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Mohsin Qureshi[a]; K. G. Varshney[a]; Fahmida Khan[a]
[a] CHEMISTRY DEPARTMENT, COLLEGE OF ENGINEERING AND TECHNOLOGY ALIGARH MUSLIM UNIVERSITY, ALIGARH, U.P., INDIA

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Quantitative Separation of Magnesium and Palladium from Numerous Metal Ions on Titanium Tungstate Papers by Electrochromatography

MOHSIN QURESHI, K. G. VARSHNEY, and
FAHMIDA KHAN

CHEMISTRY DEPARTMENT AND COLLEGE OF ENGINEERING AND TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY, ALIGARH (U.P.), INDIA

Summary

Electrochromatography of forty-six metal ions has been performed in fifteen electrolytes on papers impregnated with titanium tungstate by applying different electrical potentials and allowing different time intervals for migration. On the basis of the differential mobility of the cations, which depend on the nature of the complexes formed with the background electrolytes and the ion exchange properties of titanium tungstate, a large number of binary and ternary separations have been achieved. The separations of one metal ion from numerous metal ions have also been accomplished. For example, the following difficult and important separations have been made: Cu^{2+}–Cd^{2+}–Bi^{3+}, Ag^{+}–Cu^{2+}–Au^{3+}, Pd^{2+}–Pt^{4+}–Ir^{4+}, Hg^{2+}–Cd^{2+}–Zn^{2+}, Ag^{+}–Pt^{4+}, Au^{3+}–Pt^{4+}, Cd^{2+}–Bi^{3+}, Bi^{3+}–Pb^{2+}, Bi^{3+}–Hg^{2+}, Pd^{2+}–Ru^{3+}, Ga^{3+}–In^{3+}, La^{3+}–Ce^{4+}, Hg_2^{2+}–Hg^{2+}, Mg^{2+}–Al^{3+}, Hg^{2+} from forty-five cations, Au^{3+} from forty-one cations, Pd^{2+} from forty-three cations. Magnesium and palladium have been quantitatively separated in 100–200 μg quantities from binary mixtures as well as from synthetic mixtures containing commonly interfering metals.

INTRODUCTION

Synthetic inorganic ion exchangers are of great interest in the field of separation science. A large number of separations of metal ions have been achieved on columns of these ion exchangers because of their superior stability over organic resins in strong radiations and at high temperatures. Papers impregnated with these materials have also been used for chromatography (*1–6*) and electrophoresis (*7–9*) of metal ions. These papers are particularly useful for the separation of alkali metals and alkaline earths. They are extremely selective and give fast and clean separations of metal ions that are otherwise difficult to separate. However, no quantitative work was reported in the literature before 1968 when selenium was first separated quantitatively from metal ions on tin(IV) tungstate papers in these laboratories (*5*). The field of quantitative electrochromatographic separation is still untouched. This is due to the fact that numerous problems must be solved before reproducible results can be obtained.

Of the ion exchangers prepared in these laboratories, titanium tungstate (*10*) has proved to be fairly stable in acids. It also exhibits good ion exchange properties. It was therefore used to impregnate the papers, and electrochromatography of all common metal ions was performed on these papers. On the basis of migration of metal ions under the combined influence of electric field and ion exchange, magnesium and palladium have been quantitatively separated from numerous metal ions. The present paper summarizes such a study.

EXPERIMENTAL

Apparatus

Spectrophotometric studies were performed on Bausch and Lomb spectronic-20 colorimeter. Hanging strip type apparatus from Shandon, Ltd., London, was used as the electrochromatographic chamber.

Reagents and Chemicals

Ion exchange papers were prepared by loading the ion exchanger on Whatman No. 1 paper strips (36 × 3.5 cm). Titan Yellow and 15% titanic chloride solutions were of B.D.H. (England). Other reagents and chemicals were of reagent grade.

Preparation of Ion Exchange Papers

Titanium tungstate papers were prepared as in our previous publication (*6*).

