platinum metals,

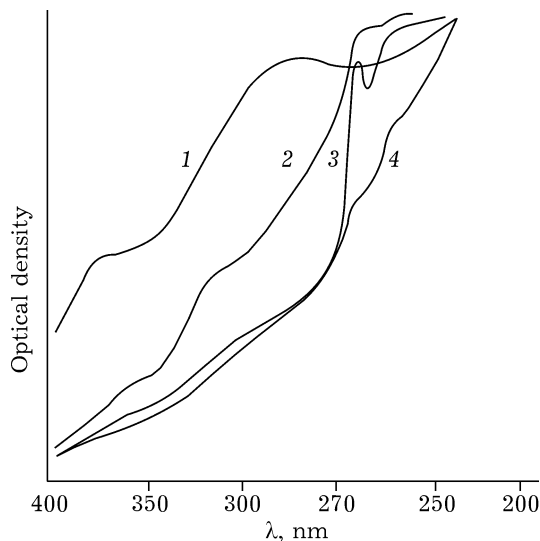


Fig. 1. Absorption spectra of ammonium compounds of Ru (1), Rh (2), Ir (3), Pt (4) that have been obtained upon their reextraction by  $\text{NH}_4\text{OH}$  solution.  $T = 20\text{--}40^\circ\text{C}$ .

a solution of muriatic acid with a concentration of  $6\text{--}7\text{ mol/dm}^3$  is applied as a reextractant.

Reextraction of platinum metals by ammonia upon the UV light irradiation proceeds to yield  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ ,  $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Ir}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  metallamines (Fig. 1). Ruthenium can be reextracted by  $(\text{NH}_4)_2\text{CO}_3$  solution to form the “ruthenic red” compound (Fig. 2). The solution of muriatic acid ( $7\text{ mol/}$

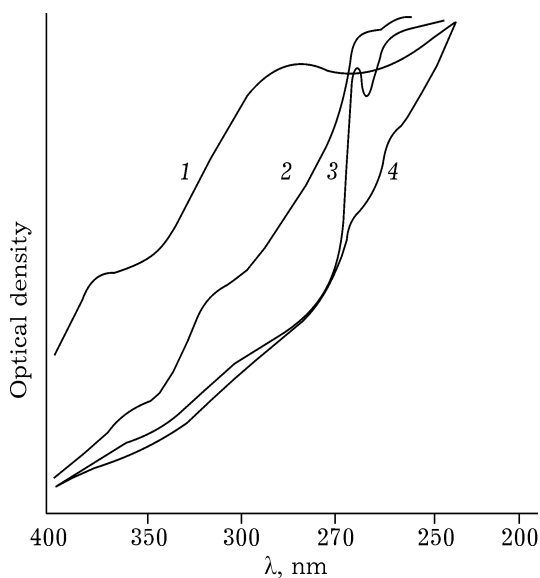


Fig. 2. Absorption spectra of “ruthenic red” (1) upon the reextraction of  $\text{RuCl}_3 \cdot 3\text{R}_2\text{S}$  ( $1\text{ M } (\text{NH}_4)_2\text{CO}_3$  solution,  $T = 30\text{--}40^\circ\text{C}$ ) and of  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  (2) ( $1\text{ M } \text{NH}_4\text{OH}$  solution,  $T = 20\text{--}40^\circ\text{C}$ ).

