

Suppression of Interfering Ions in the Analysis of Plants to Determine Fluoride Using the Fluoride Ion Selective Electrode

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Plant ashes may contain sufficient aluminium and/or iron to interfere seriously in the determination of fluoride ions when using the fluoride ion selective electrode. In the presence of these metals the known additions method gave erroneous results, as did that involving the attempted formation of complexes with ethylenediaminetetraacetic acid, disodium salt, or 1,2-cyclohexylenedinitrilotetraacetic acid. Good recoveries of fluoride ion were obtained in the presence of aluminium, iron, magnesium or silicate, using sodium citrate as the complexing agent. The application of the citrate complex method to ashes of commercial tea, high in aluminium and iron, gave recoveries of fluoride ion of greater than 90%.

Plants normally contain less than $10 \mu\text{g g}^{-1}$ of fluoride,¹ but a number are known to accumulate fluoride in their tissues. Some of the latter group biosynthesise organofluorine compounds.² Natural fluoride accumulators occur in the genera *Dichapetalum*,³ *Thea*,⁴ *Gastrolobium*,⁵ *Camellia*,⁶ *Oxylobium*,⁷ *Acacia*⁸ and *Palicourea*.⁹ Plants may also absorb fluoride into their leaves as a result of atmospheric pollution, sometimes with adverse consequences.¹⁰

Until recently, the analysis of plant material to determine fluoride was usually carried out either by the Willard - Winter distillation method,¹¹ or by diffusion of liberated hydrofluoric acid followed by its quantitative determination as the alizarin fluoro-complexonate.¹² With the introduction of the fluoride ion selective electrode, the analysis of plants to determine fluoride has been simplified, and a number of methods involving the use of this electrode have been published.¹³ These methods are not generally suitable for plants that contain substantial amounts of aluminium, iron and silica, which form complexes with fluoride in solution.

Cannon¹⁴ quotes the results of analyses of more than 80 plant species, representing all types of vegetation, showing that the average aluminium content of the plant ashes was $8\ 610 \mu\text{g g}^{-1}$, while the average iron content was $6\ 740 \mu\text{g g}^{-1}$.

Louw and Richards¹⁵ developed a method for the determination of fluoride in sugar cane, using the fluoride ion selective electrode. They expressed the belief that their method could be applied to other types of plant tissues, particularly those which contained high concentrations of aluminium, iron and silica. Louw and Richards did not, however, quote the amounts of these elements present in their samples, and in sugar cane these amounts are known to vary over a wide range, *viz.*, 0.004-0.3% for aluminium, 0.005-0.3% for iron and 1-3% for silicon.¹⁵

A variety of methods have been used to minimise the interference from aluminium, iron and silica when using the fluoride ion selective electrode, and these methods can be divided broadly into two classes, the known additions, or spike, method and the method involving addition of a compound that forms complexes preferentially with interfering elements, thus releasing fluoride ions. We have investigated the application of these methods to the determination of fluoride in plant ashes.

Experimental

The fluoride ion concentrations were determined by use of a Corning fluoride ion selective electrode and a saturated calomel reference electrode connected to a Corning - EEL, Model 12, pH meter. The sample solutions were stirred slowly with a magnetic stirrer and temperature changes were kept to a minimum by placing insulation, consisting of three asbestos mats, between the stirrer motor and the beaker containing the solution under analysis. There was a considerable variation in the time taken to reach equilibrium, those solutions most

dilute in fluoride taking the longest. Equilibrium was considered to be established when there was no change in e.m.f. over 2 min. Standard graphs were prepared from known fluoride ion concentrations introduced into the appropriate buffer solution. All reagents were of analytical-reagent grade.

The concentrations of aluminium and iron in commercial tea ashes were determined according to the methods given in the "Methods of Analysis of the Association of Official Agricultural Chemists."¹⁶ In order to determine their fluoride ion concentration 1-g samples of tea were treated with 10 ml of sodium hydroxide solution (67 g l⁻¹) and heated in nickel crucibles at 110 °C for 24 h. The crucibles were next transferred to a muffle furnace, heated at 500 °C for 2 h and then at 800 °C until the contents had fused. When cool, the fused mixture was dissolved in a mixture of glacial acetic acid (2.5 ml) and water (10 ml). The resulting solution was transferred into a calibrated flask, 5 ml of sodium citrate solution (2.5 M) were added and the solution was made up to 50 ml with water. The pH was adjusted to 8.5 with sodium hydroxide solution (67 g l⁻¹), which was added dropwise. A standard graph was prepared from known concentrations of sodium fluoride in 5 ml of sodium citrate solution (2.5 M), 10 ml of sodium hydroxide solution (67 g l⁻¹) and 2.5 ml of glacial acetic acid, adjusted to pH 8.5 and diluted to 50 ml with water.

