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Use of β-diketonate anions as eluent in non-suppressed ion chromatography

Acetylacetonate eluent for the separation of fluoride and chloride

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ABSTRACT

β-Diketones in aqueous solution exist in different chemical states owing not only to keto–enol tautomerism but also to dissociation equilibria. The use of acetylacetonate anion as the eluent in ion chromatography was effective for the elution of weakly retained anions such as fluoride and chloride. Further, by using the chelate-forming ability of β-diketones, it was found that the influence of metal cations in the sample solution on the ion chromatograms is eliminated.

INTRODUCTION

Non-suppressed ion chromatography (IC) was developed for the separation and determination of various anions [1,2], and has been widely applied to the separation and determination of many kinds of anions and cations by selecting suitable eluent ions [3,4].

Fluoride and chloride anions have been often determined by using non-suppressed IC [3,4]. However, because fluoride, in particular, is weakly retained on the anion-exchange resin, it is necessary to select an eluent with a weak driving strength to separate the fluoride peak from first system (dip) peak. Therefore, two methods can be considered: the use of a low-concentration eluent or the selection of an eluent anion with a weak driving strength. In the former instance, the sample peak is broadened because of the lack of an exchangeable eluent anion for the sample anion on the resin. The latter, however, is suitable, as hydroxide [5] and nicotinate [6] anions are useful eluents.

Further, the baseline level often fluctuates for some time after the injection of sample solutions containing metal cations. Hence it is necessary to remove or mask these metal cations in order to eliminate this phenomenon.

β-Diketones (1,3-diones), which are well known chelating reagents with metal

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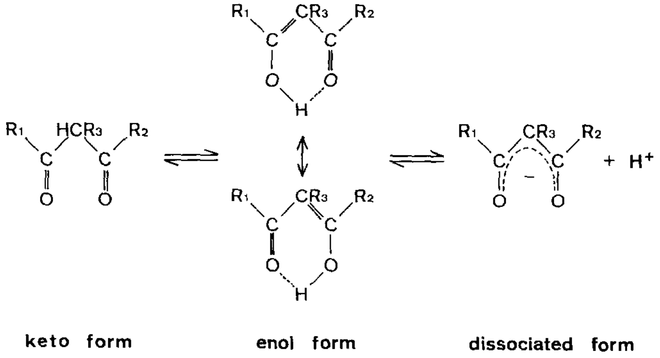
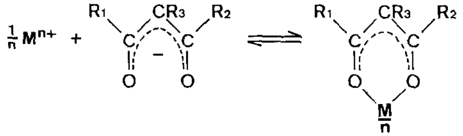
cations [7], exist in different forms owing not only to keto–enol tautomerism but also to dissociation equilibria, as follows:



It was considered that the dissociated from (β-diketonate anion) could be used as an eluent in non-suppressed IC because the driving strength of the enol group is relatively small. Moreover, by changing the side-chains (R_1, R_2 and R_3) of these reagents, one can control the driving strength of the β-diketonate anion in IC.

In addition, β-diketonate anions react with many metal ions, as follows:



Therefore, it is possible to eliminate the influence of metal ions in sample solutions without pretreatment by using β-diketonate anions as the eluent.

In this work, the acetylacetonate anion ($R_1 = R_2 = CH_3$, $R_3 = H$), which is simplest β-diketonate anion, was selected as the eluent and applied to the determination of fluoride and chloride anions.

EXPERIMENTAL

Apparatus

A Tosoh Model HLC-601 ion chromatograph system was used, consisting of a computer-controlled pump, a conductivity detector, a sample injector (100 μl) and an oven. An anion-exchange column (50 mm × 4.6 mm I.D.) packed with Tosoh TSKgel IC-Anion-PW (polymethacrylate gel, capacity 0.03 ± 0.003 mequiv./g) was used for the separation of anions. The flow-rate was maintained at 1.0 ml/min under a pressure of 40–60 kg/cm^2. The separation column and the conductivity detector were placed in an oven regulated at 30°C. The data were recorded with a Shimadzu Chromatopack C-R1A recorder.

