This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Interseparation of Platinum Metals in Concentrated Solution by Gel Permeation Chromatography

B. Limoni-Relis[a]; G. Schmuckler[a]
[a] DEPARTMENT OF CHEMISTRY, TECHNION—ISRAEL INSTITUTE OF TECHNOLOGY, HAIFA, ISRAEL

To cite this Article Limoni-Relis, B. and Schmuckler, G.(1995) 'Interseparation of Platinum Metals in Concentrated Solution by Gel Permeation Chromatography', Separation Science and Technology, 30: 3, 337 — 346
To link to this Article: DOI: 10.1080/01496399508013875
URL: http://dx.doi.org/10.1080/01496399508013875

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, **30**(3), pp. 337–346, 1995

Interseparation of Platinum Metals in Concentrated Solution by Gel Permeation Chromatography

B. LIMONI-RELIS and G. SCHMUCKLER*
DEPARTMENT OF CHEMISTRY
TECHNION—ISRAEL INSTITUTE OF TECHNOLOGY
HAIFA 32000, ISRAEL

ABSTRACT

The chromatographic interseparation of the anionic halide complexes of platinum metals in concentrated acidic solutions by certain polydextran gels as the separating medium and aqueous electrolyte solutions as eluents is described. The dextran groups of highly crosslinked gels of this type interact selectively with platinum halides via H-bonding, and these platinum group metal halides can then be easily eluted with aqueous salt or acid solutions. The separations are sharp and rapid and can be carried out at room temperature. Base metal halides do not form H-bonds with the gels and are therefore eluted from the column before the platinum metals.

INTRODUCTION

Sephadex gels have been used largely to separate organic molecules and macromolecules by differential migration. There are two features that make these gels interesting for the separation of metal complexes:

1. Sephadex gels are highly hydrophilic and can thereby absorb ions, mainly by hydrophobic interaction (1).
2. The addition of an electrolyte to the water-swollen gel causes shrinkage. This means that the ordered water shell surrounding the gel can be ruptured by simple salts, and these can serve as good eluents for metal complexes.

---

* To whom correspondence should be addressed.

Halide complexes of platinum group metals (PGMs) are strongly adsorbed on Sephadex gels from acidic aqueous solutions, and interseparation of these metals can be effected by aqueous salt solutions.

From the molecular point of view the differential migration can be subdivided into these stages:

1. Diffusion of solute molecules into the gel pores.
2. Interaction of solute molecules with the functional groups of the gel.
3. Exclusion of solute molecules from the gel and diffusion into the mobile phase.

In order to understand the separation process of some anionic PGM complexes, a number of parameters, such as distribution coefficients and equilibrium constants derived from adsorption isotherms, and kinetic data derived from breakthrough curves, were determined.

In the following it will be shown how these parameters helped in achieving sharp separations of anionic PGM complexes in aqueous solutions.

EXPERIMENTAL

Materials

Sephadex G-10 and G-15 gels 40–150μ were purchased from the Pharmacia Co., Sweden.

All the salts and acids used in the preparation of eluent solutions were reagent grade.

The metal complexes used, K_2PtCl_4, K_2PtCl_6, K_2PdCl_4, and K_2PtBr_6, were supplied by B.D.H., Poole, UK. Solutions of metal complexes were prepared in 1 N HCl.

Measurements

Metal concentrations in all effluent fractions and batch aliquots were determined with a Perkin-Elmer 403 atomic absorption spectrophotometer.

Determination of Column Parameters and Distribution Coefficients

The columns, 30.0 × 1.0 cm glass tubes fitted with sintered-glass discs, were wet-packed with Sephadex G-10 gel to a total bed volume (V_t) of 30 mL.

The column void volume, V_0, was determined as described elsewhere (2) with the aid of Blue Dextran, and was found to be 12.3 mL for Sephadex G-10. The inner volume, V_i, was determined by injecting (1 mL) 0.1 N sodium chloride solution and eluting with distilled water. Its value was found to be 6.56 mL for the same gel.

Distribution coefficients, K_D, for the metal complexes in various eluents were calculated from the equation

$$K_D = \frac{V_e - V_0}{V_i}$$

where V_e is the elution volume of the metal complex.

Construction of Adsorption Isotherms by Batch Experiments

One gram quantities of dry Sephadex G-10 were swollen in 1 N HCl and equilibrated with the PGM halide complexes at 22°C. These equilibrium data enabled the amount of PGM adsorbed on the gel (mmol/g), Q_i, to be calculated. Q_i is one of the parameters of the adsorption isotherms.

The graphical correlation of Q_i vs C_0 (solute equilibrium concentration in the contacting solution in mol/L) gave the Langmuir adsorption isotherms for each PGM complex. From the linear form of these isotherms, *a* (the total adsorption capacity) and *K* [the Langmuir equilibrium constant (mol/L)] could be calculated.