Preparation of Cation Solutions and Detectors

For qualitative studies, cation solutions and detectors were prepared and used as described earlier (*4*). For quantitative studies, a solution of magnesium (10,000 ppm Mg) was prepared by dissolving 1 g magnesium metal in dilute nitric acid, heating, and then diluting with distilled water to 100 ml. Palladium chloride was dissolved in dilute hydrochloric acid to obtain a standard palladium solution (10,000 ppm Pd).

Procedure

For qualitative studies of electrophoretic migration, the earlier method (*7*) was followed. A description of the quantitative work follows.

(a) *Magnesium from Numerous Metal Ions.* The magnesium solution (100–300 μg Mg) along with the cations to be separated were applied on the strips with the help of a lambda pipet. The strips were electrochromatographed in the electrolyte, 0.2 M $NaNO_2$ + 0.2 M sodium acetate (1:1), for 4 hr under a potential of 200 V. After the required time the pilot strips were examined for the spots of magnesium and other cations. The remaining strips were then cut according to where spots had appeared on the pilot strips, and magnesium was eluted with 50 ml of 5% v/v HCl by heating on a water bath. The blank was run in a similar way by following the entire procedure for an unspotted paper strip. After the elution was complete the strips were washed with 20 ml distilled water. The solution was evaporated to small volume (2–3 ml), and the paper strips were oxidized with an oxidizing mixture of HNO_3:$HClO_4$:H_2SO_4 in the ratio 1:3:2. The solution was then evaporated to dryness and the residue was dissolved in a little distilled water. Magnesium was determined in this solution with Titan Yellow by the standard method (11).

(*b*) *Palladium from Numerous Metal Ions.* For the separation of palladium, 0.1 M $NaNO_2$ was used as the electrolyte and the electric current was passed for 3 hr under a potential difference of 200 V. After electrochromatography the strips were taken out and half-dried. The spot area was cut into pieces and palladium was eluted with 10% HCl (40 ml) in the cold by using 20 ml twice. Spectrophotometry of palladium was done with KI as reagent (*12*).

RESULTS

The electrochromatographic behavior of forty seven metal ions on titanic tungstate papers has been studied using a number of background

TABLE 1A

Electrochromatographic Movements of Ions in Different Electrolytes on Titanium Tungstate Papers (in cm)

Solvent system ion	0.5 M HNO$_3$[b]	0.2 M HCl[b]	0.2 M HCl + 0.1 M KCl (1:1)[d]	0.2 M HCl + 0.2 M NaCl (1:1)[c]	0.2 M HCl + 0.2 M NH$_4$Cl (1:1)[e]	0.2 M HNO$_3$ + 0.2 M NaNO$_3$ (1:1)[e]	0.4 M HNO$_3$ + 0.2 M NH$_4$NO$_3$ (1:1)[a]
Ag^+	+1.0	0.00	0.00	0.00	0.00	0.00	+1.0T
Pb^{2+}	+1.5	0.00	0.00	0.00	0.00	−1.5	0.00
Hg_2^{2+}	0.00	0.00	−3.0	−2.5	−2.0	0.00	0.00
Hg^{2+}	+1.5	0.00	−4.3	−8.0	−2.0	−1.1	0.00
Tl^+	+1.7	0.00	−2.8	−2.2	−2.3	+2.0	+1.0
Bi^{3+}	0.00	−1.7	−3.2	−3.1	−2.0	0.00	−1.0
Cd^{2+}	+2.0	1.0	0.00	0.00	0.00	+3.5	0.00
Cu^{2+}	+2.1	+3.3	+3.1	+2.6	+2.7	+5.0	+1.1
As^{3+}	0.00	+2.8	+0.7	0.00	0.00	0.00	0.00
Sb^{3+}	0.00	+1.0	0.00	0.00	0.00	0.00	0.00
Ni^{2+}	+2.4	+2.0	+9.3	+3.9	+3.3	+4.5	+1.3
Co^{2+}	+3.6	+2.0	+9.0	+4.3	+4.5	+4.0	+1.5
Mn^{2+}	0.00	+4.1	+7.5	+4.2	+5.5	+4.5	+1.0
Fe^{2+}	+1.7	+1.0	+3.0T	+2.0	+3.2T	+2.2T	+1.0T
Fe^{3+}	+1.6	+1.0	+3.0T	+1.4	+3.0T	+1.7T	+1.2T
Al^{3+}	+2.3	+4.5	+7.5	+2.0	+3.5	+3.8	+1.3
Cr^{3+}	0.00	+2.8	+1.4	+5.8	+4.1	+4.0	+1.1
Zn^{2+}	+3.5	+4.0	+7.0	+3.8	+4.3	+4.8	+1.7
La^{3+}	+2.6	+2.8	+3.7	+3.0	+3.5	−1.0	+4.5
Ce^{3+}	+2.5	+2.7	+2.8	+1.6	+4.0	+3.2	+4.7
Ce^{4+}	+1.0	0.00	+1.0	0.00	0.00	0.00	+2.5T
UO_2^{2+}	+2.0	+1.0	+2.5	+4.2	+4.0	+2.7	0.00
VO^{2+}	+2.8	+1.7	+2.5	+1.9	+5.5	+3.5	0.00
Te^{4+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pd^{2+}	−2.0T	−2.8	−6.5	−6.5	−5.0	−7.0	+1.1
Pt^{4+}	−3.6	+1.7	−1.1	0.00	0.00	−5.8	−3.7T
Y^{3+}	+3.0	+2.5	+3.5	+3.4	+5.3	+3.2	0.00
Au^{3+}	0.00, −2.0	−1.0	−2.5	−4.0	−3.1	−3.8	−1.3
Ga^{3+}	+2.8	0.00	+3.0	+1.7	+5.8	−1.0	0.00