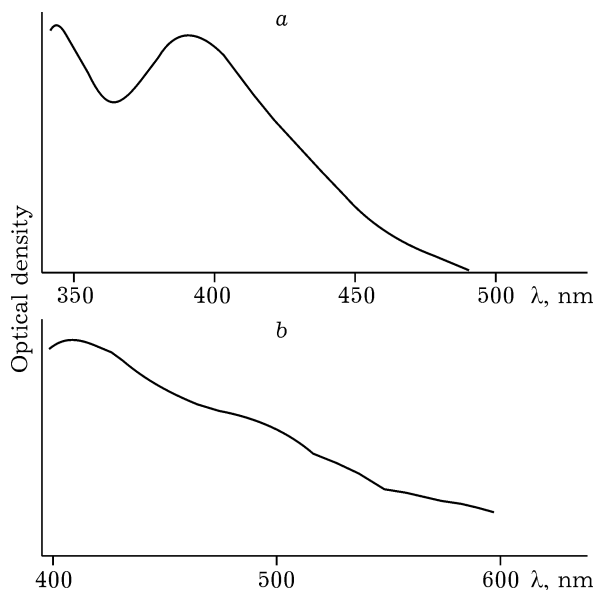


Fig. 3. Absorption spectra: a –  $\text{H}_3[\text{IrCl}_6]$  obtained upon the reextraction of  $\text{IrCl}_3 \cdot 3\text{R}_2\text{S}$  using  $7\text{ M HCl}$  solution on exposure to the UV light; b – complex of rhodium obtained upon the reextraction of  $\text{RhCl}_3 \cdot 3\text{R}_2\text{S}$  using  $\text{NaOCl} \cdot \text{HCl}$  system.  $T = 20^\circ\text{C}$ .

$\text{dm}^3$ ) recovers iridium in the form of  $[\text{IrCl}_6]^{3-}$  (Fig. 3, a). Rhodium can be reextracted by an alkaline solution of sodium hypochlorite with formation of dark blue  $\text{RhO}_3^-$ ,  $\text{RhO}_2^+$ ,  $\text{RhO}^{3+}$  solutions (see Fig. 3, b). Reextraction of platinum, rhodium, iridium and ruthenium by rongalite is followed by the formation of sulphide deposits.

Consequently, UV irradiation that exerts a significant influence on the reextraction rate has no effect on the composition of the reextracted compounds. The irradiation of extracts without any reextractant by the UV light has been performed. Depending on the distance from a light source and on the duration of the irradiation of samples, salts of various compositions can be recovered from an extract and photodecomposition of the salts to obtain a metal can be performed. Chemical analysis of the obtained salts had been performed suggesting their possible composition. Table 2 presents composition and properties of salts recovered from the extracts.

According to the radiography analysis, recovered salts have amorphous structure and metallic ruthenium is semi-amorphous.

We have succeeded in recovering the  $\text{RuCl}_3$  and  $\text{RuCl}_2$  salts and partially metal ruthenium

TABLE 2

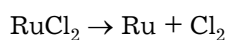
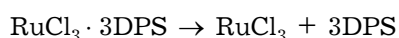
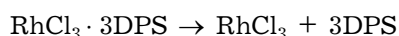
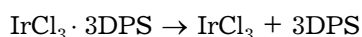
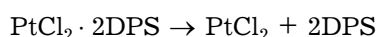
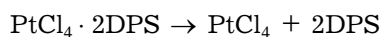
Results of the metals recovery from extracts upon the UV irradiation

Extract type	Irradiation time, h	Extraction degree, %	Recovered product		
			Composition	Chemical properties	Visual appearance of the crystals
PtCl <sub>2</sub> · 2DPS	6-8	~100	PtCl <sub>2</sub>	Insoluble in water and HCl, water solution with SnCl <sub>2</sub> is coloured in yellow	Greenish-yellow
RhCl <sub>3</sub> · 3DPS	4-5	~100	RhCl <sub>3</sub>	Insoluble in water and acids	Red
IrCl <sub>3</sub> · 3DPS	7-9	~100	IrCl <sub>2</sub>	Insoluble in acids and diluted alkalis	Grey
RuCl <sub>3</sub> · 3DPS	3-4	~100	RuCl <sub>3</sub>	Easily soluble in water, forming reddish solutions, substance is hydrolyzed when heated, releasing Ru(OH) <sub>3</sub>	Black

Note. DPS stands for dipropylsulphide.

from the ruthenic extract. IrCl<sub>2</sub> salt has been obtained from the iridic extract, PtCl<sub>4</sub> and PtCl<sub>2</sub>, from platinum extract and RhCl<sub>3</sub>, from rhodic extract (according to chemical analysis).

It can be inferred that decomposition of the complexes in an organic phase proceeds during the UV irradiation by the reactions



Hence, as compared to the recorded methods for processing the extracts, an irradiation of organic solutions by the UV light makes it possible to:

a) conduct reextraction under normal conditions, which significantly simplifies a technology of obtaining the pure metals;

b) raise an extraction degree and quality of the metal due to its selective recovery during reextraction.

