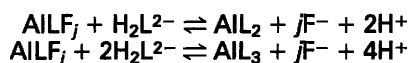


Tiron as a Masking Reagent for Aluminium in the Determination of Fluoride With an Ion-selective Electrode: Equilibrium Studies and Application

Akio Yuchi, Naoki Yanai, Hiroko Wada and Genkichi Nakagawa

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

Equilibria between aluminium fluoro complexes and Tiron (sodium 1,2-dihydroxybenzene-3,5-disulphonate; $\text{Na}_2\text{H}_2\text{L}$) were studied. Formation of the mixed ligand complexes of AlF_j ($j = 1$ or 2) defines the interference by aluminium in the determination of fluoride with ion-selective electrodes using Tiron as a masking reagent.

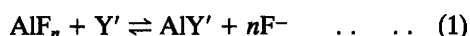


The second and even the third Tiron can react with these mixed ligand complexes to liberate fluoride together with two to four protons. Hence higher recoveries of fluoride are obtained at higher pH with a higher concentration of Tiron. At pH 6, 0.1 mol dm^{-3} Tiron solution has a tolerance limit of around 10^{-3} mol dm^{-3} of aluminium, and is superior to the corresponding solution of citrate or CDTA in releasing fluoride from aluminium. Tiron was applied to the analysis of crude cryolite and fluorspar after decomposition of the samples with aluminium chloride solution.

Keywords: Fluoride determination; ion-selective electrode; aluminium masking; mixed ligand complexes; Tiron

The determination of fluoride with ion-selective electrodes is a simple and convenient method and is widely used. However, aluminium causes serious interference in this determination owing to complexation with fluoride ion. To overcome this effect, addition of masking reagents has been preferred over prior separation because of its simplicity. Various complexing reagents, such as citrate,¹ phosphoric acid,² EDTA,³ CDTA,⁴ hydroxide ion,⁵ triethanolamine,⁶ sulphosalicylic acid,⁷ Tiron (sodium 1,2-dihydroxybenzene-3,5-disulphonate)⁸ and aluminium (triammonium aurinetricarboxylate),⁹ have been proposed, depending on the sample. The combined use of masking reagents has also been recommended.^{3,6,7,10} The performances of these masking reagents have been evaluated from various points of view, *viz.*, masking ability, detection limit of the electrode, reproducibility of the potential and response time.¹⁻²¹ In an earlier paper,⁸ we compared the masking abilities of several complexing reagents experimentally, and recommended Tiron as a highly effective masking reagent for aluminium. However, other groups later reported conflicting results.^{17,19-21}

For samples containing an excess of aluminium over fluoride, a masking reagent with high ability to release fluoride is necessary. The masking abilities have been discussed in terms of the following equilibrium^{15,16,18,19}:



where Y = masking reagent (hereafter charges of complexes are omitted for clarity), that is, masking reagents react with aluminium fluoro complexes to liberate fluoride. If this were the case, ligands with a higher conditional stability constant (K') should be more effective. Among the masking reagents commonly used, however, citrate is superior in terms of masking ability despite having the smallest conditional stability constant for its aluminium complex ($\log K' = 12.1$ for EDTA, 13.2 for CDTA and 10.5 for citrate at pH 6). Moreover, the actual recoveries of fluoride are much lower than those expected from equation (1).¹⁵

Recently we have studied the complexation equilibria between aluminium, fluoride and these three masking

reagents and found that mixed ligand complexes, AlYF_j , are formed and that the extent of the formation of the species governs the interference by aluminium in the determination of fluoride with the masking reagents.²²

In this work, we studied the equilibria between aluminium, fluoride and Tiron ($\text{Na}_2\text{H}_2\text{L}$) or catechol (H_2L), and determined their masking abilities. Tiron was successfully applied to the analysis of crude cryolite and fluorspar.

Experimental

Reagents

Potassium nitrate was recrystallised twice. Other reagents, including Tiron, were of analytical-reagent grade and were used as received.

