Application Note 41730

Analysis of Metallurgical Slags with Thermo Scientific ARL OPTIM'X WDXRF Sequential-Simultaneous Spectrometer

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Key Words

ARL OPTIM'X, spectrometer, metallurgical slags, X-ray fluorescence, XRF

Goal

To show the excellent repeatability of the Thermo Scientific™ ARL™ OPTIM'X for the analysis of slags at 200 W.

Introduction

Slags originate from various stages in the iron and steel process, e.g. blast furnace, converter, basic oxygen furnace (BOF also referred to as BOS = basic oxygen steelmaking), electric arc furnace or ladle.

In the blast furnace, slag is formed from impurities in the iron ores (known as the gangue), the flux and coke ashes. It is a complex silicate of aluminum, calcium and magnesium containing small quantities of oxides of manganese and iron as well as calcium sulfide. Slag has a double role: it permits removal of the gangue thanks to its fusibility and fluidity, it also allows exchange reaction with the liquid metal and permits a control of the process in order for the desirable elements to stay in the melt while the others are removed. As an example, in an electric arc furnace the slag formation process can be controlled by adding oxygen, carbon and slag formers to the melt.

This will promote formation of CO instead of MnO and FeO and help keep these elements in their metallic form in the melt. The basic slag formers like lime (CaO) and magnesia (MgO) help neutralize the acidity of the slag in order to save the refractory bricks of the furnace.

Instrument

The Thermo Scientific ARL OPTIM'X is a WDXRF instrument designed for ease of operation and low maintenance costs. An ARL OPTIM'X XRF spectrometer configured as a sequential-simultaneous unit was used to obtain the results presented in this application note. The instrument was fitted with a SmartGonio™ covering elements from fluorine (Z=9) to uranium (Z=92) and with a fixed channel for fluorine. A rhodium anode X-ray tube is used and the geometry of the instrument is optimized to provide the highest sensitivity. Two power versions exist, either a 50 W or the new 200 W version which has been used for the tests shown in this report. The instrument does not require external or internal water cooling, and has 10 times better spectral resolution than a conventional EDXRF instrument as well as superior precision, short and long term stability. It can analyse Na and Mg without any problem, and even F in slags when necessary. Ease of operation is obtained through the state-of-the-art OXSAS software running under Windows® 7 environment.

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Sample preparation

Slags samples were crushed and ground in a mill to less than 50 microns to avoid particle size effects. Magnetic separation of metallic residues is performed on the milled fractions before further preparation. In general the pressed powder method is used for routine elemental determinations in slags, especially when fast reporting is important.

Calibration and results

Eight certified slag standards were used for calibration of the ARL OPTIM'X at 200 W. These standard samples cover the concentration ranges shown in Table 1 on next page. A working curve is established for each element using the Multi-Variable-Regression incorporated in the OXSAS software package.

Elements	Analytical Device	Calibration Ranges (%)
CaO	SmartGonio	2.2% - 59%
SiO_2	SmartGonio	5.5% - 57%
Fe_2O_3	SmartGonio	0.44% - 30%
MgO	SmartGonio	1.5% - 14.5%
Al_2O_3	SmartGonio	0.6% - 12%
K_2O	SmartGonio	0.02% - 1.5%
MnO	SmartGonio	0.6% - 18%
TiO_2	SmartGonio	0.17% - 1.2%
P_2O_5	SmartGonio	0.02% - 11%
Na_2O	SmartGonio	0.02% - 1.5%
S	SmartGonio	0.01% - 1.5%
F	SmartGonio	0.1% - 17%
F	Fixed channel	0.1% - 17%

Table 1: Summary of concentration range and performance

Fluorine can be determined either with the SmartGonio or with a fixed channel. As shown in table 2 the performance in term of limit of detection is similar with both devices, but the fixed channel will allow much longer counting time as it is analyzing fluorine in parallel to the analysis of all the other elements on the goniometer. Hence the use of a fixed channel brings improved limit of detection and precision for fluorine as shown in the short and long term stability tests (Tables 3 and 4).

Element	Kv	MA	Type	Time 60 s LOD	Time 210 s LOD	SEE
				[ppm]	[ppm]	[%]
F Kα	30	6.67	Gonio	537	284	0.17
F Kα	30	6.67	Fixed channel	509	270	0.22

Table 2: Comparison of performance for fluorine determination using goniometer or fixed channel. LoD = limit of detection. The fixed channel will be counting for the whole time during the SmartGonio analysis.

The Standard Error of Estimate (SEE) is a measure of the accuracy of analysis. It is the average error between the certified concentrations of the standard samples and the calibration curve data.

Stability tests

In order to show the excellent repeatability of the ARL OPTIM'X for the analysis of slags at 200 W, both in short and long term, stability tests were performed. The counting time was optimized for each element measured on the SmartGonio. For short term repeatability 10 consecutive measurements were performed on a pressed slag sample.