(continued)

TABLE 1A—Continued

Solvent system ion	0.5 *M* HNO_3[b]	0.2 *M* HCl[b]	0.2 *M* HCl + 0.1 *M* KCl (1:1)[d]	0.2 *M* HCl + 0.2 *M* NaCl (1:1)[c]	0.2 *M* HCl + 0.2 *M* NH_4Cl (1:1)[e]	0.2 *M* HNO_3 + 0.2 *M* $NaNO_3$ (1:1)[e]	0.4 *M* HNO_3 + 0.2 *M* NH_4NO_3 (1:1)[a]
Ba^{2+}	+2.2	+4.0	+6.5	+5.7	+5.0	+4.2	0.00
Sr^{2+}	+3.1	+4.7	—	+5.2	+5.5	—	+1.0
Ca^{2+}	+4.8	+4.7	−8.5	+4.9	+6.5	+4.8	+0.00
Mg^{2+}	+1.6	+2.2	−2.2	+4.0	+5.7	+5.7	+1.0
Be^{2+}	—	0.00	+3.3	+4.9	+5.3	+3.8	+1.0
Zr^{4+}	0.00	+2.2	0.00	+1.8	+1.9	−2.3	−2.2
Th^{4+}	+2.2	+2.3	0.00	+2.3	+1.2	+1.5	+3.5
In^{3+}	+3.7	—	+2.2	+2.3	+3.7	+1.2	0.00
Ru^{3+}	+1.3	—	+1.0	+1.3T	+1.4	+1.7T	+1.6T
Ir^{4+}	+3.0	+2.3	+3.0	+5.8	+6.6	+4.5	+0.5
Nb^{5+}	+3.3, 0.00	−1.0	−0.7	−0.7	0.00, +4.5	+0.7	0.00
Hf^{4+}	0.00	+2.1	−1.1	0.00	0.00	0.00	+0.5
Se^{4+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mo^{6+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K^+	—	—	—	—	—	—	—
Rb^+	—	—	−2.0	+7.5	+7.9	—	+2.9
Cs^+	—	—	+9.0	+9.2	+7.7	+2.8	+2.5

[a] 40 V applied potential, 6 hr.
[b] 50 V applied potential, 6 hr.
[c] 100 V applied potential, 4 hr.
[d] 100 V applied potential, 5 hr.
[e] 200 V applied potential, 4 hr.

electrolytes. The results are given in Tables 1A and 1B. The distance of the center of the zone from the middle of the paper is given in centimeters with a positive sign indicating movement of ions towards the cathode and a negative sign used for movement toward the anode. On the basis of these results some possible important binary and ternary separations were attempted on these papers, and the results are given in Table 2. The separation of a cation from numerous metal ions also