Aluminium stock solution, 0.01 mol dm^{-3} . Prepared by dissolving the nitrate nonahydrate in 0.01 mol dm^{-3} nitric acid; the concentration was standardised by back-titration of excess of EDTA with standard copper(II) solution against 1-(2-pyridylazo)-2-naphthol indicator.²³

Potassium fluoride solution, 0.01 mol dm^{-3} . Prepared from the reagent dried for 24 h at 110 °C and stored in polyethylene containers.

Potassium hydroxide solution, 0.1 mol dm^{-3} . Prepared as described previously.²⁴

Aluminium chloride solution, 2.5%. Prepared by dissolving 2.5 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 100 cm^3 of 0.01 mol dm^{-3} hydrochloric acid.

Procedure

Equilibrium studies

The equipment used was the same as that described previously.^{22,25} The protonation constant of Tiron and the stability constants of its aluminium complexes were determined by conventional pH titrations. For measurement in ternary systems, series of solutions containing 10^{-3} mol dm^{-3} of aluminium, 10^{-2} mol dm^{-3} of Tiron or 10^{-1} mol dm^{-3} of catechol and various amounts of fluoride were prepared. The

Table 1. Equilibrium constants in Al-L and Al-L-F⁻ systems at 25°C and at 0.1 mol dm⁻³ of KNO₃

System	Equilibrium	Log(equilibrium constant)	
		L = Tiron	L = catechol
Al-L	$[\text{AIL}][\text{H}^+]^2/[\text{Al}][\text{H}_2\text{L}^{2-}]$	-3.11 ± 0.04 (-3.6)*	$(-6.08)^\dagger$
	$[\text{AIL}_2][\text{H}^+]^2/[\text{AIL}][\text{H}_2\text{L}^{2-}]$	-6.26 ± 0.09 (-6.7)	(-9.18)
	$[\text{AIL}_3][\text{H}^+]^2/[\text{AIL}_2][\text{H}_2\text{L}^{2-}]$	-9.9 ± 0.2 (-10.6)	(-13.52)
	$[\text{AHL}_2]/[\text{AIL}_2][\text{H}^+]$		(6.03)
Al-L-F ⁻	$[\text{AHL}_3]/[\text{AIL}_3][\text{H}^+]$		(8.01)
	$[\text{AIF}]/[\text{AIL}][\text{F}^-]$	4.92 ± 0.07	5.13 ± 0.07
	$[\text{AIF}_2]/[\text{AIF}][\text{F}^-]$	3.54 ± 0.07	2.9 ± 0.1

* Recalculated from the constants in reference 27 with protonation constants of $10^{12.6}$ and $10^{7.7}$.

† Reference 28.

pH was adjusted to the desired value and the ionic strength was kept at 0.1 mol dm⁻³ with potassium nitrate. After standing overnight, $-\log[\text{H}^+]$ and $-\log[\text{F}^-]$ were measured.

Analysis of cryolite and fluorspar²⁶

A 10-mg amount of powdered sample (100 mesh) was placed in a 100-cm³ round-bottomed flask and aluminium chloride solution was added so that the molar ratio of aluminium to fluoride would be slightly higher than 1. The solution was refluxed gently for 30 min by attaching a condenser. After adjustment to pH 2 with 1 + 1 hydrochloric acid and dilution to 250 cm³, a 5-cm³ aliquot was placed in a 50-cm³ calibrated flask, 10 cm³ of 0.5 mol dm⁻³ Tiron solution were added, the pH was adjusted to 6 with ammonia solution and the solution was made up to volume with water. To this solution, a 0.1–0.5-cm³ aliquot of 10⁻² mol dm⁻³ standard fluoride solution was added and the potential was measured after each addition. The content of fluoride was determined using a Gran plot.

