

MEDIUM-PRESSURE LIQUID CHROMATOGRAPHY OF PLATINUM METAL IONS ON SPHERON DEAE

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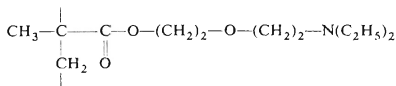
Received January 7th, 1983

Spheron DEAE (modified macroreticular hydroxyethylmethacrylate-ethylenedimethacrylate copolymer) was used for chromatographic separation and determination of Rh(III), Pd(II), and Pt(IV) in chloride medium. The most suitable composition of the mobile phase was looked for by studying the influence of hydrochloric acid concentration on the capacity ratios of the metal ions mentioned and on their resolution, as well as the influence of different additions to the mobile phase on the decrease of the high Pt(IV) retention. Using the photometric (UV) detection, the linear dependence was found up to following concentrations: Rh 200 mg l⁻¹, Pd 2 g l⁻¹, Pt 500 mg l⁻¹. The detection limit was 23 ng Rh, 62 ng Pd and 96 ng Pt in 7 µl sample injected. The reproducibility of the determination was (as relative standard deviation for $n = 3$) 1–4%, relative error 0.7–7%.

For the analytical control of platinum metal wastes (sweepings, spent catalysts, etc.), individual platinum metals content (up to 1%) can be determined by a combined fire assay and spectrophotometric methods. A much speedier solution of this problem proved to be a combined fire assay and liquid chromatographic method¹ using tri-*n*-butyl phosphate (TBP) as a stationary liquid phase. The disadvantage of this method was the column bleeding (system TBP–4M–HCl), the non-uniformity of sorbent impregnation with TBP, and a rather low column efficiency.

It has been described recently that weakly basic anion exchangers retain platinum metals (as well as gold) in chloride medium by ion exchange (*e.g.*²) or by complex formation³.

The task of this work was to prove whether a commercial copolymer modified by a diethylaminoethyl group



(Spheron DEAE) can be used for medium-pressure liquid chromatography (MPLC) separation and determination of rhodium, palladium, and platinum.

EXPERIMENTAL

A home made, all glass and PTFE (*i.e.* acid resistant) liquid chromatograph (maximum pressure.

1 MPa) was used, a nitrogen flask served as a pressure device. A glass column was filled with Spheron DEAE 1 000 (Lachema, Brno, Czechoslovakia), $d_p = 25-40 \mu\text{m}$, in the chloride form, its total exchange capacity, calculated from the nitrogen content, was $Q(\text{N}) = 1.55 \text{ mmol g}^{-1}$ (of dry resin). It was twice recycled using 2M-NaOH and 2M-HCl. Column dimensions: $L_c = 10 \text{ cm}$, $d_c = 0.4 \text{ cm}$, sample volume injected (by means of a loop) $7 \mu\text{l}$, UV detector (254 nm), cell volume $50 \mu\text{l}$, cell thickness 2.5 mm (Development workshops of Czechoslovak Academy of Sciences, Prague). The column was filled with the polymer using a slurry method after desintegrating the aggregates of the sorbent in an ultrasonic bath. The dead time was measured using chromium(III) chloride solution in the presence of lithium chloride $c(\text{Cr}) = 0.25 \text{ mol l}^{-1}$, $c(\text{LiCl}) = 4.0 \text{ mol l}^{-1}$. With respect to the kinetic inertness of chromium complexes and from the stability constants of the chloro-complexes, it follows that more than 95% of chromium will be present in the form of hydrated Cr^{3+} and CrCl_2^{2+} at the given chloride concentration and will not be retained by an anion exchanger.

Platinum metals solutions (1 g per liter) were prepared by pressure dissolution⁴ of known amounts of highest purity platinum metals (Safina, Vestec, Czechoslovakia) in a mixture of hydrochloric and nitric acids (16.5 : 1) followed by repeated evaporation just to dryness with hydrochloric acid after an addition of sodium chloride, equivalent to the amount of platinum metal used. The stock solutions of $\text{Na}_{x-n} \text{MCl}_x$ (for M^{n+}) were stored in 0.1M-HCl. The working solutions were prepared from the stock solutions and were brought up to the same hydrochloric acid concentration as in the mobile phase used.

The chemicals used for ion-pairing were of different origin: amines (Schuchardt, Munich, FGR), benzyldecyl-dimethylammonium bromide (Spora, Prague, Czechoslovakia), sodium dodecylbenzenesulphonate and dodecyl sulphate (Sandoz, Switzerland). All other chemicals were reagent grade (E. Merck, Darmstadt, FGR and Lachema, Brno, Czechoslovakia).

