

Manganese ore analysis with the ARL OPTIM'X XRF Spectrometer

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Figure 1. Thermo Scientific ARL OPTIM'X XRF Spectrometer with its 13-position sample loader.

Introduction

Manganese is a transition metal that is used in a number of highly valuable applications, including the production of alloys (i.e., stainless steels) and batteries. Manganese is particularly critical in Li-ion battery cathodes, where it is used to stabilize nickel manganese cobalt (NMC) materials, improving performance and ensuring that the battery can operate safely.

The first step in manganese production, regardless of final application, is the mining and refinement of manganese ore. Understanding the composition of the ore allows for appropriate refinement processes to be used that generate the purest materials possible. This also means that manganese ore prices can vary greatly, as high-quality ores require less refinement. This makes precise ore characterization paramount for accurate distribution and processing.

X-ray fluorescence (XRF) spectroscopy is a commonly used analytical technique for the accurate chemical analysis of ores. XRF is a preferred method in mining and refining applications as it is quick, non-destructive, and requires minimal sample preparation. In this application note, a Thermo Scientific™ ARL OPTIM'X™ XRF Spectrometer is used to analyze several elements/oxides in ores in a matter of minutes. Given the high volumes of manganese ore mined annually, every minute saved in its characterization can make a significant difference in overall throughput.

Instrumentation

The ARL OPTIM'X XRF Spectrometer is a wavelength-dispersive XRF (WDXRF) spectroscopy instrument designed for ease of use with minimal operation and maintenance costs. It is fitted with a Thermo Scientific™ SmartGonio™ Goniometer, which allows the ARL OPTIM'X Spectrometer to cover the full elemental range from fluorine (${}_{9}\text{F}$) to americium (${}_{95}\text{Am}$). Two power versions of the spectrometer exist, a 50 and 200 W version. Overall, the 200 W version typically offers 2.5x faster data acquisition compared to the 50 W version. For this application note, the 50 W version has been used. The ARL OPTIM'X Spectrometer does not require external or internal water cooling and has 10x better spectral resolution than a conventional energy-dispersive XRF (EDXRF) instrument, as well as superior precision and stability. It has reliable performance for elements such as sodium (${}_{11}\text{Na}$), magnesium (${}_{12}\text{Mg}$), and even fluorine (${}_{9}\text{F}$).

Analytical conditions

As shown in Table 1, the SmartGonio Goniometer on the 50 W ARL OPTIM'X Spectrometer was used to collect the intensity data for 12 elements in each manganese ore sample. Total analysis time was 8 minutes. Measurement time can be further fine-tuned for specific applications. Total counting time could be decreased by a factor of 2.5 with the 200 W instrument without any reduction in accuracy and precision. Total analysis time would, therefore, decrease to less than 4 minutes when the 200 W ARL OPTIM'X Spectrometer is used.

Sample preparation

Calibration was performed using 4 manganese ore certified reference materials (CRMs). Samples were fused into beads, without ignition, with a sample to flux ratio of 1:10. Ammonium nitrate oxidizer was added to the fusion mix. Table 2 shows the concentration ranges of the different oxides covered by the calibration. R^2 and standard error of estimates (SEE) values were obtained for each compound.

The sample preparation as fused beads removes any grain size effect or mineralogical effects that may spoil the X-ray fluorescence analysis. Therefore an excellent analysis accuracy is obtained especially for major and minor elements/oxides. Trace elements determination is more difficult due to the dilution of the sample where trace levels are ten times lower in the actual fused bead compared to the original sample. Hence longer counting time may be used for trace elements determination when needed. Alternatively samples are prepared as pressed pellets when best trace elements determination is required.

Name	Analysis time (s)	kV	mA
Al Ka 1,2	36	30	1.67
Ba Lb 1	36	30	1.67
Ca Ka 1,2	36	30	1.67
Fe Ka 1,2	36	30	1.67
K Ka 1,2	36	30	1.67
Mg Ka 1,2	60	30	1.67
Mn Ka 1,2	36	30	1.67
Na Ka 1,2	60	30	1.67
Si Ka 1,2	36	30	1.67
Ti Ka 1,2	36	30	1.67
P Ka 1,2	36	30	1.67
V Ka 1,2	36	30	1.67

Table 1. Analytical conditions for manganese ore characterization.

