Dynamic Sorption Preconcentration of Platinum Metals

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A method for Ru, Rh, Pd, Ir and Pt preconcentration using amine sorbent has been proposed; quantitative recovery of metals on the microcolumn has been achieved by diluting a sample with 6–8 M HCl in a flow system before injection into the micro-column.

Sorption preconcentration of platinum metals (PM) is widely used in the analysis of minerals, ores and non-ferrous metallurgy products. Sorbents containing aliphatic or heterocyclic amine groups are the most promising.[1–3] Chloride complexes of PM are selectively recovered on these sorbents from hydrochloric acid solutions.[2,4]

The variety and remarkable kinetic inertness of PM complexes in solution presents difficulties when preconcentration methods are being developed. Distribution coefficients of the main metal species are relatively low and therefore preconcentration procedures are time-consuming and the recovery of metals is often not quantitative. It is most difficult to achieve high sorption rates of ruthenium and rhodium.[2,3,5] Heating a solution has usually increased the recovery of these metals,[5] and some dynamic preconcentration methods have been described[1–3,6] but they provide an effective recovery only for a few PM.

The purpose of the present work is to develop a new approach to the preconcentration of the PM group elements using non-equilibrium conditions of dynamic sorption.

The recovery of ruthenium(III, IV), rhodium(III), palladium(II), iridium(III, IV) and platinum(IV) on microcolumns containing 0.1 ml of POL-DETA sorbent was investigated. The sorbent was synthesized based on styrene–2% divinylbenzene copolymer, and it contained 1.1 mM g^{-1} of diethylenetriamine groups.[7] Solution was pumped through the microcolumn using a peristaltic pump with a flow rate of 2–3 ml min^{-1}. The recovery of metals was determined by measuring the remaining concentration of metals in solution by electrothermal atomic absorption or with the help of a radiotracer method.

Sorption of PM from hydrochloric acid solutions on amine sorbents is caused by exchange of chloride with PM complexes on the protonated nitrogen of the functional groups. Recovery of anhydrous anionic chloride complexes is mostly effective.[8,9] The formation of amine complexes of PM is also possible, if a lengthy phase contact time and heating of solution is used.[8,10]

It was found that the recovery of palladium and iridium(IV) is quantitative over a wide acidity range: from pH 5 to 2 M HCl; iridium(III), from pH 5 to 6 M HCl (Fig. 1). The palladium complexes are labile enough and sorption of this metal from low acidity solutions proceeds due to substitution of chloride for nitrogen in the inner coordination sphere of the metal.[8] When the HCl concentration rises to 0.1 M, tetrachloropalladate, which effectively interacts with protonated nitrogen, is predominantly present in solution. Anhydrous chloro complexes of iridium, once formed, exist under low HCl concentration for a long time due to their outstanding kinetic inertness.

The greatest extent of ruthenium(IV), rhodium(III) and platinum(IV) recovery was achieved at different HCl concentrations: 1–3; 6–7 and 3 M (86%, 96% and 85%, respectively) (Figs. 2–4). Under these conditions the predominant forms of the metals in solution are $Ru_2OCl_{10}^{4-}$, $RhCl_6^{3-}$ and $PtCl_6^{2-}$.[1,12] The decrease in metal recovery at lower HCl concentrations is connected with the formation of aquachloro complexes possessing a smaller charge.

Sorption of all anionic forms of PM is suppressed under a high concentration of competitive chloride. However, these chloride concentrations are the most favourable to the formation of anhydrous chloro complexes of platinum metals. This contradiction is practically insoluble in a static sorption regime but is relatively simple to eliminate under dynamic conditions. Thus, a solution containing anhydrous chloro complexes of PM most favourable for recovery can be diluted

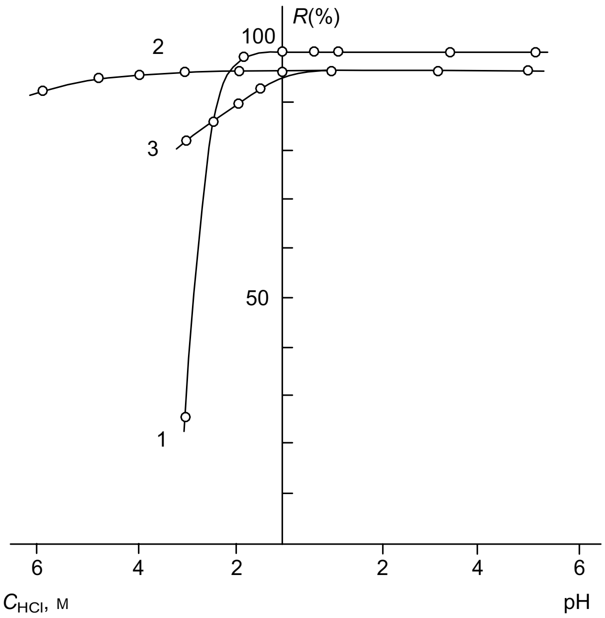

Fig. 1 Effect of HCl concentration on palladium(II) (1) and iridium(III,IV) (2,3) recovery on a POL-DETA sorbent. C_{Pd} = 5 ppm, C_{Ir} = 0.01 ppm, v = 3 ml min^{-1}.

