

POTENTIOMETRIC FLUORIDE ANALYSIS WITH IMPROVED ANALYTICAL PERFORMANCE

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Abstract

Since the 1960s SINTEF has, in collaboration with the Nordic aluminium smelters, developed methods for sampling and analysis of fluoride. Unlike conventional potentiometric analysis, this methodology involves detection of fluoride in acidic media. At low pH, the electrode kinetics is improved, resulting in faster analysis. By masking of the fluoride leakage from the ion-selective electrode, the sensitivity of the method is improved. Standard addition methodology is applied for improved analytical performance. The acidic media makes it possible to perform a direct analysis of fluoride in biological samples. In this way, fluoride is extracted from the biological matrix by the acid. The high sensitivity requires low sample masses used and thus does not interfere with the fluoride detection at the ion-selective electrode. This is far more efficient than the conventional approach of ashing the sample at elevated temperatures. Acid extraction can also be applied to filter dust samples.

Introduction

The introduction of the fluoride selective electrode in the 1960ies greatly simplified the analytical procedures for fluorine assessment as Willard-Winter [1] distillation and subsequent titration was replaced by direct assessment of the free fluoride concentration of the samples. As the fluoride selective electrode shows no response to other fluorine containing species, the total fluorine content must be made available to the electrode as fluoride. In primary aluminium production, environmental impact control is performed by monitoring the fluorine content of biological material sampled at various distances from the smelter. The digestion of the biological matrix normally involves ashing (conifer needles, grasses) or bones (alkaline fusion). Fugitive emissions of fluoride are monitored by sampling air over the roof of smelters. Filters are boiled in sodium hydroxide in order to extract the fluorine containing species. These processes are time consuming due to the temperature gradients involved and are further, due to the transfer of sample between containers, prone to introduce errors in the analytical results.

The fluoride selectivity of the ion selective electrode is ascribed to the lanthanum trifluoride membrane used. The main interfering species for this electrode is the hydroxyl ion, and this limits its application to neutral or acid samples. The free fluoride concentration is pH dependent as hydrogen fluoride is an acid with an acid constant of about 3.2. At lower pH values hydrogen fluoride is the main fluorine containing species in the solution. Standard procedures for analyzing fluoride therefore involve using a pH about 5 to have sufficient free fluoride present for analysis. The sensitivity of this methodology is limited to about 0.1 ppm. This limit is dictated by the leakage of fluoride from the lanthanum trifluoride membrane. Baumann [2] has shown that this sensitivity can be lowered by introducing fluoride complexing species, acids being amongst them. Further, it has been shown by

Moritz *et al.* [3, 4] that the fluoride electrode kinetics is superior at low pH. Aarhaug *et al.* [5] estimated the detection and quantification limits for this methodology to be 6.2 and 8.6 ppb respectively.

In aluminium primary production fluorine containing samples also contain Al^{3+} . Standard methodology suggests the use of a Total Ionic Strength Adjustment Buffer (TISAB) where a complexing agent is added to remove interference by cations like Al^{3+} , Fe^{3+} and Ca^{2+} . TISAB buffers do, however, not work well at low pH where its chelating agent is protonated.

In this paper, we present an alternative and more time efficient procedure for extraction and digestion of samples. The methodology is cold acid extraction of the fluorine from the biological matrix followed by direct potentiometric fluoride detection in the same sample beaker [6]. Phosphoric acid is proposed as an alternative to TISAB. By performing fluoride analysis at low pH, fast and sensitive analysis can be performed. The improved sensitivity allows for less sample mass to be used. This, add the effect of improved electrode kinetics allows for the quantification of fluoride for a sample containing solid material.

Although not documented in this paper, SINTEF has performed a verification program in order to justify the use of acid extraction as a viable alternative to ashing and alkaline fusion of biological matrices.

Experimental

Fluoride concentration assessment was performed by hardware from Metrohm AG. In addition to Fluoride and Silver/Silver chloride electrodes, a temperature sensor was used to monitor sample temperature. An 808 Titrand with an 1 mL burette was used to perform additions of fluoride standard ($1000 \text{ mg F}^- \text{ L}^{-1}$). An 824 Sample changer with a 26 position rack was used for automation of the analysis. A rotor was used to stir the solutions during analysis. For each series of analyses performed, the first and last beakers were used to rinse the electrodes. The 808 Titrand standard addition functionality was used to quantify the fluoride concentration in the sample beaker. Three standard additions were applied, and the maximum electrode EMF drift was set to 0.5 mV min^{-1} . Maximum delay before next standard addition was set to 0.5 seconds. A minimum measuring time of 20 seconds were enforced. Fluoride quantification was performed in two modes: Acid and TISAB. In Acid mode, Hydrochloric acid (5M, 5mL) was used as a supporting electrolyte. In TISAB mode, 1 mL TISAB III (Merck) was added to each solution. All solutions were diluted to 50 mL with deionized water. Analysis of samples containing fluoride in the concentration range 10 ppb to 20 ppm was performed. For the lower concentration range, correction for the fluoride background introduced by the hydrochloric acid and the deionized water was corrected for.