Calibration*				
Element	Min %	Max %	R^2	SEE (%)
Al_2O_3	3.900	7.320	0.9995	0.0427
BaO	0.2470	0.3950	0.9732	0.0127
CaO	0.0810	0.2700	0.9999	0.0014
Fe_2O_3	5.230	7.040	0.9999	0.0050
K_2O	1.700	2.050	0.9976	0.0090
MgO	0.1410	0.3290	0.9959	0.0060
MnO	45.32	59.47	0.9987	0.2810
Na_2O	0.2360	0.3180	0.6417	0.0246
SiO_2	9.490	24.82	0.9999	0.0224
TiO_2	0.1790	0.3360	0.9969	0.0049
P_2O_5	0.1520	0.1950	0.8034	0.0111
V_2O_5	0.0418	0.0702	0.9966	0.0009

* Data is the average of 4 manganese ore CRMs

Table 2. Concentration ranges and calibration parameter values for manganese ore components.

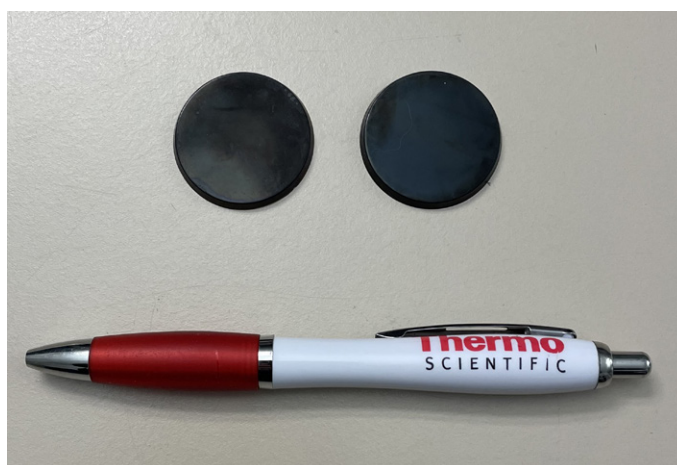


Figure 2. Two of the fused beads used for the calibration.

Calibration

Calibration curves were created to relate elemental characteristic X-ray intensities to oxide concentrations (Figure 3).

X-ray fluorescence can measure individual elements, and the results can also be related directly to the oxide forms when only one single form of each oxide is present in the sample.

