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

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To cite this Article Singh, Rama S. , Tripathi, Satyendra N. , Ghose, Animesh K. and Dey, Arun K.(1969) 'Separation of Platinum Metals by Paper Electrophoresis', Separation Science and Technology, 4: 3, 171 — 179
To link to this Article: DOI: 10.1080/01496396908052248
URL: http://dx.doi.org/10.1080/01496396908052248

SEPARATION SCIENCE, 4(3), pp. 171–179, June, 1969

Separation of Platinum Metals by Paper Electrophoresis

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Summary

Ruthenium, rhodium, palladium, osmium, iridium and platinum have been separated from a single spot in horizontal paper electrophoresis using ethylenediaminetetraacetic acid (EDTA) as background electrolyte. Electrograms were run using 0.01 *M* electrolyte, at pH 9.0, 10.5, 11.0 and 12.0. Binary, ternary, quaternary and quinary separations are possible at various pH values, but best separation occurs at pH 11.0. At this pH, ruthenium and osmium slightly overlap with each other and can be separated by cutting this zone and placing it on a fresh paper and carrying on the electrophoresis, now using 0.1 *M* EDTA at pH 6.0. Ruthenium and osmium can thus be separated from each other on the second paper. The temperature is kept at 20°C, a potential 250 V is supplied, and the developing time is 3.5 hr.

The electrophoretic separation of platinum metals has been attempted by various workers (*1–5*) using disodium salt of ethylenediaminetetraacetic acid (EDTA) as background electrolyte, but no success has been achieved for the separation of all six platinum metals when present together in a mixture, using paper electrophoresis. Ghose and Dey (*6*), however, from these laboratories, could separate the six platinum metals by paper chromatography.

The present communication describes the separation of all six platinum metals from a single spot, using EDTA as background electrolyte at pH 11.0 and 6.0. A very simple technique has been devised to separate the overlapped spot by transfer from one paper to another and subjecting to electrophoresis under a new set of conditions.

EXPERIMENTAL

Apparatus

An LKB 3276B paper electrophoresis apparatus (LKB-Produkter. Sweden), with accessories, was employed.

Filter Paper Strips

Whatman No. 1 filter paper was used for chromatography (1.5 × 46.5 cm).

Background Electrolyte

British Drug House AnalaR grade EDTA was used as the electrolyte, the concentrations being 0.1 and 0.01 *M*. The pH of the 0.1 *M* solution was maintained at 6.0 and the pH of the 0.01 *M* EDTA was varied from 9.0, to 10.5, to 11.0, and to 12.0 by the addition of NaOH.

Metal Solutions

Stock solutions (0.05 *M*) of palladous chloride, chloroplatinic acid, iridium trichloride, rhodium trichloride, ruthenium trichloride, and osmium tetraoxide in HCl (all obtained from Johnson, Matthey & Co., London) were prepared by dissolving in water and by standardization (7). Mixtures of these were prepared by mixing equal volumes of each and diluting as necessary.

Developing Reagents

Potassium iodide: 2% w/v in water.

Stannous chloride: solution was prepared by dissolving 10 g of hydrated $SnCl_2$ in 100 ml of 6 *N* HCl and adding 1 g of granular tin.

Rubeanic acid: 1% w/v in ethanol.

Thiourea: 2% w/v in water.

Procedure

The electrodes and electrode vessels were washed and dried. The base plate was kept on the horizontal surface of the table. The electrode vessels were placed in their positions and equal volumes of 0.01 *M* EDTA were poured into these vessels with the help of a glass siphon. The strips were washed with distilled water and soaked in the electrolyte. The excess electrolyte was removed by hanging the strips vertically for 1 min. and by pressing them between filter papers. These strips were then mounted in the cassette, and the mixture of the platinum metals was spotted at the previously marked center with the help of a self-filling pipette (ca. 1.5 μl).

The cassette was then covered, and a potential of 250 V was applied for 3.5 hr. After the run the strips were transferred to the drying rack, in such a way that equal lengths of each strip extended outside the rack. The ends were cut off, and the rack was placed horizontally to dry for 30 min at 120°C. The strips were developed with detecting reagents.