The Known Additions Method

The basic work on the known additions or spike method as applied to fluoride ion analysis in solution was done by Baumann.¹⁷ In order to prevent interference by metals that form complexes with fluoride she worked with solutions that were greater than 1 M in orthophosphoric acid and less than 10⁻³ M with respect to fluoride. In solutions of such high acidity most of the fluoride was complexed as hydrofluoric acid, and this acid was not sensed by the electrode.

Baumann showed that under these conditions a consistent proportion of the fluoride ion was complexed as hydrofluoric acid irrespective of the total fluoride ion concentration. She also demonstrated that results obtained by using the known additions method, giving a slope of 59 mV per decade, were comparable with those obtained directly from calibration graphs, which might not have slopes of 59 mV per decade.

In work designed to investigate the equilibria obtaining in aqueous hydrofluoric acid solution, Srinivasan and Rechnitz¹⁸ showed *inter alia* that when the concentration of hydrogen ions was 1.5 × 10⁻¹ M and the fluoride ion concentration varied from 4 × 10⁻³ to 10⁻¹ M a variable proportion of fluoride ion was uncomplexed. Table I has been obtained from data given in Table I of their paper. The difference between Baumann's results and those of Srinivasan and Rechnitz can be attributed to the fact that under Baumann's conditions of high hydrogen ion concentration and low fluoride ion concentration, hydrofluoric acid was the only complex formed in a substantial amount. In Srinivasan and Rechnitz's work, with lower hydrogen ion and higher fluoride ion concentrations, HF₂⁻ was formed to an extent which varied with the total fluoride ion concentration. The equilibria present in aqueous hydrofluoric acid are shown below [equations (2) and (3)].

TABLE I
TOTAL AND FREE FLUORIDE ION CONCENTRATIONS IN AQUEOUS SOLUTIONS OF
HYDROFLUORIC ACID AT CONSTANT HYDROGEN ION CONCENTRATIONS
(IONIC STRENGTH = 1.0 M)
Calculated from Table I of Srinivasan and Rechnitz.¹⁸

Total F ⁻ concentration/M	Free F ⁻ concentration/M	H ⁺ concentration/M	Free F ⁻ , %
4 × 10 ⁻³	3.7 × 10 ⁻⁵	0.15	0.92
8 × 10 ⁻³	6.0 × 10 ⁻⁵	0.15	0.75
2 × 10 ⁻²	2.1 × 10 ⁻⁴	0.15	1.05
4 × 10 ⁻²	4.7 × 10 ⁻⁴	0.15	1.18
6 × 10 ⁻²	8.5 × 10 ⁻⁴	0.15	1.42
8 × 10 ⁻²	1.4 × 10 ⁻³	0.15	1.75
1 × 10 ⁻¹	2.2 × 10 ⁻³	0.15	2.20

A theoretical justification for Baumann's method can be obtained by using equation (1),¹⁹ which gives the results shown in Table II.

$$\sum_0^N \beta_i [L]^i + 1 - \sum_0^N (T_1 - iT_m) \beta_i [L]^i = 0 \quad \dots \quad (1)$$

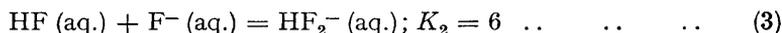
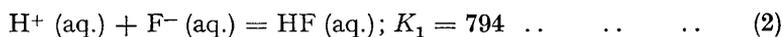
where N is the maximum co-ordination number of the metal (6 in the aluminium - fluoride system), β_i the i th over-all stability constant, $[L]$ the concentration of free ligand, T_1 the total concentration of ligand and T_m the total metal ion concentration.

TABLE II

FREE FLUORIDE ION CONCENTRATION AT 1 M TOTAL HYDROGEN ION CONCENTRATION FOR VARIOUS TOTAL FLUORIDE ION CONCENTRATIONS

Total F ⁻ concentration/M	Free F ⁻ concentration/M	Free F ⁻ , %
10 ⁻⁵	7.2 × 10 ⁻⁹	7.2 × 10 ⁻²
10 ⁻⁴	7.2 × 10 ⁻⁸	7.2 × 10 ⁻²
10 ⁻³	7.2 × 10 ⁻⁷	7.2 × 10 ⁻²

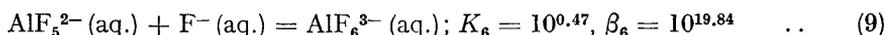
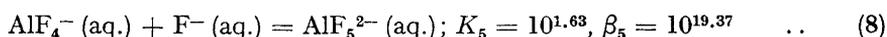
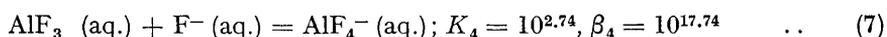
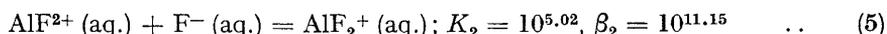
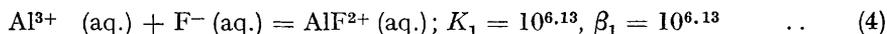
Srinivasan and Rechnitz¹⁸ found the following equilibria and equilibrium constants in aqueous hydrofluoric acid:



The ratio $K_1:K_2 = 132$.

