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Suppressed ion chromatography of inorganic anions and divalent metal cations with pyromellitic acid as eluent

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Abstract

Suppressed conductimetric detection ion chromatography (IC) using pyromellitate eluent was investigated for the simultaneous determination of common inorganic anions and divalent cations. When pyromellitate and sample anions (Cl⁻, NO₃⁻ and SO₄²⁻) in the eluent were introduced into a cation-exchange membrane suppressor in the H⁺ form after anion-exchange separation, pyromellitate and the anions were converted to pyromellitic acid and corresponding acids (HCl, HNO₃ and H₂SO₄), respectively. Since these acids are stronger than pyromellitic acid (pK_{a1} =1.92), these acids were detected conductimetrically as an increase of the concentration of H⁺ in the eluent. In contrast, divalent cation–pyromellitate complexes (Mg²⁺ –, Ca²⁺ –, Sr²⁺ –, Ba²⁺ –, Fe²⁺ –, Mn²⁺ –, Co²⁺ –, Ni²⁺ –, Zn²⁺ – and Cd²⁺ –pyromellitate complexes) were converted to pyromellitic acid by the suppressor and these divalent cations were detected as an increase of the concentration of pyromellitate eluent at pH 5.4 and a 25-cm anion-exchange column (TSKguardgel QAE-SW), both highly sensitive conductimetric detection and excellent simultaneous separation of inorganic anions (Cl⁻, NO₃⁻, I⁻, SCN⁻, SO₄²⁻ and S₂O₃²⁻) and divalent cations (Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺ and Cd²⁺) were achieved in 30 min. The detection limits (*S*/*N*=3; injection volume, 20 µl) for the anions were 0.73–2 µ*M* and those for the divalent cations were 0.21–4.7 µ*M*. © 1998 Elsevier Science B.V.

Keywords: Complexion; Metal cations; Inorganic anions; Organic acids; Pyromellitic acids

1. Introduction

Benzenepolycarboxylates, such as phthalate [1-3], trimellitate (1,2,4-benzenetricarboxylate) [2,4], trimesate (1,3,5-benzenetricarboxylate) [1-3] and pyromellitate (1,2,4,5-benzenetetracarboxylate) [2,3,5] are commonly employed as eluent ions in non-suppressed ion chromatography (IC) for various inorganic anions. Benzenetricarboxylates (trimellitate and trimesate) and benzenetetracarboxylate are exclusively applied to an indirect UV-photometric detection IC. This is due mainly to both the small differences in the conductivity between theses benzenecarboxylates and inorganic anions and their strong UV adsorption. However, recently, in order to expand the utility of benzenecarboxylate in IC, the application of benzenecarboxylate to suppressed conductivity detection IC for anions has been investigated [6,7].

In previous works [8,9], we have found that pyromellitate forms UV-adsorbing complexes with some divalent metal cations and then developed UV-photometric detection IC for the simultaneous determination of inorganic anions and some divalent metal cations. In this work, in order to demonstrate the utility of pyromellitate eluent in IC, the application of pyromellitate eluent to suppressed conductimetric detection IC with a cation-exchange membrane suppressor in the H^+ form was investigated for the simultaneous determination of inorganic anions

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and divalent metal cations. As a result, both highly sensitive conductimetric detection and excellent simultaneous separation were achieved for inorganic anions (Cl⁻, NO₃⁻, I⁻, SCN⁻, SO₄²⁻ and S₂O₃²⁻) and divalent cations (Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺ and Cd²⁺). This result strongly indicates that pyromellitate eluent is very useful not only for UV-photometric detection IC but also suppressed conductimetric detection IC for inorganic anions and divalent metal cations.

2. Experimental

2.1. Ion chromatograph

The ion chromatograph consisted of a Tosoh (Tokyo, Japan) SC-8010 chromatographic data-processor, a Tosoh CCPM eluent delivery pump at 1 ml/min, a Tosoh CCPM regenerant delivery pump at 1 ml/min, a Tosoh SD-8012 on-line degasser, a Tosoh CO-8020 column oven at 35°C, a Tosoh CM-8020 conductimetric detector, a Dionex (Sunnyvale, CA, USA) AMMS-I anion micro membrane suppressor, and a Rheodyne (Cotati, CA, USA) 9125 injector equipped with a 20-µl sample loop.