Breakthrough Curves

Columns of dimensions 20.0 × 1.0 cm were used for breakthrough curves. The total bed volume was 16.45 mL, and the flow rate was maintained at 24 mL/h. The columns were continuously loaded with 5×10^{-3} M solutions of K_2PtCl_4, K_2PtCl_6, K_2PdCl_4, and K_2PtBr_6 in 1 N HCl until the metal concentration in the eluent was equal to that in the feed solution (C_0). The concentration dependence of the breakthrough curves was tested with 5×10^{-4}, 2×10^{-3}, and 5×10^{-3} M K_2PtBr_6.

Separations

The chromatograms shown in Figs. 3 and 4 were carried out on Sephadex G-10, using glass columns of 30 × 1.0 cm dimensions and flow rates of 0.5 mL/min. The chromatogram shown in Fig. 5 was carried out on a 40 × 2.50 cm glass column, Sephadex G-15, and HCl 1 M as eluent.

RESULTS AND DISCUSSION

Fundamental Parameters

In order to gain some information on the interaction and separation possibilities of PGMs with Sephadex gels, four model compounds—

K_2PdCl_4, K_2PtCl_4, K_2PtCl_6, and K_2PtBr_6—were chosen, and the parameters of importance (viz. distribution coefficients, capacity factors, equilibrium constants, and rate constants) were determined.

Distribution coefficients were determined from elution volumes of the anionic metal complexes as described in the Experimental Section. The numerical values found are listed in Table 1, showing relatively high values as compared with those for base metals (3). From these values, and from the column parameters—V_i (inner volume of the gel) and V_0 (void volume)—the capacity factor, k', could be calculated:

$$k' = K_D \frac{V_i}{V_0} \tag{1}$$

Adsorption isotherms were derived from batch equilibrations of Sephadex G-10 with the same palladium and platinum salts in 1 N HCl. The results are summarized in Fig. 1 and show the typical shape of the convex Langmuir isotherm, for which the linear form is

$$\frac{1}{Q_i} = \frac{1}{a} + \frac{1}{KaC_0} \tag{2}$$

where Q_i = the quantity of metal salt adsorbed on the gel at equilibrium
C_0 = the concentration of the metal complex in solution (mol/L)
a = the total adsorption capacity (nmol/g)
K = the Langmuir equilibrium constant (L/mol)

The equilibrium constant was determined with Eq. (2) from the slope and intercept of the linear form of the graphs of Fig. 1.

Kinetic information on adsorption rates can be derived from the breakthrough curves determined at low flow rates for the four salts under consideration. They are presented in Fig. 2.

The adsorption rate constant, k_a, can be obtained from the slopes of

TABLE 1
Equilibrium and Kinetic Data for Palladium and Platinum Complexes

k_d (min^{-1})	k_a (L/mol·min)	k'	K_D	K_{eq} (L/mol)	Complex
12.7	86.2	2.1	3.9	6.8	K_2PtCl_4
8.9	82.1	2.5	4.8	9.2	K_2PdCl_4
1.9	36	5	9.4	18.9	K_2PtCl_6
0.4	12.2	6	11.5	30.3	K_2PtBr_6

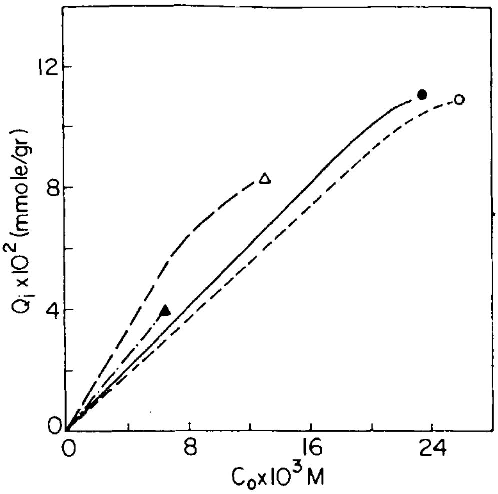

FIG. 1 Adsorption isotherms of anionic complexes of platinum and palladium on Sephadex G-10. (△) K_2PtBr_6, (▲) K_2PtCl_6, (○) K_2PtCl_4, (●) K_2PdCl_4.

