



## Lab Report XRF 142

# S8 TIGER Series 2

- Quality control of anode cokes – trace analysis by WDXRF (acc. to ISO 12980, ASTM D 6379 and YS/T 63.16)

### Introduction

Coke based anodes are vital in aluminum production and are used to conduct the current to the electrolytic bath. In addition the coke helps to remove the oxygen from the alumina as  $\text{CO}_2$ . The production of one ton of aluminum requires approximately 400 kg of anode. They are made out of petroleum coke, pitch and returns from aluminum production. The mixture is put into moulds and heated up for 2 weeks above  $1100^\circ\text{C}$ . The calcinated carbon blocks are now able to withstand the extreme conditions in the electrolytic aluminum bath.

The control of the impurities in the coke is vital to avoid cross contamination to the final aluminum products. Especially hazardous elements must be controlled in order to prevent downgrading of the metal quality. Especially Si, Fe, Pb, Ni, V, Na and Ca are influencing the aluminum quality, while Ni, V, Na and Ca have a negative impact on anode quality and power consumption. Sulfur from the anode coke will leave the cell as sulfur dioxide. Therefore the level of sulfur in the anode should be as little as possible to prevent from negative environmental impact. The same is true for the hazardous element Pb.

Wavelength dispersive X-ray fluorescence analysis (WDXRF) enables manufacturers the quick and precise control of all major impurities in the anode coke. With the S8 TIGER with 1 kW this task is easily accomplished with little installation. Based on 1 kW X-ray power the S8 TIGER Series 2 doesn't require any external cooling water or compressed air, but delivers the analytical performance one would need to control impurities in coke and coal. This lab report will show the analytical performance of the S8 TIGER Series 2 and outline the specific benefits for this task.



Figure 1: Quick and easy start of samples with TouchControl and EasyLoad of the S8 TIGER Series 2

### Instrument

The S8 TIGER 1 kW WDXRF spectrometer (Figure 1) comes equipped with an X-ray tube with close coupling between the tube, sample and detector. This optimized beam path ensures a high efficiency with optimal excitation of the elements in the sample. The compact goniometer is equipped for this application with 2 collimators (0.23° and 0.46°) and four analyzer crystals (XS-55, PET, LiF200 and LiF220). With two detectors (flow counter and scintillation counter) more than 20 elements were analyzed. Big advantage of the S8 TIGER Series 2 design is the direct loading: The sample is placed from the automatic sample handler into the measurement position. The sample chamber is quickly evacuated and the analysis starts immediately once the vacuum level

is reached. This pressure controlled start of the measurement enhances the analysis light elements in humid samples. It ensures that the vacuum level is constant and that there is no influence for the light elements by absorption of remaining water and gases in the beam path. In addition the sample is always mounted in the same distance to the tube. This leads to a better analytical precision because there are no longer any tolerances left.

### Sample preparation

The standards and samples were ground to receive a very small grain size in a tungsten carbide vessel to avoid contamination with Cr and Fe. In addition one has to be careful with Na contamination. This can be avoided by using gloves. 7 g of anode coke powder was thoroughly mixed with 1.4 g of wax and pressed with an automated press in aluminum cups.

Table 1: Concentration ranges and limits of detection for anode cokes analyzed with the S8 TIGER with 1 KW

Element	Lower Range [ppm]	Upper Range [ppm]	LOD [ppm]
F	64	4953	48
Na	59	2401	7
Mg	4	70	2,5
Al	32	1524	5,3
Si	24	180	2,4
P	1	24	1,4
S	0.89 %	4.69 %	42
K	5	35	0,8
Ca	25	387	1,4
Ti	2	28	0,6
V	32	698	3,1
Cr	3	12	3,5
Mn	1	9	0,7
Fe	99	1454	5,5
Ni	65	283	1,9
Cu	1	6	0,3
Zn	10	43	0,5
Sr	1	6	0,3
Ba	1	17	1,7
Pb	3	30	0,5

## Calibration and Measurement

To analyze the 20 elements in anode coke, the net intensities for all elements were determined by measuring peak and background intensities. In order to save valuable measurement time, the same background positions were used for several elements when possible. The measurement times were selected to meet the requirements for process control. SPECTRA<sup>plus</sup> offers automatic time optimized measurements: Based on the required counting statistical error (CSE) the measurement of an element line is stopped, once the defined CSE is achieved. This ensures that no time is wasted to measure the samples better than required and the maximum sample throughput is achieved. This function stops in addition the measurement at the defined maximum

measurement time. The typical measurement time for one sample was in the range of 19 minutes.

The calibration function was calculated based on the measurement of 14 certified reference samples covering wider concentration ranges for different grades, including returns from the aluminum process. The concentration ranges are listed in Table 1. The calibration curves for S and Ni are shown in Figures 2 and 3. The maximum calibration deviation was typically less than 1 % rel. The high linearity was achieved based on the variable alpha matrix correction enabling the analysis of samples with low and high sulfur concentration in one calibration: The absolute standard deviation improved by 10% relative with activating the variable alpha matrix correction

