



ELSEVIER

Journal of Chromatography A, 707 (1995) 384–389

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Use of β -diketonate anions as eluent in non-suppressed ion chromatography: 1,3-cyclohexanedionate as acidic eluent

Naoki Hirayama^{1,*}, Masahiro Maruo², Akinobu Shiota³, Tooru Kuwamoto⁴

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

First received 3 January 1995; revised manuscript received 7 March 1995; accepted 7 March 1995

Abstract

A new low- pK_a β -diketonate eluent for non-suppressed ion chromatography was developed for suppressing the dissociation of impurity anions without impairing the separation and determination of fluoride and chloride anions. It was found that 1,3-cyclohexanedionate is the preferred eluent, having a low pK_a originating from the structural strain of the β -diketonate group.

1. Introduction

Non-suppressed ion chromatography (IC) was developed as an effective method for the separation and determination of several anions [1,2]. This method has been improved by the development of new eluent ions [3,4] with superior elution characteristics.

We previously reported the separation and determination of fluoride and chloride anions, which are retained weakly on the anion-exchange resin, by using acetylacetonate as the eluent [5]. This compound is very suitable for the above-mentioned purpose because of its relatively low driving strength and high selectivities of monovalent inorganic anions. However, it is desirable that the pH of the eluent should be relatively low in order to suppress the dissociation of impurity anions, such as carbonate and organic anions. For this purpose, the development of a new β -diketonate eluent having a low pK_a value and characteristics similar to those of acetylacetonate is needed.

From this standpoint, we investigated two low- pK_a β -diketonate eluents: trifluoroacetylacetonate and 1,3-cyclohexanedionate. It was found that 1,3-cyclohexanedionate is the preferred elu-

* Corresponding author.

¹ Present address: Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920-11, Japan.

² Present address: Department of Ecosystem Studies, School of Environmental Science, The University of Shiga Prefecture, Hikone 522, Japan.

³ Present address: Seian Women's High School, Kamigyo-ku, Kyoto 602, Japan.

⁴ Present address: Hiroshima Jogakuin College, Higashi-ku, Hiroshima 732, Japan.

ent anion for the separation and determination of fluoride and chloride anions at relatively low pH in the anion-exchange column used.

2. Experimental

2.1. Apparatus

A Tosoh Model HLC-601 ion chromatograph system was used, consisting of a computer-controlled pump, a conductivity detector, a sample injector (100 μ l) and an oven. An anion-exchange column (50 mm \times 4.6 mm I.D.) packed with Tosoh TSKgel IC-Anion-PW (poly-methacrylate 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/cm². 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 instrument.

2.2. Eluents

Acetylacetone (2,4-pentanedione, Hacac; $pK_a = 8.99$ [6]) was purified by a previously reported method [5,7]. A 100-ml portion of analytical-reagent grade acetylacetone was shaken with 10 ml of dilute ammonia (1 + 10) and shaken with two 10-ml portions of distilled water. This solution was distilled at 136°C.

Trifluoroacetylacetone (1,1,1-trifluoropentane-2,4-dione, H·TFA; $pK_a = 6.09$ [8]) was purified by the method of Matsubara and Kuwamoto [9] to remove highly acidic impurities. A 10-ml portion of analytical-reagent grade trifluoroacetylacetone was refluxed in the presence of 1 g of disodium hydrogenphosphate and distilled at 107°C.

1,3-Cyclohexanedione (dihydroresorcinol, H·CHD; $pK_a = 5.26$ [6]) was purified by dissolving analytical-reagent grade 1,3-cyclohexanedione in chloroform and recrystallizing the reagent by adding benzene.

β -Diketone–sodium hydroxide solutions as eluents were prepared by dissolving the purified

β -diketones in distilled water and adding 1 M sodium hydroxide solution to adjust the eluent pH.

Sodium benzoate ($pK_a = 4.202$ [6]) and sodium acetate ($pK_a = 4.757$ [6]) eluents were prepared by dissolving the analytical-reagent grade salts in distilled water. Trifluoroacetic acid ($pK_a = 0.50$ [8]), resorcinol (*m*-dihydroxybenzene; $pK_{a_1} = 9.44$, $pK_{a_2} = 12.32$ [8]) and phenol ($pK_a = 9.98$ [6]) were dissolved in distilled water and used as eluents; the pH of these solutions was adjusted with 1 M sodium hydroxide solution.

All of these eluent solutions were deaerated before use.

2.3. Standard sample solutions

Stock standard solutions of 100 mM sodium fluoride ($pK_a = 3.17$ [6]), sodium chloride, sodium nitrite ($pK_a = 3.15$ [6]), sodium bromide, sodium nitrate and sodium carbonate ($pK_{a_1} = 6.35$, $pK_{a_2} = 10.33$ [6]) were prepared by dissolving the analytical-reagent grade salts in water. Working standard solutions were obtained by diluting the stock standard solutions with distilled water.