Results and Discussion

Equilibrium Studies

Protonation constants

At pH lower than 6, H₂L²⁻ is the main species of Tiron in solution. The second protonation constant, $K_2 = [\text{H}_2\text{L}^{2-}]/[\text{HL}^{3-}][\text{H}^+]$, was determined potentiometrically to be $10^{7.62}$, which was in good agreement with the value of $10^{7.66}$ reported by Havelková and Bartušek.²⁷ The corresponding constant for catechol ($10^{9.22}$) was taken from the literature.²⁸

Complexation of aluminium with Tiron

The complex formation of aluminium with Tiron is expressed as follows:



The equilibrium constants were determined by pH titration of solutions containing various amounts of aluminium and Tiron and the results are given in Table 1. The protonated complexes, AHL₂ and AHL₃, which are found in the Al-catechol system,²⁸ are not formed in the Al-Tiron system, probably because of the lower basicity of Tiron than catechol (see above).

Formation of the mixed ligand complexes

The distribution of each species in the Al-Tiron system was calculated with the constants obtained above and is shown as a function of $-\log[\text{H}^+]$ in Fig. 1(a). The reactions of these species with fluoride ion were studied at the various $-\log[\text{H}^+]$ values indicated by arrows in Fig. 1(a). The average number of fluoride ions bound to aluminium, \bar{n} , is shown as a function of $-\log[\text{F}^-]$ in Fig. 1(b).

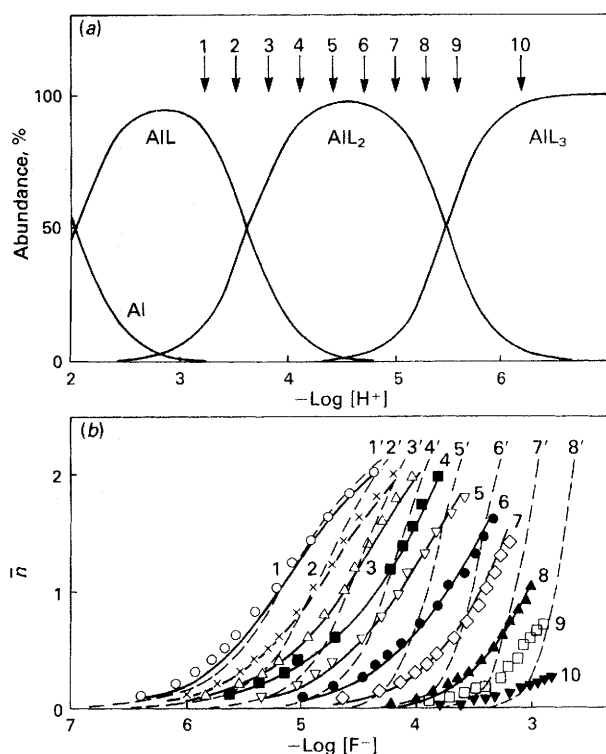


Fig. 1. (a) Distribution of species for Al-Tiron system. $C_{\text{Al}} = 10^{-3}$ mol dm⁻³; $C_{\text{L}} = 10^{-2}$ mol dm⁻³. The numbers 1–10 correspond to the experimental conditions in (b). (b) \bar{n} vs. $-\log[\text{F}^-]$ for the Al-Tiron-F⁻ system. Dotted lines (denoted by primed numbers) were calculated by assuming no mixed ligand complex formation. Solid lines (denoted by unprimed numbers) were calculated with the constants obtained

If there were only AIL_m and AIF_n, the \bar{n} vs. $-\log[\text{F}^-]$ plots would be the dotted lines shown. The considerable deviation of the experimental points from these lines indicates the formation of the mixed ligand complexes. The possibilities of various mixed ligand complexes with the general formula AIL_iF_j participating in the equilibria were examined for citrate, CDTA and EDTA.²²



It was concluded that the 1:1 complex AIL forms mixed ligand complexes AILF and AILF₂, but AIL₂ and AIL₃ do not. The constants obtained in these systems are summarised in Table 1.

Determination of Fluoride in the Presence of Aluminium

In general, the release of fluoride ion from aluminium varies with the masking reagent used, its concentration, pH and the concentrations of fluoride and aluminium.