TABLE 1B

Electrochromatographic Movements of Ions in Different Electrolytes on Titanium Tungstate Papers (in cm)

Solvent system ion	0.1 *M* NaNO$_2$[b]	1.0 *M* NaNO$_2$[e]	0.1 *M* NaNO$_2$ + 0.1 *M* KCl (1:1)[c]	0.1 *M* NH$_4$Cl + 0.1 *M* NaNO$_2$ (1:1)[a]	0.2 *M* Sodium acetate + 0.1 *M* NaNO$_2$ (1:1)[a]	0.1 *M* Sodium citrate + 0.1 *M* NaNO$_2$ (1:1)[c]	0.1 *M* Sodium citrate[f]	0.1 *M* Sodium acetate[d]
Ag^+	+0.4	−0.6	−1.0	0.00	0.00	−0.7	0.00	0.00
Pb^{2+}	0.00	0.00	0.00	−0.8	−0.3	−1.8T	0.00	0.00
Hg_2^{2+}	−0.5	0.00, −3.0	0.00	0.00	−1.0	0.00	0.00	0.00
Hg^{2+}	−1.0	−2.7	0.00, −2.8	+3.0	+1.2	+6.3T	−0.9	+0.2T
Tl^+	0.00	0.00	+0.4	0.00	+0.8	0.00	0.00	+1.5T
Bi^{3+}	0.00	0.00	0.00	0.00	0.00	—	+0.8T	0.00
Cd^{2+}	+2.1	−1.7	+1.4	−2.5	+0.5	−1.2	+0.4T	+1.7T
Cu^{2+}	+0.8	0.00	+1.0	−2.0	+0.5	−4.1	−2.8	+1.1
As^{3+}	0.00	0.00	0.00	0.00	0.00	−2.3	−0.2	0.00
Sb^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	−1.3T	0.00
Ni^{2+}	+1.3	+1.7	+6.0	−3.5	+0.7	−3.1	−0.30	+2.3
Co^{2+}	+1.1	+1.1	+4.5	−2.8	+0.8	−3.7	−3.5	+1.5T
Mn^{2+}	+1.5	+0.8	+4.0	−4.5	+1.0	−1.5	−1.1	+3.0
Fe^{2+}	0.00	0.00	+0.5	—	—	—	—	—
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00, −5.6	−1.8	+0.5
Al^{3+}	0.00	+0.4	+1.3	−3.0T	0.00	0.00	−1.6T	+0.7
Sr^{3+}	+0.5	0.00	+1.3	−2.8	0.00, −4.0	−2.4	−1.1	+1.1T
Zn^{2+}	+1.0	+2.0T	+4.9	−4.4	−1.2	−3.7	−1.2	+2.7
La^{3+}	+0.7	+0.00	+1.2	0.00	+0.5	—	−0.2	+1.8
Ce^{3+}	+1.3	+0.00	+2.0T	−2.7T	+1.2	—	+0.5	+2.3
Ce^{4+}	+0.4	0.00	+0.7	−0.00	0.00	−1.6T	−0.8	0.00
UO_2^{2+}	0.00	0.00	0.00	−2.0	0.00	0.00, −2.6	−0.6	0.00
VO^{2+}	−5.2T	0.00	+1.2	−2.7	0.00, −4.7	−8.2T	−2.2T	+1.2T
Te^{4+}	0.00	0.00	0.00	0.00	—	−1.9	−1.2	0.00

(continued)