2.2. Analytical column

A stainless steel analytical column (250×4.6 mm I.D.) packed with a Tosoh TSKguardgel QAE-SW (silica with anion-exchange capacity ca. 0.3 mequiv./ g and particle size ca. 5 μ m) was employed in this study.

2.3. Chemicals

All chemicals were of analytical-reagent grade. Pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) was purchased from Aldrich (Milwaukee, WI, USA) and the other chemicals were purchased from Wako (Osaka, Japan). Distilled deionized water (DIW) was used for the preparation of standard solutions and eluents.

The pH of the pyromellitic acid eluent was adjusted with a 1 *M* NaOH solution.

The regenerant for the AMMS-I was prepared by diluting 1 *M* sulfuric acid with DIW.

3. Results and discussion

3.1. Effect of the eluent pH on retention behavior of inorganic anions and divalent cations

In previous fundamental studies [8,9], we have reported that alkaline earth and divalent transition metal cations (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Cd^{2+}) formed complexes with pyromellitate and the complexes were retained on the anion-exchanger (TSKguardgel QAE-SW) in the IC using pyromellitate eluent. Therefore, in order to achieve the simultaneous separation of inorganic anions, alkaline earth and transition metal cations on the TSKguardgel QAE-SW column, the effect of pH of the 0.15 m*M* pyromellitate eluent on the retention behavior was investigated in detail.

As shown in Fig. 1A, the retention volumes of inorganic anions, except phosphate, decreased with increasing the pH of eluent. This is due to an increase of eluent strength of pyromellitate by promoting the degree of dissociation of pyromellitic acid ($pK_{a1}=1.92$, $pK_{a2}=2.82$, $pK_{a3}=4.49$ and $pK_{a4}=5.64$). The retention volume of phosphate increased at pH>5.5. This is due to an increase of affinity between phosphate and anion-exchanger by promoting the degree of dissociation of phosphoric acid ($pK_{a1}=2.15$, $pK_{a2}=7.20$ and $pK_{a3}=11.75$).

On the other hand, as shown in Fig. 1B, the retention volumes of alkaline earth and transition metal cations increased with increasing the pH of the eluent. The retention behavior of transition metal cations was similar to that of alkaline earth metal cations. The peak shapes of these cations tended to be tailed with increasing the pH of the eluent. Especially, the peak of Zn^{2+} , which disappeared at pH>6, is perhaps due to the peak broadening. This might be because the stability of the divalent cation– pyromellitate complexes increased with increasing the pH of eluent, and thus the complexes formed were strongly retained on the column.

When considering the retention volumes of inorganic anions and divalent cations, the peak shape of



Fig. 1. Effect of pH of eluent on retention volumes of (A) inorganic anions and (B) divalent cations. Column, TSKguardgel QAE-SW; column size, 250×4.6 mm I.D.; column temperature, 35° C; eluent, 0.15 m*M* pyromellitate; flow-rate, 1 ml/min; injection volume, 20 µl; sample concentration: 0.2 m*M* for monovalent anions, 0.15 m*M* for divalent anions and 0.05 m*M* for divalent cations. Symbols: (A) \bullet , PO₄⁻⁷; \bigcirc , Cl⁻⁷; \blacktriangle , NO₂⁻⁷; \triangle , Br⁻⁷; \blacksquare , NO₃⁻⁷; \square , I⁻⁷; \blacklozenge , Mn²⁺; \triangle , Co²⁺; \blacksquare , Ni²⁺; \square , Zn²⁺; \blacklozenge , Cd²⁺.

divalent cations and the chemical stability of the silica-based anion exchanger, the optimum pH of eluent was concluded to be ca. 5.5.

3.2. Effect of pyromellitate concentration on retention behavior of anions and divalent cations

In order to simultaneously separate inorganic anions and divalent cations, the effect of the concentration of pyromellitate in the eluent at pH 5.4 on the retention behavior was investigated.

