



# Application of commercially available anion exchange resins for preconcentration of palladium(II) complexes from chloride–nitrate solutions

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## ABSTRACT

The possibility of selective preconcentration of palladium(II) complexes by the polystyrene-divinylbenzene (Varion ATM, ADM) and polyacrylate (Varion ADAM) anion exchangers and the mechanism of their sorption onto these anion exchangers were investigated. The aim of this study was to find an appropriate model for the kinetics of Pd(II) complexes sorption and examine the influence of acids concentration and phase contact time on palladium(II) preconcentration.

The rate constants for the three models (pseudo-first and pseudo-second and intraparticle diffusion) and the correlation coefficients have been calculated in order to assess which model provides the best fit predicted data with experimental results. The pseudo-second order equation provides the best fit to experimental data.

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## 1. Introduction

Preconcentration is an inevitable step in the determination of noble metals traces. In this procedure the analytes are preconcentrated from dilute solutions and separated from matrix elements which cause interferences during their determination. Ion exchange, solvent extraction, coprecipitation are the most commonly used preconcentration methods [1,2].

Ion exchange methods are mostly based on the separation of anionic chlorocomplexes of platinum metals from the matrix elements which occur in the cationic forms in dilute acid solutions.

At present various types of commercially available cation and anion exchangers Varion, are used in preconcentration processes [3,4], water treatment [5–9], removal [7,10–12], purification and separation processes [10,13].

The most popular Varion ion exchange resins are anion (Varion AD, ADA, ADM, ADAM, AT, ATM, AT-400, AT-660) and cation (Varion KS, KSM) exchange resins.

Literature does not provide the reply to the question about sorption behaviour of PGM metals and their preconcentration processes onto the Varion exchange resins. Its data on PGM metals are limited and incomplete. Due to this fact Varion ADM, ATM and ADAM are interesting and worth considering in the preconcentration process of palladium(II).

Hubicki and Leszczyńska [14] used strongly (Varion AP), intermediate and weakly basic anion exchangers for palladium(II)

removal from the chloride and chloride–nitrate solutions. Moreover, the effect of the addition of macrocomponents such as zinc(II) or aluminium(III) on the palladium(II) sorption from solutions under examination was observed. The strongly basic anion exchangers – Varion AP and Lewatit MP-500 as well as the weakly basic anion exchanger Duolite A-6 cannot be used in Pd(II) ions sorption from the solutions containing zinc(II) due to competitive sorptions of  $[ZnCl_4]^{2-}$  complexes towards  $[PdCl_4]^{2-}$ . Duolite A-30 and Duolite A-7 give more promising results therefore the application of these resins for Pd(II) ions sorption in the presence of zinc(II) is worth considering. The affinity series of the anion exchangers towards palladium(II) complexes in solutions containing aluminium(III) was determined and is as follows:

Varion AP > Duolite A-7 > Lewatit MP 500 > Duolite

A-6 > Duolite A 30 B.

Leśniewska et al. [13] used cationic resins; Dowex 50 WX-8, Dowex 50 WX-2, Dowex HCR-S, Varion KS, Cellex-P for elimination of interferences during the palladium determination. After elimination of matrix ions (Al, Fe, Pb, Zn, Ni, Cu, Y) the anion exchange sorbent Cellex-T was used for palladium and platinum separation.

The aim of the paper was to study the possibility of palladium(II) complexes preconcentration from the chloride–nitrate solutions ( $0.1 \div 0.9 \text{ M HCl} - 0.9 \div 0.1 \text{ M HNO}_3 - 100 \text{ mg/dm}^3 \text{ Pd(II)}$ ), in order to understand the mechanisms of palladium(II) complexes sorption, find a suitable model for the kinetics and examined the influence of acids concentration and phases contact time.

Therefore applicability of the following anion exchange resins: Varion ADAM (weakly basic ion exchanger), Varion ATM (strongly

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## Nomenclature

$d_z$	anion exchanger bed density (g/cm <sup>3</sup> )
$C_o$	initial concentration of Pd(II) (mg/dm <sup>3</sup> )
$C_r$	working ion exchange capacity (g/cm <sup>3</sup> )
$C_t$	concentration of Pd(II) ions in solution after time $t$ (mg/dm <sup>3</sup> )
$h$	initial sorption rate (mg/g min)
$k_1$	equilibrium rate constant of the pseudo-second order sorption (1/min)
$k_2$	equilibrium rate constant of the pseudo-second order sorption (g/mg min).
$k_{int}$	interparticle diffusion rate constant (mg/g min <sup>1/2</sup> )
$m_j$	weight of the dry ion exchanger (g)
$q_1, q_2$	amounts of Pd(II) adsorbed at equilibrium for the pseudo-first and second order sorptions (mg/g)
$q_t$	amount of Pd(II) adsorbed at $t$ (mg/g)
$U$	effluent volume at $C=0.5C/C_o$ (cm <sup>3</sup> )
$U_o$	dead volume in the column (cm <sup>3</sup> )
$V$	volume of the solutions (dm <sup>3</sup> )
$V_i$	void (inter-particle) anion exchanger bed volume (cm <sup>3</sup> )
$V_j$	volume of ion exchanger bed put into the columns (cm <sup>3</sup> )
$V_p$	volume of effluent between the first fraction and that to the breakthrough point (cm <sup>3</sup> )

### Greek letters

$\lambda_{Pd(II)}$	mass distribution coefficient of Pd(II)
$\lambda'_{Pd(II)}$	bed distribution coefficient of Pd(II)

basic ion exchanger, Type 1), Varion ADM (strongly basic ion exchanger, Type 2) was studied. Preconcentration of palladium(II) complexes from the chloride–nitrate solutions was carried out under dynamic and static conditions with a different phases contact time.