For the investigation of the effect of counter cations in the sample, several solutions of metal chloride salts (the same as those used in the previous study [5]) were used.

3. Results and discussion

3.1. Selectivities of monovalent sample anions

Ion chromatography is used to separate many kinds of anions in common sample solutions. Therefore, the selectivities of the sample anions are very important factors for the selection of the eluent anion.

The low pK_a of TFA⁻ originates from the change in the charge distribution in the β -diketone group caused by the substitution of fluorine atoms, which are electron-withdrawing, for the three hydrogen atoms of acac⁻. In contrast, the

low pK_a of CHD^- originates from the structural strain of the group caused by cyclization. These structural differences suggested possible differences in the anion selectivities between these two eluents.

Table 1 shows the selectivities of inorganic monovalent anions with several β -diketonates and other organic eluents. These values hardly changed by varying the eluent concentration and pH and, therefore, it is conceivable that these values reflect the characteristics of the eluent anions.

One of the merits of using an acac^- eluent is the relatively high selectivities of monovalent anions. The values were much better than for those obtained with a benzoate eluent. The selectivities were slightly worse than those observed using an acetate eluent, but the acac^- eluent is more effective because of the sensitivities [5]. Therefore, for practical use, it is desirable that the low- pK_a β -diketonate eluent has similar selectivities to the acac^- eluent.

From the decrease in the selectivities with a TFA^- eluent compared with an acac^- , which was similar to that with a trifluoroacetate eluent compared with an acetate, it was suggested that a design of a new eluent by fluorination is not suitable. On using CHD^- eluent, in contrast, the selectivities were almost the same as those with

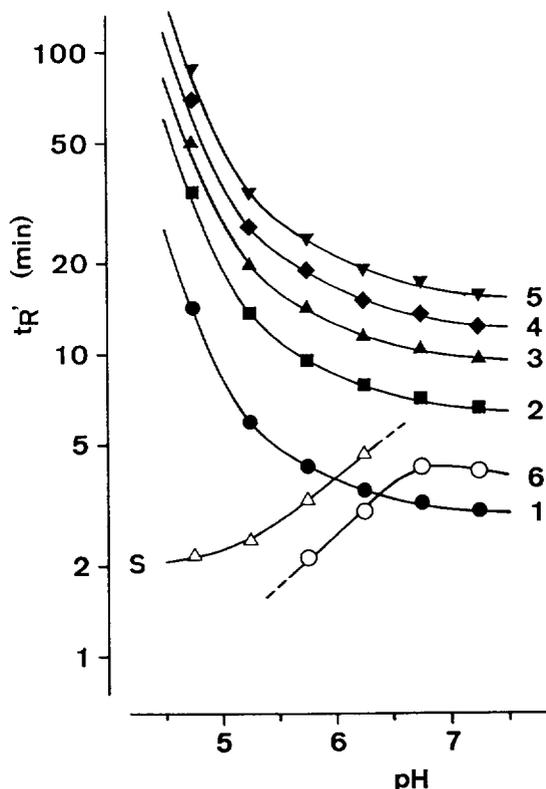


Fig. 1. Relationship between the retention times of anions and the eluent pH. Sample: 1 = fluoride; 2 = chloride; 3 = nitrite; 4 = bromide; 5 = nitrate; 6 = carbonate. S = second system peak. Eluent: 5.0 mM $\text{H} \cdot \text{CHD}^- \text{NaOH}$.

Table 1
Selectivities of monovalent anions

Eluent anion	Concentration (mM)	pH	A = Cl^- , B = F^-	A = NO_2^- , B = Cl^-	A = Br^- , B = NO_2^-	A = NO_3^- , B = Br^-
acac	5.0	9.00	2.33	1.45	1.32	1.28
TFA	5.0	6.09	1.79	1.29	1.23	1.19
CHD	5.0	5.26	2.32	1.46	1.32	1.30
Benzoate	2.5	6.80	1.81	1.30	1.26	1.20
Acetate	10.0	7.45	2.65	1.63	1.28	1.34
Trifluoroacetate	1.0	5.50	1.90	1.35	1.28	1.21
Resorcinolate	5.0	9.44	1.73	1.31	1.21	1.20
Phenolate	5.0	9.98	1.72	1.29	1.22	1.19

Selectivity: $\alpha(\text{A}, \text{B}) = t'_R(\text{A})/t'_R(\text{B}) [=k'(\text{A})/k'(\text{B})]$.

acac⁻ eluent and it was found that the design of a low-pH eluent by cyclization is very useful.

In addition, the use of a resorcinolate eluent resulted in very similar selectivities to those with a phenolate eluent rather than CHD⁻. It was also concluded that the characteristic of the β -diketonate as eluent anion is maintained by the existence of the keto-form structure.