In conventional ion-exchange chromatography, it is well known that the relationship between the log eluent concentration $(\log[E^{x^{-}}])$ and the log capacity factor $(\log k')$ of solute ion is linear [10];

$$\log k' = -(x/y)\log[\mathrm{E}^{x^{-}}] + C$$

Where x is the charge of the solute ion, y is the charge of eluent ion and C is constant.

As shown in Fig. 2A, the relationships were linear for inorganic anions and the slope values for divalent anions were about twice those of monovalent anions. These results indicated that these inorganic anions were predominantly separated by an anion-exchange mechanism.

On the other hand, as shown in Fig. 2B, the relationships were not linear for all divalent cations. The retention behavior of transition metal cations was similar to that of alkaline earth metal cations. These results strongly suggested that these divalent cation–pyromellitate complexes were not predominantly separated by an anion-exchange mechanism. The details for this retention mechanism will be the subject of future work.

Considering Fig. 2A and B, the optimum eluent concentration for the simultaneous separation of inorganic anions and divalent cations was concluded to be 0.15 mM.

3.3. Effect of H^+ -form suppressor on conductimetric detector response of anions and divalent cations

Fig. 3A and B show the chromatograms of inorganic anions (Cl⁻, NO₃⁻, I⁻, SCN⁻, SO₄²⁻, S₂O₃⁻) and divalent cations (Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺ and Cd²⁺) with and without the





Fig. 2. Effect of concentration of eluent on capacity factors of (A) inorganic anions and (B) divalent cations. Eluent, pyromellitate at pH 5.4; other conditions as in Fig. 1.



Fig. 3. Chromatograms of inorganic anions and divalent cations with (A) and without (B) cation-exchange membrane suppressor in H⁺ form Eluent, 0.15 m*M* pyromellitate at pH 5.4; detection, conductivity; regenerant, 10 m*M* sulfuric acid, 1 ml/min; sample, mixture of 0.05 m*M* CaCl₂, CdCl₂, Co(NO₃)₂, Ni(NO₃)₂, MgSO₄, MnSO₄ and ZnSO₄, 0.15 m*M* Na₂S₂O₃ and 0.2 m*M* KI and KSCN. Peaks: 1, Mg²⁺; 2, Ca²⁺; 3, Cl⁻; 4, Mn²⁺; 5, Co²⁺; 6, NO₃⁻; 7, Ni²⁺; 8, I⁻; 9, Zn²⁺; 10, SO₄²⁻; 11, SCN⁻; 12, Cd²⁺; 13, S₂O₃²⁻. Other conditions as in Fig. 2.

cation-exchange membrane suppressor in the H⁺ form under the optimum eluent conditions (0.15 mM pyromellitate at pH 5.4). The conductimetric detector responses of these anions and divalent cations were drastically enhanced by using the suppressor. As shown in Table 1, the conductimetric detector responses of anionic solutes with pK_{a1} values <2.2

Table 1

Conductimetric detector responses (CDR) and pK_{a1} values of inorganic anions, organic acids and divalent cations under the optimun chromatographic conditions

Solute	CDR	p <i>K</i> _{a1}	Solute	CDR	p <i>K</i> _{a1}
$\overline{\text{CO}_{3}^{2-}}$	(-)	6.35	Formic acid	(-)	3.57
$PO4^{3-}$	(+)	2.15	Acetic acid	(-)	4.76
\mathbf{F}^{-}	(-)	3.17	Propionic acid	(-)	4.87
Cl^{-}	(+)	a	Butyric acid	(-)	4.82
NO^{2-}	(-)	3.22	Valeric acid	(-)	4.86
Br-	(+)	a	Lactic acid	(-)	3.89
NO ³⁻	(+)	a	Benzoic acid	(-)	4.20
I^-	(+)	a	Maleic acid	(+)	1.94
SCN^{-}	(+)	a	Malonic acid	(-)	2.84
SO_4^{2-}	(+)	a	Succinic acid	(-)	4.21
$S_2O_3^{2-}$	(+)	a	Malic acid	(-)	3.46
2 9			Tartaric acid	(-)	3.04
Mg^{2+}	(+)		Phthalic acid	(-)	2.95
Ca ²⁺	(+)		Fumalic acid	(-)	3.02
Sr^{2+}	(+)		Citric acid	(-)	3.13
Ba ²⁺	(+)				
Fe ²⁺	(+)				
Mn ²⁺	(+)		Pyromellitic acid		1.92
Co ²⁺	(+)		•		
Ni ²⁺	(+)				
Zn^{2+}	(+)				
Cd^{2+}	(+)				