Detection of Zones

A stannous chloride–potassium iodide test solution, as proposed by Burstall (*8*) was used to detect platinum, palladium, and rhodium. Ruthenium was detected by rubeanic acid. Thiourea and 0.5 *N* HCl were used for detecting osmium. Iridium was detected after platinum, palladium, and rhodium, by dipping the strip into concentrated HNO_3 and treating it with potassium iodine + stannous chloride (*1*) (Table 1).

TABLE 1

Detection of Metal Ions

Metal ion	Reagent	Color
Ru(III)	Rubeanic acid	Blue
Rh(III)	KI + $SnCl_2$	Orange to maroon
Pd(II)	KI + $SnCl_2$	Pink to dark purple
Ir(III)	KI + $SnCl_2$ in presence of conc. HNO_3	Brown
Os(VIII)	Thiourea + 0.5 *N* HCl	Red
Pt(IV)	KI + $SnCl_2$	Yellow to brownish yellow

RESULTS

A large number of separations were carried out using 0.01 *M* EDTA at various pH, namely, 9.0, 10.5, 11.0, and 12.0. The best separation could be achieved at pH 11.0 (Table 2); the values for the distance moved (R_L and R_T) by the metal ions are given in parentheses. Positions of the spots at different pH values of EDTA electrolyte are shown in Fig. 1. In every case ruthenium and osmium overlapped.

TABLE 2

Separations of the Platinum Metals in 0.01 *M* EDTA as Background Electrolyte

pH of EDTA	R_L and R_T of the metal ions in cm	Possible separations
9.0	Pt(IV) (5.0–3.5)	[Os–Ir–Pd–Pt]
	Pd(II) (3.0–2.0)	[Ru–Ir–Pd–Pt]
	Rh(III) (2.5–2.0)	[Os–Rh–Pt]
	Ir(III) (2.4–1.8)	[Ru–Pd–Pt]
	Os(VIII) (0.0–0.0)	[Os–Ir–Pt]
	Ru(III) (0.0–0.0)	[Ru–Rh–Pt]
		[Os–Ir–Pd]
10.5	Pt(IV) (13.2–10.5)	[Os–Rh–Pd–Pt]
	Pd(II) (6.0–5.5)	[Ru–Rh–Pd–Pt]
	Rh(III) (4.8–3.4)	[Os–Ir–Pd–Pt]
	Ir(III) (4.5–3.0)	[Ru–Ir–Pd–Pt]
	Os(VIII) (0.0–0.0)	
	Ru(III) (0.0–0.0)	
11.0	Pt(IV) (15.5–14.0)	[Os–Ru–Rh–Ir–Pd–Pt]
	Pd(II) (9.0–8.2)	[Os–Rh–Ir–Pd–Pt]
	Ir(III) (5.8–4.5)	[Ru–Rh–Ir–Pd–Pt]
	Rh(III) (3.0–2.5)	
	Os(VIII) (1.0–0.1 toward cathode)	
	Ru(III) (0.0–0.0)	
12.0	Pt(IV) (12.0–11.0)	[Os–Ru–Rh–Ir–Pt]
	Pd(II) (7.5–5.3)	[Os–Ru–Rh–Pd–Pt]
	Ir(III) (6.0–4.0)	
	Rh(III) (3.0–2.0)	
	Os(VIII) (1.0–0.1, toward cathode)	

TABLE 3

Separation of Platinum Metals in 0.1 *M* EDTA as Background Electrolyte

pH of EDTA	R_L and R_T of the metal ions in cm	Possible separation
6.0	Pt(IV) (7.0–5.5)	[Pt–Pd–Ru–Os]
	Pd(II) (5.0–4.4)	[Pt–Ir–Rh–Os]
	Ir(III) (4.8–4.6)	[Pt–Pd–Rh–Os]
	Ru(III) (4.0–3.2)	[Pt–Ir–Ru–Os]
	Rh(III) (3.0–2.0)	
	Os(VIII) (−0.3–0.0)	