Thus, under conditions where two (or more) successive equilibria are present, a constant proportion of the ligand is present at equilibrium only under certain conditions, *viz.*, a very high concentration of the cation and a very low concentration of the ligand.

For the complexes of aluminium (Al³⁺) with fluoride (F⁻), stepwise (K) and over-all (β) stability constants are as follows²⁰:



Note that $K_1:K_2 = 13$.

In order to appreciate the significance of this information in terms of the complexing of fluoride by aluminium in fluoride ion determinations using the known additions method, we have calculated the theoretical concentration of free fluoride ion in solutions containing aluminium and fluoride, at concentrations that are usual in plant analysis,¹⁴ by use of equation (1). If we assume that the aluminium ion concentration is 10⁻³ M, and that the unspiked solution has a total fluoride ion concentration of 10⁻⁴ M, solution of equation (1) gives a free ligand (F⁻) concentration of 8.2 × 10⁻⁸ M and 99.92% of the fluoride is complexed. If we were now to add a spike of negligible volume, which increased the total [F⁻] to 10⁻³ M, solution of the equation now gives [L] = 3.2 × 10⁻⁶ M and 99.7% of the fluoride is complexed. These results are summarised in Table III.

It is clear that under these conditions the proportion of fluoride ion complexed before and after spiking is not the same and that the spike method will give erroneous results. Because the total fluoride concentration has been increased 10-fold, the more concentrated solution should have a potential 59 mV less than the weaker. When complex formation has occurred, as is shown in Table III, instead of the ratios of free fluoride ion concentration after spiking to before spiking being 10:1, the theoretical value, they will be 39:1 and 32:1. Results calculated for the fluoride ion concentration in the original solutions will be much lower

TABLE III

PERCENTAGE OF FLUORIDE IONS COMPLEXED WITH VARIOUS ALUMINIUM AND FLUORIDE ION CONCENTRATIONS AS CALCULATED FROM EQUATION (1)

The stability constants used in the calculations were those listed in reference 20, which were determined in a neutral solution with an ionic strength of 0.53 M.

Total Al ³⁺ concentration/M	Total F ⁻ concentration/M	Free F ⁻ concentration/M	F ⁻ complexed, %
10 ⁻³	10 ⁻⁴	8.2 × 10 ⁻⁸	99.92
10 ⁻³	10 ⁻³	3.2 × 10 ⁻⁶	99.68
10 ⁻²	10 ⁻³	8.2 × 10 ⁻⁸	99.99
10 ⁻²	10 ⁻²	2.7 × 10 ⁻⁶	99.97

than they should be. It can be demonstrated²¹ that the effect of increasing the fluoride ion concentration while maintaining a constant aluminium ion concentration is to increase the proportion of complexes with co-ordination numbers greater than 1. This effect is shown in Table IV.

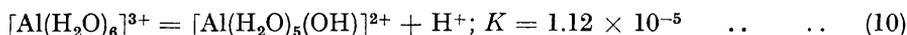
TABLE IV

DISTRIBUTION OF ALUMINIUM FLUORIDE COMPLEXES AS PERCENTAGES OF TOTAL COMPLEXED SPECIES

Calculated from Rossotti and Rossotti.²¹

Total Al ³⁺ concentration/M	Total F ⁻ concentration/M	Complexed species					
		AlF ²⁺	AlF ₂ ⁺	AlF ₃	AlF ₄ ⁻	AlF ₅ ²⁻	AlF ₆ ³⁻
10 ⁻³	10 ⁻⁴	99.1	0.85	0	0	0	0
10 ⁻³	10 ⁻³	75.4	24.0	0.55	0.0015	0	0
10 ⁻²	10 ⁻³	99.1	0.85	0	0	0	0
10 ⁻²	10 ⁻²	78.7	20.9	0.4	0	0	0

Unfortunately, these theoretical results cannot be verified in solutions containing aluminium and fluoride ions as the only complexing species as the aluminium ion is appreciably acidic, showing the following equilibrium in water²²:



If the pH of the aluminium ion solution is adjusted to 5, the lowest pH at which fluoride ion determinations are normally carried out with the fluoride ion electrode, the aluminium begins to precipitate as hydroxyaluminium complexes, disturbing the aluminium - fluoride equilibria. Precipitation of these complexes can be prevented by using an acetate, or other, buffer, but such a buffer will also affect the aluminium - fluoride equilibria because the buffer must be complexing to some extent with aluminium in order to render it soluble in water at this pH. A similar argument applies to iron(III) ions, which also form a complex with fluoride.

