

Evaluation of the potentiometric determination of trace fluoride in natural and drinking water with a fluoride ISE

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Abstract

The performance of the fluoride ion selective electrode (F-ISE) potentiometric method was evaluated for fluoride determination in natural and drinking water and the pitfalls that could prevent accurate analyses were assessed. Guidelines are provided for the accurate implementation of the F-ISE method for low-level F⁻ determination in the routine analytical laboratory. The following aspects were evaluated: minimising electrode drift, electrode care and optimisation, the use of different TISAB (total ion strength adjustment buffer) solutions, calibration procedures for trace F⁻, interference correction procedures, matrix effects, and the determination of the analytical parameters. The methodologies and procedures proposed in this work were applied in an SABS proficiency testing programme (Water Check Programme-2004) which included low-level F⁻ determination in natural water and synthetic samples with varying amounts of possible interfering elements. The accuracy of the results was excellent confirming the versatility of F-ISE for low-level F⁻ determinations in routine laboratories provided that the correct analytical procedures are followed and common pitfalls are avoided.

Keywords: F⁻ determination, F-ISE, F⁻ in drinking water

Introduction

South Africa has approved the mandatory implementation of water fluoridation of municipal water. The ability to measure fluoride accurately in natural and drinking water at concentration levels < 1 mg/l is an obvious prerequisite for the safe and effective implementation of water fluoridation. A recent study (Noh and Coetzee, 2006) has shown that the proficiency of many analytical laboratories in South Africa to determine F⁻ at these low levels is inadequate. The current study investigates the reasons for this less than satisfactory performance of South African laboratories and evaluates the fluoride ion selective ion (F-ISE) potentiometric method, the most common instrumental technique used for fluoride determination in water. The specific aim is to study the performance of the F-ISE method for low-level (< 1 mg/l) F⁻ determination, determine the pitfalls that could prevent accurate analyses, and provide guidelines for the successful implementation of F-ISE in the routine analytical laboratory.

Fluoride (F⁻) in water can be determined in a number of ways, using instrumental methods such as potentiometry with ion-selective electrodes (ISE) (Richard 1969; Wang, 1995; McCaffrey, 1994; Lopes da Conceição, 2000; Van Staden, 2000; US EPA Method 13B), spectrophotometry (Bellack 1958; Crosby et al., 1968; Cabello-Tomas and West, 1969; Wada et al. 1985; Yuchi et al., 1995; Khalifa and Hafez, 1998; Oszwaldowski et al., 1998; Faraj-Zadeh and Kalhor, 2001; Nishimoto et al., 2001; Garrido et al., 2002; US EPA method 13A), inductively coupled plasma-mass spectrometry (Bayón et al., 1999; Okamoto, 2001), complexometry (Pickering, 1986; Saha, 1993), capillary ion analysis (Bondoux and Jones, 1995; Saad et al., 1998), and ion chromatography (IC) (Jones, 1992; Moskvina et al., 1998; Jackson, 2001; Dionex (Application Note 133, 135, 140 and 154).

The fluoride ion selective electrode (F-ISE) is the most widely used for the determination of F⁻ due to its simplicity and short analysis time while ion chromatography (IC) offers a useful alternative because of good selectivity and sensitivity. Although the SPANDS method achieved high sensitivity, this method is now less frequently used in routine analytical laboratories as it is labour-intensive, has poor selectivity, and is time-consuming (Crosby et al., 1968; MacLeod and Crist, 1973; Oszwaldowski et al., 1998). Apart from these three, the other methods listed above are not used in routine F⁻ determinations. F-ISE was found to be the most common method in South Africa (Noh and Coetzee, 2006), for the routine determination of F⁻ at trace concentration levels.

The current study was undertaken to evaluate ISE, for low-level F⁻ determination, to compile guidelines on how to avoid common pitfalls, and how to apply the method accurately for trace F⁻ determination in natural and drinking water. The following aspects were evaluated: minimising electrode drift, electrode care and optimisation, the use of different TISAB solutions (total ion strength adjustment buffer), calibration procedures for trace F⁻, interference correction procedures, matrix effects, and the determination of the analytical parameters.

Experimental details

Instrumentation

The F⁻ concentration was measured using an F-ISE (9404 sc Orion Research Inc., MA, USA) in combination with an Ag/AgCl single junction reference electrode (Orion Model 90-01) connected to the read-out device, ORION 960 Auto Chemistry System (Orion Research Inc., MA, USA).

Standards and reagent solutions

Stock F⁻ solution and F⁻ standards

A 1 000 mg F⁻/l sodium F⁻ stock solution was prepared by

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dissolving 0.221 g NaF (pro analysi, MERCK) in a 100 ml polystyrene volumetric flask with deionised water. Standards of the required concentration were prepared by appropriate dilution of the stock solution using 18 M Ω .cm deionised water.

Total ionic strength adjustment buffers (TISAB) for F-ISE

Total ionic strength adjustment buffers (TISAB) are important reagents for the determination of F⁻ using ISE. There are several different formulations to make up TISAB solutions. The preparation procedure of each TISAB solution used in this study is described below.

TISAB III

TISAB III is commercially available from Thermo Orion (Orion Research Inc., Beverly, MA, USA, Cat. No.940911). It contains CDTA (trans-1,2-cyclohexylenedinitrilo) tetra-acetic acid) and ammonium acetate (CH₃COONH₄) buffer at pH 5.5. The recommended volume ratio between TISAB and test solution is 1:10. 20 ml of test solution and 2 ml of TISAB III mixed in a plastic beaker was used in this study.

TISAB IV

It contains TRIS buffer at pH 8.5 and is used for high levels of Al interference. 84 ml concentrated HCl (36 to 38%), 242 g tris(hydroxymethyl) aminomethane, and 230 g sodium tartrate (Na₂C₄H₄O₆ · 2H₂O), were added to 500 ml deionised water, allowed to dissolve, and then made up to 1 l in a volumetric flask with deionised water. The recommended volume ratio between TISAB and test solution (Orion, 1982) is 1:1. In this study, 10 ml of test solution and 10 ml of TISAB IV were mixed in a plastic beaker.