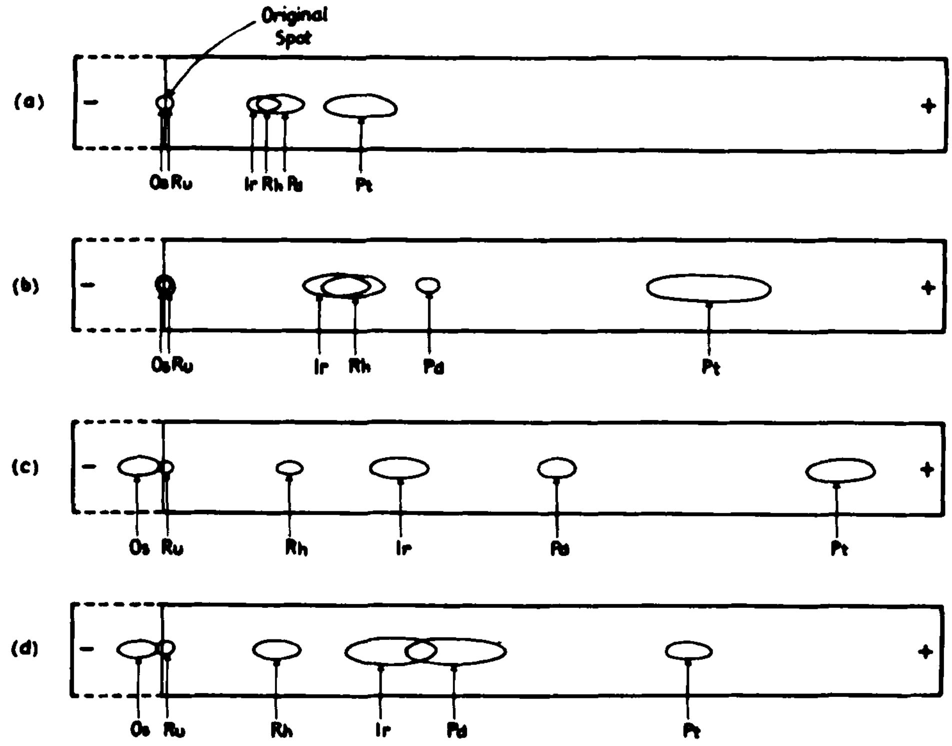

FIG. 1. Positions of the spots on the electrochromatograms at different pH values of the background electrolyte. (a) pH = 9.0; (b) pH = 10.5; (c) pH = 11.0; (d) pH = 12.0.

In another set of experiments, the concentration of EDTA was changed to 0.1 *M*; the pH was kept at 6.0; voltage and time were as before. At this concentration of EDTA, a clear-cut separation between ruthenium and osmium was obtained. The positions of the metal ions are shown in Fig. 2. Table 3 shows the separation at this concentration of EDTA.

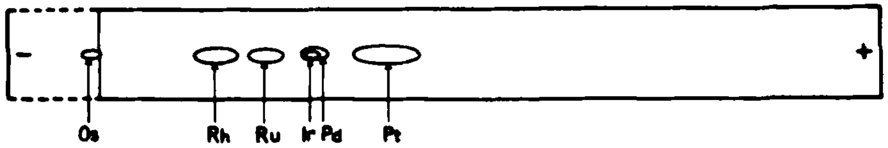

FIG. 2. Position of the spots using 0.1 *M* EDTA as background electrolyte at pH 6.0.

