

## The customer application

**SINTEF Materials and Chemistry, Trondheim, Norway:**

**Sintalyzer –**

**a completely automated analysis system for fluoride determination in the aluminum industry**



SINTEF was established in 1950 and is today the largest independent research organization in Scandinavia. More than 1700 employees, of whom about 1350 work in Trondheim and 350 in Oslo, develop new products and methods for industry and the public sector. Research is concentrated on the areas of technology, natural science, medicine and social science. SINTEF cooperates closely with the Norwegian University of Science and Technology (NTNU) in Trondheim and the University of Oslo..

### **Introduction**

For almost 40 years SINTEF has been involved with the environmental aspects of aluminum production. Monitoring fluoride emissions has assumed particular importance in this context. However, the aqueous solutions from the aluminum industry are difficult to analyze, as complex formation interferes with the determination of fluoride.

The analysis system developed by SINTEF and based on Metrohm instruments solves the above-mentioned problems. The seventh version of the Sintalyzer has recently been released.

### **Instruments and accessories used**

- 799 GPT Titrino with 1 mL Exchange Unit and micro buret tip
- 781 pH/Ion Meter
- 824 Easy Sample Changer with 759 Swing Head, 802 Rod Stirrer and rack for 26 samples
- 6.0502.150 ion-selective fluoride electrode and 6.0726.100 double-junction Ag/AgCl reference electrode
- Pt 1000 temperature sensor
- PC with Windows™ operating system and three RS 232 interfaces



The Sintalyzer system for fully automatic fluoride determination.

## Description of the analytical method

Sample solutions from the aluminum industry cannot be analyzed by the standard method using TISAB solution. The aluminum, silicon and iron contained in the samples form stable fluoro complexes and would therefore interfere with the fluoride determination, leading to low-bias results.

The Sintalyzer system uses several buffer solutions specifically adapted to the samples to be investigated. This, together with proper sample preparation, allows the fluoride to be determined exactly and completely.

The standard addition technique is used. In order to avoid dilution of the original matrix, micro volumes of a highly concentrated standard solution are added. Thanks to the dosing device's high resolution of 10'000 steps per cylinder volume and the use of the 1 mL Exchange Unit it is possible to add even such small volumes extremely accurately. In order to prevent diffusion of the standard solution into the sample, an anti-diffusion buret tip is used.

The Sintalyzer software controls the standard addition procedure that has been specially developed and optimized to suit the given samples. The program monitors the potential values measured by the 781 pH/Ion Meter. As soon as the potential has stabilized, the program calculates the necessary volume of standard solution and transmits this to the 799 GPT Titrino. The standard additions are carried out in such a way that a constant potential difference is always obtained. The Sintalyzer software subjects the measured values to a linear regression analysis and then calculates the fluoride concentration of the sample from the initial potential and the regression data.

The screenshot shows the main interface of the Sintalyzer software. It includes a menu bar (File, Options, Help), a logo, and various input fields for analysis parameters. The 'Analysis' section contains buttons for 'Open Com', 'Reset all units', 'Software', 'Execute control', 'HControl', 'HFlow', 'Manual analysis', and 'Automatic analysis'. The 'Database operations' section has 'View report' and 'Report and database utility' buttons. There are also checkboxes for 'Autoincrement beaker number' and 'Autoincrement journal number', and a 'Start at beaker no.' field with a 'Clear gid' button.

Pos	Beaker no.	Journal no.	Sample reference	Dilution factor	Aliquot [ml]
1	1	1110-1	Cathode	0.5	5
2	2	1110-2	Cathode	0.5	10
3	3	1110-3	Anode	1	5
4	4	1110-4	Anode	1	10

Main page of the Sintalyzer software.

Rapid fluoride determination depends on the fast measurement of the electrode potential after each standard addition. The Sintalyzer software uses an algorithm that has been specially matched to the response behavior of the fluoride ISE.

For storing the analytical data, the Sintalyzer software provides a database that offers both comprehensive statistics functions and a report generator. Search filters allow the user to draw up, for example, comparison charts or to graphically display the chronological sequence of measured values. Data export to a LIMS system is also possible without any problems.

### Analytical report

Determination of fluoride with SINTALYZER

06.07.2004 Analyst: May-Tove Sorbo

Sample changer: automatic  
 Customer: Okid Prebako/Sorbo  
 Sample type:  
 Method:

Sample temperature: 0 °C Number of standard additions: 1  
 Concentration of std.: 1000 mg/l Time of stability: 0 min  
 Dispensing rate: 0 ml/min Blank value: 0.55 µg