Fluoride complexation by Al^{3+} ions was illustrated by spiking a solution containing $10 \mu\text{g}$ of fluoride with aliquots of and AlCl_3

solution while recording the fluoride selective electrode EMF. The procedure was repeated for a solution containing 10 µg of fluoride added orthophosphoric acid (5 M, 5 mL) to illustrate the interaction of Al³⁺ with PO₄³⁻. The complexation was also illustrated by spiking fluoride to samples of hydrochloric acid, one of them containing AlCl₃ (100 µg)

Results

The direct comparison between Acid and TISAB mode titration are shown in Table 1. All series were performed subsequently, without removing outliers. The first analysis was removed from each series due to the history effect, as higher concentrations were performed first. The series performed at 0,01 and 0,02 ppm were corrected for background fluoride content.

Table 1. Acid and TISAB mode potentiometric titration of fluoride.

Type	Acid	TISAB	Acid	TISAB	Acid	TISAB	Acid	TISAB	Acid	TISAB
Conc. Solution (ppm)	0,01	0,01	0,02	0,02	0,2	0,2	2	2	20	20
µg F ⁻ sample	0,5	0,5	1	1	10	10	100	100	1000	1000
	0,58	0,38	1,00	0,92	9,42	9,41	102,1	98,2	1029,1	1011,9
	0,59	0,26	1,03	0,93	9,55	9,45	98,1	101,5	985,6	1017,0
	0,51	0,31	1,00	0,95	9,50	9,34	92,8	101,9	1004,4	1020,7
	0,52	0,47	1,00	0,92	9,45	9,33	95,8	100,4	961,6	1009,6
	0,53	0,26	1,06	0,94	9,46	9,18	98,9	101,3	989,3	1009,5
	0,57	0,39	0,98	0,92	9,58	9,65	98,8	102,4	976,5	1011,6
	0,54	0,25	1,02	0,79	9,59	9,03	94,0	103,7	958,2	1017,6
	0,49	0,22	1,02	0,92	9,42	9,09	98,9	116,8	985,5	1021,7
	0,52	0,27	1,02	0,92	9,57	9,12	96,0	118,6	976,5	1005,3
Average (ppm)	0,54	0,31	1,01	0,91	9,50	9,29	97,3	105,0	985,2	1013,9
SD (ppm)	0,04	0,08	0,02	0,05	0,07	0,20	2,87	7,39	21,65	5,61
RSD (ppm)	6,6	26,4	2,2	5,1	0,7	2,2	3,0	7,0	2,2	0,6
Relative error (%)	7,7	-37,6	1,5	-8,8	-5,0	-7,1	-2,8	5,0	-1,5	1,4
Analysis time (min)	42	81	45	57	31	43	38	39	50	44

For the two series of highest fluoride concentration, the analytical performance is similar. At lower concentration levels, it can be seen that the analytical performance of TISAB mode is inferior when it comes to both precision and accuracy. Further, the analysis time at the 10 ppb level is twice that of the Acid mode. The analytical performance of the Acid mode has previously been reported by Aarhaug [7], although not compared directly with TISAB mode analysis.

The applicability of phosphoric acid as an alternative to TISAB was evaluated by adding Al³⁺ to sample solutions of hydrochloric acid with and without orthophosphoric acid present. The comparison is shown in Figure 1. The background value of fluoride ascribed to phosphoric acid was three times higher than that of hydrochloric acid. This can be seen by the lower ordinate intercept.

Clearly, the neat hydrochloric acid loses more fluoride to Al³⁺ complexation than when adding orthophosphoric acid. The increase in EMF for the experiment containing orthophosphoric acid can be ascribed to the dilution of the 10 µg fluoride solution. The dilution factor is however the same for both experiments.

The methodology presented is currently used by most aluminium smelters in Scandinavia. To exemplify the excellent analytical performance, two examples from the 2012 round robin test are presented.

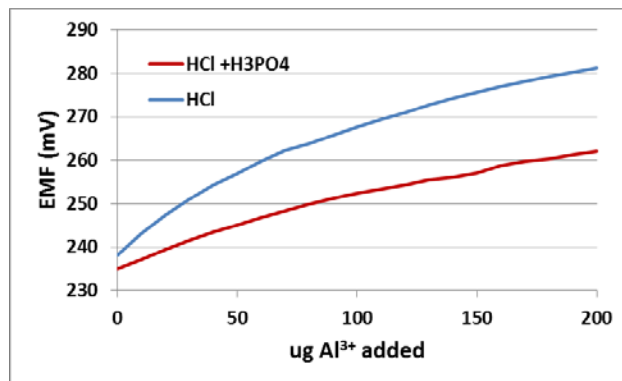


Figure 1. Phosphoric acid complexation of Al³⁺.