^aCompletely dissociated; (-) negative detector response; (+) positive detector response.

were positive (increasing conductivity) and those of anionic solute with pK_{a1} values >2.8 were negative (decreasing conductivity). In contrast, the conductimetric detector responses of all detectable divalent cations were positive. Therefore, the effect of the suppressor on the conductimetric detector responses of anions and divalent cations is discussed in detail.

3.3.1. The detector responses for anionic solutes

When pyromellitate is introduced into the suppressor, pyromellitate is converted to pyromellitic acid and the pH of eluent decreases (e.g. the pH of 0.15 mM pyromellitate eluent after the suppressor is measured to be ca. 3.6).

$$C_6H_2(COOH)_x(COONa)_{4-x} \rightarrow (suppressor-H^+)$$

 $\rightarrow C_6H_4(COOH)_4$

Anionic solutes are also converted to corresponding acids by the suppressor.

 $NaA \rightarrow (suppressor-H^+) \rightarrow HA$

Strong acids are completely dissociated in the eluent, while pyromellitic acid ($pK_{a1} = 1.92$, $pK_{a2} = 2.82$, $pK_{a3} = 4.49$ and $pK_{a4} = 5.64$) and weak acids are partly dissociated. These acids are mainly detected conductimetrically as the change of the concentration of H⁺ with the highest conductivity in the eluent. As for strong acids, due to an increase of the concentration of H⁺, a high and positive conductimetric detector response is obtained. In contrast, as for acids weaker than pyromellitic acid, due to a decrease of the concentration of H⁺, the detector response is negative and the response strongly depends on the differences in the acidity between these acids and pyromellitic acid.

3.3.2. The detector responses of divalent cations

When divalent cation–pyromellitate complexes $(Mg^{2+}-, Ca^{2+}-, Sr^{2+}-, Ba^{2+}-, Cd^{2+}-, Co^{2+}-, Fe^{2+}-, Co^{2+}-, Mn^{2+}-, Ni^{2+}-, and Zn^{2+}-pyromellitate complexes) are introduced into the suppressor, these complexes are converted to pyromellitic acid, and then the concentration of pyromellitic acid in the eluent increases.$

$$M^{2+}$$
-pyromellitate \rightarrow (suppressor- H^+)
 $\rightarrow C_6 H_2$ (COOH)₄

Due to partial dissociation of pyromellitic acid in the eluent, divalent cations are mainly detected conductimetrically as an increase of the concentration of H^+ in the eluent. As a result, a high and positive conductimetric detector response is obtained.

Fig. 4A and B show calibration graphs obtained by plotting peak area against the concentration of strongly acidic anions (Cl⁻, NO₃⁻ and SO₄²⁻) and divalent cations (Mg²⁺, Ca²⁺, Mn²⁺ and Cd²⁺). Linear calibration graphs were obtained at least up to 1 m*M* for these anions and cations. The slope of SO₄²⁻ was ca. twice that of Cl⁻ and NO₃⁻. This means that these anions were mainly detected conductimetrically as their corresponding acid (HCl, HNO₃ and H₂SO₄). As shown in Fig. 4B, the slopes of these divalent cations slightly decreased with increasing the retention volumes. A detailed study of the slight difference will be subject of future work.

Table 2 shows the detection limits with and without the suppressor, as well as by suppressed conductimetric detection IC using a HCO_3^{-}/CO_3^{2-}



Fig. 4. Calibration graphs of (A) inorganic anions and (B) divalent cations. Symbols: (A) \oplus , Cl⁻; \blacktriangle , NO₃⁻; \blacksquare , SO₄²⁻. (B) \oplus , Mg²⁺; \blacklozenge , Ca²⁺; \blacksquare , Mn²⁺; \blacklozenge , Cd²⁺. Chromatographic conditions as in Fig. 3A.

