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## THE QUALITATIVE CHROMATOGRAPHIC ANALYSIS OF THE PLATINUM METALS AND GOLD ON PAPER IMPREGNATED WITH AMBERLITE LA-1 HYDROCHLORIDE

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### SUMMARY

Mixtures of Au(III), Ru(III), Rh(III), Pd(II), Os(III), Ir(III) and Pt(IV) were analysed qualitatively by reversed phase extraction chromatography on paper impregnated with Amberlite LA-1 hydrochloride and developed with 6 *M* HCl using the descending or circular technique or Matthias' method. The sensitivities of colour tests for the metals investigated have also been determined. The time of analysis depends on the chromatographic technique applied and varies from 1 h (circular technique) to 3.5 h (Matthias' method).

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### INTRODUCTION

The separation and analysis of the platinum metals is of interest to many laboratories. The most promising separation techniques include extraction and chromatographic methods, which permit the separation of some of these metals or their separation from gold or other accompanying metals. In the first chromatographic experiments undertaken by Lederer<sup>1</sup> and Burstall *et al.*<sup>2,3</sup>, the paper chromatography technique was used, with mixtures of hydrochloric acid and butanol or ethyl methyl ketone as the mobile phase. Kember and Wells<sup>4</sup> quantitatively determined platinum, palladium, rhodium and iridium after their separation by paper chromatography. Almost all of the papers published up to 1968 on the chromatography of platinum metals were covered in a review by Varshal *et al.*<sup>5</sup> and some results have been summarized by Lederer and Majani<sup>6</sup> in the form of tables. The most commonly used technique is the paper chromatography technique, but other chromatographic techniques have also been investigated, *viz.* thin-layer chromatography<sup>7-10</sup>, ion exchange<sup>11,12</sup> or combined methods, for instance, paper chromatography plus ion exchange<sup>13</sup>. In most experiments, mixtures of oxygen-containing solvents with HCl were used as the mobile phase. The systems investigated did not permit the separation of all of the platinum metals and the duration of the paper chromatographic analysis was rather long.

Recently, a very useful method for separating many metals has been developed —the so-called reversed-phase extraction chromatography, introduced in inorganic

analysis by Siekierski and Kotlińska<sup>14</sup> and by Winchester<sup>15</sup>. There have been only a few applications of this technique in the chromatographic separation of the platinum metals. Cerrai and Testa<sup>16</sup> investigated the chromatographic behaviour of numerous metals on paper impregnated with tri-*n*-octylphosphine oxide and separated the mixture Au-Pt-Pd-Ir by the column technique on cellulose treated with this extractant<sup>17</sup>. Cerrai and Ghersini<sup>18</sup> carried out systematic chromatographic investigations of many metals in the system di-(2-ethylhexyl)orthophosphoric acid-HCl, but the results obtained did not permit the separation of the platinum metals in this system. More promising results were obtained with supports treated with tributyl phosphate, which enabled Au to be separated from Pt<sup>19</sup> as well as the components of Au-Pt-Pd<sup>20</sup> and Au-Pd-Pt-Rh mixtures<sup>21</sup>. The chromatographic spectra of many metals in the systems liquid anion exchanger-HCl<sup>22,23</sup> or HBr<sup>23,24</sup> indicate the possibility of separating some of the platinum metals; however, this was demonstrated only for the mixture Pt-Pd-Ru<sup>25</sup>.

Chromatography on the paper impregnated with Amberlite LA-1 or tri-*n*-octylamine(TOA) salts combined with selective spraying reagents appeared to be useful in the systematic analysis of cations of the analytical groups IIA<sup>26</sup> and IIB<sup>27</sup>, which include the platinum metals. For this reason, in the present work a method for the qualitative chromatographic analysis of mixtures of the platinum metals and gold in the system Amberlite LA-1-HCl was investigated.

## MATERIALS AND METHODS

Amberlite LA-1 (Serva, G.F.R.) was used without further purification as the liquid anion exchanger. All other reagents and metal salts were of analytical-reagent grade. The solutions of palladium, platinum and osmium were prepared by dissolving the metals in *aqua regia*, evaporating the solutions almost to dryness, dissolving them in small amounts of concentrated HCl and diluting the solutions with distilled water so as to give suitable concentrations. Solutions of other metal ions were obtained by dissolving suitable salts —(NH<sub>4</sub>)<sub>3</sub>RhCl<sub>6</sub>, (NH<sub>4</sub>)<sub>3</sub>IrCl<sub>6</sub>, HAuCl<sub>4</sub> and RuCl<sub>3</sub>— in distilled water that had been slightly acidified with HCl. In all experiments, 3 μl (single ions) or 5 μl volumes (mixtures of metals) were spotted on the starting line. The concentrations of the metals in the solutions were: Pt(IV) 0.64, Pd(II) 0.3, Ru(III) 0.78, Rh(III) 0.4 and Ir(III), Os(III) and Au(III) 1% (w/v). In order to determine the sensitivities of the colour reactions under chromatographic conditions, some experiments were carried out with more dilute solutions of the metals.