TABLE 1B—Continued

Solvent system ion	0.1 M $NaNO_2$[b]	1.0 M $NaNO_2$[e]	0.1 M $NaNO_2$ + 0.1 M KCl (1:1)[c]	0.1 M NH_4Cl + 0.1 M $NaNO_2$ (1:1)[a]	0.2 M Sodium acetate + 0.1 M $NaNO_2$ (1:1)[a]	0.1 M Sodium citrate + 0.1 M $NaNO_2$ (1:1)[c]	0.1 M Sodium citrate[f]	0.1 M Sodium acetate[d]
Pd^{2+}	−8.7	−3.8	−9.3	−4.7	−2.4	−8.6	−1.8T	−0.5
Pt^{4+}	+1.7	—	−4.3T	−0.4	−3.0	−4.5	−2.7	−4.9T
Y^{3+}	+0.5	0.00	+1.5	−2.0	+0.8	−1.4	−2.4	+1.6
Au^{3+}	−0.8	0.00	0.00	−0.6	−1.2	−1.0	−1.4	−2.2
Ga^{3+}	+0.6	0.00	+1.0	−3.0	−2.3	−1.7	0.00	0.00
Ba^{2+}	+0.3	—	−1.1	−2.5	0.00	0.00	0.00, −3.2	—
Sr^{2+}	—	—	−0.9	−4.0	0.00	0.00	0.00, −3.8	—
Ca^{2+}	+3.2T	+1.7	0.00	−1.6	−6.1	−0.7	+1.6	+2.9T
Mg^{2+}	+4.2	+4.6	+7.0	+2.5	+4.8	+2.1	—	+9.9
Be^{2+}	+0.6	0.00	+3.0T	−4.4	+1.0	—	−1.1	+3.0
Zr^{4+}	0.00	0.00	0.00	0.00	−1.7	0.00	—	+1.3T
Th^{4+}	0.00	0.00	0.00	−1.7T	0.00	—	—	0.00
In^{3+}	—	—	—	−0.4	0.00	−1.8	−1.8	0.00
Ru^{3+}	0.00	−1.1T	−0.3	+0.5	−0.9	0.00, −3.0	−0.3	0.00
Ir^{4+}	+0.5	0.00	−2.0	+2.0	0.00	−1.5	0.00	0.00
Nb^{5+}	0.00	—	—	0.00	−1.7	0.00	—	−1.3T
Hf^{4+}	+1.9T	—	—	—	—	—	—	—
Se^{4+}	−0.0	0.00	−1.1	—	−0.8	−1.5	−1.1	−0.85
Mo^{6+}	−0.5	0.00	0.00	0.00	0.00	+4.7	+3.1	0.00
K^{+}	+4.1	+7.2	—	+7.3	+4.5	−6.1	+2.1	+6.1
Rb^{+}	+6.0	+5.6	0.0	0.00	+1.8	+3.7	+0.6	+5.0
Cs^{+}	+6.8	+4.8T	+5.4T	−3.5	+1.7	+4.1	+1.0	+7.1

[a] 100 V applied potential, 4 hr.
[b] 200 V applied potential, 3 hr.
[c] 200 V applied potential, 4 hr.
[d] 300 V applied potential, 4 hr.
[e] 80 V applied potential, 5 hr.
[f] 140 V applied potential, 4 hr.

TABLE 2

Separations Actually Achieved on Titanium Tungstate Papers by Electrochromatography