Due to the fact that palladium(II) and other noble metals can be brought to the solutions (leaching process) using diluted aqua regia, a mixture of mineral acids such as e.g., sulfuric, nitric and hydrochloric acids, a mixture of hydrochloric acid and sodium chloride as well as a mixture of hot hydrochloric acid and gaseous chlorine, chloride – nitrate solutions were considered in our studies [1,2,15]. Moreover, recovery processes of palladium(II) from scrap materials are carried out usually from chloride or chloride–nitrate solutions.

## 2. Experimental

### 2.1. Characteristics of the anion exchange resins used in the studies

Varion ADAM is a weakly basic anion exchange resin including tertiary amine functional groups ( $-N(CH_3)_2$ ) on the polyacrylate matrix. It has a macroporous structure, of the total ion exchange capacity 1.2 meq/cm<sup>3</sup>, particle sizes 0.315–1.25 mm. It can be used in the operating pH range from 0 to 14.

Varion ATM and ADM are strongly basic anion exchange resins. Both resins are macroporous, polystyrenic but belonging to different types. Varion ATM is a strongly basic anion exchange resin Type 1 while Varion ADM Type 2. Type 1 anion exchange resin has three methyl groups ( $-N^+(CH_3)_3$ ) whereas in Type 2 an ethanol group replaces one of the methyl groups ( $-N^+(CH_3)_2C_2H_4OH$ ). The total ion exchange capacity and particle sizes is equal 1.2 meq/cm<sup>3</sup> and 0.315–1.25 mm, respectively for both anion resins.

### 2.2. Methods

#### 2.2.1. Static method

The static method was used to determine the amount of palladium(II) complexes sorbed onto anion exchange resins. Laboratory experiment was carried out in the conical 100 cm<sup>3</sup> flasks dosed with a ground-in stopper. 20 cm<sup>3</sup> proper aqueous phase (chloride–nitrate solutions: 0.1 M HCl – 0.9 M HNO<sub>3</sub>; 0.2 M HCl – 0.8 M HNO<sub>3</sub>; 0.5 M HCl – 0.5 M HNO<sub>3</sub>; 0.8 M HCl – 0.2 M HNO<sub>3</sub>; 0.9 M HCl – 0.1 M HNO<sub>3</sub>) containing 100 mg/dm<sup>3</sup> Pd(II) and 0.2 g ion exchanger were put into a conical flask and shaken mechanically using the laboratory shaker, (Elphin+, type 357, produced in Poland) for 1–240 min at 20 °C. Then the anion exchanger was filtered off in order to determine the concentration of palladium(II) complexes in the solution. The amount of palladium(II) complexes [PdCl<sub>4</sub>]<sup>2-</sup> sorbed onto anion exchangers,  $q_t$ , was calculated by the mass-balance relationship (Eq. (1)):

$$q_t = (C_o - C_t) \frac{V}{m_j} \quad (1)$$

where  $C_o$  is the initial concentration of Pd(II) complexes in the aqueous phase,  $C_t$  is the concentration of Pd(II) complexes in solution after time  $t$ ,  $V$  is the volume of the solution,  $m_j$  is the weight of the dry ion exchanger used [16–17].

#### 2.2.2. Kinetic investigations

Kinetics of palladium(II) complexes sorption from the chloride–nitrate solutions by the static method was studied. In order to investigate the mechanism of sorption and potential rate controlling steps, the pseudo-first and second order equations and the interparticle diffusion equation have been used to test the experimental data. The rate constants for the three models have been determined and the correlation coefficients have been calculated in order to assess which model provides the best fit of the predicted data with the experimental results.

In order to investigate the mechanism of sorption and potential rate controlling steps the pseudo-first and -second order kinetic models have been used. The Legergren's equation and the pseudo-first order equation are generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \quad (2)$$

After integration and applying the boundary conditions such as  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , the integrated form of Eq. (2) becomes:

$$\log(q_1 - q_t) = \log q_1 - \frac{k_1}{2.303} t \quad (3)$$

where  $q_1$  and  $q_t$  are the amounts of palladium(II) complexes sorbed at equilibrium and at  $t$ , respectively, and  $k_1$  is the rate constant of the pseudo-first order sorption [17–20].

The pseudo-second order equation based on adsorption equilibrium capacity was also used in the data analysis. Such an equation can be expressed as [20,21]:

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \quad (4)$$

Integrating this equation for the boundary conditions gives:

$$\frac{1}{(q_2 - q_t)} = \frac{1}{q_2} + k_2 t \quad (5)$$

where  $q_2$  is the amount of palladium(II) complexes sorbed at equilibrium,  $k_2$  is the equilibrium rate constant of the pseudo-second order sorption.

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