If the iron(III) and aluminium ions are not completely complexed by the buffer, the known additions method will give results that are too low. Thus, when a known fluoride ion concentration (6.4×10^{-2} M) was determined with the fluoride ion selective electrode, by use of the known additions method, in solutions containing aluminium or iron(III) ions and buffered with sodium chloride (0.5 M) - sodium acetate (0.5 M) at pH 5.3, values of 5.8×10^{-2} M (with 0.02 M Al³⁺) and 5.5×10^{-2} M (with 0.02 M Fe³⁺) for fluoride were obtained.

Complexing fluoride with aluminium ions or other species can have another effect, which renders the known additions method valueless. Fluoride ion concentrations can only be measured with the fluoride ion selective electrode down to about 10⁻⁶ M; below this concentration the potential tends to become constant and the method would give erroneously high results.²³ It is shown in Table V, where the concentration of fluoride ion was determined at pH 5 in the presence of 0.2 M aluminium nitrate solution, that erroneously high results are obtained even when the concentration of fluoride is as high as 1.6×10^{-2} M. In order to keep the aluminium in solution, and to provide a constant ionic background, the solutions were buffered with sodium chloride (0.5 M) - sodium acetate (0.5 M) solution.

Carlson and Keeney²⁴ state that "the method of standard additions may be applicable to samples which contain concentrations of complexing agents in excess of those of the ion sought. The basis of this method is that the addition of a known amount of the ion does not change the ratio of complexed to non-complexed ion in the sample solution. Thus, the ratio of the activities before and after addition of the standard would be the same as it would be if no complexes were present. The log nature of the response of the electrode causes the change in potential with the addition of standard to be constant no matter what the nature of the complex species." Mowbray²⁵ states that the metal must be present in a higher concentration than the ligand for the spike method to be effective. This contention is not found to be true in practice when the complexing ion is aluminium, as is evident from Table V.

TABLE V

DETERMINATION OF FLUORIDE ION CONCENTRATIONS IN SOLUTIONS 0.02 M IN ALUMINIUM NITRATE AND BUFFERED WITH 0.5 M SODIUM CHLORIDE - 0.5 M SODIUM ACETATE AT pH 5

Determined from a standard graph (sg) and by the known additions method (kam).

Actual F ⁻ concentration/M	F ⁻ concentration/M (sg)*	F ⁻ concentration/M (kam)
1×10^{-3}	1.6×10^{-4}	7.5×10^{-1}
4×10^{-3}	1.6×10^{-4}	9.4×10^{-1}
1×10^{-2}	1.6×10^{-4}	1.0
1.6×10^{-2}	1.8×10^{-4}	1.0

* The standard graph was prepared by determining the potential of known concentrations of fluoride ion in a solution buffered with 0.5 M sodium chloride - 0.5 M sodium acetate.

It is also claimed that the known additions method overcomes the effect of having an unknown ionic strength in solution. Baker¹³ states that the standard additions technique, by its very nature, cancels out the effects caused by differing pH values and ionic strengths encountered between standards and actual samples. "The calibration curve is, as it were, prepared in the sample solution." This is not borne out in practice, as varying ionic strengths may affect the position of the slope and the theoretical Nernst relationship between the concentration of fluoride ion and the measured e.m.f. It can be seen from Table VI that both the experimental slopes and the measured e.m.f. vary with the nature of the ions in solution, even when these ions do not form complexes with fluoride. Such effects are unpredictable and lead to varying results when the fluoride ion concentration is determined by the known additions method (Table VI).

TABLE VI

EXPERIMENTAL SLOPES AND E.M.F. RECORDED BY THE FLUORIDE ION ELECTRODE FOR CONCENTRATIONS OF FLUORIDE ION IN SOLUTION IN WATER, 0.5 M SODIUM CHLORIDE, 0.5 M SODIUM ACETATE AND 0.5 M SODIUM CHLORIDE - 0.5 M SODIUM ACETATE, AND THE FLUORIDE ION CONCENTRATIONS DETERMINED BY THE KNOWN ADDITIONS METHOD (kam)

Actual F ⁻ concentration $\times 10^3/M$	E.m.f./mV				F ⁻ concentration $\times 10^3$ (kam)/M			
	H ₂ O	NaCl	NaAc	NaCl - NaAc	H ₂ O	NaCl	NaAc	NaCl - NaAc
1.0	110	115	109	116	0.8	1.1	1.1	1.0
4.0	74	80	75	81	4.0	4.0	4.0	3.8
10.0	49	58	51	57	11.0	9.5	10.0	9.5
16.0	37	46	39	48	15.0	15.9	15.0	14.0
64.0	3	11	5	13	58.0	63.0	63.0	55.0
Slope	60	58	58	57				

The Formation of Complexes

In order to suppress the complexation of fluoride by a number of metal ions during water analysis, Frant and Ross²⁶ originally made use of a very small concentration of citrate in an acetate buffer at pH 5.5. Subsequently ethylenediaminetetraacetic acid, disodium salt

(EDTA) was substituted for the citrate. Harwood²⁷ later showed that 1,2-cyclohexylene-dinitrilotetraacetic acid (CDTA) was superior to EDTA in water analysis. However, a 5 g l⁻¹ solution of CDTA, when added 1 + 1 to the water to be analysed, gave a 97% recovery of fluoride in the presence of 2 μg g⁻¹ of aluminium, 91% with 5 μg g⁻¹ of aluminium and only 84% with 10 μg g⁻¹ of aluminium. In the analysis of plants the portion of sample solution taken for fluoride ion analysis may contain up to several hundred μg g⁻¹ of aluminium ions. (Harwood cites the stability constants of EDTA and CDTA incorrectly as 16.1 and 17.6 respectively; these values are in fact for log *K*.)