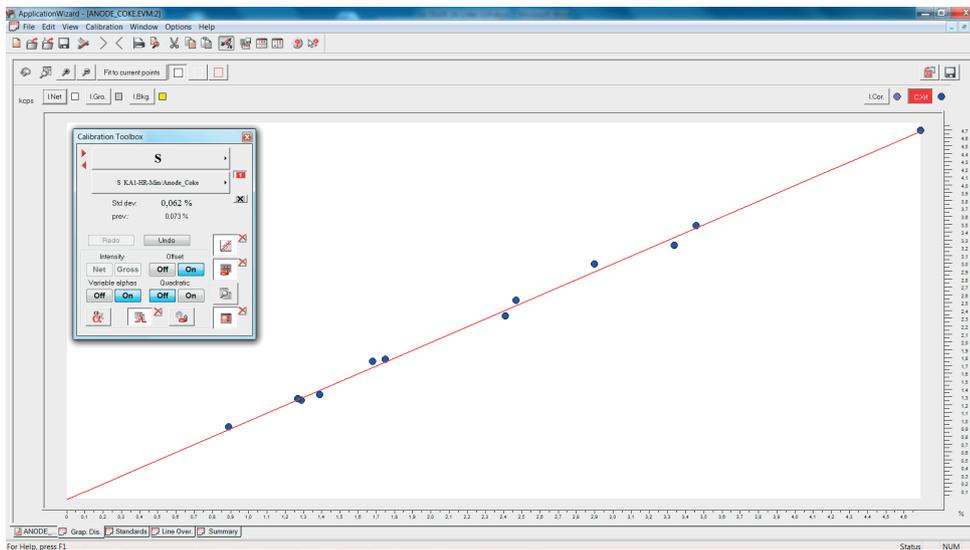


Figure 2: Calibration curve for S, covering the concentration range up to 4.7 %

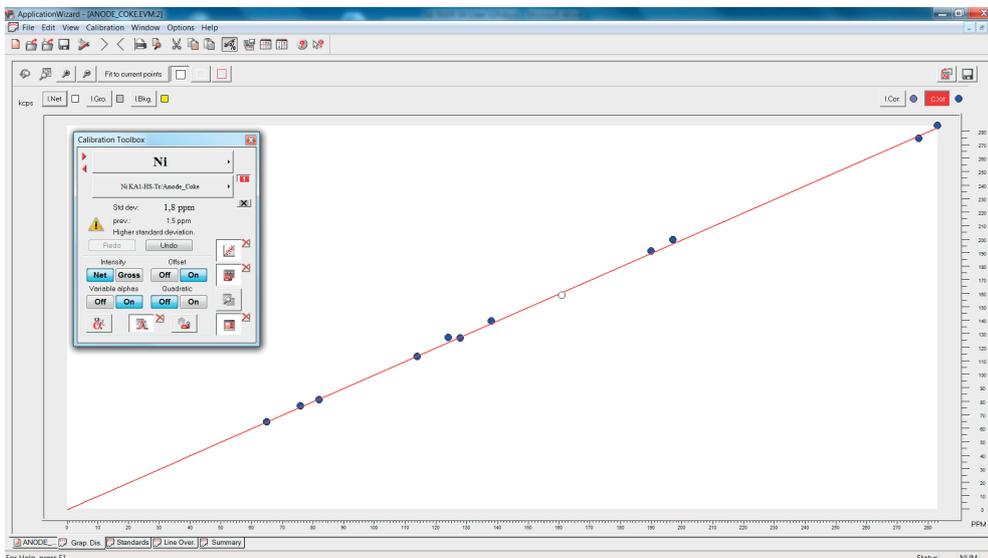


Figure 3: Calibration curve for Ni, covering the concentration range up to 300 ppm with a standard deviation of less than 2 ppm

Table 2: Results of the repeatability test for anode coke, measured 10 times

Time	Average	Std.Dev.	Rel.Std. Dev.	Certified Conc.
S (%)	0.57	0.00	0.85	0.60
Ni (PPM)	3.4	0.5	14.4	4
Si (PPM)	78.8	12.0	15.3	70
Fe (PPM)	127.0	0.8	0.6	130.0
Na (PPM)	36.0	0.0	0.0	n.a.
Al (PPM)	45.4	1.5	3.3	50
Ca (PPM)	65.7	0.5	0.7	63
K (PPM)	13.8	0.6	4.3	12
Mg (PPM)	5.2	0.4	7.7	6
Cl (PPM)	241.5	1.7	0.7	230
Cr (PPM)	9.0	0.1	1.1	1
Mn (PPM)	6.0	0.6	10.5	6.0
P (PPM)	21.1	0.3	1.4	11
Pb (PPM)	448.8	1.1	0.2	450
Ti (PPM)	9.9	0.7	7.1	4
Zn (PPM)	569.3	0.8	0.1	570
C (%)	99.26	0.00	0.0	99.3

The recovery of the minor elements, such as iron, calcium, chlorine, zinc and lead was in the range of 97 to 105 %. The determination of carbon as matrix elements was possible subtracting the sum of all other elements, the alignment with the certified concentration was excellent. The recovery for trace elements in the lower range of the calibration was higher with typical 10 % rel.

## Results

Anode cokes are quickly checked and verified for their usability in aluminum production with WDXRF. Quick sample preparation with simple grinding and pressing forms within less than 5 minutes a stable specimen which is accurately and precisely analyzed with 19 minutes maximum measurement time on the S8 TIGER Series 2 with 1 kW power. With detection limits down to the sub-ppm range even the analysis of hazardous elements is possible in addition to elements with higher concentrations. A wider variety of different cokes can be analyzed based on just one calibration due to the variable alpha matrix coefficients: Even higher variation of major and minor elements is compensated efficiently. This variable alpha model is unique to Bruker's analytical software SPECTRA<sup>plus</sup>.

The installation of the S8 TIGER Series 2 with 1 kW is quick, no other supply than standard power and P10 gas is required. With less requirements for power and no need for water chiller the operating costs are uniquely low. With more than 70 samples per day, the sample throughput is high enough for medium size labs, in addition the same instrument configuration also enables users to analyse raw materials such as Bauxite or final aluminum products..

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