Low-level TISAB (LLT)

This TISAB solution is used when measuring samples containing less than 0.4 mg/l F⁻ and no F⁻ complexing agents, such as Fe or Al, are present. 57 ml acetic acid and 58 g sodium chloride were added in 500 ml distilled water and the pH was adjusted to 5.5 by adding drops of 5 M NaOH after cooling the solution, then made up to 1 l in a volumetric flask with deionised water. The recommended volume ratio between TISAB and test solution is 1:1. 10 ml of test solution and 10 ml of Low-level TISAB mixed in a plastic beaker was used in this study.

Results and discussion

Electrode drift

One of the main problems in ISE measurement is the drift in electrode potential during a sequence of measurements. 0.02, 0.1, 1, 2 mg/l spiked samples of F⁻ in deionised water were prepared together with TISAB III in 100 ml polystyrene volumetric flasks. The uncertainty, due to fluctuating potential values during the first few seconds after immersion of the electrode, was controlled by the following procedure: The reference electrode was placed in the beaker first, followed after 3 min by the F⁻ electrode. The potential was recorded from 3 min after immersion of the F⁻ electrode for 1 h and drift values were calculated by subtraction. These experiments were repeated 3 times for each sample. The electrodes were rinsed by spraying with a jet of deionised water and gently dabbed dry with a soft tissue before measurement.

A summary of results, showing the average drift (mV/h) and standard deviation obtained in this experiment, is given in Table 1.

[F ⁻] Known	0.02 mg/l	0.1 mg/l	1 mg/l	2 mg/l
Average drift (mV/h)	1.30 ± 0.53	1.23 ± 0.32	1.03 ± 0.06	0.73 ± 0.15

These results show that the average drift values of the F⁻ electrode were bigger when the concentrations of F⁻ were lower. This trend is evident in the standard deviations. This confirms that, as expected, lower concentrations of F⁻ were more severely influenced by drift and show poor precision.

Four different procedures were designed to minimise electrode drift and then tested. The four procedures were:

Procedure 1

Both electrodes, reference electrode and F-ISE, were immersed in the storage solution (100 mg/l F⁻) over night in between measurements. The potential of the 0.1 mg/l F⁻ test solution was measured, without preconditioning, for 1 h using TISAB III on three consecutive days.

Procedure 2

Both electrodes (reference electrode and F-ISE) were immersed in the storage solution (100 mg/l F⁻) overnight. Before the first potential measurement of the test solutions, the electrodes were immersed in the pre-conditioning solution (0.1 mg/l) for 20 min. The test solution, 0.1 mg/l, was then measured for 1 h using TISAB III the potential recorded. After finishing the first measurement, the electrodes were immersed into the storage solution again for 50 min to allow the electrodes to be equilibrated under similar conditions as before (Procedure 1). The procedure was then repeated twice on the same day.

Procedure 3

Preconditioning was used on the test solutions (0.02 mg/l and 0.1 mg/l) only for the first measurement in a series. The procedure was then repeated twice on the same day.

Procedure 4

The F⁻ electrode was conditioned by brushing the membrane with F⁻ toothpaste according to the following procedure (Thermo Orion, Application Note). A small amount of F⁻ toothpaste (Mentadent P Herbal toothpaste, F⁻ System, Lever Pond's (Pty) Ltd., Durban) was squeezed from the tube on to a toothbrush. The F-ISE membrane was then brushed softly using this toothbrush and then the electrode was rinsed by spraying with a jet of deionised water until there was no toothpaste on the membrane and gently dabbed dry with a soft tissue. After cleaning the F-ISE, it was stored dry in air. The reference electrode was stored in deionised water. The test solutions (0.02 mg/l and 0.1 mg/l) were measured 3 times without any preconditioning or exposure to the storage solution using TISAB III.

For Procedure 1, the drift in each run was quite different and the electrode response was not reproducible, although the same electrodes and solutions were used. For Procedure 2 the electrode response was reproducible but the response time to obtain a stable reading was not improved. The results obtained for Procedure 3 and Procedure 4 are shown in Figs. 1 and 2, respectively.

Procedure 4 shows very stable electrode response, shorter equilibration time, and low drift. This indicates that proper conditioning of F-ISE is a very efficient way for minimising the electrode drift and improving equilibration time.

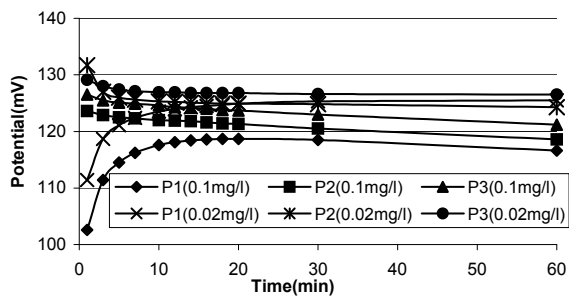


Figure 1
Electrode response (Procedure 3): TISAB III at 0.02 mg/l and 0.1 mg/l F⁻

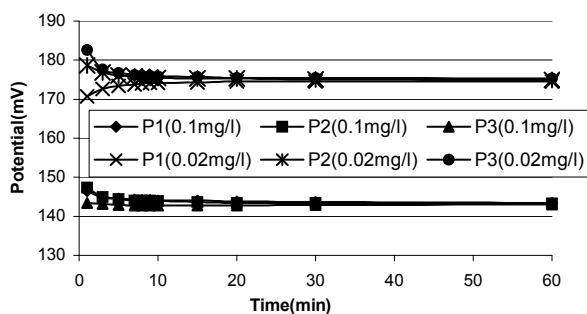


Figure 2
Electrode response (Procedure 4): TISAB III at 0.02 mg/l and 0.1 mg/l F⁻

The effect of different TISAB solutions on calibration for low-level F⁻ determinations

In the case of ISE methods, calibration is carried out by immersing the electrodes in a series of solutions of known concentration and by plotting a graph of the mV reading versus the log of the activity. For electrodes with Nernstian response, this should give a straight line over the whole linear concentration range. At lower F⁻ concentrations linearity in F-ISE calibration curves is no longer possible and the curves typically move away from linearity as the concentrations decrease below 0.1 mg/l. This places important demands on calibration procedures if accurate results are to be achieved for lower concentrations. In this section the use of multi-standard calibration procedures for low-level F⁻ determinations and the efficiency of different TISAB solutions were investigated.