The stability constants of the complexes of aluminium and iron with EDTA and CDTA are strongly pH dependent, an important factor that seems to have been overlooked by previous workers. The co-ordinating power of these ligands depends on the extent to which the carboxyl groups are ionised; thus co-ordinating power decreases with decreasing pH. This relationship is shown in Table VII. Moreover, the reaction between aluminium and EDTA is not instantaneous²⁸ and at higher pH values aluminium forms very inert hydroxo complexes. The limiting pH above which the latter complexes will be formed can be calculated from equation (11).²⁹

$$[H^+] = (10^{-8} [Al^{3+}])^{1/3} \quad \dots \quad (11)$$

Hence, complex formation with aluminium by EDTA may only be complete at pH 3.3 with 10⁻² M Al³⁺ or pH 4 with 10⁻⁴ M Al³⁺, and at these pH values EDTA itself is not a very effective ligand (Table VII). In fact, fluoride can be used as a masking agent for aluminium against EDTA if a 5–6-fold excess of fluoride over aluminium is added, as in boiling solutions fluoride displaces EDTA from its aluminium complex.³⁰

TABLE VII

LOGARITHMS OF THE EFFECTIVE STABILITY CONSTANT, *K*_{eff}, FOR THE ALUMINIUM ION - EDTA, ALUMINIUM ION - CDTA, IRON(III) ION - EDTA AND IRON(III) ION - CDTA COMPLEXES AT AN IONIC STRENGTH OF 0.1 M

Calculated from Tables II and III of Schwartzbach and Flaschka.²⁸

Complex	pH											
	1	2	3	4	5	6	7	8	9	10	11	12
Al ³⁺ - EDTA	-1.9	2.6	5.5	7.7	9.6	11.4	12.9	13.8	14.8	15.7	16.0	16.1
Al ³⁺ - CDTA	-2.1	1.8	5.1	7.7	9.8	11.6	12.6	13.9	14.9	15.9	16.9	17.8
Fe ³⁺ - EDTA	7.1	11.6	14.5	16.7	18.6	20.4	21.8	22.8	23.8	24.6	25.0	25.1
Fe ³⁺ - CDTA	8.9	12.8	16.1	18.7	20.8	22.6	23.7	24.9	25.9	26.9	27.9	28.8

As can be seen from Table VIII, the recovery of fluoride when determined in the presence of a solution 0.02 M in aluminium nitrate and 0.04 M in EDTA at pH 8.5 was very low. At pH values less than 8.5 the free fluoride ion concentration was too small to be detected if the concentration of added fluoride was less than 6 × 10⁻³ M. Clearly, fluoride forms complexes more efficiently with the Al³⁺ ion than does EDTA.

As neither EDTA nor CDTA is suitable as a masking agent we investigated the use of sodium citrate at various pH values. Oliver and Clayton,³¹ working with fluoride minerals and with the electrolyte used in the Hall process for aluminium production, showed that with 500 μg g⁻¹ of aluminium in solution there was a linear relationship between log [F⁻] and potential over a wide range, when a buffer that was 0.5 M in potassium acetate and 1 M

TABLE VIII

DETERMINATION OF FLUORIDE ION CONCENTRATIONS IN SOLUTIONS 0.04 M IN EDTA AND 0.02 M IN ALUMINIUM NITRATE AT pH 8.5

Actual F ⁻ concentration/M	Experimental* F ⁻ concentration/M
2 × 10 ⁻³	4.5 × 10 ⁻⁴
4 × 10 ⁻³	8.0 × 10 ⁻⁴
6 × 10 ⁻³	9.0 × 10 ⁻⁴
8 × 10 ⁻³	1.1 × 10 ⁻³
1 × 10 ⁻²	1.5 × 10 ⁻³

* Determined from a standard graph prepared from solutions 0.04 M in EDTA.

in sodium citrate, adjusted to pH 8, was used. Buck and Reismann,³² after ashing plant material and fusing the ash with sodium hydroxide, determined the fluoride ions in a solution that was 0.71 M with respect to citrate at pH 5.7. These last workers found that aluminium and magnesium interfered and that the relative error with magnesium decreased with increasing citrate concentration. The relative error with aluminium decreased with increasing pH, and was only 0.5% at pH 8.3. These workers advocated the use of CDTA to eliminate interference from magnesium.

