

Note

Separation of selenate, selenite, tellurate and tellurite by means of isotachopheresis

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Isotachopheresis (ITP) is a relatively new method for the separation and determination of various anions and cations¹. It is a powerful technique for analyzing not only simple organic samples² but also biochemical samples³. We have already shown the utility of ITP for the separation of metal cations using complex-forming and ion-pairing equilibria^{4–6}.

However, there have been few studies of inorganic anions, except for the common anions such as chloride, sulphate, nitrate, phosphate, etc. Therefore, we investigated the utility of ITP for analysis of metal oxo anions which may undergo polymerization in solution at low pH, using ion-pairing equilibria⁷.

The purpose of the present study was to investigate a rapid and simple method for the separation and determination of another group of oxo anions, selenate, selenite, tellurate and tellurite by means of ITP. The effect of the pH of the leading electrolyte and the kind of counter ion on the effective mobilities and the separable range of the above four anions were also examined.

EXPERIMENTAL

All reagent grade chemicals were used without further purification. The sodium salts of selenate, selenite and tellurite were purchased from Wako Pure Chemicals (Osaka, Japan) and sodium tellurate were obtained from Kanto Chemical Co. (Tokyo, Japan). The stock solutions were prepared by dissolving the sodium salts in twice distilled water, and a standard solution containing all four ions were made by mixing the individual stock solutions. The leading and terminal electrolyte systems are shown in Table I. The apparatus was as described previously⁷.

RESULTS AND DISCUSSION

All experiments were carried out at a high pH in the leading electrolyte, because selenite, tellurate and tellurite ions are weak acids with low effective mobilities at low pH. The PR values of the weak acids increased with increasing pH of the leading electrolyte owing to their dissociation into more negatively charged ions, as shown in Fig. 1. The PR value represents the ratio of the potential gradient of the leading ion zone to that of the sample ion zone⁸. Selenate is so strong an acid that its PR value scarcely changes.

TABLE I
LEADING AND TERMINATING ELECTROLYTE SYSTEMS

Leading electrolyte*	pH	Driving current (μA)
(1) 0.01 M Cl^- + Tris	7.0–8.5	100
(2) 0.01 M Cl^- + NH_3	9.0–10.0	125
(3) 0.01 M Cl^- + NH_3 + additive**	10.0	125
Terminating electrolyte		
(4) 0.01 M TES*** + Tris	7.5	
(5) 0.01 M β -Alanine + $Ba(OH)_2$	11.0	

* 0.025% Poly(vinyl alcohol) (PVA) was added.

** 2 mM $Ni(phen)_3^{2+}$ or $Co(en)_3^{3+}$ were added as ion-pairing reagents.

*** N-Tris(hydroxymethyl)methyl-2-aminoethanesulphonic acid.

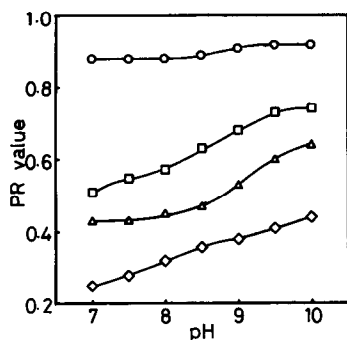


Fig. 1. Effect of pH of the leading electrolyte on the PR values of SeO_4^{2-} (○—○), SeO_3^{2-} (□—□), TeO_3^{2-} (△—△) and TeO_4^{2-} (◇—◇). Conditions as in Table I.

To obtain a sufficient separation of the four anions it was preferable to use the ion-pairing equilibria between the nickel(II)–1,10-phenanthroline, $Ni(phen)_3^{2+}$, or cobalt(III)–ethylenediamine, $Co(en)_3^{3+}$, complexes and the anions, with which the separable range was expanded from 5 to 8.8 nmol. Other 1,10-phenanthroline complexes, e.g., of Fe(II), Co(II), Cu(II), were not useful for this determination.

The effective mobilities of the anions, particularly of selenate and selenite, decreased with increasing concentration of cobalt(III)–ethylenediamine complex in the leading electrolyte, as shown in Fig. 2. However, they were approximately constant with increasing concentration of nickel(II)–1,10-phenanthroline complex in the leading electrolyte. It is seen from Fig. 2 that the PR values of the anions were influenced by the charge of the counter ion, especially in the cases of selenate and selenite. Typical isotachopherograms are shown in Fig. 3. When the concentration of cobalt(III)–ethylenediamine complex was 2 mM in the leading electrolyte, selenite and tellurite ions underwent “enforced” isotachophoretic migration. This phenomenon may be attributed to the “u inversion” migration mode⁹. Selenate, selenite, tellurite and tellurate were separated in this order by means of isotachopheresis using

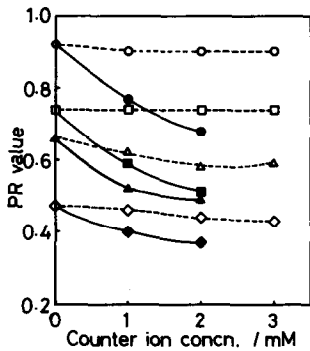


Fig. 2. Effect of counter ion on the PR values of SeO_4^{2-} (○, ●), SeO_3^{2-} (□, ■), TeO_3^{2-} (△, ▲) and TeO_4^{2-} (◇, ◆). Counter ions: $\text{Ni}(\text{phen})_3^{2+}$ (broken line); $\text{Co}(\text{en})_3^{3+}$ (solid line).

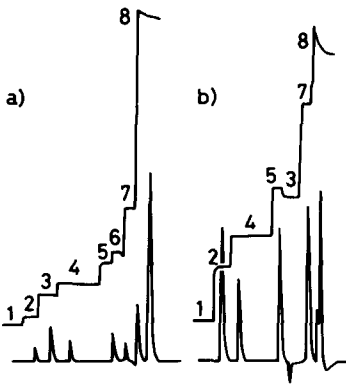


Fig. 3. Isotachopherograms of selenate, selenite, tellurate and tellurite in the presence of 2 mM $\text{Ni}(\text{phen})_3^{2+}$ (a), and 2 mM $\text{Co}(\text{en})_3^{3+}$ (b). Leading electrolyte: 0.01 M Cl^- , NH_3 , pH 10.0, 0.025% PVA. Migration current: 125 μA . Sample: 4 μl of a mixed solution, $1.3 \cdot 10^{-3}$ M. Zones: 1 = Cl^- ; 2 = SeO_4^{2-} ; 3 = SeO_3^{2-} ; 4 = CO_3^{2-} ; 5 = TeO_3^{2-} ; 6 = HCO_3^- ; 7 = TeO_4^{2-} ; 8 = β -alanine.

ion-pairing equilibria between the metal complex and the anions. The analysis time was about 15 min.

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