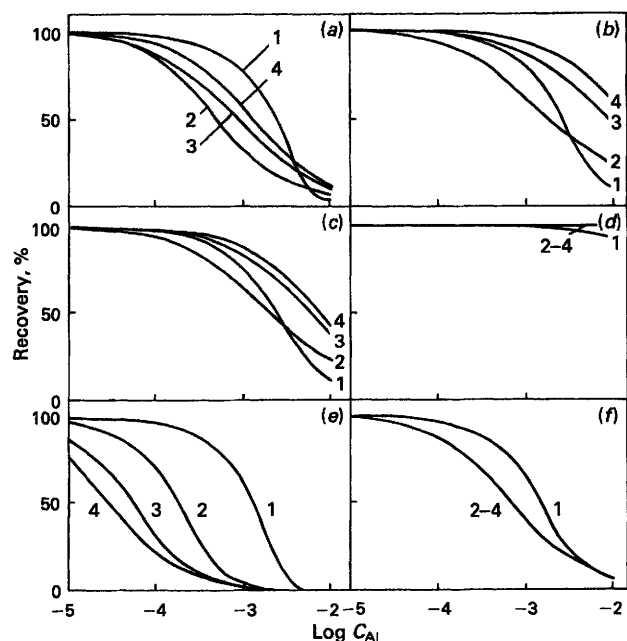


Fig. 2. Calculated recovery of fluoride vs. $\log C_{Al}$ in masking aluminium. C_F : (1) 10^{-2} ; (2) 10^{-3} ; (3) 10^{-4} ; and (4) 10^{-5} mol dm^{-3} . (a) 0.1 mol dm^{-3} citrate, pH 5; (b) 0.1 mol dm^{-3} citrate, pH 6; (c) 0.1 mol dm^{-3} Tiron, pH 5; (d) 0.1 mol dm^{-3} Tiron, pH 6; (e) 0.1 mol dm^{-3} catechol, pH 5; and (f) 0.1 mol dm^{-3} catechol, pH 6

Determination and comparison of masking abilities

Here we consider the analysis of a solution containing fluoride of concentration C_F with a masking reagent of concentration C_L at a certain pH, with a fluoride recovery R in the presence of aluminium of concentration C_{Al} . Such an aluminium concentration can be calculated from the other parameters and the equilibrium constants concerned.

The concentration of free fluoride is given by

$$[F^-] = C_F R \quad \dots \quad (4)$$

The average number of fluoride ions bound to aluminium, \bar{n} , can be calculated using only $[F^-]$, C_L , pH and the equilibrium constants with the equation

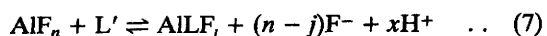
$$\bar{n} = \frac{\sum n[AIF_n] + \sum j[AiLF_j]}{\sum [AIF_n] + \sum [AiLF_j] + \sum [(AIL_m)']} \quad \dots \quad (5)$$

where $(AIL_m)'$ represents protonated and deprotonated species of AIL_m . Then C_{Al} , giving R , is obtained with the following equation, derived from the definition of $\bar{n} = (C_F - [F^-])/C_{Al}$:

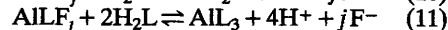
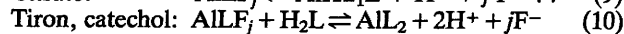
$$C_{Al} = C_F(1 - R)/\bar{n} \quad \dots \quad (6)$$

Fig. 2 shows the relationship between the recoveries of fluoride and the total concentration of aluminium thus calculated for 0.1 mol dm^{-3} of citrate, Tiron and catechol at pH 5 and 6.

When an excess of a masking reagent such as CDTA, EDTA, citrate or Tiron is added to a solution containing aluminium and fluoride, the following reaction proceeds completely to the right with $n-j$ fluoride ions liberated at C_F less than 10^{-3} mol dm^{-3} :



Therefore, the recovery of fluoride in the determination with an ion-selective electrode is governed by the release of fluoride from the resulting mixed ligand complexes.



With CDTA or EDTA, AiL is in equilibrium with $AiLF$ as given by equation (8). This equilibrium shifts more to the right for CDTA than for EDTA, as expected from a comparison of the stability constants of the mixed ligand complexes, $AiLF$.²² Hence CDTA is more effective than EDTA, but in some instances it is not sufficient. Higher concentrations of these reagents do not improve their masking ability.