Whatman No. 4 chromatographic paper was treated with a benzene solution of Amberlite LA-1 hydrochloride, obtained by shaking a 0.1 M solution of Amberlite LA-1 in benzene with an equal volume of 1 N HCl, separating the phases and filtering through cellulose. The paper strips were passed through the organic solution three times and compressed between two sheets of paper in order to remove the excess of impregnating solution. The paper strips were then air dried in order to remove the diluent of the liquid anion exchanger. The solutions of the metals investigated were spotted on to the paper strips, which were developed with aqueous solutions of hydrochloric acid of suitable concentrations. Three paper chromatographic techniques were used: the circular technique for a distance of 10 cm (developing time 1 h), the descending technique for a distance of 16 cm (developing time 1 h 20 min) and Mat-

this' method (descending technique) for a distance of 27 cm (time of analysis 3.5 h). After development, the paper was dried and the metals were detected on the paper by spraying with solutions of suitable reagents. The following reagent solutions were used (concentrations in % w/v): 5% KI in water; 5% SnCl<sub>2</sub> in 2 N HCl; a saturated solution of thiourea in 1 N HCl or in 6 N HNO<sub>3</sub>; 0.5% rubeanic acid in ethanol; 0.3% potassium xanthogenate in water-ethanol; 0.5% *p*-nitrosodimethylaniline in methanol; 1% Ce(SO<sub>4</sub>)<sub>2</sub> in water; and 0.5% 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol.

## RESULTS AND DISCUSSION

It follows from earlier papers<sup>22,23</sup> that the most promising liquid anion-exchange system for separating the platinum metals seems to be a secondary amine salt-HCl system because tertiary amine salts have too high an affinity for the chloride complexes of some platinum metals. Therefore, all experiments were performed on paper impregnated with the hydrochloride of a secondary long-chain amine, Amberlite LA-1. One of the parameters that controls the  $R_F$  values of metals in reversed-phase paper chromatography is the concentration of the complexing anions. In Table I, the experimental  $R_F$  values for the metal ions investigated are presented for various concentrations of hydrochloric acid used as eluent, the papers being impregnated with a 0.1 M solution of Amberlite LA-1 hydrochloride in benzene.

In further investigations, 6 M hydrochloric acid was used as the mobile phase. At that concentration of HCl, it is possible to separate mixtures of Au(III), Os(III), Pt(IV) and Pd(II) with Ru(III), Ir(III) or Rh(III). As Ru(III), Ir(III) and Rh(III) form a single zone in this system, the use of selective spray reagents for the identification of those metals is necessary. A number of reagents were tested for their suitability for this purpose, and the results obtained are given in Table II.

The following reagents were chosen as being suitable for the complete analysis.

(1) The identification of iridium, ruthenium and osmium can be achieved simultaneously by using a solution of thiourea in 6 N nitric acid, the temperature of the reaction being controlled. Osmium forms a rose-coloured complex, Os(NH<sub>2</sub>·

TABLE I

$R_F \times 100$  VALUES FOR THE PLATINUM METALS AND GOLD AS FUNCTIONS OF THE MOLARITY OF THE HCl ELUENT

Paper treated with Amberlite LA-1 hydrochloride. Descending technique for a distance of 16 cm; operating temperature  $20 \pm 1^\circ$ .

Metal	HCl concentration (mole/l)					
	0.5	1.0	2.0	4.0	6.0	8.0
Au(III)	0	0	0	0	0	0
Os(III)	8	8	8	10	16	20
Pt(IV)	8	8	8	10	30	40
Pd(II)	10 ↓ *	10 ↓	15	22	48	60
Ru(III)	75 ↓	80 ↓	80 ↓	80	85	85
Rh(III)	75	75	80	80	85	85
Ir(III)	95	95	95	95	95	95

\* ↓ = Tailing of spot.

TABLE II  
 COLOUR TESTS FOR THE PLATINUM METALS AND GOLD OBTAINED ON PAPER TREATED WITH AMBERLITE LA-1 HYDRO-  
 CHLORIDE USING 6 M HCl AS THE MOBILE PHASE

<i>Metal</i>	<i>Thiourea in HCl</i>	<i>6 M HNO<sub>3</sub> after heating</i>	<i>KI</i>	<i>SnCl<sub>2</sub> after heating</i>	<i>SnCl<sub>2</sub> + KI</i>	<i>Rubeanic acid</i>	<i>Ceric sulphate</i>	<i>Potassium xanthogenate</i>	<i>p-Nitrosodi- methylaniline</i>	<i>PAN + NH<sub>3</sub></i>
Au(III)			Yellow- orange	Black		Yellow	Yellow	Grey	Brown	
Os(III)	Rose		Orange- brown			Black		Brown	Brown	Brown- violet
Pt(IV)			Yellow	Yellow	Orange	Pale rose		Beige		
Pd(II)			Orange- brown	Orange	Violet or green-blue	Yellow		Beige	Red	Blue- green
Ru(III)	Blue					Blue- green		Yellow	Blue	
Ir(III)		Brown					Brown			
Rh(III)				Yellow	Brown			Pale rose	Pale rose	

$\text{CS}\cdot\text{NH}_3)_6^{3+}$ , with thiourea at room temperature, whereas ruthenium gives a blue spot. The intensity of the colour increases at first during heating of the chromatogram in an oven; however, when the temperature increases to about  $110^\circ$ , the blue spot of ruthenium disappears after 10 min and the spot of osmium fades; simultaneously, the brown spot of iridium appears. This effect is due to the reaction of the metals with nitric acid; a volatile ruthenium oxide is formed and colourless compounds of iridium(III) are oxidized to brown compounds of Ir(IV). The sensitivities of the reactions under chromatographic conditions are  $1.5 \cdot 10^{-5}$  g for Ir(III),  $7.5 \cdot 10^{-7}$  g for Ru(III) and  $7.5 \cdot 10^{-6}$  g for Os(III).