Selection of appropriate TISAB for low-level F⁻ determinations

F⁻ determination over the concentration range 0.02 mg/l to 1 000 mg/l was studied using three different TISAB solutions: LLT, TISAB III and TISAB IV. 20 ml of standard solution without TISAB, 20 ml of standards and 2 ml of TISAB III, 10 ml of standard and 10 ml of TISAB IV and LLT were prepared in 50 ml plastic beakers. The potential of standards was measured from low to high concentration and the meter reading was taken after a constant value had been attained (drift < 0.1 mV/min). The calibration graph for each TISAB is given in Fig. 3.

All graphs, except the graphs obtained using TISAB IV, showed a linear relationship above 0.1 mg/l F⁻ concentration but only LLT and TISAB III did not show excessive curvature below 0.1 mg/l. Only these two were therefore considered for further investigation.

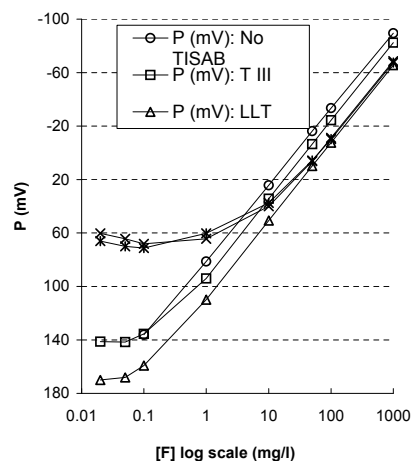


Figure 3
Calibration curves for different types of TISAB. TISAB IV curves show excessive curvature below 10 mg/l

Low-level (0.01 to 3 mg/l) F⁻ calibration using TISAB III and LLT

A two-point calibration is sufficient when the measurement is done in the linear range of the calibration curve. Three or more standards are, however, recommended in order to confirm the linearity. If the curve is non-linear more standards are needed in order to define the curve in the non-linear range. The slope of the calibration graph is about 54 mV/decade for monovalent ions such as F⁻ (Nico, 2000). Figure 4 shows calibration lines obtained for three standard series in the concentration range 0.05 to 3 mg/l. This concentration range includes the non-linear portion below about 0.1 mg/l where the electrode response becomes progressively less as the concentration reduces.

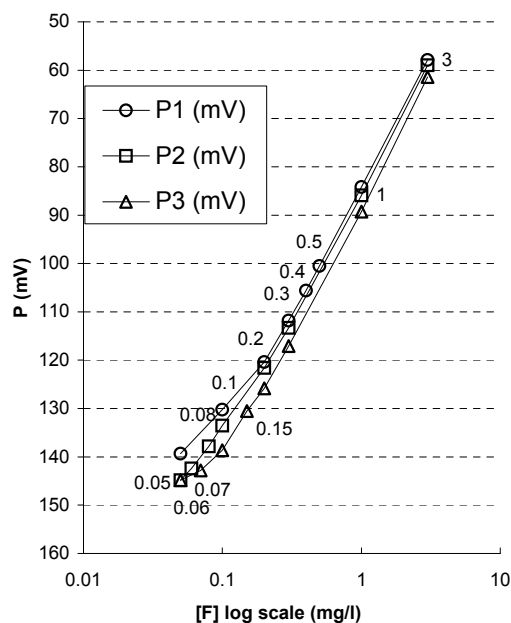


Figure 4
Multi-point calibration graph using TISAB III

The analytical parameters, slope, intercept and correlation coefficient for the second calibration curve (P2) are given as example in Table 2.

Standards range (mg/l)	Slope	Y-intercept	R ²
0.05-3	-48.156	84.995	0.9940
0.06-3	-49.039	84.890	0.9951
0.08-3	-50.014	84.830	0.9959
0.1-3	-51.038	84.850	0.9963
0.2-3	-53.323	85.022	0.9993

The value of R² estimates the linearity of each curve. It is necessary to have R² at least 0.999 for the confirmation of linearity but the results show R² values less than 0.999 when the calibration points of lower than 0.2 mg/l are included. Obviously linearity is not confirmed for data points below 0.2 mg/l. This presents a problem for determination of F⁻ at concentration range below 0.2 mg/l, as can be seen in Table 3 where this calibration curve was used to determine F⁻ in deionised water samples with known F⁻ concentration.

Table 3 shows the importance of using the proper calibration function for accurate determination of sample concentration.

The results, obtained by using the function for the range 0.05-3 where the slope was outside the ideal range and the linearity < 0.999, show large errors. The results for the calibration line based on the range 0.1 to 3 mg/l and 0.2 to 3 mg/l are reasonable, but not very good. An additional problem was that sample concentrations, less than 0.1 mg/l for the calibration range 0.1 to 3 mg/l and less than 0.2 mg/l for calibration range from 0.2 to 3 mg/l, could not be determined accurately since these were out of the calibration range. Other regression models were then applied to the data to see whether a different calculation procedure could improve the results for F⁻ concentrations below 0.2 mg/l. A summary of the results using non-linear regression functions is given in Table 4.

The results in Table 4 are very inaccurate effectively precluding the use of non-linear regressions models, such as exponential and polynomial functions, for setting up calibration curves.