Background electrolyte	Electrical potential applied (V)	Time (hr)	Separations actually achieved
0.5 *M* HNO_3	50	6	Mo^{6+}(0.00)–Cr^{3+}(+4.2) Mo^{6+}(0.00)–Co^{2+}(+4.3) Mo^{6+}(0.00)–V^{4+}(+4.2) Mo^{6+}(0.00)–Ni^{2+}(+2.4) Ag^{+}(0.00)–Pt^{4+}(−1.7) Ru^{3+}(0.00)–Pt^{4+}(−2.4) Au^{3+}(−1.3)–Pt^{4+}(−2.7)
0.2 *M* HCl	50	6	Cd^{2+}(0.00)–Zn^{2+}(+2.7) Cd^{2+}(0.00)–Bi^{3+}(−3.2) Bi^{3+}(−2.8)–Pb^{2+}(0.00) Bi^{3+}(−2.8)–UO_2^{2+}(+1.8) Bi^{3+}(−2.8)–Cu^{2+}(+3.3) Bi^{3+}(−2.4)–Hg^{2+}(0.00) Bi^{3+}(−2.6)–Tl^{+}(0.00) Ag^{+}(0.00)–Pt^{4+}(−2.7) Ag^{+}(0.00)–Pd^{2+}(−3.7)
0.2 *M* HCl + 0.1 *M* KCl (1:1)	100	5	Cu^{2+}(+2.8)–Cd^{2+}(−0.7)–Bi^{3+}(−2.8) Ir^{4+}(+3.3)–Ru^{3+}(+1.1) Cd^{2+}(+2.0)–Zn^{2+}(+8.0) Ag^{+}(0.00)–Tl^{+}(−2.1)
0.2 *M* HCl + 0.2 *M* NaCl (1:1)	100	4	Pd^{2+}(−6.0)–Ru^{3+}(0.00) Ag^{+}(0.00)–Cu^{2+}(+2.0)–Au^{3+}(−2.4) Pd^{2+}(−4.0)–Pt^{4+}(0.00)–Ir^{4+}(+1.6) Hg^{2+}(−4.5)–Cd^{2+}(+2.5)–Zn^{2+}(+4.8)
0.2 *M* HCl + 0.2 *M* NH_4Cl (1:1)	100	4	Ga^{3+}(+4.5)–In^{3+}(+1.7) La^{3+}(+4.5)–Ce^{4+}(0.00)
0.16 *M* HNO_3 + 0.2 *M* NH_4NO_3 (1:1)	100	4	Hg_2^{2+}(0.00)–Hg^{2+}(−2.4) Ga^{3+}(−1.4)–Tl^{+}(+0.5)
0.1 *M* $NaNO_3$	200	3	Mg^{2+}(+3.2)–Be^{2+}(+0.3) Mg^{2+}(+4.0)–Ba^{2+}(+0.7) Mg^{2+}(+3.9)–Al^{3+}(+0.5) Mg^{2+}(+2.9)–Sr^{2+}(+0.5)

TABLE 3

Separation of One Cation from Numerous Metal Ions on Titanium Tungstate Papers by Electrochromatography

Ions	Background electrolytes	Interfering ions	Electrical potential applied (V)	Time (hr)
Mo^{6+}(0.00) from 27 cations	0.5 *M* Nitric acid	Hg_2^{2+}, Bi^{3+}, As^{3+}, Sb^{3+}, Sn^{2+}, Sn^{4+}, Mn^{2+}, Zr^{4+}, Se^{4+}, Te^{4+}, Hf^{4+}, Nb^{5+}, Ru^{3+}, Pd^{2+}	50	6
Bi^{3+}(−1.7) from 38 cations	0.2 *M* Hydrochloric acid	Au^{3+}, Pd^{2+}, Nb^{5+}	50	6
Cu^{2+}(+3.1) from 35 cations	0.2 *M* Hydrochloric acid + 0.1 *M* potassium chloride (1:1)	Fe^{2+}, Fe^{3+}, La^{3+}, Ir^{4+}, Ga^{3+}, In^{3+}, Se^{4+}	100	5
Hg^{2+}(−8.0) from 45 cations	0.2 *M* Hydrochloric acid + 0.2 *M* sodium chloride (1:1)	Pd^{2+}	100	4
Au^{3+}(−3.8) from 41 cations	0.2 *M* Nitric acid + 0.1 *M* sodium nitrate (1:1)	Pt^{4+}	200	4
Pd^{2+}(−8.7) from 43 cations	0.1 *M* Sodium nitrite	V^{4+}	200	3
Mg^{2+}(−4.8)	0.2 *M* Sodium nitrite + 0.2 *M* sodium acetate (1:1)	K^+	100	4

appeared probable, and mixtures containing possible interfering metal ions have been tested. The results are summarized in Table 3. A comparison of the electrochromatographic behavior of some metal ions on Whatman No. 1 and impregnated papers is shown in Table 4.