Figure 2 shows the result of the fluoride titration for samples with and without Al^{3+} ions present.

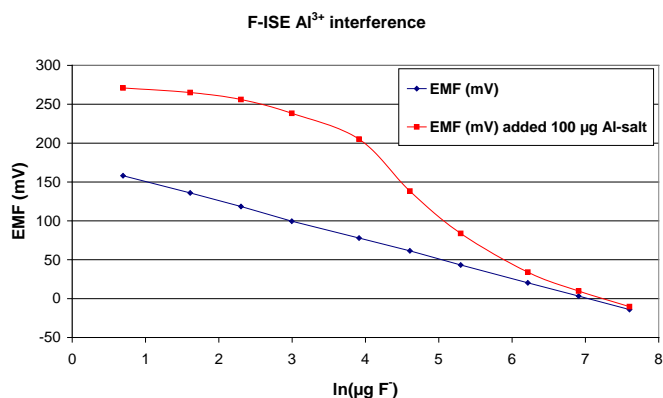


Figure 2. Fluoride titration of samples with and without Al^{3+} present.

For the sample without Al^{3+} added, the linear correlation found between electrode EMF and the natural logarithm of the fluoride concentration is close to the theoretical correlation given by the Nernst equation with a slope of about -59 mV . With the presence of Al^{3+} , an increase in electrode EMF is observable due to complexation of fluoride by Al^{3+} . Figure 2 also clearly illustrates that the effect of complexation is constant for a fixed level of interfering ions. Thus, the effect diminishes and are insignificant at the highest concentrations of fluoride.

In Figure 3 the results of the cold extraction of fluorine from grass is shown. Although the extraction time used by most smelters is "left overnight", this can be reduced to a few hours by means of an ultrasound bath. Sample masses used were in the range 0.5 to 2 g. The result show that there is, with one exception, very good correlation between the laboratories.

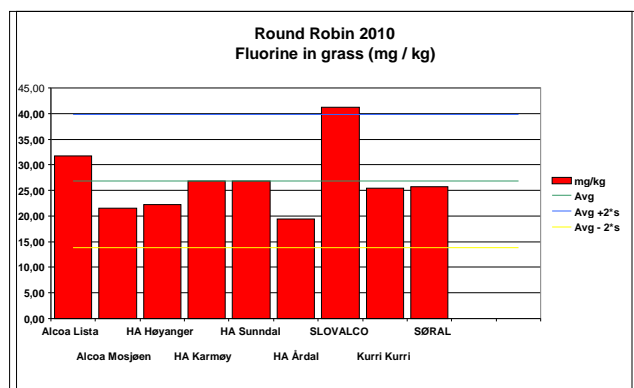


Figure 3. Round Robin: Fluoride in grass quantification (mg/kg). Green line indicates average value, while yellow and blue lines define the ± 2 standard deviation interval.

To illustrate the applicability of direct analysis of solid materials, the round robin results from the analysis of secondary alumina is shown in Figure 4. Sample masses used were in the range 0.1 to 0.5 g.

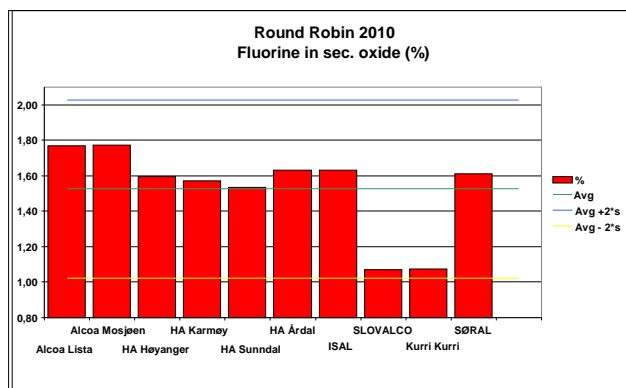


Figure 4. Round robin: Fluoride in secondary alumina (%). Green line indicates average value, while yellow and blue lines define the ± 2 standard deviation interval.

The results show good correlation between the contributing smelters from the Nordic countries. Low, yet within the two standard deviation interval, results were observed for the other contributing smelters.

Conclusion

By performing fluoride quantification in Acid mode, the sample pretreatment can be greatly simplified. Although improved fluoride sensitivity is not necessary a requirement where sample concentrations are high, this can be used to lower the sample mass when measuring the fluoride concentration in a beaker containing the sample mass. By combing the extraction and analysis steps, time and cost of analysis can be reduced.

This methodology is currently in use by nine smelters worldwide. No hardware requirements are required in order to perform Acid mode fluoride analysis. Beneficial to analytical performance is however a titrator capable of performing quantification by multipoint standard addition.

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