The measurements were then repeated after reconditioning the electrode with fluoride tooth paste as before. Comparative results before and after cleaning are shown in Table 5.

This table clearly shows that the slope was very much improved after conditioning the electrode. This proves that electrode conditioning can restore the efficiency of the electrode. The calibration function and the calculated F⁻ values are given in Table 6.

Calibration range	0.05 to 3 mg/l			0.1 to 3 mg/l			0.2 to 3 mg/l		
Function	Y=-48.156x+84.995			Y=-51.038x+84.85			Y=-53.323x+85.022		
R ²	0.9940			0.9963			0.9993		
Known [F] (mg/l)	Calculated [F] (mg/l)	SD (N=2)	% Error	Calculated [F] (mg/l)	SD (N=2)	% Error	Calculated [F] (mg/l)	SD (N=2)	% Error
0.07	0.062	0.005	-10.9	0.072	0.005	3.6	0.082	0.006	16.7
0.09	0.076	0.006	-15.2	0.088	0.007	-2.6	0.098	0.007	8.9
0.12	0.093	0.001	-22.2	0.106	0.001	-11.7	0.118	0.001	-2.0
0.15	0.114	0.001	-23.8	0.128	0.001	-14.4	0.141	0.001	-5.8
0.18	0.137	0.000	-23.8	0.152	0.000	-15.3	0.166	0.001	-7.5
0.4	0.343	0.005	-14.4	0.362	0.005	-9.6	0.380	0.005	-4.9
0.5	0.442	0.010	-11.5	0.460	0.010	-7.9	0.479	0.010	-4.1
0.8	0.761	0.010	-4.8	0.768	0.010	-4.0	0.783	0.010	-2.2
1.5	1.567	0.000	4.5	1.518	0.000	1.2	1.502	0.000	0.1
2.0	2.123	0.007	6.2	2.021	0.006	1.1	1.976	0.006	-1.2
2.5	2.775	0.009	11.0	2.602	0.008	4.1	2.517	0.008	0.7

Calibration range	Low level between 0.05 to 0.2 mg/l for measuring < 0.2 mg/l sample								
Function	Exponential function			Polynomial function			Linear regression		
R ²	Y=99.279 e ^{-0.2942x}			Y=704.1x ² -331.26x+159.68			Y=-39.047x+94.484		
Known [F] (mg/l)	Calculated [F] (mg/l)	SD (N=2)	% Error	Calculated [F] (mg/l)	SD (N=2)	% Error	Calculated [F] (mg/l)	SD (N=2)	% Error
0.07	0.057	0.005	-18.6	0.057	0.006	-18.6	0.057	0.005	-18.3
0.09	0.073	0.007	-18.9	0.075	0.008	-16.7	0.073	0.008	-18.6
0.12	0.092	0.001	-23.3	0.095	0.001	-20.8	0.094	0.001	-21.6
0.15	0.119	0.002	-20.7	0.118	0.001	-21.3	0.121	0.002	-19.6
0.18	0.150	0.001	-16.7	0.144	0.001	-20.0	0.151	0.001	-16.1

Status		Before cleaning (second run)		After cleaning	
[F] (mg/l)	Log F	P (mV)	Slope	P (mV)	Slope
0.05	-1.301	144.8	-	154.0	-
0.06	-1.222	142.4	-30.3	150.5	-44.2
0.08	-1.097	137.8	-36.8	145.0	-44.0
0.1	-1.000	133.5	-44.4	140.3	-48.5
0.2	-0.699	121.6	-39.5	124.7	-51.8
1	0.000	85.9	-51.1	85.9	-55.5
3	0.477	59.0	-56.4	58.6	-57.2

Calibration range	0.05 to 3 mg/l			0.08 to 3 mg/l			0.1 to 3 mg/l		
Function	Y=-53.937x+85.408			Y=-54.989x+85.399			Y=-55.411x+85.449		
R ²	0.9990			0.9997			0.9998		
Known [F] (mg/l)	Calculated [F] (mg/l)	SD (N=2)	% Error	Calculated [F] (mg/l)	SD (N=2)	% Error	Calculated [F] (mg/l)	SD (N=2)	% Error
0.07	0.074	0.003	5.7	0.078	0.003	11.10	0.079	0.003	12.9
0.09	0.090	0.004	0.1	0.094	0.004	4.8	0.096	0.004	6.7
0.15	0.153	0.000	1.7	0.158	0.000	5.4	0.161	0.000	7.3
0.5	0.482	0.017	-3.6	0.489	0.017	-2.2	0.493	0.017	-1.4
0.8	0.788	0.005	-1.5	0.791	0.005	-1.1	0.794	0.005	-0.8
1.5	1.523	0.014	1.6	1.510	0.013	0.7	1.509	0.013	0.6
2	2.089	0.006	4.5	2.059	0.006	3.0	2.052	0.006	2.6

Compared to the results in Table 3, the linearity (R²) was very much improved after electrode conditioning and the slope in each range, -53.9, -54.9 and -55.4, was within the ideal range. All calculated F⁻ values based on these calibration curves were accurate. These results emphasise the importance of using a reliable calibration function for the low-level F⁻ determination and the crucial role of electrode conditioning in attaining accurate analytical results.

The same analysis was repeated using LLT. The results were similar but TISAB III showed better linearity (See Fig. 5) and has the advantage of containing a decomplexing agent for Al-F complexes. Table 7 (next page) shows comparative results for the determination of F⁻ in spiked tap water samples using TISAB III and LLT.

After calibration, the background value, which is the F⁻ concentration in raw tap water before adding F⁻, was measured and found to be 0.167 mg/l for TISAB III and 0.159 mg/l for LLT. The value, 0.167 mg/l, obtained from TISAB III, was considered to be more reliable since more accurate results had been achieved using TISAB III in previous experiments that had been done with laboratory-deionised water. In addition, the % recovery, obtained using TISAB III, was better and within the recovery limit. The results from LLT show one outlier at 73%, for the 0.1 mg/l F⁻ sample. Compared to the results for TISAB III, the % recovery from LLT was worse than that of TISAB III. This confirms the use of TISAB III instead of LLT for F⁻ determination in natural and drinking water samples.