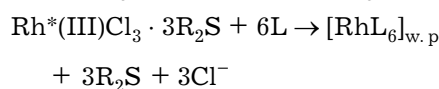
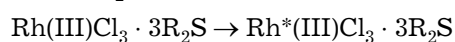
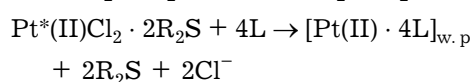
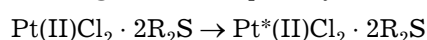
It should be noted that this method is especially promising as regards ruthenium. A number of reagents in a combination with the UV light can be used for analytical purposes. For instance, thiourea can be used for ruthenium determination in solutions of organic monosulphides and

iridium can be determined in the form of [IrCl<sub>6</sub>]<sup>3-</sup> (reextractant is a solution of 7 M HCl).

## CONCLUSIONS

Initiation of reextraction reactions (reactions of an inner-sphere replacement of R<sub>2</sub>S molecules by alternative addenda) can be performed not only in thermal way and by the use of accelerating reagents, but also photochemically. By virtue of the fact that the visible light has no influence upon the reactions in question, the activation of the reextraction process occurred by the UV light from a PRK-2 sun-lamp. In this case, the reextraction proceeded much more effectively than upon a thermal or oxidation-reduction action. During the UV irradiation, a labilization of complexes and R<sub>2</sub>S elimination from the internal sphere of an extracted complex occurs (the Me-SR<sub>2</sub> bond is weakened upon the photoexcitation).

With photochemical excitation, central atom, that is, chelating agent, being in an excited state, gains a greater capacity for the replacement-exchange events to pass by the reactions



where  $Pt^*(II)$  and  $Rh^*(III)$  are excited states, L is an attacking ligand (a charge at the complex is omitted). On the other hand, since the light is a source of electrons for complexes in an organic phase and the complexes are an electron sink, then it is impossible to rule out a potential for oxidation-reduction processes to pass, which is especially typical of ruthenium that shows a tendency to be reduced to metal. It has also been found [6] that oxidation-reduction reactions are not typical of the photochemistry of rhodium amino complexes similar to  $[RhA_5X]^{2+}$ ,  $[RhA_4X_2]^+$ . It can be assumed that the reextraction reactions under the effect of the UV light are caused by an electron phototransfer, which leads to the reduction of the central atom and to the formation of a labile complex in the organic phase, the complex being a site for elimination of the extractant molecules.

Depending on the nature of the medium and reextractants, the reextraction capability of metals varies, which forms the basis of their selective separation when both of them are present. Accordingly, a reextraction of iridium (III) in the medium of 7 M HCl under the effect of the UV light proceeds easier as compared to Rh, Pt and Ru (the quantitative extraction of iridium occurs for 10 min, while Rh, Ru and Pt cannot be extracted at all).

Fast passing of iridium from an organic into an aqueous phase, as compared to rhodium, ruthenium and platinum, is caused probably by the fact that the absorption of the UV light by iridium occurs more intensively than the absorption by Rh, Pt, Ru and HCl. In addition, it has been known that chloride ions in the highly acid medium are capable to reduce iridium. In our case, a possibility is not ruled out for iridium to be reduced by a chlorine radical that is formed in the HCl solution.

The reextraction rate depends on the donor capacity of reextractant ligands. Therefore, we can speak in this case about an intermediate compound that is formed in the organic phase with a reextractant ligand (instead of the chloride-ligand) in the internal sphere.

With allowance made for the interference of the ligands, the replacement rate in the internal sphere of the complex will also be dependent on the ligand that is at its *trance*-position.

It has been found that during photochemical reextraction, along with a thermal one, the

medium exerts a considerable influence on the labilization of the Me-S bond. To take an example, the efficiency of a thiourea action on the process of reextraction of Rh and Pt in the HCl medium is higher than in water.

High performance of the reextraction process for platinum metals upon an irradiation is also attributable to the fact that an activation of the reextractant molecules as well occurs during the UV irradiation, *i.e.* a strengthening of the donor properties of the entering ligands, which is caused by a transient formation of free radicals.

Process of photochemical reextraction depends also on the nature of an extractant. If a synthetic sulphide (DPS, DBS, DHS) is the ligand, then the reextraction proceeds somewhat quicker than in the case of oil sulphides.

Thus, an essence of the reextraction mechanism for platinum metals that are exposed to the UV light consists in a labilization of the complex and in the reduction of the central atom, a chelating agent, to lower oxidation states, *i.e.* its transformation into the speciations that are more susceptible to replacement-exchange reactions.

## Acknowledgements

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