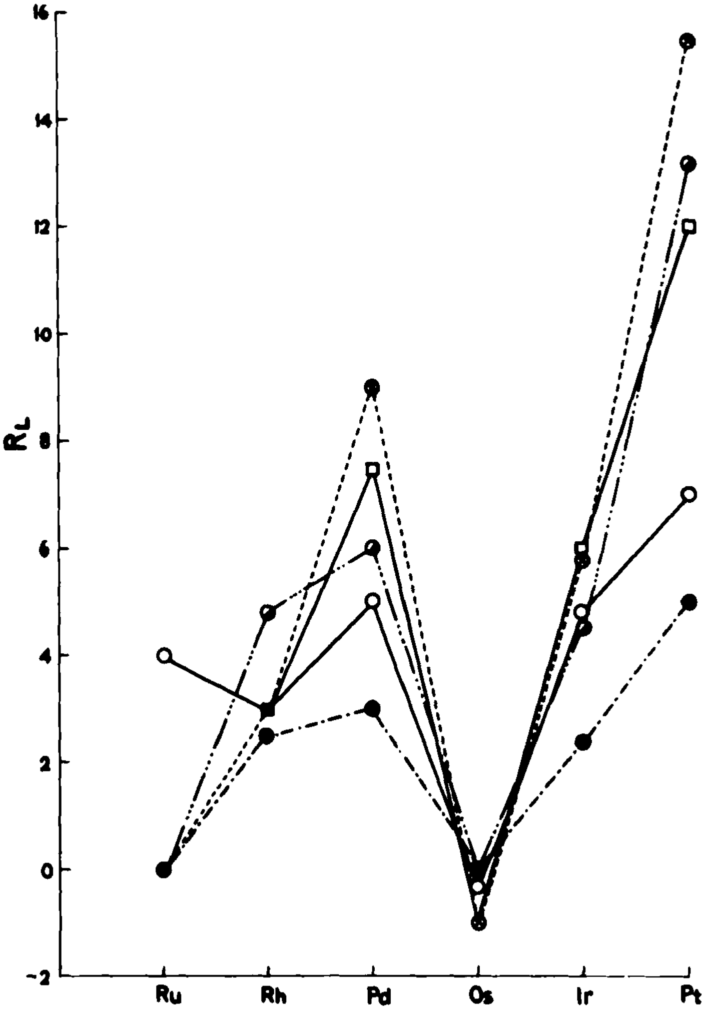

FIG. 3. R_L values of the platinum metals. pH 6.0 (—○—○); pH 9.0 (—●—.—.●); pH 10.5 (—◑—...—...—◑); pH 11.0 (---⊗---⊗); pH 12.0 (—□—□).

The separations are represented in Figs. 3 (R_L values) and 4 (R_T values).

A modified method has been devised for the separation of overlapped metal ions by transferring the spot containing the overlapped metal ions from one electrochromatogram to another as follows.

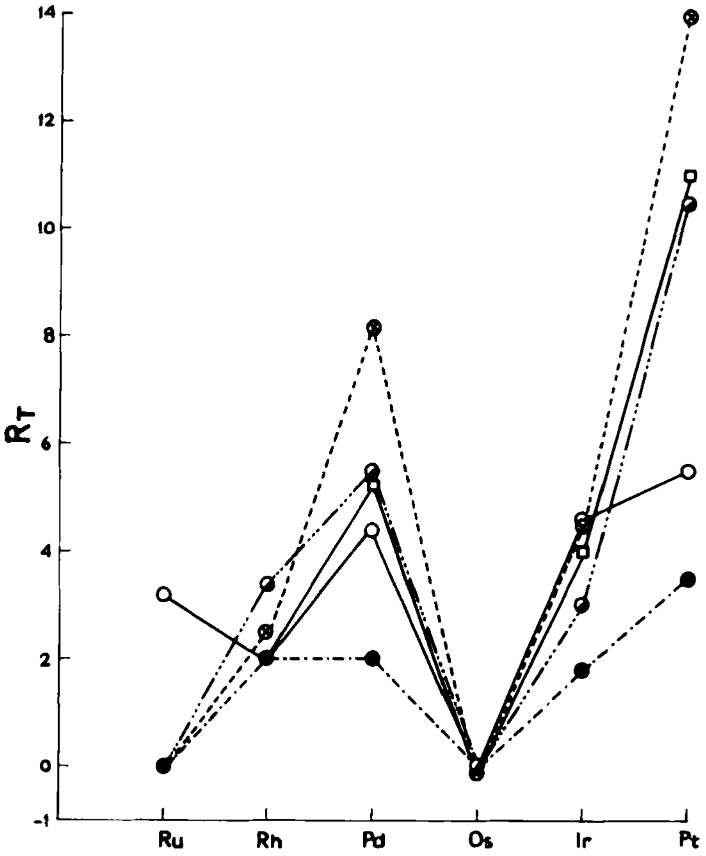

FIG. 4. R_T values of the platinum metals. pH 6.0 (—○—○); pH 9.0 (—●—.—.—●); pH 10.5 (—◑—...—...—◑); pH 11.0 (---⊗---⊗); pH 12.0 (—□—□).