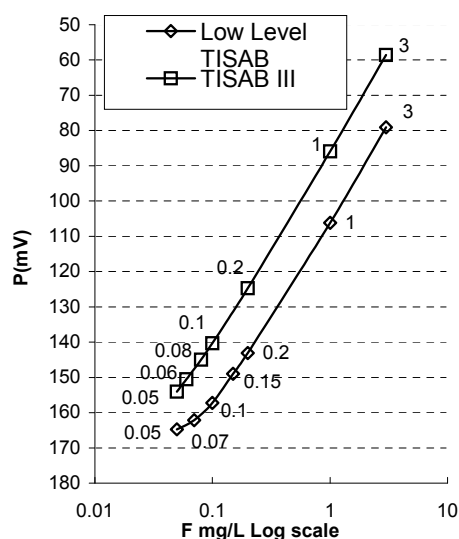


Figure 5
Calibration curves for LLT and TISAB III after electrode conditioning

Interference study

The cations, Al³⁺, Fe³⁺, Ca²⁺, Mg²⁺, Cu²⁺ as well as the anions, Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻ and colloids (SiO₂) were studied to determine their influence on the analysis of low-level F⁻. Two approaches were used.

TISAB type	TISAB III				LLT			
Calibration range	0.1 to 3 mg/ℓ				0.1 to 3 mg/ℓ			
Function	Y=-54.627x+84.945				Y=-54.872x+107.14			
R ²	0.9994				0.9993			
Matrix type	*Back ground [F](C)	Added [F] (s)	Fortified conc. (C ₂)	LFM **R %	*Back ground [F](C)	Added [F] (s)	Fortified conc. (C ₂)	LFM R %
Tap water	0.167	0.1	0.270	103.0	0.159	0.1	0.232	73.0
		0.2	0.360	96.5		0.2	0.347	94.0
		0.5	0.640	94.6		0.5	0.618	91.8
		1	1.178	101.1		1	1.103	94.4
		2	2.208	102.1		2	2.200	102.1

*Background [F]: concentration before adding F, **% R:% Recovery

Interfering substance: Ion	Concentration interference (mg/ℓ)	Known [F] (mg/ℓ)					
		0.5		1		2	
		Measured [F](mg/ℓ)	% R*	Measured [F](mg/ℓ)	% R	Measured [F](mg/ℓ)	% R
PO ₄ ³⁻ (as NaH ₂ PO ₄ ·6H ₂ O)	0	0.494	98.9	1.009	100.9	2.015	100.7
	1	0.538	107.6	0.956	95.6	1.946	97.3
	10	0.465	92.9	0.978	97.8	1.963	98.1
	50	0.465	92.9	0.978	97.8	1.929	96.5
	100	0.460	92.1	0.996	99.6	1.946	97.3
SO ₄ ²⁻ (as Na ₂ SO ₄)	0	0.499	99.8	0.980	98.0	2.038	101.9
	1	0.481	96.1	0.971	97.1	2.097	104.9
	10	0.479	95.7	0.988	98.8	2.115	105.7
	50	0.481	96.1	0.988	98.8	2.106	105.3
Cl ⁻ (as KCl)	0	0.528	105.7	1.026	102.6	2.003	100.1
	1	0.511	102.2	1.006	100.6	2.028	101.4
	10	0.507	101.4	1.026	102.6	2.061	103.1
	50	0.505	101.0	0.997	99.7	2.028	101.4
NO ₃ ⁻ (as NaNO ₃)	0	0.205	102.5	0.503	100.6	0.998	99.8
	1	0.204	102.0	0.478	95.6	0.990	99.0
	10	0.207	103.5	0.476	95.2	0.994	99.4
	50	0.199	99.5	0.480	96.0	0.990	99.0
Al ³⁺ (as AlCl ₃ ·6H ₂ O)	0	0.505	101	0.994	99.4	2.044	102.2
	1	0.477	95.4	0.876	87.6	1.923	96.2
	10	0.353	70.6	0.677	67.7	1.363	68.2
	50	0.161	32.2	0.295	29.5	0.575	28.8
	100	0.107	21.4	0.168	16.8	0.310	15.5
Fe ³⁺ (as Fe(NO ₃) ₃ ·9H ₂ O)	0	0.507	101.4	0.981	98.1	2.028	101.4
	1	0.441	88.1	0.900	90.0	1.829	91.4
	10	0.444	88.8	0.911	91.1	1.867	93.4
	50	0.461	92.2	0.914	91.4	1.844	92.2
Mg ²⁺ (As MgSO ₄)	0	0.495	99.1	0.989	98.9	2.100	105.0
	1	0.503	100.6	1.058	105.8	2.043	102.2
	5	0.502	100.3	1.030	103.0	2.035	101.7
Ca ³⁺ (As CaCl ₃)	0	0.495	99.1	0.989	98.9	2.100	105.0
	1	0.506	101.2	1.019	101.9	2.083	104.1
	5	0.515	102.9	1.039	103.9	2.159	108.0
Cu ²⁺ (as CuCl ₂ ·2H ₂ O)	0	0.494	98.9	1.009	100.9	2.015	100.7
	1	0.538	107.6	0.956	95.6	1.946	97.3
	10	0.465	92.9	0.978	97.8	1.963	98.1
	50	0.465	92.9	0.978	97.8	1.929	96.5
Interfering substance: Colloid	Interference conc. (mg/ℓ)	Known [F] (mg/ℓ)					
		0.2		0.5		1	
		Measured [F](mg/ℓ)	% R	Measured [F](mg/ℓ)	% R	Measured [F](mg/ℓ)	% R
SiO ₂ (As SiO ₂ powder)	0	0.196	97.8	0.485	96.9	0.982	98.2
	60	0.201	100.7	0.490	97.9	1.003	100.3
	180	0.195	97.5	0.480	96.0	0.973	97.3

*R=Recovery

- Sample solutions were spiked with one interfering species at a time and the effect on F⁻ determination was assessed
- Sample solutions were spiked with a mixture of interfering species to assess whether synergistic effects were present.