TABLE IX

DETERMINATION OF FLUORIDE ION CONCENTRATIONS AT pH 8.5 IN THE PRESENCE OF 0.02 M ALUMINIUM NITRATE OR 0.02 M IRON(III) NITRATE, AND EITHER 0.25 M SODIUM CITRATE OR 0.5 M SODIUM CHLORIDE - 0.5 M SODIUM ACETATE - 0.25 M SODIUM CITRATE

Actual F ⁻ concentration/M	F ⁻ (Al ³⁺) concentration/M		F ⁻ (Fe ³⁺) concentration/M	
	Na ₃ citrate*	Buffer†	Na ₃ citrate*	Buffer†
1 × 10 ⁻³	1.1 × 10 ⁻³	9.7 × 10 ⁻⁴	1.2 × 10 ⁻³	1.2 × 10 ⁻³
4 × 10 ⁻³	4.2 × 10 ⁻³	2.1 × 10 ⁻³	4.0 × 10 ⁻³	4.0 × 10 ⁻³
1 × 10 ⁻²	1.0 × 10 ⁻²	5.0 × 10 ⁻³	1.0 × 10 ⁻²	1.1 × 10 ⁻²
1.6 × 10 ⁻²	1.6 × 10 ⁻²	7.9 × 10 ⁻³	1.6 × 10 ⁻²	1.7 × 10 ⁻²
6.4 × 10 ⁻²	6.4 × 10 ⁻²	4.5 × 10 ⁻²	6.3 × 10 ⁻²	7.2 × 10 ⁻²

* Values determined from a standard graph prepared from solutions 0.25 M in sodium citrate.

† Values determined from a standard graph prepared from solutions containing 0.5 M sodium chloride - 0.5 M sodium acetate - 0.25 M sodium citrate.

Our results show that in the presence of aluminium or iron in the concentrations likely to be met in the ashes of plants that accumulate these metals, a buffer of 0.25 M sodium citrate solution at pH 8.5 gives good recoveries of fluoride and is preferable to a 0.5 M sodium chloride - 0.5 M sodium acetate - 0.25 M sodium citrate buffer at this pH (Table IX). Determinations made by using a standard graph prepared in a solution that was 0.25 M with respect to sodium citrate gave slightly more accurate results than those obtained by the known additions method (Table X). At pH 6.5 citrate is not a good complexing agent for aluminium, the recovery of fluoride at this pH being too low when determined from the standard graph and too high when the known additions method is applied (Table XI).

TABLE X

DETERMINATION OF FLUORIDE ION CONCENTRATIONS BY THE KNOWN ADDITIONS METHOD AT pH 8.5 IN THE PRESENCE OF 0.02 M ALUMINIUM NITRATE OR 0.02 M IRON(III) NITRATE AND EITHER 0.25 M SODIUM CITRATE OR 0.5 M SODIUM CHLORIDE - 0.5 M SODIUM ACETATE - 0.25 M SODIUM CITRATE

Actual F ⁻ concentration/M	F ⁻ (Al ³⁺) concentration/M		F ⁻ (Fe ³⁺) concentration/M	
	Na ₃ citrate	Buffer	Na ₃ citrate	Buffer
1.0 × 10 ⁻³	1.1 × 10 ⁻³	1.3 × 10 ⁻³	1.2 × 10 ⁻³	1.3 × 10 ⁻³
4.0 × 10 ⁻³	4.0 × 10 ⁻³	2.7 × 10 ⁻³	4.0 × 10 ⁻³	3.9 × 10 ⁻³
1.0 × 10 ⁻²	1.0 × 10 ⁻²	6.1 × 10 ⁻³	9.5 × 10 ⁻³	9.2 × 10 ⁻³
1.6 × 10 ⁻²	1.5 × 10 ⁻²	8.8 × 10 ⁻³	1.6 × 10 ⁻²	1.5 × 10 ⁻²
6.4 × 10 ⁻²	5.0 × 10 ⁻²	4.0 × 10 ⁻²	5.8 × 10 ⁻²	5.8 × 10 ⁻²

The recovery of fluoride from solutions containing magnesium or silicate ions in concentrations comparable with those found in the ashes of plants that accumulate magnesium or silica is good when a 0.25 M sodium citrate buffer solution is used at pH 8.5 and the determination is made from the standard graph. The known additions method gives less accurate results (Table XII).

Although silicon is known to form a complex with fluoride at low pH values there is little interference from silicate at pH 8.5 (Table XIII) and the addition of citrate is not necessary, providing aluminium, iron and magnesium are absent.