Average concentration and standard deviations are shown in Table 3. The total counting time per run on the goniometer is set at 270 s in this example and can be decreased to 210 s when a fluorine fixed channel is used.

For long term repeatability test, the same pressed specimen was analyzed every 30 minutes over 12 hours. The total counting time per run on the SmartGonio was set at 270 s and can be decreased to 210 s when a F fixed channel is fitted. Average concentrations and standard deviations are shown in Table 4.

	CaO	SiO_2	Fe_2O_3	MgO	Al_2O_3	S	MnO	K_2O	P_2O_5	Na_2O	TiO_2	F Gonio	F Mono
# 1	39.62	35.33	0.987	5.42	10.01	0.945	2.43	1.51	0.642	1.38	0.810	0.504	0.484
# 2	39.61	35.36	0.984	5.43	10.04	0.949	2.43	1.52	0.641	1.38	0.814	0.496	0.473
# 3	39.61	35.28	0.986	5.44	10.05	0.948	2.43	1.52	0.643	1.38	0.813	0.462	0.496
# 4	39.54	35.36	0.988	5.46	10.06	0.949	2.42	1.51	0.640	1.39	0.812	0.466	0.483
# 5	39.62	35.34	0.979	5.44	10.02	0.949	2.42	1.51	0.639	1.40	0.814	0.483	0.481
# 6	39.58	35.36	0.988	5.46	10.05	0.947	2.43	1.50	0.638	1.39	0.808	0.501	0.470
# 7	39.63	35.38	0.988	5.45	10.07	0.950	2.43	1.51	0.640	1.39	0.819	0.503	0.495
# 8	39.56	35.33	0.983	5.46	10.08	0.952	2.42	1.51	0.641	1.40	0.815	0.511	0.470
# 9	39.63	35.36	0.985	5.46	10.07	0.953	2.42	1.51	0.642	1.40	0.811	0.466	0.498
# 10	39.63	35.35	0.988	5.45	10.06	0.956	2.42	1.51	0.636	1.38	0.812	0.509	0.472
AVG	39.61	35.35	0.986	5.45	10.05	0.950	2.425	1.511	0.640	1.39	0.813	0.490	0.482
SD	0.032	0.026	0.003	0.013	0.023	0.003	0.005	0.005	0.002	0.008	0.003	0.019	0.011
Time	10 s	10 s	10 s	20 s	20 s	30 s	20 s	20 s	20 s	30 s	20 s	60 s	210 s

Table 3: Results of a precision test (10 runs) for a sequential-simultaneous configuration: total counting time per run is 270 s and can be decreased to 210 s when a fluorine fixed channel is used.

	CaO	SiO_2	Fe_2O_3	MgO	Al_2O_3	S	MnO	K_2O	P_2O_5	Na_2O	TiO_2	F Gonio	F Mono
# 1	39.56	35.37	0.991	5.47	10.04	0.952	2.42	1.51	0.646	1.38	0.814	0.496	0.480
# 2	39.64	35.33	0.983	5.42	10.06	0.956	2.43	1.51	0.644	1.39	0.806	0.481	0.485
# 3	39.53	35.30	0.987	5.43	10.06	0.951	2.43	1.51	0.648	1.41	0.815	0.497	0.473
# 4	39.69	35.40	0.988	5.47	10.07	0.956	2.42	1.51	0.643	1.38	0.810	0.452	0.483
	..	..	..	..	..	..	..	..	..	..	..	..	..
# 22	39.59	35.31	0.992	5.45	10.06	0.951	2.43	1.52	0.642	1.40	0.806	0.491	0.479
# 23	39.66	35.30	0.987	5.44	10.03	0.957	2.43	1.51	0.647	1.39	0.805	0.453	0.484
# 24	39.59	35.42	0.984	5.45	10.08	0.953	2.43	1.51	0.646	1.40	0.810	0.475	0.495
AVG	39.59	35.32	0.989	5.45	10.05	0.954	2.426	1.513	0.644	1.393	0.811	0.491	0.481
SD	0.040	0.052	0.004	0.018	0.015	0.003	0.005	0.004	0.003	0.008	0.004	0.023	0.012
Time	10 s	10 s	10 s	20 s	20 s	30 s	20 s	20 s	20 s	30 s	20 s	60 s	210 s

Table 4: Results of an overnight reproducibility test for a pressed slag sample over 12 hours

Conclusion

The ARL OPTIM'X WDXRF instrument permits successful analysis of various elements in slags. Good repeatability and reproducibility is obtained with 270 s of total counting time with the SmartGonio for all elements including fluorine. When a fixed channel for F is fitted the total counting time can be decreased to 210 s while improving the precision on F due the longer counting time that can be used on the fixed channel. If better results are required for any element the counting time for that particular element can be increased.

If better results are required for any element the counting time for that particular element can be increased, but in view of the excellent standard deviations obtained the counting time for some elements could even be decreased, e.g. to 10s for MnO, K_2O and TiO_2 thus reducing the total counting time to just 3 minutes for 12 elements.

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