Single compound ion interference

A series of standards and synthetic sample mixtures were prepared by the appropriate dilution of the stock solutions with deionised water and adding TISAB III in appropriate amounts. One interfering chemical at a time was chosen for investigating the interference effect on the F⁻ determination. The results are given in Table 8.

Obviously, anion interferences yield insignificant error, but the cation interferences, such as Al and Fe, were problematic even after adding TISAB III. The efficiency of TISAB III for de-complexation of Al-F and Fe-F complexes decreases at Al level > 1 mg/l.

The stability constants of metal-CDTA complexes are higher than those of metal-F⁻ complexes (Douglas, 1979). CDTA could therefore effectively de-complex metal from metal-F⁻ complexes, which would release free F⁻ ions. Therefore the % recoveries of each test solution were very much improved after adding TISAB III. However, the % recoveries of F⁻, in presence of 1 mg/l Al were 95.4%, 87.6% and 96.2% and, in presence of 10 mg/l Al were 70.6%, 67.7% and 68.2% for 0.5 mg/l, 1 mg/l and 2 mg/l F⁻ respectively. This indicates that TISAB III could not perfectly solve the Al interference. As the Al concentration increases, 1, 10, 50 and 100 mg/l the % recovery of F⁻ decrease drastically. Similar results have been reported by Duff and Stuart (1975) using a different type of TISAB, (triethanolamine (TEA) buffer and citrate buffer). Harwood (1968) showed that iron exhibited an effect, but at the concentrations normally found in natural waters this effect will be insignificant. He also noted that Al interference is a major obstacle, even at the levels normally

found in water. It was therefore necessary in the current study to investigate ways of overcoming Al interference on low-level F⁻ determination. The results given in Table 9 show that even if Al is present at 0.1 mg/l, it results in measurable suppression of the determined F⁻ concentration.

From Table 9, the Al tolerance for 95% F⁻ recovery is 0.1 mg/l Al for 0.2 mg/l F⁻ and 0.5 mg/l F⁻, and 0.2 mg/l for 1 mg/l F⁻. Different procedures and approaches with varying degrees of success have been reported in the literature to limit the effect of Al interference (Harwood, 1968; Duff and Stuart, 1975; Nicholson and Duff, 1981; Frenzel and Brätter, 1986; Pickering, 1986; Okutani et al., 1989; Trojanowicz et al., 1998). In the determination of F⁻ with an ISE in the presence of Al, release of the F⁻ from Al-F complex is essential and for this purpose several masking agents have been examined. Tri-ammonium citrate (TAC) buffer, employing CDTA and tri-ammonium citrate as complexing agents, was found to be most efficient in terms of masking ability. In their detailed study Nicholson and Duff (Nicholson and Duff, 1981) noted that 24 h following buffer addition would be beneficial in terms of an increased F⁻ recovery. These results were remarkable and potentially useful in the current application, provided it could be proven to be efficient with modern generation electrodes. Experiments were therefore done to confirm this result.

Firstly, TAC buffer was prepared using TISAB III as basis. The calculated value of TAC was 1M. The results of F⁻ determination with this buffer compared with results obtained using TISAB III are summarised in Table 10.

The results show that Al concentrations up to 5 mg/l were tolerated for 94% recovery at 1 mg/l F⁻. The recovery was therefore very much improved employing the TAC buffer. This experiment confirmed the fact that TAC buffer is greatly superior to TISAB III without TAC in terms of masking Al interference.

Interfering substance	Interference conc. (mg/l)	Known [F] (mg/l)					
		0.2		0.5		1	
		Measured [F](mg/l)	% R*	Measured [F](mg/l)	% R	Measured [F](mg/l)	% R
Al (as AlCl ₃ ·6H ₂ O)	0	0.198	99.0	0.489	97.8	0.995	99.5
	0.1	0.193	96.5	0.470	94.0	0.956	95.6
	0.2	0.188	94.0	0.430	86.0	0.956	95.6
	0.5	0.187	93.5	0.430	86.0	0.884	88.4
	1	0.186	93.0	0.445	89.0	0.855	85.5

Interfering Substance	Interference Conc. (mg/l)	1 mg/l F ⁻			
		TISAB Type			
		*TISAB III		TAC buffer	
		Measured [F](mg/l)	% R*	Measured [F](mg/l)	% R
Al (as AlCl ₃ ·6H ₂ O)	0	0.994	99.4	1.024	102.4
	1	0.876	87.6	0.962	96.2
	5	-	-	0.942	94.2
	10	0.677	67.7	0.904	90.4
	50	0.295	29.5	0.666	66.6
	100	0.168	16.8	0.509	50.9

* TISAB III results was cited from Table 9

TABLE 11
The effectiveness of time allowed for decomplexing using TISAB III on F⁻ determination in presence of 1 mg/l and 10 mg/l Al at 1 mg/l F⁻

Time (h)	Fs/Fr (1Al+1F)	Fs/Fr (10Al+1F)
0.02 (1 min)	0.85	0.60
0.17 (10 min)	0.86	0.60
0.33 (20 min)	0.86	0.60
0.5 (30 min)	0.87	0.61
1	0.87	0.61
2	0.88	0.62
3	0.91	0.62
4	0.93	0.62
5	0.94	0.62
6	0.93	0.63
7	0.95	0.63
8	0.95	0.63
9.5	0.95	0.63
10.5	0.95	0.63
24	0.95	0.64

An experiment was designed to determine the effectiveness of allowing decomplexing time after addition of TISAB III. A reference solution, 1 mg/l F_s(F_s) and a sample solution, mixture of 1 mg/l F_s and 1 mg/l Al (F_s) were made up. After calibration, using standards 0.1, 0.5 and 3 mg/l F⁻ concentrations of these two solutions were determined at several times from 1 min to 24 h. Since this experiment took a long time, the electrode drift had to be considered. Therefore, the ratio (F_s/F_p), instead of single measurement (F_s), was calculated to compensate the electrode drift. The results are shown in Table 11.