Detection limits (S/N=3) of inorganic anions and divalent cations with (A) and without (B) suppressor using pyromellitate eluent and (C) with suppressor using HCO₃⁻/CO₃²⁻ eluent

Ion	Detection limits (μM)			
	A^{a}	B ^b	C°	
Anion				
PO_4^{3-}	1.5	1.4	1.1	
Cl^{-}	0.73	31	0.38	
NO_2^-	5.3 ^d	43 ^d	0.63	
Br ⁻	0.89	18	0.52	
NO_3^-	0.89	40	0.63	
I _	1.6	25	1.7	
SCN^{-}	2.0	52 ^d	2.0	
SO_4^{2-}	0.82	9.1	0.51	
$S_2O_3^{2-}$	1.1	7.0	0.99	
Cation				
Mg^{2+}	0.27	0.21		
Ca ²⁺	0.34	0.30		
Mn ²⁺	0.49	0.59		
Co ²⁺	0.47	0.59		
Ni ²⁺	1.4	2.2	_	
Zn^{2+}	2.7	4.7	_	
Cd ²⁺	1.3	3.5	_	

^aEluent gackground conductivity, ca. 99 μ S/cm; noise level, 0.0033 μ S/cm.

^bEluent gackground conductivity, ca. 52 μ S/cm; noise level, 0.0019 μ S/cm.

^cEluent, 2 m*M* NaHCO₃–1.6 m*M* Na₂CO₃; column, TSKgel IC-Anion PW; eluent background conductivity, ca. 22 μ S/cm; noise level, 0.0030 μ S/cm.

^dNegative peak response.

eluent for inorganic anions and divalent cations. As shown in Table 2, a highly sensitive conductimetric detection of anions and divalent cations was achieved by the suppressed conductimetric detection IC using pyromellitate eluent.

3.4. Reproducibility

The relative standard deviations of the detector response (peak height) of the anions and divalent cations in Fig. 3A were less than 1.0% (n=8). Reproducible chromatograms were obtained during repeated chromatographic runs.

3.5. Application

The present method was applied to the simultaneous determination of common inorganic anions and divalent cations in acid rain and river water samples. The samples were analyzed after filtration with a 0.45- μ m membrane filter. Fig. 5A and B show typical chromatograms of acid rain and river water samples, respectively. The peak resolution among inorganic anions (Cl⁻, NO₃⁻ and SO₄²⁻) and divalent cations (Mg²⁺ and Ca²⁺) was quite satisfactory.



Fig. 5. Chromatograms of (A) rain and (B) river water samples. Peaks: (concentration, m*M*): (A) 1, Mg^{2+} (0.005); 2, Ca^{2+} (0.005); 3, Cl^{-} (0.060); 4, NO_{3}^{-} (0.007); 5, SO_{4}^{2-} (0.016). (B) 1, Mg^{2+} (0.037); 2, Ca^{2+} (0.21); 3, Cl^{-} (0.16); 4, NO_{3}^{-} (0.021); 5, SO_{4}^{2} (0.14); 6, HCO_{3}^{-} . Chromatographic conditions as in Fig. 3A.

As shown in Fig. 5B, when the river water sample was analyzed, the peak of HCO_3^- appeared and the retention volume was close to that of Ca^{2+} . However, since the conductimetric detector response of Ca^{2+} was above 50 times that of HCO_3^- , it was considered that HCO_3^- caused almost no interference in the determination of Ca^{2+} using the peak height method.

4. Conclusion

In order to enhance the detection sensitivity of inorganic anions and divalent cations by conductimetric detection IC using pyromellitate eluent, the effect of the cation-exchange membrane suppressor in the H^+ form was investigated. By using the suppressor, the conductimetric detection sensitivity of strongly acidic anions and divalent cations was strongly enhanced, and excellent simultaneous separation and highly sensitive conductimetric detection for both inorganic anions and divalent cations were achieved. The result expanded the utility of pyromellitate eluent in IC for the simultaneous determination of inorganic anions and divalent cations.

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