From the above, we selected the CHD⁻ anion as the preferred eluent for the separation and determination of fluoride, chloride and other monovalent anions in low-pH solutions.

3.2. Optimum chromatographic conditions

Fig. 1 shows the relationship between the retention times of sample anions and the eluent pH at a fixed eluent concentration (5.0 mM). With increasing eluent pH, the peaks of monovalent anions were eluted rapidly. However, at high pH, a second system peak [10], which corresponds to the peak of CHD⁻ itself, or the peak of monovalent carbonate anion was overlapped with the peak of fluoride by increasing the ratios of charged carbonate species. On the other hand, with decreasing pH, the concentration of CHD⁻ as an eluent anion was decreased and the retention times were increased.

Fig. 2 shows the relationship between the retention times and the concentration of H·CHD at a fixed eluent pH (5.26). With decreasing concentration, the retention time was increased. On the other hand, with increasing the concentration, the peak of the fluoride anion overlapped with second system peak.

For convenience, possible interactions between pH and concentration effects were assumed to be negligible; the optimum eluent pH and concentration of H·CHD were chosen as 5.26 and 5.0 mM, respectively. At this optimum condition, the detection limits ($S/N = 2$) of fluoride and chloride were 1.2 μM (23 ng/ml) and 0.8 μM (29 ng/ml), respectively, which were slightly better than those on acac⁻ eluent, 1.2 μM (23 ng/ml) and 1.5 μM (55 ng/ml) [5], respectively.

Fig. 3 shows the ion chromatograms of fluoride and chloride anions under the optimum

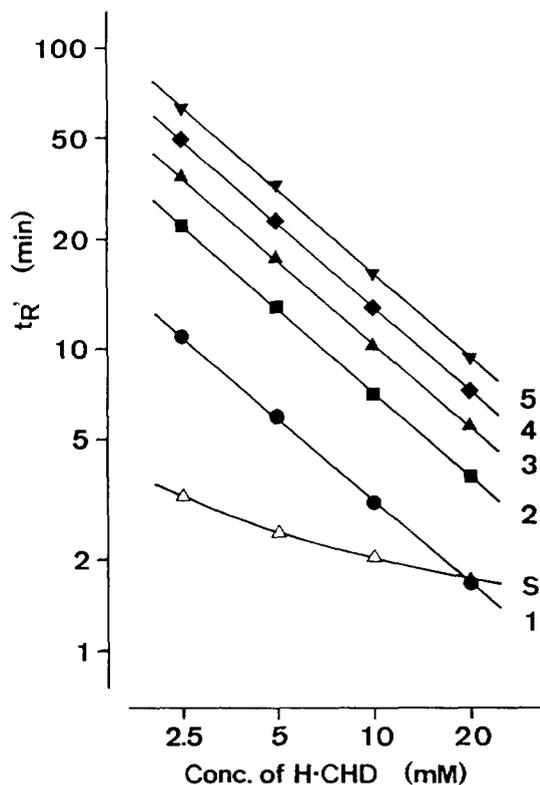


Fig. 2. Relationship between the retention times and the concentration of H·CHD. Sample: 1 = fluoride; 2 = chloride; 3 = nitrite; 4 = bromide; 5 = nitrate. S = second system peak. Eluent: H·CHD–NaOH (pH 5.26).

conditions with the acac⁻ and CHD⁻ eluents. These elution behaviours were very similar to each other.

3.3. Comparison of the influences of metal cations in the sample with acac⁻ and CHD⁻ eluents

It is well known that β -diketones form chelate compounds with many kinds of metal cations [11]. In a previous study [5], we investigated the elimination of the fluctuation of the baseline level in the chromatogram by metal cations in the sample by calculating the ratio of the deviation at the front of the peak of F⁻ (0.5 mM) to the peak height. It was found that an acac⁻

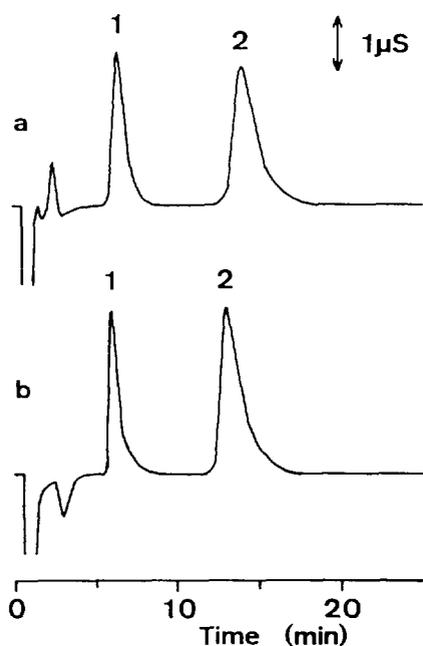


Fig. 3. Ion chromatograms with β -diketonate eluents. Sample: 1 = 0.5 mM (9.5 μ g/ml) fluoride; 2 = 0.5 mM (17.8 μ g/ml) chloride. Eluent: (a) 5.0 mM Hacac-NaOH (pH 9.00); (b) 5.0 mM H·CHD-NaOH (pH 5.26).

eluent has this eliminating ability except for the case when Mg^{2+} or Mn^{2+} is present.

