

# Application of the ion-exchanger Cellex P for the selective separation of some metal ions

## Part 4. Separation of platinum metal ions in the presence of amines\*

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### Anwendung des Ionenaustauschers Cellex P zur selektiven Trennung von Metallionen.

#### Teil 4. Trennung von Platinmetallen in Gegenwart von Aminen

**Zusammenfassung.** Bei den Untersuchungen zur Trennung von Platinmetallen am Cellulose-Ionenaustauscher Cellex P wurden die größten Affinitätsunterschiede für Pd, Pt und Ir bei Verwendung von Ethylendiamin als Komplexbildner festgestellt. Die Trennung von Pd/Pt und Pd/Ir wurde über einen weiten Konzentrationsbereich unter dynamischen Bedingungen untersucht. Das Verfahren wurde zur Analyse von Pd-Ir-Legierungen eingesetzt (98% Pd, 2% Ir; gefunden 97,8% Pd, 1,98% Ir).

**Summary.** The possibility of using amines as complexing agents for the separation of some platinum metal ions on the cellulose ion-exchanger Cellex P has been investigated. The greatest affinity differences for palladium and platinum or iridium are obtained in the presence of ethylenediamine. The separation of Pd-Pt and Pd-Ir pairs has been tested over a wide range of concentration ratios under dynamic conditions. The method can be used for the analysis of Pd-Ir alloys (98% Pd, 2% Ir; found 97.5% Pd, 1.98% Ir).

The aim of this paper was to verify the usefulness of cellulose ion-exchanger with phosphonic groups — Cellex P, for the separation of some platinum metals. Ethylenediamine was used to improve the selectivity of the exchanger.

According to the literature [1, 2] and the results of our research [3], the conventional ion-exchangers with cross-linked polystyrene matrix are also not very convenient for the separation of platinum metal ions. As we pointed out in our previous papers [4–6], Cellex P is very useful for the selective separation of some metal ions, provided suitable complexing agents are chosen.

Preliminary separation of platinum before their determination is often necessary, especially when they are present in non-equal weight ratio — even if such a highly selective method as atomic absorption spectrometry (AAS) is used.

In the present paper, the separation of palladium from iridium or platinum is described for equivalent and non-equivalent weight ratios using Cellex P ion-exchanger.

### Experimental

**Ion-exchanger.** For static and dynamic investigations the phosphonic ion-exchanger Cellex P (Bio Rad Laboratories) was used. It was regenerated according to the procedure described by the manufacturers [7]. The exchange capacity determined according to [4] equals 0.94 meq/g.

**Metal ion solutions.** The solutions of Rh, Pd and Ir were prepared by dissolving appropriate amounts of the chlorides, p. a., of the metals (Koch-Light Lab.) in twice-distilled water. The solution of Pt was obtained by diluting a solution of  $H_2PtCl_6$  of definite concentration. The solutions were standardized gravimetrically or by AAS in comparison with the spectral standards.

**Amine solutions.** Standard amine solutions were prepared by dissolving a weighed sample of the appropriate amine (Merck and Fluka AG) in twice-distilled water.

**Apparatus.** Beckman model 1272 atomic absorption spectrophotometer with Pye Unicam GRM 1268 graphite atomizer and Unilam model 1288 burner. Pehameter Elpo model N-517, Poland.

Calomel and glass electrodes by Radiometer type G202B, Denmark.

**Sorption of metal ions by the batch method.** The retention of the metal ions on the ion-exchanger Cellex P was carried out in the following systems:

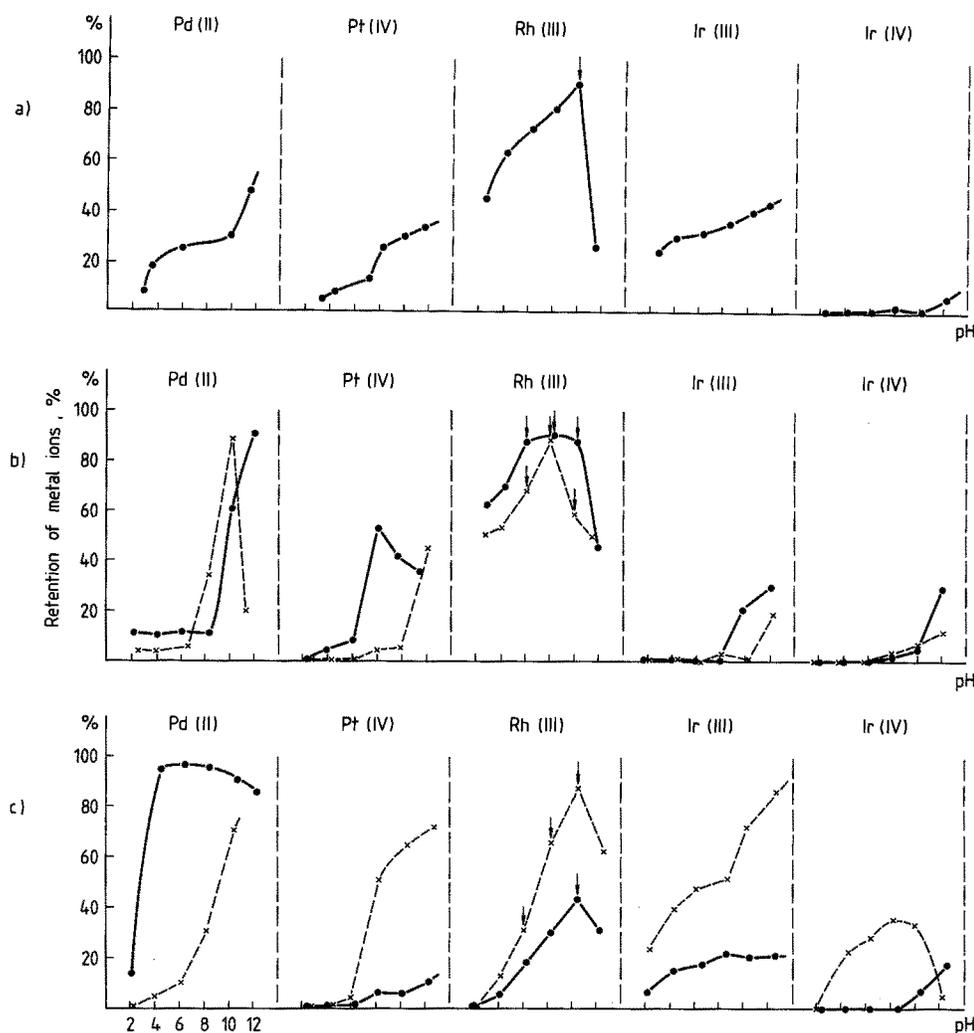
1. Cellex P—Me = 1:25
2. Cellex P—Me—amine = 1:25:20

The following amines were used: ethylenediamine, 1,3-diaminopropane triethylenetetramine (triene) and tetraethylenepentaamine (tetrene). The retention of metal ions was investigated as a function of pH and has been expressed in percentage in relation to the initial quantity of the metal ions in the solution. The results are presented in Fig. 1.

**Procedure.** The sample of ion-exchanger (0.20 g in hydrogen form) was mixed with 20 ml of the solution. The pH of the solution was adjusted to the desired pH using HCl or NaOH. The sample was shaken for 8 h and then the metal ion concentration in the solution was determined by AAS.

**Column separation.** The solution of the mixture of Pd and Pt or Ir in the presence of ethylenediamine (molar ratio en: Pd = 2:1) was introduced into the column. The pH of the solution should be kept within the range of 9.5–10.5. Palladium is retained on the column while platinum or

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**Fig. 1 a—c**  
Retention of platinum metal ions on the ion-exchanger Cellex P as a function of the pH-value. **a** in the absence of amine; **b** x, with 1,3-diaminopropane, o, with ethylenediamine; **c** x, with triene, o, with tetrene

iridium is carried through. The metal ions (Pt or Ir) which remained in void and interstitial spaces were washed out with about 10 ml of twice-distilled water. Palladium (1.20 mg) was eluted with 30 ml of 1 M HCl. When the quantity of Pd amounted to 30 mg the volume of the eluent was increased to 100 ml of 1 M HCl. The flow rate of the sample containing metal ions was 2 ml/min and of the eluent 3 ml/min.

**Analysis of Pd-Ir alloy.** A weighed sample of the alloy (0.1114 g) was dissolved in aqua regia and the solution was evaporated to dryness. The residue was dissolved in 5 ml of 0.1 M HCl and diluted with twice-distilled water to 50 ml. 5 ml of the above solution in the presence of ethylenediamine at pH about 10 was introduced into the column (1.0 g of the resin). Palladium and iridium were eluted as described above.

## Results and discussion

Our preliminary dynamic experiments showed that the differentiation of the Cellex P affinity towards chloro-complexes of palladium and platinum or iridium is too small to enable their quantitative separation. Pd(II) was only partially retained on the resin phase and was passing into

effluent as anionic complex. Therefore, we decided to transform Pd(II) into amine complexes. For finding out the most suitable palladium-amine complexes we investigated the usefulness of the following amines: ethylenediamine, 1,3-diaminopropane, triethylenetetramine (trien) and tetraethylenepentaamine (tetrene).

In spite of expected disagreement between static and dynamic results due to inert properties of platinum metals, we investigated the sorption behaviour of Pd(II), Pt(IV), Ir(IV), Ir(III) and Rh(III) by the batch technique as a function of pH-value. These investigations also help to establish that pH-value which corresponds to the greatest differentiation of the metal ion affinity towards the ion-exchanger. In the static experiments the molar ratio of the components in the system Cellex P:Me:amine was equal to 25:1:29 (Fig. 1).