Eluents

Acetylacetone (2,4-pentanedione, Hacac, pK_a = 8.99 [8]) was purified by the method of Steinbach and Freiser [9]. A 100-ml volume of analytical-reagent grade

TABLE I

COUNTER CATIONS USED, STABILITY CONSTANTS OF $M(acac)_i^{(n-i)+}$ COMPLEXES AT 25°C [8] AND REAGENTS USED

Cation	Log β_1[a]	Log β_2[a]	Log β_3[a]	Reagent
Li^+	–			LiCl
Na^+	–			NaCl
Mg^{2+}	3.65	6.25		$MgCl_2$
Al^{3+}	8.6[b]	16.5[b]	22.3[b]	$AlCl_3 \cdot 6H_2O$
K^+	–			KCl
Ca^{2+}	–	–		$CaCl_2 \cdot 2H_2O$
Cr^{3+}	–	–	–	$CrCl_3 \cdot 6H_2O$
Mn^{2+}	4.21	7.30		$MnCl_2 \cdot 4H_2O$
Fe^{2+}	5.07[b]	8.67[b]		$FeSO_4 \cdot 7H_2O$
Fe^{3+}	9.8[b]	18.8[b]	26.2[b]	$FeCl_3 \cdot 6H_2O$
Co^{2+}	5.40	9.54		$CoCl_2 \cdot 6H_2O$
Ni^{2+}	6.00	10.60		$NiCl_2$
Cu^{2+}	8.25	15.05		$CuCl_2 \cdot 2H_2O$
Zn^{2+}	5.06	9.00		$ZnCl_2$

[a] $\beta_i = [M(acac)_i^{(n-i)+}]/[M^{n+}][acac^-]^i$ (M^{n+} is the metal ion).
[b] at 30°C.

acetylacetone was shaken with 10 ml of dilute ammonia (1:10) and shaken with two 10-ml portions of distilled water. This solution were distilled at 136°C.

Acetylacetone–sodium hydroxide (sodium acetylacetonate, Naacac) solutions as eluents were prepared by dissolving the purified acetylacetone in distilled water and adding 1 *M* sodium hydroxide solution to control the eluent pH.

Sodium salicylate (NaSa), sodium benzoate (NaBz) and sodium acetate (NaOAc) eluents were prepared by dissolving analytical-reagent grade reagents in distilled water.

All of these eluent solutions were deaerated before use.

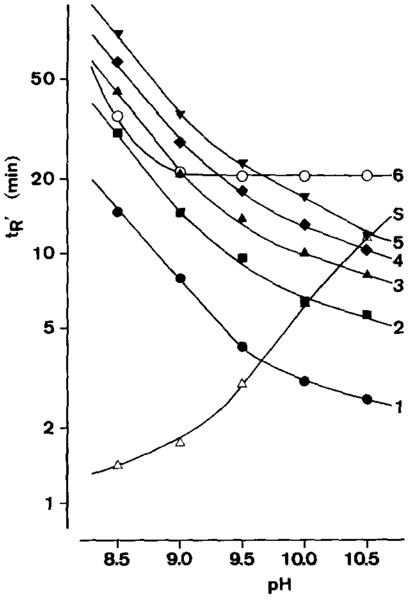
Standard sample solutions

Stock standard solutions of 100 m*M* sodium fluoride, chloride, nitrite, bromide nitrate and carbonate were prepared by from analytical-reagent grade salts. Working standard solutions were obtained by diluting the stock solutions with distilled water.

Counter cations used in the investigation are shown in Table I. Stock standard solutions of 100 mequiv./l of each cation were prepared by from analytical-reagent grade reagents as shown in Table I. Working standard solutions were obtained by diluting the stock solutions with distilled water. The stability constants (β_i) of metal complexes with $acac^-$ are given in Table I [8].

River water

As an example of an application, river-water samples collected from the Otada river and the Muko river (both in Nishinomiya City, Hyogo, Japan) on May 2nd, 1990, were used after filtration through a 0.2-μm Millipore filter.