With citrate, on the other hand, the deprotonated species $AiH_{-j}L$ ($AiH_{-j}L$ denotes the species further deprotonated from AiL irrespective of its structure, where L is the triply charged anion of citrate²⁸) is in equilibrium with $AiLF_j$ as in equation (9), and higher recoveries are expected at higher pH. An increase in citrate concentration slightly improves the recoveries over those expected from equation (9).¹⁷

With Tiron or catechol, fluoride ions are expelled from the mixed ligand complexes by the formation of AiL_2 and AiL_3 [equations (10) and (11)], so higher recoveries are obtained with increasing Tiron concentration. The masking abilities are enhanced with an increase in pH more markedly than with citrate, as two to four protons are released on complexation as shown by equations (10) and (11). The conflicting results obtained with Tiron may be due to experiments being performed at different pH; Tanikawa *et al.* at pH 6 and 8,⁸ Kauranen at pH 5,¹⁷ Nicholson and Duff at pH 5.4,²⁰ Ballczo and Sager¹⁹ and Sager²¹ at pH 6.5. The behaviour of catechol is similar to that of Tiron, but it is less effective. Equations (7), (10) and (11) shift less to the right for catechol, because the stability constants of $AiLF_j$ are almost the same whereas those of AiL_2 and AiL_3 are smaller by 10^3 compared with Tiron. As shown in Fig. 2, Tiron is the most effective at pH 6 of the masking reagents examined.

Dynamic range and response time

It has been observed that the presence of citrate, acetate or phosphate causes a premature departure from a linear response at lower concentration levels.^{1,10,11} With Tiron, on the other hand, the dynamic range is extended to as low as $10^{-5.5}$ mol dm^{-3} , which is comparable to that achieved without any masking reagents. The detection limit of the electrode is in principle governed by the dissolution of the LaF_3 membrane, which will be enhanced by complexation of the lanthanum ion. As the stability of the lanthanum complex with Tiron is low under these conditions, the dissolution is not affected as much in this system.

The response of the ion-selective electrode in Tiron solution is relatively fast (less than 5 min) if the electrode is conditioned with a standard solution containing Tiron. When the electrodes are used continuously in Tiron solution for a long period, the standard potential decreases slightly, *e.g.*, by 1 mV after 4 h. This effect can be avoided by measuring the standard potential every hour.

Recoveries of fluoride from artificial samples

Fluoride ion concentrations in artificial samples were determined by direct potentiometry. Some of the results are presented in Table 2.

The recovery is higher with a higher concentration of Tiron (Nos. 2 and 10), and at higher pH (Nos. 4, 6 and 10). In addition, when a sample solution was diluted while keeping the concentration ratio of fluoride to aluminium constant, the recovery became higher (Nos. 1, 2 and 3, or 5, 6 and 7 or 8, 9, 11 and 12). This is because mixed ligand complexes with any masking reagents are more dissociated in a dilute solution as described previously.¹⁵

As a rough guide, the tolerance limit of aluminium is 10^{-3} mol dm^{-3} with $C_L = 0.1$ mol dm^{-3} at pH 6, and 10^{-4} mol dm^{-3} with $C_L = 0.1$ mol dm^{-3} at pH 5.5.

Table 2. Recoveries of fluoride with Tiron used as a masking reagent for aluminium

No.	C_L / mol dm ⁻³	pH	C_{Al} / mol dm ⁻³	C_F / mol dm ⁻³	Recovery, %
1	0.01	6	10 ⁻²	10 ⁻²	3, 3
2			10 ⁻³	10 ⁻³	78, 81, 82
3			10 ⁻⁴	10 ⁻⁴	104, 104
4	0.1	5	10 ⁻³	10 ⁻³	66, 66
5		5.5	10 ⁻²	10 ⁻²	34, 38
6			10 ⁻³	10 ⁻³	88, 89, 89
7			10 ⁻⁴	10 ⁻⁴	103
8		6	10 ⁻¹	10 ⁻²	0.04, 0.06
9			10 ⁻²	10 ⁻³	74, 78
10			10 ⁻³	10 ⁻³	98, 99, 101
11			10 ⁻³	10 ⁻⁴	99, 104
12			10 ⁻³	10 ⁻⁴	101, 106