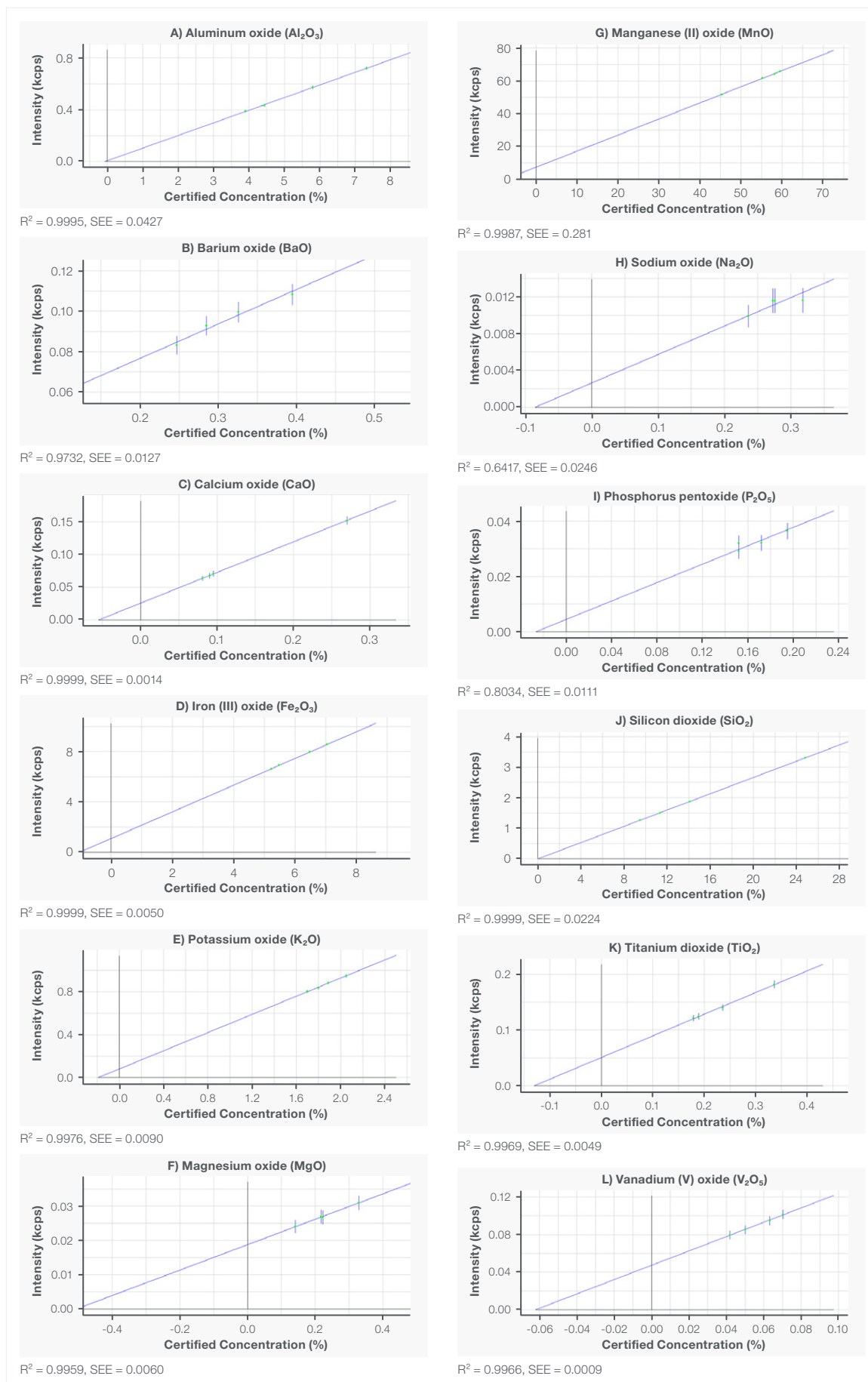


Figure 3. Calibration curves for a selection of oxides found in manganese ore.

Validation and precision

Two manganese ore reference materials (170a and 171) were used to validate the calibration (Table 3). CRM reference values are compared with the average of 10 replicate analyses of the two CRMs. Tables 4 and 5 show the repeatability of the 10 replicates for each CRM.

Sample ID		170a			171		
Element	Unit	CRM	Average	Difference	CRM	Average	Difference
Al ₂ O ₃	%	4.44	4.40	-0.04	7.32	7.34	0.02
BaO	%	0.326	0.340	0.014	0.247	0.247	-0.000
CaO	%	0.090	0.091	0.001	0.081	0.087	0.006
Fe ₂ O ₃	%	6.49	6.45	-0.04	5.23	5.18	-0.05
K ₂ O	%	1.70	1.70	-0.00	2.05	2.03	-0.02
MgO	%	0.222	0.213	-0.009	0.217	0.222	0.005
MnO	%	58.18	58.07	-0.11	45.32	45.10	-0.22
Na ₂ O	%	0.276	0.291	0.015	0.236	0.248	0.012
P ₂ O ₅	%	0.152	0.182	0.030	0.152	0.164	0.012
SiO ₂	%	11.34	11.28	-0.06	24.82	24.71	-0.11
TiO ₂	%	0.179	0.178	-0.001	0.336	0.338	0.002
V ₂ O ₅	%	0.070	0.068	-0.002	0.042	0.041	-0.001

Table 3. Analysis of reference manganese ores with the ARL OPTIM'X Spectrometer.