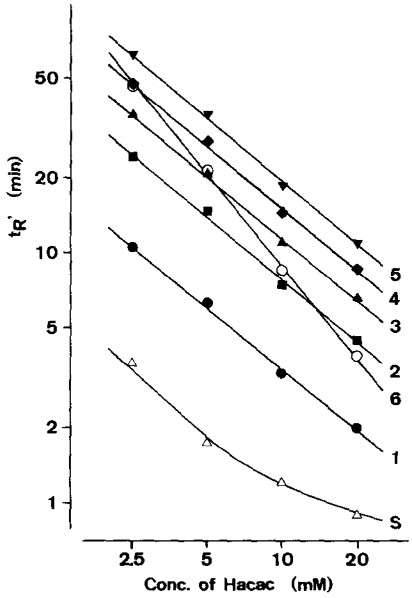


Fig. 1. Relationship between retention times (t'_R) of anions and eluent pH. Sample: 1 = fluoride; 2 = chloride; 3 = nitrite; 4 = bromide; 5 = nitrate; 6 = carbonate. S = second system peak. Eluent: 5.0 m*M* Hacac–NaOH.

Fig. 2. Relationship between retention times and concentration of Hacac. Sample: 1 = fluoride; 2 = chloride; 3 = nitrite; 4 = bromide; 5 = nitrate; 6 = carbonate. S = second system peak. Eluent: Hacac–NaOH (pH 9.0).

RESULTS AND DISCUSSION

Optimum chromatographic conditions

In non-suppressed IC, it is necessary to consider two system (dip) peaks [10], the first being due to the difference in the conductance of the eluent and sample water band, and the latter to the compensation for the first system peak. In order to reduce the errors in quantitative analysis, the selection of optimum chromatographic conditions such that the position of the sample anion peak is separated from those of the system peaks was investigated.

Fig. 1 shows the relationship between the retention times of sample anions and eluent pH at a fixed eluent concentration (5.0 m*M*). With increasing eluent pH, the fluoride peak was eluted rapidly and near to the first system peak, and the second system peak overlapped with several peaks of the sample anions. On the other hand, with decreasing pH, the degree of dissociation of Hacac was decreased and the retention times were increased.

Fig. 2 shows the relationship between the retention times and the concentration of Hacac at a fixed eluent pH (9.0). With decreasing concentration, the retention time increased. On the other hand, with increasing concentration, the fluoride peak was near to the second system peak and the peaks of chloride and carbonate overlapped.

Based on these results, the optimum eluent pH and concentration of Hacac

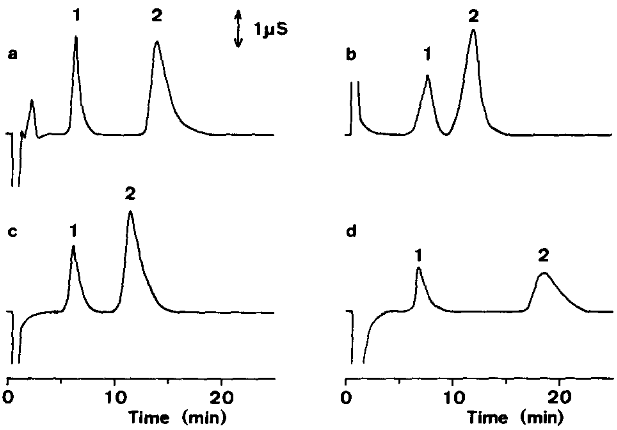


Fig. 3. Ion chromatograms obtained with different eluent anions. Sample: 1 = 0.5 m*M* (9.5 μg/ml) fluoride; 2 = 0.5 m*M* (17.8 μg/ml) chloride. Eluent: (a) 5.0 m*M* Hacac–NaOH (pH 9.0); (b) 0.5 m*M* NaSa (pH 6.2); (c) 1.5 m*M* NaBz (pH 6.5); (d) 5.0 m*M* NaOAc (pH 7.7).

were selected as 9.0 and 5.0 m*M*, respectively. Under these optimum conditions, the detection limits (signal-to-noise ratio = 2) of fluoride and chloride were 1.2 μ*M* (23 ng/ml) and 1.5 μ*M* (55 ng/ml), respectively.