For the quantitative separation of magnesium and palladium from numerous metal ions of common interest, binary mixtures containing known amounts of magnesium or palladium along with other cation of interest were prepared. Electrochromatography was then performed, and magnesium and palladium were eluted by the methods described

TABLE 4

Comparison of Electrochromatographic Behavior of Some Metal Ions on Whatman No. 1 and Titanium Tungstate Papers

Cations	Background electrolyte	Whatman No. 1 papers	Titanium tungstate papers
Mo^{6+}	0.5 *M* NHO_3	0.00	0.00
Bi^{3+}	0.2 *M* HCl	−1.3	−1.7
Cu^{2+}	0.2 *M* HCl + 0.1 *M* KCl (1:1)	+2.1	+3.1
Hg^{2+}	0.2 *M* HCl + 0.2 *M* NaCl (1:1)	+3.7	−8.0
Au^{3+}	0.2 *M* HNO_3 + 0.1 *M* $NaNO_3$ (1:1)	−4.0	−3.8
Pd^{2+}	0.1 *M* $NaNO_2$	−0.5	−8.7
Mg^{2+}	0.1 *M* $NaNO_2$	0.00	+4.2

earlier. They were determined spectrophotometrically as usual and the results are summarized in Tables 5 and 6.

Separation of magnesium and palladium was also performed quantitatively in synthetic mixtures containing the cations that commonly interfere with these metals. For magnesium, the following two mixtures

TABLE 5

Quantitative Separation of Magnesium in Binary Mixtures

Sample No.	Mixture	Amount of Mg applied (μg)	Amount of Mg found (μg)	% Error
1	Mg–Al	99	94	−5
2	Mg–Be	99	94	−5
3	Mg–Be	99	101	+2
4	Mg–Sr	99	94	−5
5	Mg–Ba	99	101	+2
6	Mg–Ba	99	101	+2
7	Mg–Mn	99	95	−5
8	Mg–Mn	99	101	+2
9	Mg–Al	198	185	−6.5
10	Mg–Be	198	194	−2

TABLE 6

Quantitative Separation of Palladium in Binary Mixtures

Sample No.	Mixture	Amount of Pd applied (μg)	Amount of Pd found (μg)	% Error
1	Pd–Ni	100	102.5	+2.5
2	Pd–Ni	100	95	−5
3	Pd–As	100	95	−5
4	Pd–As	100	100	0.00
5	Pd–Mg	100	100	0.00
6	Pd–Mg	100	95	−5
7	Pd–Mn	100	95	−5
8	Pd–Mn	100	100	0.00
9	Pd–Hg	100	100	0.00
10	Pd–Hg	100	102.5	+2.5
11	Pd–Cu	100	100	0.00
12	Pd–Cu	100	95	−5
13	Pd–Co	100	102.5	+2.5
14	Pd–Co	100	100	0.00
15	Pd–Fe	100	95	−5
16	Pd–Fe	100	102.5	+2.5
17	Pd–Ru	100	102.5	+2.5
18	Pd–Ru	100	102.5	+2.5
19	Pd–Ga	100	102.5	+2.5
20	Pd–Ga	100	102.5	+2.5

TABLE 7

Quantitative Separation of Magnesium from Synthetic Mixture

Sample No.	Amount of Mg applied (μg)	Amount of Mg found (μg)	% Error
1	99	105	+5
2	99	105	+5
3	99	101	+2
4	99	90	+9
5	99	101	+2
6	198	202	+2
7	198	224	+13
8	198	212	+7
9	198	192	−3
10	198	192	−3

TABLE 8

Quantitative Separation of Palladium from Synthetic Mixture

Sample No.	Amount of Pd applied (μg)	Amount of Pd found (μg)	% Error
1	100	100	0.00
2	100	100	0.00
3	100	100	0.00
4	100	102.5	+2.5
5	100	100	0.00
6	100	102.5	+2.5
7	100	95	−5

were prepared by mixing 1 ml of each of the cation solutions containing 10,000 μg: (a) Cd^{2+}, Sn^{4+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Zn^{2+}, Ba^{2+}, Sr^{2+}, Be^{2+}, and Cr^{3+}; and (b) Ni^{2+}, Co^{2+}, As^{3+}, Hg^{2+}, V^{4+}, In^{3+}, Ga^{3+}, Cu^{2+}, and Pd^{2+}. These mixtures and the standard magnesium solution (10,000 ppm Mg) were mixed in the volume ratio 1:1 and this mixture was applied on the paper strips with the aid of a lambda pipet (20 to 40 λ). For palladium, 1 ml of each of the solutions of the following cations (10,000 ppm cation in each case) were mixed: Cu^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Fe^{3+}, Ga^{3+}, Ru^{3+}, Mg^{2+}, and As^{3+}. This mixture and the standard palladium solution (10,000 ppm Pd) were again mixed in the volume ratio 1:1. This was applied with the aid of a lambda pipet (20 λ) as in the case of magnesium. The results of these determinations are summarized in Tables 7 and 8.