Table 3. Determination of fluoride in cryolite and fluorspar

Sample	Fluoride, %	
	This work	After steam distillation
Cryolite . . .	52.3, 53.3, 53.4	52.7, 53.0
Fluorspar . .	47.7, 48.3	47.8, 48.1

Determination of fluoride in crude cryolite and fluorspar

Crude cryolite and fluorspar were analysed using a Gran plot after decomposition of the sample with aluminium chloride solution.²⁶ All the points on each plot lay on a straight line. As shown in Table 3, the results were in good agreement with those obtained after steam distillation.

The authors gratefully acknowledge a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 61127007).

References

1. Frant, M. S., and Ross, J. W., *Anal. Chem.*, 1968, **40**, 1169.
2. Baumann, E. W., *Anal. Chim. Acta*, 1968, **42**, 127.

3. Crosby, N. T., Dennis, A. L., and Stevens, J. G., *Analyst*, 1968, **93**, 643.
4. Harwood, J. E., *Water Res.*, 1969, **3**, 273.
5. Oliver, R. T., and Clayton, A. G., *Anal. Chim. Acta*, 1970, **51**, 409.
6. Duff, E. J., and Stuart, J. L., *Talanta*, 1972, **19**, 76.
7. Palmer, T. A., *Talanta*, 1972, **19**, 1141.
8. Tanikawa, S., Kirihara, H., Shiraiishi, N., Nakagawa, G., and Kodama, K., *Anal. Lett.*, 1975, **8**, 879.
9. Tzimou-Tsitouridou, R., Kabasakalis, B., and Alexiades, C. A., *Microchem. J.*, 1985, **32**, 373.
10. Peters, M. A., and Ladd, D. M., *Talanta*, 1971, **18**, 655.
11. Edmond, C. R., *Anal. Chem.*, 1969, **41**, 1327.
12. Ingram, B. L., *Anal. Chem.*, 1970, **42**, 1825.
13. Louw, C. W., and Richards, J. F., *Analyst*, 1972, **97**, 334.
14. Noshiro, M., and Jitsugiri, Y., *Nippon Kagaku Kaishi*, 1972, 350.
15. Shiraiishi, N., Murata, Y., Nakagawa, G., and Kodama, K., *Anal. Lett.*, 1973, **6**, 893.
16. Vickery, B., and Vickery, M. L., *Analyst*, 1976, **101**, 445.
17. Kauranen, P., *Anal. Lett.*, 1977, **10**, 451.
18. Troll, G., Farzaneh, A., and Cammann, K., *Chem. Geol.*, 1977, **20**, 295.
19. Ballczo, H., and Sager, M., *Fresenius Z. Anal. Chem.*, 1979, **298**, 382.
20. Nicholson, K., and Duff, E. J., *Anal. Lett.*, 1981, **14**, 493.
21. Sager, M., *Monatsh. Chem.*, 1987, **118**, 25.
22. Yuchi, A., Ueda, K., Wada, H., and Nakagawa, G., *Anal. Chim. Acta*, 1986, **186**, 313.
23. Murate, S., Nakagawa, G., and Kodama, K., *Bunseki Kagaku*, 1974, **23**, 242.
24. Powell, J. E., and Hiller, M. A., *J. Chem. Educ.*, 1957, **34**, 330.
25. Yuchi, A., Hotta, H., Wada, H., and Nakagawa, G., *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1379.
26. Tanikawa, S., Kirihara, H., Shiraiishi, N., Nakagawa, G., and Kodama, K., *Bunseki Kagaku*, 1975, **24**, 559.
27. Havelková, L., and Bartušek, M., *Collect. Czech. Chem. Commun.*, 1969, **34**, 3722.
28. Motekaitis, R. J., and Martell, A. E., *Inorg. Chem.*, 1984, **23**, 18.

Paper 8/01368C

Received April 6th, 1988

Accepted May 25th, 1988