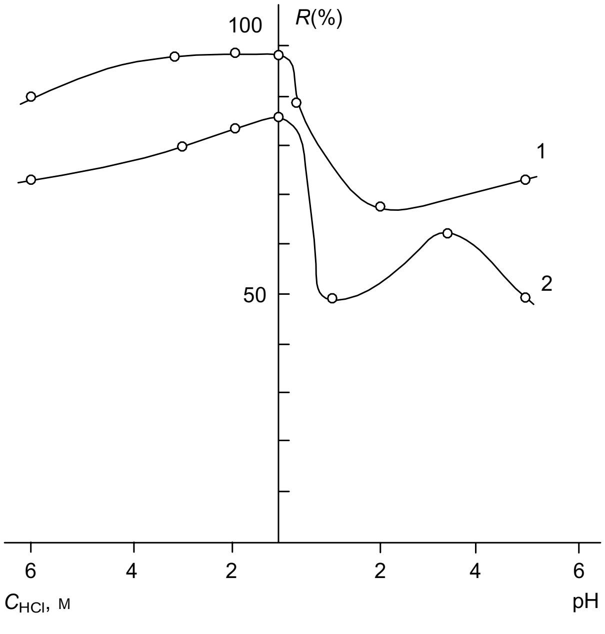

Fig. 2 Effect of HCl concentration on ruthenium(IV) recovery on a POL–DETA sorbent. 1, recovery using dilution before injection into microcolumn; 2, without dilution. C_{Ru} = 5 ppm, v = 3 ml min^{-1}.

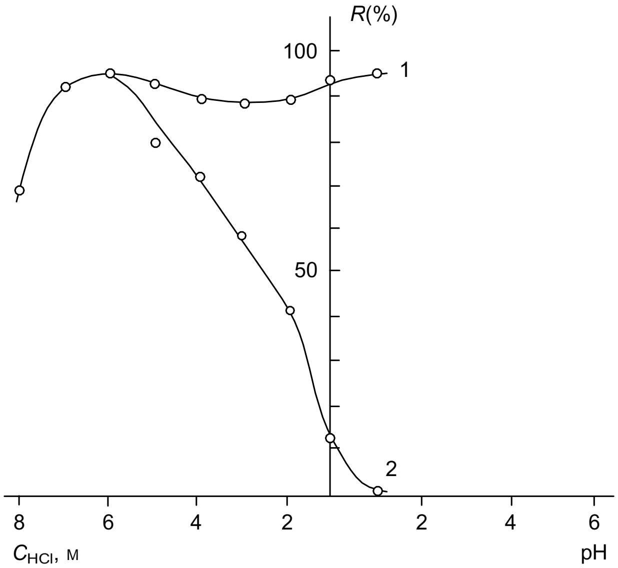

Fig. 3 Effect of HCl concentration on rhodium(III) recovery on a POL–DETA sorbent. 1, recovery using dilution before injection into microcolumn; 2, without dilution. $C_{Rh} = 0.36$ ppm, v = 3 ml min^{-1}.

directly in a flow system before injection into a microcolumn to reduce the chloride concentration. In this case anhydrous chloro complexes of PM exist long enough to be transported to sorbent functional groups.

The results obtained are presented in Figs. 2–4. Recovery of ruthenium is quantitative when a solution containing initially 6–8 M HCl is diluted to 1–3 M HCl; rhodium, to pH 1–7 M HCl; platinum, to 1–3 M HCl. Simultaneous preconcentration of PM is achieved by sample dilution to 1–2 M HCl.

The influence of the main matrix elements, iron(III) and copper(II), on the recovery of PM was investigated (Table 1). It was found that PM were quantitatively extracted from solutions containing up to 20–40 g dm^{-3} of iron and copper.

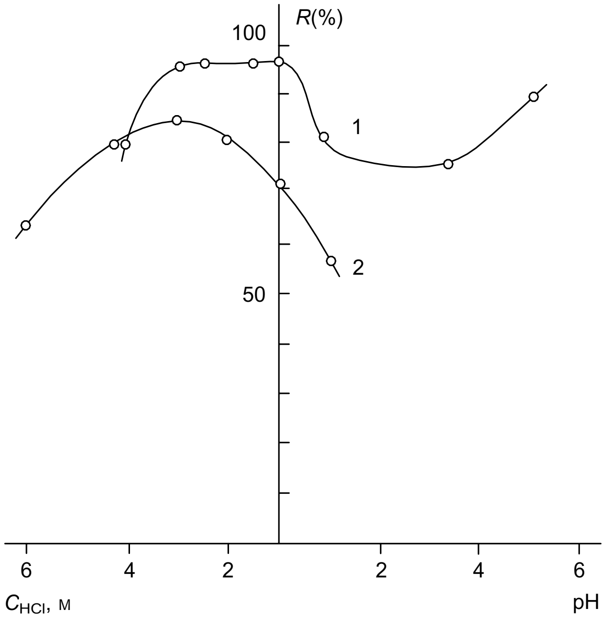

Fig. 4 Effect of HCl concentration on platinum(IV) recovery on a POL–DETA sorbent. 1, recovery using dilution before injection into microcolumn; 2, without dilution. $C_{Pt} = 7$ ppm, v = 3 ml min^{-1}.