All statistical treatment was performed at a 95% probability.

RESULTS AND DISCUSSION

Fig. 1 shows the dependence of capacity ratio (k) for Rh and Pd on hydrochloric acid activity. The activity was calculated using activity coefficients given in⁵. As a measure of separation efficiency of the system, not only the resolution (R_{ij}) for palladium and rhodium but also the resolution per time ($R_{ij}t_{R,j}^{-1}$) was studied in dependence on hydrochloric acid concentration in the mobile phase and on its flow rate. The results obtained are in Table I.

The resolution of Pd from Pt was always better than the resolution of Rh from Pd. Therefore, and because of a high retention time of platinum, only the resolution of the pair Rh-Pd was taken as a measure of column separation efficiency.

The effect of different cationic as well as anionic additions to the mobile phase (5M-HCl) in different concentrations on the resolution of Rh-Pd or Pd-Pt was studied. The results are in Fig. 2.

The influence of the exchange of H^+ for Li^+ -ions in the mobile phase on the capacity ratios and on the resolution was tested keeping the sum $c(\text{Li}^+) + c(\text{H}^+) = 5 \text{ mol l}^{-1}$. The results can be seen in Table II. The most suitable mobile phase composition was found to be: $c(\text{HCl}) = 5.0 \text{ mol l}^{-1}$, $c(\text{NaClO}_4) = 0.10 \text{ mol l}^{-1}$. It has been also proved that the best column separation efficiency was obtained with

equal hydrochloric acid concentrations both in the sample solution injected and in the mobile phase (5.0 mol l^{-1}). Using the conditions given the following dependence of resolution on the mobile phase flow rate was found (given as flow rate in ml min^{-1} : $R_{\text{Rh,Pd}}, R_{\text{Pd,Pt}}$): 0.5: 1.77, 2.02; 0.8: 1.51, 1.45; 1.0: 1.53, 1.36.

The chromatogram of the sample containing 0.1 g l^{-1} Rh, 0.5 g l^{-1} Pd and 0.45 g l^{-1} Pt is shown in Fig. 3. It was run under conditions given in the caption of that figure. For the determination of the three platinum metals, the dependence of the peak height (h) on the mass concentration of the metal (ρ) was followed. Using a least square method the regression coefficients of the linear dependence $h = f(\rho)$ were found from sets of 6–12 experimental data. The linear range of the calibration dependence was tested using the correlation coefficient (r). The calibration dependences are summarized in Table III. The limit of detection (\bar{x}) was estimated from the

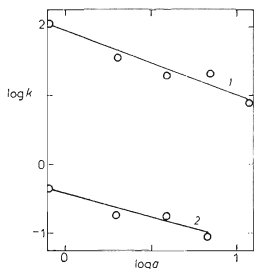


FIG. 1

Dependence of capacity ratio for Rh (1) and Pd (2) on hydrochloric acid activity. Dead volume $V_M = 0.97\text{--}1.01 \text{ cm}^3$, total porosity $\epsilon_{\text{tot}} = 0.77\text{--}0.81$

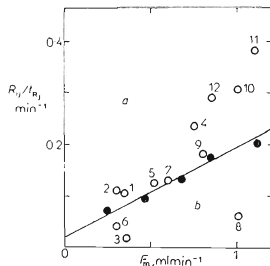


FIG. 2

Dependence of resolution $R_{\text{Rh,Pd}}$ on the additions to the mobile phase. Mobile phase: 5.00 mol l^{-1} HCl. ● no addition, ○ additions corresponding to the points: 1 $1 \cdot 10^{-4} \text{ mol l}^{-1}$ triethylamine, 2 $5 \cdot 10^{-2} \text{ mol l}^{-1}$ triethylamine, 3 $5 \cdot 10^{-2} \text{ mol l}^{-1}$ tert-butylamine, 4 $5 \cdot 10^{-2} \text{ mol l}^{-1}$ n-butylamine, 5 satur. soln. octadecylamine, 6 $1 \cdot 10^{-3} \text{ mol l}^{-1}$ benzyldodecyltrimethylammonium bromide, 7 $5 \cdot 10^{-2} \text{ mol l}^{-1}$ NH_4Cl , 8 satur. soln. Na *p*-dodecylbenzenesulphonate, 9 0.5 mol l^{-1} HClO_4 , 10 0.08 mol l^{-1} NaClO_4 , 11 0.10 mol l^{-1} NaClO_4 , 12 0.12 mol l^{-1} NaClO_4

standard deviation of the base line noise (s) and from the blank (\bar{x}_0) using the equation $\bar{x} = \bar{x}_0 + ws$ (see⁶). The reproducibility of the determination is given as a relative standard deviation for three parallel determinations and was calculated from the range. The accuracy is represented by relative error (Δ). All the characteristics are given in Table IV.