Comparison between elution behaviour of Naacac and other eluents

Fig. 3 shows ion chromatograms of fluoride and chloride obtained using several eluents having similar driving strengths, and Table II gives data for the elution behaviour of fluoride.

As the driving strength of Sa^- is high, the concentration has to be low for the separation of the fluoride peak and the first system peak. Therefore, leading of the peak shape occurred owing to the lack of an exchangeable eluent anion for the sample anion on the resin, and the values of the plate number (N) and symmetry (S) became worse.

Bz^- has suitable driving strength for the elution of fluoride. However, the peak was broadened and the N value became poorer because of some interaction between Bz^- and the resin.

TABLE II

COMPARISON OF ELUTION BEHAVIOUR WITH DIFFERENT ELUENTS

Sample: 0.5 m*M* (9.5 μg/ml) fluoride.

Eluent	Retention time, t'_R (min)	Plate number, N	Symmetry, S	Peak area[a], Y
5.0 m*M* Naacac (pH 9.0)	6.09	412	1.11	1.70
0.5 m*M* NaSa (pH 6.2)	7.39	203	0.52	1.55
1.5 m*M* NaBz (pH 6.5)	5.77	212	1.67	1.52
5.0 m*M* NaOAc (pH 7.7)	6.30	255	2.00	1.00

[a] Relative value with Y(NaOAc) = 1.

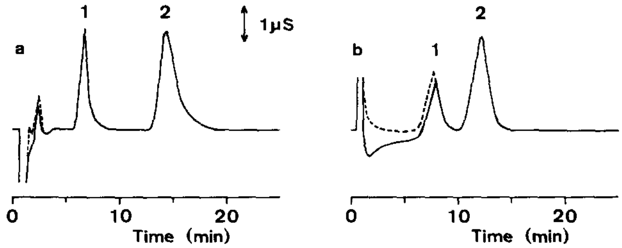


Fig. 4. Ion chromatograms obtained with iron (III) cation present in the sample. Sample: 1 = 0.5 m*M* (9.5 μg/ml) fluoride; 2 = 0.5 m*M* (17.8 μg/ml) chloride. Cations: solid lines, 0.5 m*M* Na^+ and 0.17 m*M* (0.5 mequiv./1) Fe^{3+}; dashed lines, 1.0 m*M* Na^+. Eluent: (a) 5.0 m*M* Hacac–NaOH (pH 9.0); (b) 0.5 m*M* NaSa (pH 6.2).

AcO^- has a low driving strength and can be used at high concentrations as an eluent. However, because the driving strength is too low, tailing occurred on the fluoride peak and the *N* and *S* values became worse. Moreover, the peak area (*Y*) of fluoride became small because the AcO^- anion has a relativley high conductivity.

Finally, $acac^-$ was found to be suitable as an eluent with regard to *N*, *S* and *Y* values. This result seems to be due to the following reasons: (1) $acac^-$ has suitable driving strength for the separation of fluoride and the first system peak (referring to N); (2) uncharged Hacac was adsorbed on the resin and suppressed the interaction between charged $acac^-$ and the resin (referring to *S*); and (3) the conductivity of $acac^-$ is suitable for the detection of fluoride (referring to *Y*).

TABLE III

COMPARISON OF THE DEVIATION OF THE BASELINE ON CHROMATOGRAM CAUSED BY METAL CATIONS IN THE SAMPLE WITH SEVERAL ELUENTS

Sample: 0.5 m*M* (9.5 μg/ml) fluoride and 0.5 m*M* (17.8 μg/ml) chloride [or 0.25 m*M* (24.0 μg/ml) sulphate]. Cation: 0.5 m*M* Na^+ and 0.5 mequiv./l metal cation.