The decomplexing ability of the buffer was followed from the moment the buffer was added to the F⁻ containing sample, until a stable potential plateau was obtained. This result show that in TISAB III, 24 h decomplexing gave improved F⁻ recovery in the presence of 1 mg/l Al, but there was no significant improvement at 10 mg/l Al.

Allowing 24 h for decomplexation in cases where Al interference is expected and where TISAB III is used, would not be practical in many routine analysis laboratories. The use of TAC containing TISAB buffers would then be the obvious alternative.

Multi-compound interferences

To assess whether interference effects for multicomponent mixtures are additive or even synergistic, sample solutions were spiked with various mixtures of interfering species and measured after the addition of TISAB III. The concentrations of interfering substances were: Al³⁺ 1 mg/l, Mg²⁺ 10 mg/l, Ca²⁺

TABLE 12
Effects of multiple interferences on the determination of F⁻ with TISAB III

Interfering compound* numbers	Interfering substances	[F] Known (mg/l)	[F] Measured (mg/l)	%R
0	F Only	0.2	0.199	99.4
2	Al + Mg		0.195	97.3
	Al + Fe		0.189	94.6
	Al + Ca		0.192	96.0
	Ca + Mg		0.203	101.4
	Ca + Fe		0.192	95.8
	Mg + Fe		0.200	100.2
0	F only		0.197	98.7
3	Al + Ca + Mg		0.181	90.4
	Al + Ca + Fe		0.175	87.4
	Al + Mg + Fe		0.176	88.1
	Ca + Mg + Fe		0.181	90.4
4	Al + Ca + Mg + Fe		0.185	92.7
5	Al + Ca + Mg + Fe + PO ₄		0.177	88.6
0	F only		0.5	0.492
2	Al + Mg	0.462		92.5
	Al + Fe	0.449		89.9
	Al + Ca	0.459		91.8
	Ca + Mg	0.482		96.4
	Ca + Fe	0.468		93.7
	Mg + Fe	0.482		96.4
0	F only	0.492		98.4
3	Al + Ca + Mg	0.442		88.5
	Al + Ca + Fe	0.446		89.2
	Al + Mg + Fe	0.441		88.3
	Ca + Mg + Fe	0.470		94.1
4	Al + Ca + Mg + Fe	0.437		87.4
5	Al + Ca + Mg + Fe + PO ₄	0.439		87.7
0	F only	1		1.004
2	Al + Mg		0.880	88.0
	Al + Fe		0.887	88.7
	Al + Ca		0.896	89.6
	Ca + Mg		0.975	97.5
	Ca + Fe		0.975	97.5
	Mg + Fe		0.979	97.9
0	F only		1.004	100.4
3	Al + Ca + Mg		0.853	85.3
	Al + Ca + Fe		0.850	85.0
	Ca + Mg + Fe		0.953	95.3
	Al + Mg + Fe		0.860	86.0
4	Al + Ca + Mg + Fe		0.839	83.9
5	Al + Ca + Mg + Fe + PO ₄		0.829	82.9

10 mg/l, Fe²⁺ 1 mg/l and PO₄³⁻ 10 mg/l at 0.2, 0.5 and 1 mg/l F⁻. The results are given in Table 12.

Compared to the single compound interference test results in Table 8, a decrease in trend of F⁻ recovery was observed when the number of interfering elements increased; in other words, synergistic effects were observed in the presence of many interfering substances.

Analytical parameters

Typical repeatabilities achievable in routine determinations with a properly conditioned electrode and following the procedures discussed in this study are summarised in Table 13.

This can be maintained over long periods of time as is illustrated by the results of long term tests in Table 14. A 0.2 mg/l and 1 mg/l F⁻ test solutions were measured at regular intervals over a period of 9 months. The results confirm excellent stability and reliability of electrode, solutions and measuring setup.

[F] Conc. (mg/l)	Mean potential (mV)	SD (N=10)	% RSD (repeatability)
0.02	156.0	2.17	1.4
0.05	148.2	0.78	0.5
0.1	138.5	0.60	0.4
0.5	105.5	0.24	0.2
1.0	89.7	0.20	0.2
2.0	73.4	0.18	0.3

Date	[F] Known			
	0.2 mg/l		1 mg/l	
	[F] Measured	% Recovery	[F] Measured	% Recovery
11/08/2003	0.202	101.0	0.970	97.0
30/09/2003	0.195	97.5	0.982	98.2
12/03/2004	0.195	97.5	0.982	98.2
11/05/2004	0.200	100.0	0.986	98.6

Table 14 shows that samples containing F⁻ 0.2 and 1 mg F⁻/l can be stable for at least 9 months.

The qualitative detection limit for F⁻ was determined as the lowest concentration at which an equilibrium potential could be obtained. This was determined as 0.02 mg/l. The quantitative detection limit was determined as the lowest concentration of F⁻ needed to produce a potential that could be obtained in equilibrium and produce a linear calibration curve. The quantitative detection limits were determined as 0.05 mg/l.

A working range of 0.1 to 1 000 mg/l is normally recommended for F⁻ determination (Orion, 1982), but for low-level measurement, a working range 0.1 to 3 mg/l is recommended to obtain accurate results. With a well-conditioned electrode, the lowest calibration point can be extended up to 0.05 mg/l (see Fig. 5).