The platinum metal ions capacity ratio dependence on the hydrochloric acid activity can differentiate between the two possible sorption mechanisms of Spheron DEAE. Because of the presence of a substituted nitrogen atom in the modifying chain, Spheron DEAE can sorb certain metals by complex formation or by ion-ex-

TABLE I

Dependence of resolution $R_{Rh/Pd}$ and of resolution per time $R_{Rh/Pd}/t_{R,Pd}$ on hydrochloric acid concentration and on flow rate (F_m)

$c(\text{HCl})$ mol l^{-1}	F_m ml min^{-1}	$R_{Rh/Pd}$	$R_{Rh/Pd}/t_{R,Pd}$ min^{-1}
5.00	1.15	1.81	0.204
5.00	0.85	2.19	0.177
5.00	0.68	2.07	0.134
5.00	0.47	2.40	0.095
5.00	0.25	3.18	0.073
4.00	0.50	2.70	0.094
3.00	0.30	4.08	0.058
2.00	0.77	2.94	0.065
1.00		distortion of peaks	

TABLE II

Dependence of capacity ratios and resolution of Rh, Pd, and Pt on the mobile phase composition (exchange of H^+ for Li^+)

$c(\text{HCl})$ mol l^{-1}	$c(\text{LiCl})$ mol l^{-1}	k_{Rh}	k_{Pd}	k_{Pt}	$R_{Rh/Pd}$	$R_{Pd/Pt}$
5.00	0	0.13	9.50	74	1.81	2.57
4.00	1.00	0.05	8.34	70	1.69	1.16
3.00	2.00	0.06	11.8	105	1.73	— ^a
0	5.00	0.11	28.5	109	2.23	— ^a

^a Not measured because of a very long retention time of Pt.

change, acting as a weakly basic anion-exchanger according to the equation



(the bar over the symbol denotes the species present in the polymer phase)

TABLE III

Calibration dependences for the chromatographic determination of Rh, Pd or Pt

Metal	$h = f(\rho)$	n	r	linear range $mg\ l^{-1}$
Rh	$4.90 + 0.916\rho$	12	0.9992	200
Pd	$2.14 + 0.0611\rho$	10	0.9979	2 000
Pt	0.0640ρ	6	0.9905	500

TABLE IV

Limit of detection, accuracy and reproducibility for the chromatographic determination of Rh, Pd or Pt

Metal	Limit of detn. $mg\ l^{-1}$	Δ %	s_r %
Rh	0.30	+7.0	1.1
Pd	50.1	-2.2	3.7
Pt	81.2	-0.7	4.1

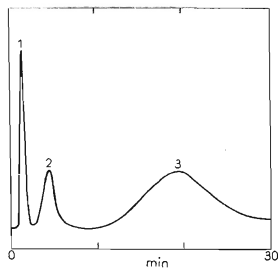


FIG. 3

Chromatogram of a mixture containing 0.1 g Rh(III), 0.5 g Pd(II) and 0.45 g Pt(IV) in 1 l. Mobile phase: 5M-HCl + 0.1M-NaClO₄. F_m 1.0 ml min⁻¹. Peak 1 Rh, 2 Pd, 3 Pt

The capacity ratio (k) of a platinum metal ion in a chromatographic system with Spheron DEAE as a stationary phase is equal to its mass distribution ratio (D_m). Thus, following dependence of capacity ratio on chloride activity can be written:

$$k = D_m = D_g \frac{m_s}{V_m} = K_{nCl}^{MCl_n^{n-}} \left(\frac{a_{Cl,s}}{a_{Cl,m}} \right)^{-n} \frac{m_s}{V_m} \quad (1)$$

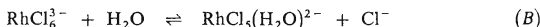
D_g being distribution coefficient, m_s and V_m mass and volume of the stationary and mobile phases, resp., and $K_{nCl}^{MCl_n^{n-}}$ selectivity coefficient.