Cation	Deviation (ratio to peak height of 0.5 m*M* F^-, %)			
	5.0 m*M* Naacac (pH 9.0)	0.5 m*M* NaSa (pH 6.2)	1.5 m*M* NaBz (pH 6.5)	5.0 m*M* NaOAc (pH 7.7)
Li^+	0.0	0.0	−0.5	−0.8
Na^+	0.0	0.0	−0.5	−0.8
Mg^{2+}	−6.8	0.0	+4.7	−4.9
Al^{3+}	0.0	−8.1	−6.3	−0.8
K^+	0.0	0.0	−0.5	−0.8
Ca^{2+}	0.0	+2.5	+6.8	−20.3
Cr^{3+}	0.0	−3.1	−5.3	+4.1
Mn^{2+}	−13.9	+1.9	+10.5	−13.8
Fe^{2+}	0.0	−5.0	−1.1	−7.3
Fe^{3+}	+0.3	−9.3	−4.7	−7.3
Co^{2+}	−0.7	+0.6	+7.4	−17.1
Ni^{2+}	−0.7	0.0	+2.6	−3.3
Cu^{2+}	0.0	−4.3	−4.7	0.0
Zn^{2+}	−1.1	−8.1	−4.7	−9.8

Hence it was concluded that acac$^-$ is the preferred eluent for the separation and determination of fluoride and chloride anions.

Comparison between the influence of metal cations in the sample on Naacac and other eluents

Fig. 4 shows chromatograms of fluoride and chloride in the presence of Fe^{3+} in the sample with Naacac and NaSa eluents. With NaSa as eluent, Fe^{3+} influenced the baseline and the fluoride peak. In contrast, with Naacac as eluent, Fe^{3+} did not interfere.

Table III shows the influences of fourteen metal cations in the sample on the baselines of chromatograms obtained with the use of four eluents. With three eluents (not Naacac), several cations influenced the baselines. On the other hand, with Naacac as eluent, only Mg^{2+} and Mn^{2+}, which have relatively low stability constants of their complexes with acac$^-$ (see Table I [8]), influenced the baselines. It was concluded that most of the metal cations form acac chelates and elute rapidly from the column, and that acac$^-$ is the preferred eluent for eliminating the influence of metal cations in the sample.

Application to river-water samples

The Otada river, a branch stream of the Muko river, contains relatively large amounts of fluoride and calcium owing to the presence of biotite granite, in which calcium fluoride is enriched [11,12]. To evaluate this method, fluoride and chloride were measured in several samples collected from the two rivers. The results, shown in Table IV, were compared with those given in a previous paper [11].

It has been speculated that high concentrations of chloride in samples 6–9 and

TABLE IV

CONCENTRATIONS OF FLUORIDE AND CHLORIDE ANIONS IN THE OTADA AND MUKO RIVERS

River	Sample No.	Previous paper [11]		This method	
		F$^-$ (μg/ml)[a]	Cl$^-$ (μg/ml)[b]	F$^-$ (μg/ml)	Cl$^-$ (μg/ml)
Otada	1	1.89	4.6	1.30	3.81
	2	0.96	5.6	1.17	5.58
	3	1.05	8.9	1.40	9.45
	3	1.78	2.9		
	5	2.46	4.8		
	6			2.03	114
	7	1.66	142		
	8			1.64	65.1
	9	2.25	640	1.70	154
	10	2.18	3.2	1.49	3.26
	11	1.58	160		
Muko	12			0.22	44.1
	13			0.52	41.7

[a] Direct photometric method with lanthanum–alizarin complexone chelate [13].

[b] Mercury(II) thiocyanate method.

11 (Otada river) are caused by mineral spring water located at the river side [11,12], and that samples 12 and 13 (Muko river) are contaminated by domestic sewage. The present results agreed approximately with those obtained previously [11] and hence this ion chromatographic method seems very useful for the determination of fluoride and chloride in natural water samples containing metal cations without pretreatment of the sample solution or intricate handling.

CONCLUSION

The use of acac$^-$ as the eluent has been shown to be useful for the separation and determination of fluoride and chloride, which are retained very weakly on anion-exchange resins. This eluent has a relatively low driving strength and was very effective for separating the fluoride peak from the first (or second) system peak. Fluoride and chloride were measured with relatively high sensitivities by using this eluent. Further, because acac$^-$ is a very effective chelating reagent, it successfully eliminated the influence of metal cations in the sample solution on the baseline of the chromatogram. In addition, Hacac is a very weak acid ($pK_a = 8.99$ [8]) and it is considered that Hacac–NaOH solution can also be used as the eluent in suppressed IC.

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