Methodology recommendations

F-ISE is a simple and accurate method for low-level F⁻ determination. Electrode drift is one of the main problems, especially at low concentrations. To minimise electrode drift and improve the equilibration time, it is recommended that F⁻ ion selective electrodes are stored dry in air and the reference electrode in deionised water. Cleaning the electrode regularly with F⁻ toothpaste is a very effective way to minimise electrode drift as well as improve the linearity of electrode response. It is recommended to use low-level standards, such as 0.1, 1 and 3 mg/l, for low-level determination. TISAB is normally added to samples and standards in ISE measurement in order to maintain a constant ionic strength for both standards and samples, optimise the pH, and de-complex interference ions. Low-level TISAB and TISAB III are available for low-level measurements, but TISAB III is recommended in natural samples, which contain many unknown interferences. Since low-level TISAB does not contain any de-complexation agent, such as CDTA, it cannot be used in natural samples. Most ionic interferences, except the Al ion, which readily form stable complexes with F⁻ ions, can be removed by using TISAB III. The Al tolerance for 95% F⁻ recovery is 0.2

mg/l and 0.1 mg/l for 1 mg/l F⁻ and 0.2 mg/l F⁻, respectively. Tri-ammonium citrate (TAC) buffer, can improve the Al tolerance up to 5 mg/l for 94% F⁻ recovery, and is recommended in the presence of high Al concentrations. However, TISAB III can be applied for most natural samples since the Al level is mostly below 0.2 mg/l. It should be noted, however, that many natural waters exist where the aluminium concentration is way above 0.2 mg/l, for example in humic mountain waters where the pH is below 6 pH units, and also with acid mine drainage where aluminium often far exceeds 1 mg/l. Aluminium in drinking water above 1 mg/l is also possible where break-through of aluminium salt flocculant has occurred, where operational optimisation processes have failed.

Synergistic effects in ISE have been demonstrated when many interfering substances are present.

Methodology application for the analysis of natural and drinking water

The methodologies and operational procedures that were developed and refined in this study were applied to the analysis of natural waters such as river water and synthetic water samples containing various potential interfering ions. The samples were obtained from the SABS as part of their ongoing Water Check Programme. This programme is a high-frequency inter-laboratory proficiency testing programme with the objective of providing a rapid report-back service to participants for self-evaluation. A set of F⁻-containing solutions with different matrix compositions and some containing elements that could interfere with the fluoride determination, was included in the test samples sent out to the participating laboratories. This was done to evaluate the effect of matrix composition and common interferences on routine F⁻ determination in South Africa. A secondary aim was to collect information with regard to the types of analytical technique currently used in South Africa for F⁻ determination and to compare their performance capabilities (Noh and Coetzee, 2006).

The set of 7 samples used in the fluoride proficiency study contained two unpreserved natural water samples, a river water (Sample 2004/03/1) and a borehole water (Sample 2004/03/2) sample, and 5 synthetic water sample concentrates (Samples 2004/03/4/5/6/7 and 8). The composition of the synthetic samples is given in Table 15. The synthetic samples were prepared using AR grade chemicals. The sample compositions were designed to assess the effect of Al interference (Sample 2004/03/4) the F⁻ concentration level (Sample 2004/03/4/6/7), and varying matrix composition such as the inclusion of formate ions (Sample 2004/03/6 and 7) on F⁻ determination.

Species	Sample number 2004/03/...				
	4	5	6	7	8
Na ⁺					
Ca ²⁺	-	0.8	0.8	0.8	-
Mg ²⁺	-	0.8	0.8	0.8	-
Al ³⁺	1	-	-	-	-
F ⁻	0.25	0.10	0.54	1.50	0.90
Formate	-	-	4	4	-
Cl ⁻	18.77	27.23	22.66	32.90	24.61
NO ₃ ⁻	-	4	4	4	-
PO ₄ ³⁻	-	4	4	4	-
SO ₄ ²⁻	13.77	20.09	24.47	32.00	40.86

Sample number	True mg/ℓ	Found this study	Median	% Error	Robust SD	%RSD	N
1	-	0.14	0.16	-	0.07	44	62
2	-	0.19	0.20	-	0.06	30	63
4	0.25	0.23	0.22	-12.0	0.12	55	61
5	0.10	0.10	0.13	+30.0	0.10	77	63
6	0.54	0.49	0.50	-7.4	0.10	20	66
7	1.50	1.45	1.42	-5.3	0.19	13	66
8	0.90	0.88	0.91	+1.1	0.10	11	65

Samples for analyses were prepared by pipetting 20 ml of the concentrate solutions into 500 ml volumetric flasks and diluting to volume with deionised water.

The results obtained using the methodologies developed in this work are summarised in Table 16 compared to the results obtained in the proficiency tests from other participating laboratories in South Africa. A complete report on the Water Check Programme results is published elsewhere (Noh and Coetzee, 2006).

The Water Check Programme makes use of robust statistics, applying down-weighting of outlying data without excluding such data for data evaluation. For this study, all the original values, outliers included, were recaptured electronically in the reporting process adopted by the SABS. The Z-score for each result is calculated and an average Z-score then calculated for each laboratory. The Z-scores are calculated as follows:

$$Z\text{-score} = \frac{x - \bar{x}}{s}, \quad \bar{x} = \text{robust mean (median) in case of natural samples}$$

or

$$Z\text{-score} = \frac{x - t}{s}, \quad t = \text{true value in case of synthetic samples}$$

The results obtained in this study achieved the lowest Z-score of 0.18 of all the 66 participating laboratories confirming the importance of following the correct procedures as proposed in this work and thus avoiding the numerous pitfalls.

Conclusion

The methodologies developed in this study were applied in a Water Check Programme, a proficiency testing programme with very good results. It proves that F⁻-ISE potentiometry could be successfully applied in low level F⁻ determinations such as would typically be required in a fluoridation programme provided that good laboratory practice peculiar to this technique, is diligently followed.

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