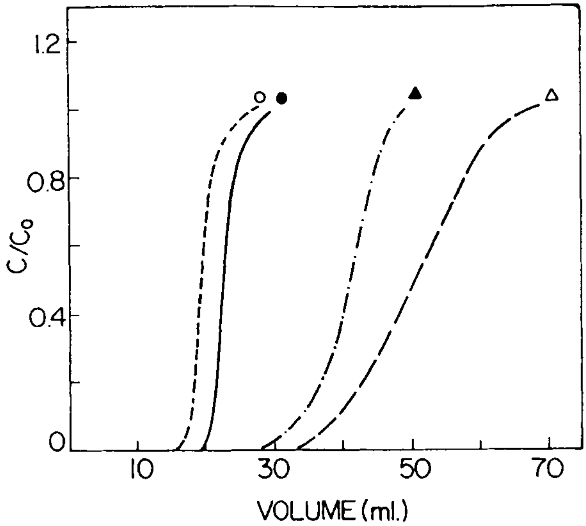

FIG. 2 Breakthrough curves of anionic complexes of platinum and palladium on Sephadex G-10. (△) K_2PtBr_6, (▲) K_2PtCl_6, (●) K_2PdCl_4, (○) K_2PtCl_4.

the breakthrough curves at midpoint according to Thomas (4):

$$\text{Slope at midpoint} = \frac{1}{4}\frac{k_a C_0}{F} \tag{3}$$

where C_0 = the salt concentration (in 1 N HCl) passing through the column

F = the flow rate (0.4 mL/min)

The numerical results of k_a are also summarized in Table 1. Since there is a simple relationship between rate constants and the equilibrium constant,

$$K_{eq} = k_a/k_d \tag{4}$$

the desorption rate constants can easily be calculated, and they are also included in Table 1.

Some important conclusions can be drawn from the numerical values presented in Table 1:

1. Sephadex gels are known to be highly hydrophilic, and their interaction with hydrophobic PGM chlorocomplexes is fast and strong. The strength of the interaction is indicated by high K_D values, while the high adsorption rate is manifested by high k_a values.
2. The desorption rate constants in Table 1 are much smaller than the adsorption rates, and they decrease as the polarizability of the anion increases. There is also a decrease in the adsorption rates from K_2PtCl_4 to K_2PtBr_6, which can be explained as a competition between hydrophobic and steric effects. There is only a small difference in k_a values between K_2PtCl_4 and K_2PdCl_4 because the steric effects are similar and the hydrophobicities are also almost the same, whereas with the Pt(IV) salts the steric effect is much more pronounced and the hydrophobicity of K_2PtBr_6 is higher than that of K2PtCl6.
3. The breakthrough curves in Fig. 2 also show the similarity in kinetic data between K_2PtCl_4 and K_2PdCl_4, whereas for K_2PtCl_6 and K_2PtBr_6 much higher elution volumes are needed, and the slopes of the curves are much smaller.
4. Sephadex G-10, which was used for the data of Table 1, is the most highly crosslinked gel with the smallest pore size in the Sephadex series. Similar experiments were carried out with Sephadex G-25 (which has larger pores and a higher water uptake), but these showed higher adsorption rates and lower selectivities for the salts dealt with.

Elution Profiles

In considering a choice of eluents for the chlorocomplexes of PGMs, it must be borne in mind that any aqueous eluent should contain halides in order to avoid hydrolysis of the PGM complexes. In Fig. 3 the elution profile of four PGM metal chlorides (each metal at a concentration of 1000 ppm) is shown on a Sephadex G-10 column (V_t = 30 mL), aqueous NaCl 1 N having been used as the eluent.

The chromatogram shows a sharp separation of the four metal salts. If ruthenium and osmium halides are added to the mixture, Ru will emerge before rhodium and Os after iridium. The order of elution thus follows the positions of these metals in the periodic table. Improvements in the separation can be achieved by using a Sephadex gel of higher porosity, such as G-15 or G-25, or by some additive to the halide eluent that enhances the desorption rate of the PGMs, e.g., perchlorates or thiocyanates.

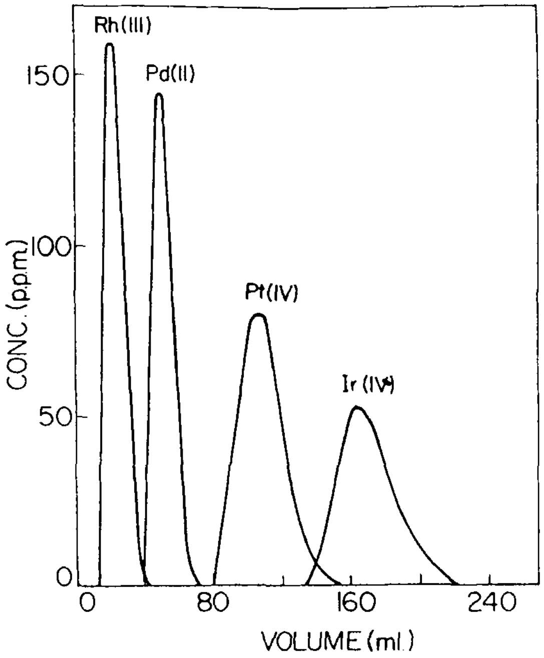

FIG. 3 A chromatogram of PGM chlorides (1000 ppm each) on Sephadex G-10, using 1 N NaCl as eluent.