DISCUSSION

Electrochromatographic studies on the papers impregnated with titanium tungstate have revealed interesting results which are summarized in Table 1A and 1B. Important binary and ternary separations achieved on these papers are given in Table 2. The separations of Mo^{6+}, Bi^{3+}, Cu^{2+}, Hg^{2+}, Au^{3+}, Pd^{2+}, and Mg^{2+} from numerous metal ions in corresponding background electrolytes are given in Table 3. The separation of Hg^{2+} from numerous metal ions in 0.2 *M* HCl + 0.2 *M* NaCl (1:1) is probably due to the formation of a negativelv charged chloride complex $(HgCl_4)^{2-}$ and Pd^{2+} in 0.1 *M* $NaNO_2$ due to the strong affinity of palladium for nitrite. In both cases migration on titanium tungstate papers is greater compared to the migration on plain Whatman No. 1 papers. The separation of Au^{3+} from numerous metal ions in 0.2 *M* HNO_3 + 0.1 *M* $NaNO_3$ is probably due to the formation of $Au(NO_3)_4^-$. The results of electrochromatographic migration of important metal ions on plain Whatman No. 1 papers are given in Table 4 for comparison. It is clear from this table that the migration of metal ions on plain and on ion exchange papers differs. Therefore, not only the nature of the background electrolyte but also the ion exchange paper are responsible for cleaner and faster separation on these papers.

To remove magnesium from the paper, we first tried oxidizing the paper strips with the mixture HNO_3:$HClO_4$:H_2SO_4. In this case the titanium tungstate gel, being insoluble, adsorbed the color of the solution developed with Titan Yellow. This reduced the intensity of the color. Elution was therefore made by heating the paper strips with 10% HCl.

In this case also some of the titanium tungstate dissolved from the paper and interfered in the spectrophotometry of magnesium. Finally, 5% HCl proved to be an ideal eluting solvent in which the problem mentioned above did not arise. Palladium was an altogether different case. The oxidation method did not work because of the reason discussed above. When the paper strips were allowed to dry after the electrochromatography, the spot of palladium which was yellow on the wet strip turned black due to the reduction of palladium to its metallic state by sodium nitrite which was used as an electrolyte. Palladium could not, therefore, be taken out by elution with HCl. To avoid this problem, palladium was eluted from the wet paper with 40 ml of 10% HCl, and it was found that elution was fast and quantitative even in the cold.

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REFERENCES

1. G. Alberti, *Chromatogr. Rev.*, **8**, 246 (1966).
2. M. Qureshi, *Fifth International Symposium on Chromatography and Electrophoresis*, Brussels, 1968, p. 197.

3. M. Qureshi and S. Z. Qureshi, *J. Chromatogr.*, **22**, 198 (1966).
4. M. Qureshi, I. Akhtar, and K. N. Mathur, *Anal. Chem.*, **39**, 1766 (1967).
5. M. Qureshi and K. N. Mathur, *Anal. Chim. Acta*, **41**, 560 (1968).
6. M. Qureshi and W. Husain, *Separ. Sci.*, **4**, 197 (1969).
7. M. Qureshi and A. H. Israili, *Anal. Chim. Acta*, **41**, 523 (1968).
8. G. Alberti, A. Conte, G. Grassini, and M. Lederer, *J. Electroanal. Chem.*, **4**, 301 (1962).
9. Ying-Bo-Hai, *Acta Chim. Sinica*, **31**, 263 (1965).
10. M. Qureshi and J. P. Gupta, *J. Chem. Soc., A*, **1969**, 1755.
11. H. A. J. Pieters, W. J. Hanssen, and J. J. Geurts, *Anal. Chim. Acta*, **2**, 241 (1948).
12. J. G. Fraser, F. E. Beamish, and W. A. E. McBryde, *Anal. Chem.*, **26**, 495 (1954).

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