Table 1 Recovery (%) of platinum metals on a POL-DETA sorbent in the presence of iron and copper.

Matrix element	Element concentration/ g dm^{-3}	Ru^{IV}	Rh^{III}	Pd^{II}	Ir^{III}	Ir^{IV}	Pt^{IV}
Fe^{III}	10.0	98	96	99	–	96	98
	20.0	99	93	100	96	93	98
	30.0	98	90	95	96	89	97
	40.0	96	60	–	95	–	94
	50.0	95	–	81	–	82	–
	60.0	94	49	–	95	–	–
Cu^{II}	10.0	98	96	–	96	96	98
	20.0	98	97	99	96	93	98
	30.0	98	96	99	95	89	97
	40.0	98	92	99	–	–	92
	50.0	98	91	87	92	71	–
	60.0	96	80	–	87	–	87

References

1 X. Chang, Y. Li, X. Luo, G. Zhan, Zh. Su and J. Gao, *Anal. Chim. Acta*, 1991, **245**, 13.

2 G. V. Myasoedova, I. I. Antokol'skaya, L. I. Bol'shakova, F. I. Danilova, I. A. Fedotova, E. B. Varshal, E. E. Rakovskii and S. B. Savvin, *Zh. Anal. Khim.*, 1982, **37**, 1837 [*J. Anal. Chem. USSR (Engl. Transl.)*, 1982, **37**, 1427].

3 V. M. Ivanov, G. N. Gorbunova, G. V. Kudryavtsev, G. V. Lisichkin and T. I. Shurupova, *Zh. Anal. Khim.*, 1984, **39**, 504 [*J. Anal. Chem. USSR (Engl. Transl.)*, 1984, **39**, 402].

4 V. A. Shestakov, G. I. Malofeeva, O. M. Petrukhin, O. A. Shiryaeva, E. V. Marcheva, Yu. I. Murinov, Yu. E. Nikitin and Yu. A. Zolotov, *Zh. Anal. Khim.*, 1984, **39**, 311 [*J. Anal. Chem. USSR (Engl. Transl.)*, 1984, **39**, 245].

5 N. M. Kuz'min, A. V. Dementyev, I. V. Kubrakova and G. V. Myasoedova, *Zh. Anal. Khim.*, 1990, **45**, 46 [*J. Anal. Chem. USSR (Engl. Transl.)*, 1990, **45**, 30].

6 G. I. Malofeeva, O. M. Petrukhin, M. V. Akhmanova, P. A. Gembitskii, N. A. Klescheeva and T. V. Danilova, *Zh. Neorg. Khim.*, 1992, **37**, 649 (*Russ. J. Inorg. Chem.*, 1992, **37**, 323).

7 G. I. Tsysin, I. V. Mikhura, A. A. Formanovskii and Yu. A. Zolotov, *Mikrochim. Acta*, 1991, **III**, 53.

8 N. N. Kazanova, O. M. Petrukhin, I. I. Antipova-Karataeva, G. I. Malofeeva, E. V. Marcheva and Yu. I. Murinov, *Koord. Khim.*, 1986, **12**, 108 [*Sov. J. Coord. Chem. (Engl. Transl.)*, 1986, **12**, 69].

9 Yu. N. Kukushkin, S. A. Simanova, E. Kalalova, Z. Radova, L. K. Mel'gunova, V. N. Pak, L. V. Konovalov and J. Kalal, *Zh. Prikl. Khim.*, 1979, **52**, 2207 [*J. Appl. Chem. USSR (Engl. Transl.)*, 1979, **52**, 2085].

10 E. Kalalova, M. Kolarova and P. Thuy, *Collect. Czech. Chem. Commun.*, 1988, **53**, 3050.

11 S. I. Ginzburg, N. A. Ezerskaya, I. V. Prokofyeva, N. V. Fedorenko, V. I. Shlenskaya and N. K. Bel'skii, *Analiticheskaya khimiya platinovykh metallov* (*Analytical chemistry of platinum metals*), Nauka, Moscow, 1972 (in Russian).

12 *Khimiya i spektroskopiya galogenidov platinovykh metallov* (*Chemistry and spectroscopy of halogenides of platinum metals*), Universitetskoe, Minsk, 1990, p. 279 (in Russian).

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