A chromatogram of Pd, Pt, and Ir chlorides is shown in Fig. 4. $NaClO_4$ was added to the eluent, NaCl; other conditions were equal to those of the experiments on which Fig. 3 is based. It is evident that the elution volumes needed are smaller, while the resolution is as good as that in Fig. 3.

Optimization of separation conditions was achieved by using Sephadex G-15 in the separator column and aqueous HCl 1 M as eluent. Figure 5 shows the separation of a concentrated technical solution of PGMs that also contained some base metals, such as Fe, Cu, and Ni. Base-metal chlorides do not interact strongly with Sephadex gels and therefore emerge early from the column.

Figure 5 demonstrates the practical feasibility of PGM interseparation and the separation of PGMs from base metals. These results have been patented (5).

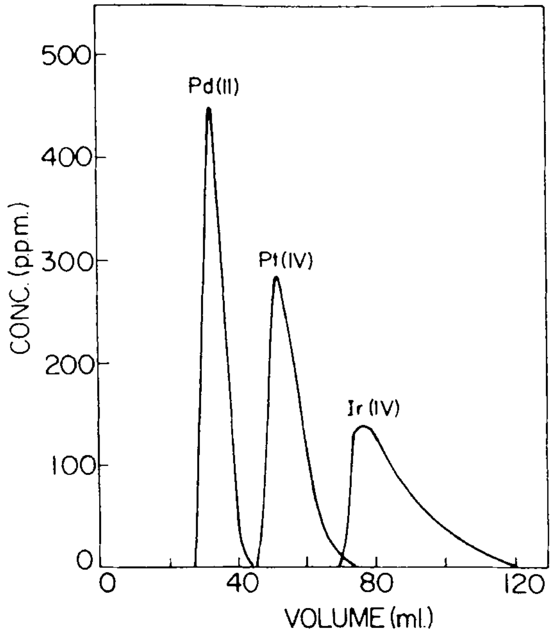

FIG. 4 A chromatogram of PGM chlorides on Sephadex G-10, using 0.1 N $NaClO_4$ in 1 N NaCl as eluent.

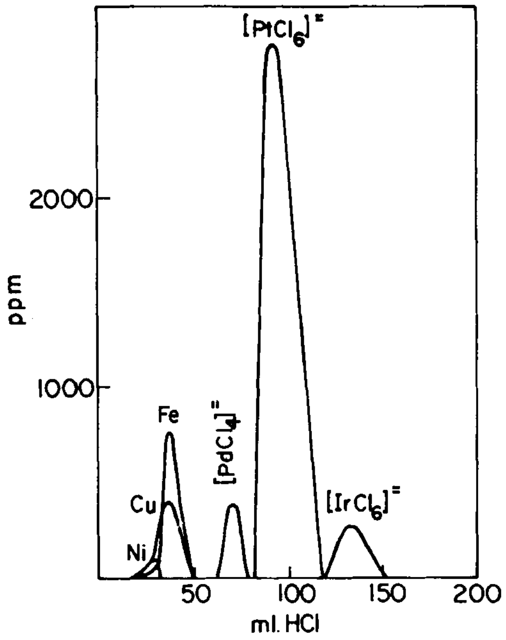

FIG. 5 A chromatogram of a technical solution of PGMs and base metals on Sephadex G-15 using 1 N HCl as eluent.

CONCLUSION

The use of Sephadex gels for achieving sharp chromatographic separations of concentrated acidic PGM solutions, as demonstrated in this work, has been incorporated in a patent because of its practical feasibility.

In order to make the separation selective, highly crosslinked small-pore Sephadex gels must be applied. The small molecules of PGM halides—much smaller than the biomolecules for which Sephadex gels are usually prescribed—diffuse easily into the gel pores and are probably retained in the gel because of halide-hydrogen bond interactions. These weak interactions, which can be altered by electrolyte solutions of the eluent, render this separation very efficient.

It is interesting to note that the separation is carried out from concentrated solutions in contrast to ion-exchange separations, where dilute solutions are usually processed.

REFERENCES

1. B. Stenlund, "Polyelectrolyte Effects in Gel Chromatography," *Adv. Chromatogr., 14* (1976).
2. B. Limoni and G. Schmuckler, *J. Chromatogr., 135*, 173 (1977).
3. P. A. Neddermeyer and L. B. Rogers, *Anal. Chem., 40*, 755 (1968).
4. H. C. Thomas, *Ann. N. J. Acad. Sci., 49*, 161 (1948).
5. G. Schmuckler, US Patent 4, 885, 143 (1989).

Received by editor April 29, 1994