Dynamic experiments proved the usefulness of the amines for the separation of platinum metals. The best results were obtained if ethylenediamine was used. In the presence of 1,3-diaminopropane and triene difficulties with the quantitative elution of platinum were observed. The optimum molar ratio of ethylenediamine to Pd(II) in the feed solution was 2:1. With lower molar ratios of ethylenediamine to palladium, the latter was partially passing into the effluent. It was also established that the optimum pH of the feed solution should be kept in the range

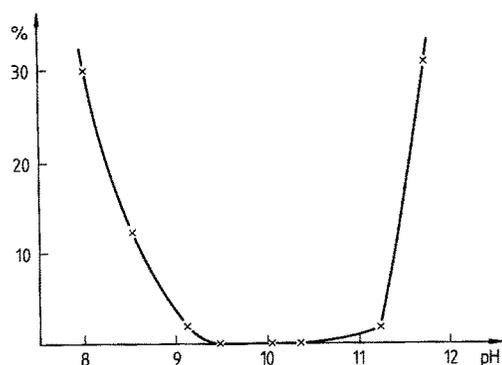


Fig. 2. Elution of palladium in the presence of ethylenediamine as a function of the pH-value of the feed solution

Table 1. Results of separation of Pd from Ir (average of 6 measurements)

Ion-exchanger, g	Added, mg		Found, mg		Error, %	
	Pd	Ir	Pd	Ir	Pd	Ir
0.1	0.012	1.03	0.0118	1.02	1.7	1.0
0.2	1.20	1.03	1.19	1.01	0.8	1.9
	1.20	0.20	1.18	0.195	1.7	2.5
	1.20	2.06	1.19	2.03	0.8	1.5
0.6	6.0	1.03	5.97	1.02	0.5	1.0
	6.0	0.20	5.94	0.196	1.0	2.0
1.0	12.0	0.20	11.93	0.194	0.6	3.0
	12.0	1.03	11.91	1.02	0.7	1.0
	12.0	2.06	11.95	2.03	0.4	1.5
2.0	30.0	0.20	29.75	0.195	0.8	2.5
	30.0	1.03	29.70	1.01	1.0	1.9
	30.0	2.06	29.80	2.04	0.7	1.0
	30.0	0.10	29.69	0.095	1.0	5.0

9.5–10.5 (good agreement with the static measurements was obtained). In that pH-range palladium is quantitatively bound to the resin (Fig. 2). Platinum, as it was to be expected, passes into the effluent as anionic species. 10 ml of twice-distilled water was enough for the quantitative elution of platinum remaining in the void and interstitial volume of the column.

To save time, the column procedure was performed on micro-scale. The amounts of platinum metals taken into the experiments were limited by the sensitivity of AAS as the detection method. It appears that the separation of 0.012 mg of palladium from 1.15 mg of platinum or 1.03 mg of iridium needs a bed height of only 1 cm (0.1 g of ion-exchanger). The analysis takes less than 1 h. If the amount of palladium is increased, the bed height should be increased also (Tables 1, 2).

The separation of a pair of platinum metals, in which palladium is in excess is an „inverse separation“ problem.

Table 2. Results of separation of Pd from Pt (average of 6 measurements)

Ion-exchanger, g	Added, mg		Found, mg		Error, %	
	Pd	Ir	Pd	Ir	Pd	Ir
0.1	0.012	1.15	0.0118	1.14	1.7	0.8
0.2	1.20	1.15	1.19	1.14	0.8	0.8
	1.20	3.45	1.18	3.43	1.7	0.6
	1.20	0.16	1.19	0.155	0.8	3.1
0.6	6.0	1.15	5.95	1.13	0.8	1.7
	6.0	0.16	5.94	0.154	1.0	5.0
	6.0	3.45	5.97	3.42	0.5	0.9
1.0	12.0	0.16	11.94	0.153	0.5	3.8
	12.0	1.15	11.95	1.14	0.4	0.9
2.0	30.0	0.03	29.90	0.028	0.3	5.7
	30.0	0.16	29.76	0.155	0.8	3.1
	30.0	0.32	29.74	0.315	0.9	1.6
	30.0	1.15	29.80	1.13	0.7	1.7
	30.0	3.45	30.81	3.42	0.6	0.9

Usually, metal ions more strongly retained on the resin are at lower concentration level than metal ions not retained. The system Me—Cellex P—amine enables the separation of metal ions by the method of “inverse separation” due to the great affinity of Pd(II) to Cellex P and the great difference in the affinity of metal ions to be separated.

It is noteworthy that iridium may be separated from palladium regardless of its valance state. Ir(III) as well as Ir(IV) are passing into the effluent as anionic species. The Pd-Ir separation has been applied to the analysis of Pd-Ir alloy (Pd 98%, Ir 2%; found Pd  $97.5 \pm 0.6\%$ , Ir  $1.98 \pm 0.04\%$  with 95% confidence limits). The retention curves in function of pH obtained by static experiments (Fig. 1) may be misleading for the separation of a pair of platinum metal ions concerned. This is due to the inert properties of platinum metals. However, static experiments may give valuable information concerning the pH-influence on the metal ion-exchanger affinity differentiation as in our experiments with ethylenediamine.

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