TABLE XI

DETERMINATION OF FLUORIDE ION CONCENTRATIONS BY THE STANDARD GRAPH (sg) AND KNOWN ADDITIONS (kam) METHODS IN THE PRESENCE OF 0.02 M ALUMINIUM NITRATE AND 0.25 M SODIUM CITRATE AT pH 6.5

Actual F ⁻ concentration/M	Experimental F ⁻ concentration/M (sg)*	Experimental F ⁻ concentration/M (kam)
1×10^{-3}	7.4×10^{-4}	1.4×10^{-3}
4×10^{-3}	3.4×10^{-3}	6.6×10^{-3}
1×10^{-2}	7.4×10^{-3}	1.4×10^{-2}
1.6×10^{-2}	1.2×10^{-2}	2.5×10^{-2}
6.4×10^{-2}	3.8×10^{-2}	2.5×10^{-1}

* Determined from a standard graph prepared from solutions 0.25 M in sodium citrate.

Thus, the method that gives the best recoveries of fluoride in the presence of aluminium, iron and magnesium is that in which 0.25 M sodium citrate solution is used to complex the metal ions at pH 8.5 and determination of fluoride ion concentration is made from the standard graph.

TABLE XII

DETERMINATION OF FLUORIDE ION CONCENTRATIONS BY THE STANDARD GRAPH (sg) AND KNOWN ADDITIONS (kam) METHODS AT pH 8.5 IN THE PRESENCE OF 0.25 M SODIUM CITRATE AND EITHER 0.016 M MAGNESIUM NITRATE OR 0.004 M SODIUM SILICATE

Actual F ⁻ concentration/M	F ⁻ (Mg ²⁺) concentration/M		F ⁻ (Si ₂ O ₅ ²⁻) concentration/M	
	sg*	kam	sg*	kam
	1×10^{-3}	1.0×10^{-3}	1.1×10^{-3}	1.1×10^{-3}
4×10^{-3}	4.0×10^{-3}	4.2×10^{-3}	4.2×10^{-3}	4.3×10^{-3}
1×10^{-2}	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}	1.1×10^{-2}
1.6×10^{-2}	1.6×10^{-2}	1.5×10^{-2}	1.6×10^{-2}	1.7×10^{-2}
6.4×10^{-2}	6.4×10^{-2}	6.3×10^{-2}	6.4×10^{-2}	6.6×10^{-2}

* Determined from a standard graph prepared from solutions 0.25 M in sodium citrate.

No work seems to have been done on metal ion - citrate complexes at pH 8.5, so it can only be assumed that the efficacy of citrate as a complexing agent at this pH is related to its increased ionisation at higher pH values. As is mentioned above, a similar effect is found with EDTA.

That the metal ions become strongly bound to citrate ions seems certain from the above results, but only in the instance of iron(III) - citrate complexes has a very large equilibrium constant been found.³³

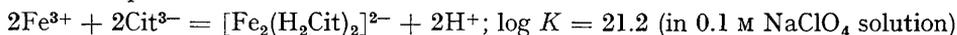
TABLE XIII

DETERMINATION OF FLUORIDE ION CONCENTRATIONS BY THE STANDARD GRAPH (sg) AND KNOWN ADDITIONS (kam) METHODS IN THE PRESENCE OF 0.004 M SODIUM SILICATE AT pH 5

Actual F ⁻ concentration/M	Experimental F ⁻ concentration/M (sg)*	Experimental F ⁻ concentration/M (kam)
1×10^{-3}	1.0×10^{-3}	1.5×10^{-3}
4×10^{-3}	4.0×10^{-3}	4.5×10^{-3}
1×10^{-2}	9.8×10^{-3}	1.0×10^{-2}
1.6×10^{-2}	1.6×10^{-2}	1.6×10^{-2}
6.4×10^{-2}	6.4×10^{-2}	6.3×10^{-2}

* Determined from a standard graph of sodium fluoride in solution in water.

A summary of known equilibrium constants for iron(III) - citrate^{33,34} and magnesium - citrate³⁴ complexes is as follows:



No work has been done on Si - citrate³⁻ or Al³⁺ - citrate³⁻ complexes.

Application of the Method to Plant Ashes

The tea plant is known to accumulate up to 17 000 $\mu\text{g g}^{-1}$ of aluminium.³⁵ The ash from a tea plant sample will therefore contain sufficient of this element to interfere considerably with the determination of fluoride ions, unless the aluminium is removed by complexation with citrate ions. By use of the fluoride ion selective electrode and a 0.25 M sodium citrate buffer solution we determined the total fluoride ion concentration in 1-g samples of commercial tea containing an average of 2 050 $\mu\text{g g}^{-1}$ of aluminium and 2 800 $\mu\text{g g}^{-1}$ of iron.