The ratio m_s/V_m is a constant for a given column arrangement and the same holds for the chloride activity in the stationary phase supposing a low platinum metal concentration in the system. Thus, a simplified equation can be written

$$k = C a_{Cl,m}^{-n} \quad (2)$$

The slope of the linear dependence $\log k = \log C - n \log a_{Cl,m}$ should correspond to the charge of the prevailing species of the platinum metal in the solution or better, to the charge of the species exchanged for chloride ion. The found slopes are -0.81 for Rh and -1.02 for Pd.

From the thermodynamic point of view, the prevailing species in the mobile phase (1-5M-HCl) should be $RhCl_5(H_2O)^{2-}$ and $RhCl_6^{3-}$, and $PdCl_4^{2-}$ according to the published values of stability constants for chlorocomplexes of platinum metals^{7,8}. From the kinetic study of chlororhodium(III) complexes^{9,10} it follows, however, that the half times τ for the reactions



and



are rather short ($\tau_b \approx 4$ min, $\tau_c \approx 3.5$ min in 5M-HCl).

Thus, according to the slopes of the linear dependences, the charge of the anions exchanged is approx. -1 and the found dependence $k = f(a_{Cl,m})$ proves that the anion-exchange mechanism is governing the sorption of platinum metals on Spheron DEAE in a chloride medium.

The conditions for the best separation were set in such a manner that the resolution was $R_{ij} \geq 1.5$ and $R_{ij}/t_{R,j}$ was as high as possible. The best results were obtained with 5M-HCl as a mobile phase. However, platinum(IV) had a very high capacity ratio ($k > 70$) under such conditions and it was not decreased by substituting part or all hydrochloric acid by lithium chloride. On the contrary, with increasing content of lithium chloride in the mixture, the platinum capacity ratio increased. Such an in-

fluence of lithium ion was already observed with strongly basic anion-exchanger¹¹ and with Spheron DEAE too, when gold was sorbed as AuCl_4^{3-} (see¹²).

We tried the ion-pairing effect for decreasing the platinum capacity ratio. From the cationic additions, only lower amines (triethylamine and somewhat tert-butylamine) acted in the desired manner, decreasing the capacity ratios of all platinum metals tested, forming probably an ion-pair of the type $\{\text{Et}_3\text{NH}^+, \text{MCl}_{n+1}^-\}$ with an ion M^{n+} in the mobile phase. On the contrary, octadecyl amine and benzyl dodecyl dimethylammonium bromide increased capacity ratios, which cannot be explained from our experimental results. The presence of ammonium ion in concentration low enough not to form a precipitate of $(\text{NH}_4)_2\text{PtCl}_6$ decreased somewhat the capacity ratios.

The retention of the complex anions containing platinum metals could also be decreased by occupying the sorption sites in the polymer by another anion. We tested some anionic surfactants for this purpose. Their effect, however, was not favorable. The retention of platinum metal ions was only slightly influenced but the column efficiency was markedly decreased. Moreover, these surfactants were strongly held by the sorbent and their removal from the column was very lengthy.

The best results were obtained when perchlorate was added to the mobile phase. The selectivity coefficient $K_{\text{Cl}^-}^{\text{ClO}_4^-}$ for Spheron DEAE has not been estimated up to now. It has a high value for a strongly basic anion-exchanger, e.g. 150 for Dowex 1 (see¹³). It has been also found¹⁴ that capacity ratios of the precious metals on strongly basic anion-exchangers decrease in the presence of perchlorate. Thus, the conclusion can be drawn that perchlorate ion successfully competes for the functional group in the polymer with the chloro-complexes of precious metals and decreases, in that way, their capacity ratios.

The best conditions for the chromatographic separation and determination of rhodium, palladium and platinum are: column length 10 cm, mobile phase composition — $c(\text{HCl}) = 5.0 \text{ mol l}^{-1}$, $c(\text{NaClO}_4) = 0.1 \text{ mol l}^{-1}$, flow rate 1.0 ml min^{-1} , sample acidity $c(\text{HCl}) = 5.0 \text{ mol l}^{-1}$.

The calibration dependence is linear in the given concentration range and the agreement of the calculated regression lines with the experimental points is very good as shown by high values of correlation coefficients. The limit of detection can be still decreased using a more sophisticated chromatograph. The reproducibility of the determination is very good. The method was tested on the determination of the platinum metals in sweeps containing 0.1 to 1% each of the metal. The analysis time, after preparing the solution from the button, was 25 min.

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Translated by the author (F. V.).