Element	Al ₂ O ₃	BaO	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	V ₂ O ₅
Counting time	36 s	36 s	36 s	36 s	36 s	60 s	36 s	60 s	36 s	36 s	36 s	36 s
Unit	%	%	%	%	%	%	%	%	%	%	%	%
Run 1	4.37	0.353	0.095	6.45	1.71	0.234	58.11	0.285	0.185	11.23	0.180	0.065
Run 2	4.41	0.328	0.091	6.45	1.69	0.230	57.92	0.298	0.187	11.32	0.181	0.068
Run 3	4.38	0.333	0.094	6.45	1.71	0.202	58.10	0.291	0.187	11.21	0.183	0.064
Run 4	4.45	0.334	0.086	6.47	1.70	0.195	58.13	0.278	0.183	11.32	0.175	0.069
Run 5	4.36	0.342	0.089	6.46	1.70	0.236	58.11	0.303	0.188	11.29	0.175	0.068
Run 6	4.42	0.349	0.089	6.45	1.69	0.231	57.97	0.294	0.168	11.31	0.179	0.068
Run 7	4.42	0.330	0.091	6.44	1.68	0.207	58.10	0.300	0.181	11.34	0.177	0.071
Run 8	4.40	0.364	0.092	6.47	1.70	0.197	58.15	0.267	0.181	11.26	0.183	0.067
Run 9	4.36	0.328	0.093	6.45	1.70	0.209	58.07	0.297	0.186	11.25	0.176	0.069
Run 10	4.40	0.336	0.086	6.44	1.68	0.193	58.06	0.296	0.173	11.33	0.174	0.067
Average	4.40	0.340	0.091	6.45	1.70	0.213	58.07	0.291	0.182	11.28	0.178	0.068
SD	0.029	0.012	0.003	0.011	0.011	0.017	0.072	0.011	0.007	0.045	0.003	0.002

Table 4. Repeatability of manganese ore (170a) analysis using the ARL OPTIM'X Spectrometer.

Element	Al ₂ O ₃	BaO	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	V ₂ O ₅
Counting time	36 s	36 s	36 s	36 s	36 s	60 s	36 s	60 s	36 s	36 s	36 s	36 s
Unit	%	%	%	%	%	%	%	%	%	%	%	%
Run 1	7.39	0.253	0.084	5.19	2.02	0.233	45.12	0.234	0.179	24.62	0.333	0.0418
Run 2	7.24	0.263	0.087	5.18	2.02	0.203	45.07	0.267	0.164	24.69	0.339	0.0402
Run 3	7.39	0.247	0.090	5.18	2.04	0.243	45.08	0.247	0.166	24.50	0.333	0.0442
Run 4	7.27	0.236	0.084	5.18	2.02	0.192	45.15	0.239	0.170	24.76	0.333	0.0388
Run 5	7.29	0.244	0.088	5.19	2.02	0.241	45.13	0.242	0.162	24.77	0.341	0.0425
Run 6	7.34	0.241	0.085	5.19	2.03	0.238	45.08	0.253	0.163	24.73	0.339	0.0381
Run 7	7.33	0.259	0.084	5.19	2.04	0.222	45.12	0.225	0.159	24.81	0.345	0.0393
Run 8	7.39	0.244	0.091	5.17	2.03	0.220	45.05	0.265	0.169	24.77	0.332	0.0404
Run 9	7.43	0.232	0.088	5.18	2.03	0.209	45.08	0.261	0.154	24.71	0.341	0.0416
Run 10	7.31	0.254	0.085	5.19	2.02	0.221	45.13	0.249	0.157	24.70	0.348	0.0391
Average	7.34	0.247	0.087	5.18	2.03	0.222	45.10	0.248	0.164	24.71	0.338	0.0406
SD	0.062	0.010	0.003	0.007	0.010	0.017	0.032	0.014	0.007	0.090	0.006	0.0019

Table 5. Repeatability of manganese ore (171) analysis using the ARL OPTIM'X Spectrometer.

Conclusion

This application note has shown the suitability of the ARL OPTIM'X Spectrometer for the analysis of manganese ore samples. This compact instrument allows for fast and reliable analysis combined with excellent repeatability. A total analysis time of 8 minutes was required with the 50 W ARL OPTIM'X Spectrometer. Obviously the sample preparation as fused beads dilutes the sample 10 times which means that the trace elements levels are very low in the actual fused beads. This explains the poor precision for traces, notably for V_2O_5 . Measurement time can be further fine-tuned for specific applications, e.g., increasing counting time in order to improve precision for trace or major elements. Total counting time could be decreased by a factor of 2.5 by using the 200 W version of the ARL OPTIM'X Spectrometer, while still achieve the same accuracy and precision. In such case, total analysis time would decrease to less than 4 minutes, including loading and pumping time.

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