Journal no	Beaker no	Sample reference	Weight [g]	Tot. vol [ml]	Aliquote [ml]	Content Beaker [µg]	Content Sample [%]	Regr. SD [%]
1	1	std 2.5 ppm	0	0	0	24.46	0.00	1.14
2	2	std 2.5 ppm	0	0	0	26.03	0.00	1.18
3	3	std 2.5 ppm	0	0	0	26.61	0.00	5.05
4	4	std 5.0 ppm	0	0	0	48.22	0.00	1.43
5	5	std 5.0 ppm	0	0	0	49.24	0.00	0.59
6	6	std 5.0 ppm	0	0	0	50.60	0.01	1.73
7	7	OkidK-III	0.0527	250	10	33.54	1.56	1.98
8	8	OkidK-III	0.0527	250	10	32.45	1.51	0.49
9	9	OkidK-III	0.1037	250	10	142.76	3.43	2.79
10	10	OkidK-IV	0.0517	250	10	57.32	2.75	3.60
11	11	OkidK-IV	0.1024	250	10	75.49	1.83	5.71
12	12	OkidK-V	0.0526	250	10	43.49	2.04	4.16
13	13	OkidK-V	0.1049	250	10	67.81	1.60	6.85
14	14	Okid sile : 8	0.0516	250	10	36.22	1.73	5.22
15	15	Okid sile : 8	0.1022	250	10	52.85	1.28	7.43
1	1	OkidK-III	0.0527	250	10	65.67	3.09	3.68
2	2	OkidK-III	0.0527	250	10	44.91	2.10	1.37
3	3	OkidK-III	0.1037	250	10	80.69	1.93	3.03

Example of a Sintalyzer analytical report.

### Results and discussion

The measured values obtained with the automated Sintalyzer system show an excellent repeatability. Even for very low fluoride concentrations the relative standard deviation is less than 5% (see table below). The optimal working range of the system is normally between 10 and 150 µg fluoride (absolute mass in the beaker).

#### Repeatability for the analysis of fluoride standards of different concentrations (in each case at least a 10-fold determination was carried out)

Concentration of fluoride standard (mmol/L)	Mass of fluoride in the beaker (µg)	Absolute standard deviation (µg)	Relative standard deviation (%)
2	100	0.56	0.55
1	50	0.48	0.93
0.2	10	0.13	1.3
0.1	5	0.087	1.6
0.04	2	0.058	2.5
0.01	0.5	0.034	4.5

The accuracy of the analytical method is also demonstrated in the following table. Two fluoride standard solutions with concentrations of 2 and 0.2 mmol/L (corresponding to 100 and 10 µg fluoride in the beaker) were each subjected to a 14-fold determination.

*Blessed is the man who, having nothing to say, abstains from giving us wordy evidence of the fact.*

George Eliot

## Results of the analysis of two fluoride standards with concentrations of 2 and 0.2 mmol/L

	Fluoride standard 2 mmol/L (100 µg fluoride in the beaker)		Fluoride standard 0.2 mmol/L (10 µg fluoride in the beaker)	
	Determined mass of fluoride (µg)	Standard deviation of linear regression (µg)	Determined mass of fluoride (µg)	Standard deviation of linear regression (µg)
1	100.18	0.17	10.03	0.94
2	99.89	0.14	10.08	1.21
3	100.14	0.37	9.98	0.32
4	100.00	1.41	10.17	0.64
5	99.67	0.24	10.12	0.64
6	103.16	1.64	10.08	0.77
7	100.13	0.57	10.14	0.56
8	100.22	0.26	10.25	0.32
9	99.79	0.48	10.03	0.72
10	100.32	0.22	10.11	0.14
11	100.26	0.47	10.19	0.49
12	100.39	0.14	10.06	0.37
13	100.66	0.00	10.05	0.52
14	100.08	0.00	10.17	0.58
Mean value (µg)	100.35	0.44	10.10	0.59
s <sub>rel</sub> (%)	0.84		0.73	
Rel. error (%)	0.35		1.04	

## Conclusions

The Sintalyzer is a completely automated analysis system for the determination of fluoride by direct potentiometry that has been specially designed to meet the requirements of the aluminum industry. In the Scandinavian countries all the aluminum producers are now using this system and it has already been installed in Germany, India and Slovakia.

In comparison with alternative determination methods such as, for example, X-ray fluorescence analysis (XRFA), the Sintalyzer system offers the advantage of much lower investment costs. Service and maintenance requirements are also considerably lower.

The Sintalyzer package contains ready-to-use methods covering all the usual matrices encountered in the aluminum industry. The system is certified according to the Norwegian quality standard and supports the user in GLP-compliant work.

Although the Sintalyzer was primarily developed for determining the fluoride content of sample solutions in the aluminum industry, the analytical method can also be modified for use with other matrices. It is also possible to replace the fluoride ISE by a different ion-selective electrode, which opens up many new applications.

We would like to warmly thank Thor Anders Aarhaug, the manager of the Sintalyzer development project at SINTEF Materials and Chemistry in Trondheim, for permission to describe this interesting application in Metrohm Information.



Thor Anders Aarhaug working with the Sintalyzer.