The separation of platinum, palladium, rhodium, and iridium are achieved on the first paper *ABCD* from the spot of the mixture of the six metal ions (Fig. 5a) using 0.01 *M* EDTA solution at pH 11.0 as background electrolyte. Here ruthenium and osmium overlapped with each other as shown. The portion *abcd* containing the two overlapped metal ions, ruthenium and osmium, is cut from the paper *ABCD*. This portion is placed at the center of another fresh paper *A'B'C'D'* soaked in 0.1 *M* EDTA, kept on the cassette (Fig. 5b). The concentration of EDTA is now kept 0.1 *M* and the pH is maintained at 6.0. The voltage applied was 250 V and time allowed was 3.5 hr. A clear-cut separation

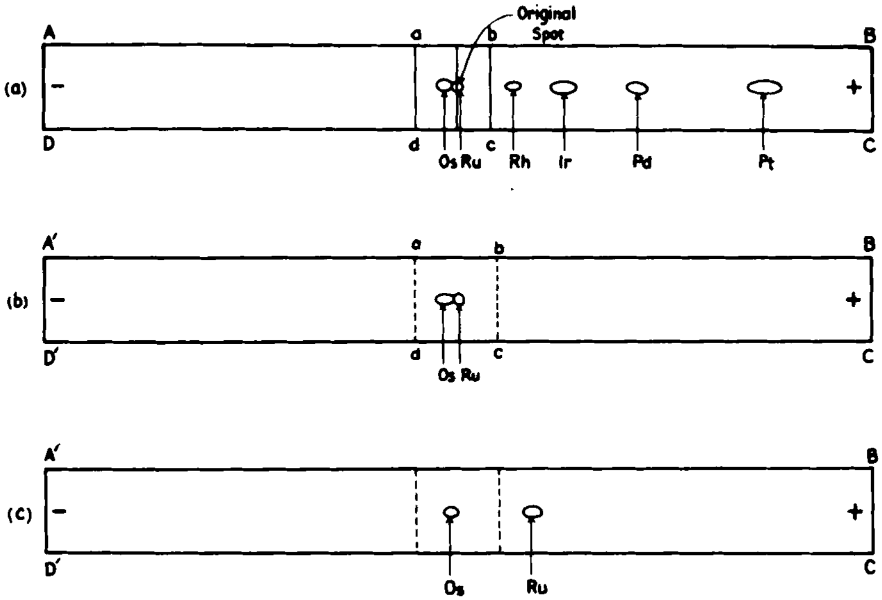

FIG. 5. Transfer of overlapped spots and their separation. (a) Separations of Pt, Pd, Ir, and Rh from Os and Ru. (b) Portion containing osmium and ruthenium is placed on a fresh electrochromatogram and electrophoresis is carried out. (c) Separation of osmium and ruthenium using 0.1 *M* EDTA at pH 6.0.

between ruthenium and osmium is achieved on the paper *A′B′C′D′*—osmium remains on the portion *abcd* and ruthenium moves to the paper *A′B′C′D′* (Fig. 5c).

DISCUSSION

Table 1 shows that by changing the pH of the background electrolyte with 0.01 *M* EDTA, binary, ternary, quaternary, and quinary mixtures of the platinum metals can be separated. At pH 9.0 and 10.5 when the concentration of EDTA is 0.01 *M*, ruthenium and osmium remain overlapped at the original spot. Iridium and rhodium also move closely together. Rhodium leads iridium up to pH 10.5 but, as soon as the pH is increased from 10.5 to 11.0, there is a clear separation of iridium and rhodium, and now iridium leads rhodium. At this pH there is also a separation between osmium and ruthenium. Osmium–EDTA complex at this pH moves toward the negative electrode forming a cationic complex. At this pH, all the other platinum metals, including platinum, palladium, iridium, and rhodium, are clearly separated from each other. As the pH is changed from 11.0 to 12.0, iridium moves further and overlaps with palladium. Thus by using 0.01 *M* EDTA at pH 11.0, the best separation of all six metal ions is possible.

As the concentration of EDTA is changed to 0.1 *M*, ruthenium moves toward the positive electrode forming an anionic complex with excess EDTA at pH 6.0.

The lowest and highest concentrations of the metal ions which could be separated and detected in the spots are

Ru, 0.8–5.1 mg/ml	Os, 1.5–9.5 mg/ml
Rh, 0.8–5.1 mg/ml	Ir, 1.5–9.5 mg/ml
Pd, 0.1–5.3 mg/ml	Pt, 0.2–9.8 mg/ml

Acknowledgments

The authors are thankful to the Council of Scientific and Industrial Research and the University Grants Commission, New Delhi, for financial support.

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Received by editor March 5, 1969
Submitted for publication April 8, 1969