(2a) The presence of Au(III), Pd(II), Pt(IV) and Rh(III) can be demonstrated by reaction with tin(II) chloride. After spraying the paper strips, the black spot of gold, the yellow-orange spot of platinum and the rose-brown spot of palladium (depending on concentration) are revealed immediately. After heating the chromatogram to about  $80^\circ$ , the intense yellow spot of rhodium appears. By using this reaction, it is possible to detect  $1.5 \cdot 10^{-6}$  g of Au(III), Pt(IV) and Pd(II) and  $3 \cdot 10^{-6}$  g of Rh(III).

(2b) More contrasting colours of the spots of Pd(II), Pt(IV) and Rh(III) can be obtained by spraying the chromatogram with tin(II) chloride solution followed by treatment with a solution of potassium iodide. Platinum forms an orange spot, palladium a green-blue spot and rhodium a brown spot, their intensities increasing after the chromatogram is heated to about  $80^\circ$ . This test is more sensitive for palladium and rhodium in comparison with the previous reaction and permits the detection of  $1.5 \cdot 10^{-7}$  g of Pd(II) and  $1.5 \cdot 10^{-6}$  g of Rh(III).

Paper chromatographic analyses of mixtures of the platinum metals and gold carried out by using the descending and circular techniques and Matthias' method are shown in Figs. 1-3.

The selective colour reactions require the chromatogram to be cut into two parts, so the mixture investigated should be spotted at two positions. If more parts

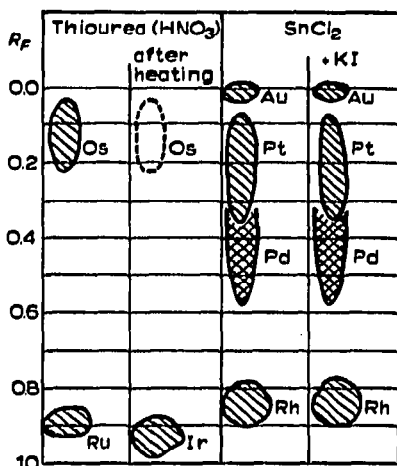


Fig. 1. Selective detection on chromatograms obtained in the system Amberlite LA-1-6 M HCl by the descending technique.

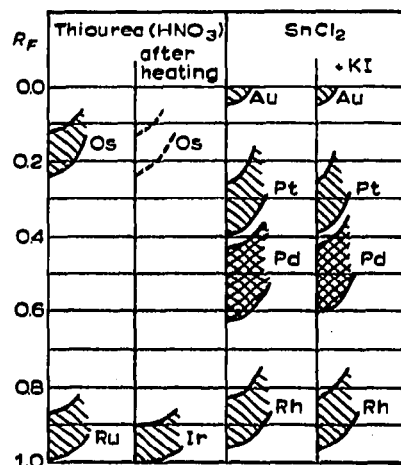


Fig. 2. As Fig. 1, using Matthias' method.

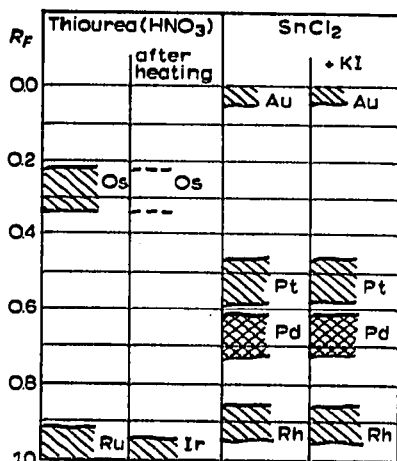


Fig. 3. As Fig. 1, using the circular technique.

of chromatogram are available (for instance, in the circular technique or Matthias' method), it is possible to confirm the results of analysis with additional colour tests (for instance, for Ir(III) with ceric sulphate and for Pd(II) and Os(III) with PAN solution); however, this is not essential.

It can be seen from Figs. 1–3 that the best separation of the pair Pt–Pd is obtained by using Matthias' method or the circular technique, whereas the circular technique is the most suitable for the separation of gold and osmium. In spite of elongated spots of platinum and palladium obtained when the descending technique was used, nevertheless, all three investigated chromatographic techniques seem to be suitable for the qualitative analysis of the platinum metals and the choice of the method depends on the amounts or concentrations of the components of the mixture being investigated. In view of its rapidity, the circular technique is recommended if the sample size is sufficient.

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