TABLE XIV

RECOVERY OF SODIUM FLUORIDE ADDED TO THE ASH OF COMMERCIAL TEA SAMPLES DETERMINED WITH A FLUORIDE ION SELECTIVE ELECTRODE IN THE PRESENCE OF 0.25 M SODIUM CITRATE AT pH 8.5

F ⁻ added to ash from 1 g of tea in 50 ml of solution $\times 10^4/\text{mol}$	F ⁻ determined $\times 10^4/\text{mol}$			Recovery of added fluoride, %			Average recovery of added fluoride, %
	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C	
0	1.55	2.90	1.50	—	—	—	—
2	3.47	4.76	3.30	96	93	90	93 \pm 3
5	6.76	7.40	6.45	104	90	99	98 \pm 8
8	9.90	10.25	9.50	104	92	100	99 \pm 7
32	34.22	32.00	33.15	102	91	99	97 \pm 6

Known amounts of sodium fluoride were added to the ash from 1-g samples of tea and the total fluoride ion concentration was again determined. The results given in Table XIV show that the recovery of fluoride was better than 90% when the determination was made from a standard graph prepared from samples dissolved in a solution containing sodium citrate at a concentration of 0.25 M.

References

- Bollard, E. G., and Butler, G. W., *A. Rev. Pl. Physiol.*, 1966, **17**, 89.
- Vickery, B., and Vickery, M. L., *Vet. Bull., Weybridge*, 1973, **43**, 537.
- Vickery, B., and Vickery, M. L., *Phytochem.*, 1972, **11**, 1905.
- Zimmerman, P. W., Hitchcock, A. E., and Givertsman, J., *Contr. Boyce Thomson Inst. Pl. Res.*, 1957, **19**, 49.
- McEwan, T., *Nature, Lond.*, 1964, **201**, 827.
- Venkateswarlu, P., Armstrong, W. D., and Singer, L., *Pl. Physiol.*, 1965, **40**, 255.
- Aplin, T. E. H., *J. Agric. West Aust.*, 1971, **12**, 154.
- Oelrichs, P. B., and McEwan, T., *Q. J. Agric. Sci.*, 1962, **19**, 1.
- de Oliveira, M. M., *Experientia*, 1963, **19**, 586.
- Lovelace, J., Miller, G. W., and Welkie, G. W., *Atmos. Envir.*, 1968, **2**, 187.
- Willard, H. H., and Winter, O. B., *Ind. Engng Chem. Analyt. Edn*, 1933, **5**, 7.
- Hall, R. J., *Analyst*, 1968, **93**, 461.
- Baker, R. L., *Analyt. Chem.*, 1972, **44**, 1326.
- Cannon, H. L., *Science, N.Y.*, 1960, **132**, 591.
- Louw, C. W., and Richards, J. F., *Analyst*, 1972, **97**, 334.
- "Methods of Analysis of the Association of Official Agricultural Chemists," Tenth Edition, Association of Official Agricultural Chemists, Washington, D.C., 1965, p. 34.
- Baumann, E. W., *Analytica Chim. Acta*, 1968, **42**, 127.
- Srinivasan, K., and Rechnitz, G. A., *Analyt. Chem.*, 1968, **40**, 509.
- Beck, M. T., "Chemistry of Complex Equilibria," Van Nostrand Reinhold Company, London, 1970, p. 78.
- Sillén, L. G., and Martell, A. E., *Compilers*, "Stability Constants of Metal - Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p. 264.

21. Rossotti, F. R., and Rossotti, H., "The Determination of Stability Constants," McGraw-Hill Book Co. Inc., New York, 1961, p. 40.
22. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," Second Edition, Wiley Eastern Private Ltd., New Delhi, 1972, p. 437.
23. Edmond, C. R., *Bull. Aust. Dev. Lab.*, 1969, 7, 1.
24. Carlson, R. M., and Keeney, D. R., "Instrumental Methods of Analysis of Soils and Plant Tissue," Soil Science Society of America, Madison, Wisc., 1971, p. 39.
25. Mowbray, J. H., "Corning Applications Note," No. 3, Corning Glass Works, Medfield, Mass., 1969.
26. Frant, M. S., and Ross, J. W., *Analyt. Chem.*, 1968, 7, 1169.
27. Harwood, J. E., *Wat. Res.*, 1969, 3, 273.
28. Schwarzenbach, G., and Flaschka, H., "Complexometric Titrations," Second English Edition, Methuen, London, 1969, p. 185.
29. Schwarzenbach, G., and Flaschka, H., "Complexometric Titrations," Second English Edition, Methuen, London, 1969, p. 184.
30. Schwarzenbach, G., and Flaschka, H., "Complexometric Titrations," Second English Edition, Methuen, London, 1969, p. 188.
31. Oliver, R. T., and Clayton, A. G., *Analytica Chim. Acta*, 1970, 51, 409.
32. Buck, M., and Reismann, G., *Fluoride*, 1971, 4, 5.
33. Sillén, L. G., and Martell, A. E., *Compilers*, "Stability Constants of Metal - Ion Complexes, Supplement No. 1," Special Publication No. 25, The Chemical Society, London, 1971, p. 412.
34. Sillén, L. G., and Martell, A. E., *Compilers*, "Stability Constants of Metal - Ion Complexes," Special Publication No 17, The Chemical Society, London, 1964, p. 479.
35. Eden, T., "Tea," Second Edition, Longmans, Green and Co., London, 1965, p. 11.

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