CHD⁻ does not have a chelating strength like acac⁻ because of the structural strain in the β -diketonate group caused by the six-membered ring. Therefore, it is considered that the eliminating ability of a CHD⁻ eluent is relatively low.

Table 2 shows the influences of fourteen metal cations in a sample on the baselines of the chromatograms using an acetate eluent [5], an acac⁻ eluent [5] and a CHD⁻ eluent. In general, the values of the deviation on CHD⁻ were larger than those on acac⁻. However, the values were all less than 5% except for Zn^{2+} . In addition, the shapes of first and second system peaks were hardly changed by the co-existence of the metal cations. From this result, it was considered that a CHD⁻ eluent can eliminate sufficiently the fluctuation of the baseline level by metal cations, in spite of its relatively weak masking ability. Further, it is remarkable that the values of the deviation for Mg^{2+} and Mn^{2+} with the CHD⁻ eluent were much smaller than those with the acac⁻ eluent.

Table 2

Comparison of the deviation of the baseline on the chromatogram caused by metal cations in the sample with β -diketonate eluents

Cation	Deviation: ratio to peak height of 0.5 mM F (%) , n = 3		
	5.0 mM NaOAc ^a (pH 7.70) [5]	5.0 mM Hacac-NaOH (pH 9.00) [5]	5.0 mM H·CHD-NaOH (pH 5.26)
Li ⁺	-0.8	0.0	0.0
Na ⁺	-0.8	0.0	0.0
Mg ²⁺	-4.9	-6.8	0.0
Al ³⁺	-0.8	0.0	+0.2
K ⁺	-0.8	0.0	0.0
Ca ²⁺	-20.3	0.0	+2.8
Cr ³⁺	+4.1	0.0	-1.4
Mn ²⁺	-13.8	-13.9	+2.2
Fe ²⁺	-7.3	0.0	+0.6
Fe ³⁺	-7.3	+0.3	0.0
Co ²⁺	-17.1	-0.7	+3.0
Ni ²⁺	-3.3	-0.7	+4.6
Cu ²⁺	0.0	0.0	-0.5
Zn ²⁺	-9.8	-1.1	+5.5

Sample: 0.5 mM (9.5 μ g/ml) fluoride and 0.5 mM (17.8 μ g/ml) chloride [or 0.25 mM (24.0 μ g/ml) sulfate]. Cation: 0.5 mM Na⁺ and 0.5 mequiv./l metal cation.

^a Sodium acetate.

4. Conclusions

We investigated the use of a CHD^- eluent at relatively low pH for the separation and determination of fluoride and chloride, which are retained very weakly on an anion-exchange resin. A CHD^- eluent has very similar characteristics to an acac^- eluent. Fluoride and chloride were measured with high sensitivities by using this eluent. Further, the CHD^- eluent reduces fluctuations in the baseline of the chromatograms caused by metal cations in the sample.

References

- [1] D.T. Gjerde, J.S. Fritz and G. Schmuckler, *J. Chromatogr.*, 186 (1979) 509.
- [2] D.T. Gjerde, G. Schmuckler and J.S. Fritz, *J. Chromatogr.*, 187 (1980) 35.
- [3] J.G. Tarter (Editor), *Ion Chromatography*, Marcel Dekker, New York, 1987.
- [4] D.T. Gjerde and J.S. Fritz, *Ion Chromatography*, Hüthig, Heidelberg, 2nd ed., 1987.
- [5] N. Hirayama, M. Maruo, A. Shiota and T. Kuwamoto, *J. Chromatogr.*, 523 (1990) 257.
- [6] S. Kotrlý and L. Šůcha, *Handbook of Chemical Equilibria in Analytical Chemistry*, Ellis Horwood, Chichester, 1985.
- [7] J.F. Steinbach and H. Freiser, *Anal. Chem.*, 25 (1953) 881.
- [8] J.A. Dean (Editor), *Lange's Handbook of Chemistry*, McGraw-Hill, New York, 13th ed., 1985.
- [9] N. Matsubara and T. Kuwamoto, *Anal. Chim. Acta*, 161 (1984) 101.
- [10] T. Okada and T. Kuwamoto, *Anal. Chem.*, 56 (1984) 2073.
- [11] R.C. Mehrotra, R. Bohra and D.P. Gaur, *Metal β -Diketonates and Allied Derivatives*, Academic Press, London, 1978.