DOES SIZE MATTER? CAN PORTABLE XRF BE USED FOR PROCESS CONTROL?

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ABSTRACT

In this paper a case study will be presented where an identical set of reference materials was used to calibrate a Wavelength Dispersive X-ray Fluorescence Spectrometer, an Energy Dispersive Benchtop spectrometer, and a Handheld Energy Dispersive Spectrometer.

The data will show that the capabilities between the three variations of the technique are comparable, the key factor to this being possible is the introduction of the Silicon Drift Detector (SDD) for handheld XRF. The biggest restrictive factor remains sample preparation which is often neglected when portable systems are used.

Specific limitations will be discussed regarding light elements and the consequences of low power systems that necessitate much longer analysis times.

In conclusion it was found that a portable system theoretically has the same capabilities, and can obtain the same quality data as a laboratory system for perfectly prepared material and long enough measuring times. In practice there are limitations and they have to be balanced against the advantage of bringing the spectrometer closer to the process and thus eliminating long turnaround times.

Laboratory Wavelength Dispersive XRF instruments, are not going to be extinct soon, because, as far as uncertainties due to counting statistics, detection limits and speed of analysis go, they are still the perfect process control tool, but portable systems can be a valuable tool in giving quick turnaround, on site data. Ideally the different techniques should be used in conjunction.

INTRODUCTION

A Ferrochrome smelter was looking for a feasible option to get quick turnaround analysis on metal ingots and slags. Their quality control was done by an off-site laboratory and turnaround times were too long for effective process control. A handheld XRF was evaluated to see if it could provide analytical results of adequate accuracy and precision in order to use it directly adjacent to the furnaces for tap control with as little sample preparation as possible.

As part of this exercise the data obtained from a handheld XRF was compared to that obtained from a desk top EDXRF and a floor standing WDXRF. The three systems were calibrated with an identical set of reference materials, optimising conditions for each instrument. The calibration statistics, countrates, and detection limits are compared. Also, the effect of sample preparation on analysis results using the handheld spectrometer were evaluated.

EXPERIMENTAL

Apparatus

Bruker S1Titan S600 Handheld EDXRF (energy dispersive) spectrometer

The Titan is a 4W system with a Rh target x-ray tube and Silicon Drift Detector (SDD). The following settings were used for measurement using EASYCAL™ empirical setup: Excitation: 15kV 30uA Analysis time: 60sec, no filter used. Measurements were done under an air atmosphere in an instrument stand.

Thermo Quant’X EDXRF benchtop spectrometer

The Quant’X is a 50W system with a Rh target x-ray tube and Silicon Drift Detector. The following conditions were applied:

Table 1: Analytical Parameters for a Thermo Quant’X

Elemental Line	Medium	Filter	Analysis time (seconds)	kV	mA
NaKα1,2	vacuum	none	30	4kV	automatic
Mg Kα1,2	vacuum	none	30	4kV	automatic
Al Kα1,2	vacuum	none	30	4kV	automatic
SiKα1,2	vacuum	none	30	4kV	automatic
PKα1,2	vacuum	none	30	4kV	automatic
SKα1,2	vacuum	none	30	4kV	automatic
CaKα1,2	vacuum	cellulose	30	8kV	automatic
K Kα1,2	vacuum	cellulose	30	8kV	automatic
TiKα1,2	vacuum	aluminium	30	12kV	automatic
VKα1,2	vacuum	aluminium	30	12kV	automatic
CrKα1,2	vacuum	aluminium	30	12kV	automatic
MnKα1,2	vacuum	aluminium	30	12kV	automatic
FeKα1,2	vacuum	palladium	30	16kV	automatic
NiKα1,2	vacuum	palladium	30	16kV	automatic

Thermo ARL9900 WDXRF (wavelength dispersive) floor standing XRF spectrometer

The ARL9900 is 4.2 kW wavelength dispersive spectrometer equipped with a Rh target x-ray tube, a flow proportional and scintillation detector, crystals and collimators for optimum counting statistics on each element of interest.

The following measurement parameters were used (Table 2) for measurement on the ARL 9900. All measurements were taken under vacuum.

Table 2: Analytical Parameters for a ThermoARL9900

Elemental Line	Crystal	Detector	Collimator	Analysis time (seconds)	kV	mA
Mg Kα1,2	AXO6	FPC	coarse	40	30kV	80mA
Al Kα1,2	PET	FPC	medium	20	30kV	80mA
SKα1,2	GER111	FPC	medium	40	30kV	80mA
SiKαm	Fixed Channel Monochromator	Sealed gas detector	fine	40	30kV	80mA
PKαm	Fixed Chanel Monochromator	Sealed gas detector	fine	40	30kV	80mA
CaKαm	Fixed Channel Monochromator	Sealed gas detector	fine	40	30kV	80mA
TiKαm	Fixed Channel Monochromator	Sealed gas detector	fine	40	50kV	50mA
CrKαm	Fixed Channel Monochromator	Sealed gas detector	fine	40	50kV	50mA
MnKαm	Fixed Channel Monochromator	Sealed gas detector	fine	40	50kV	50mA
FeKαm	Fixed Channel Monochromator	Sealed gas detector	fine	40	50kV	50mA

Standards

An identical set of reference materials were used for calibration on all three instruments. These were prepared by Qotho Services Laboratory as part of their industry specific proficiency scheme (Qotho 2019). Qotho methodology for certification is based on the consensus value of the measurement, using a network of competent laboratories, and following a stringent and robust statistical evaluation protocol, as per the requirements of ISO 13528 (International Organization for Standardization, 2005) . The samples are acquired as finely ground samples (90% <75um). The following set of reference materials shown in Table 3 were used.

Table 3: Reference Materials used for Chromite calibration (weight %)

Reference material	Al2O3	CaO	Cr2O3	FeO	MgO	MnO	P	S	SiO2	TiO2
Blank	0	0	0	0	0	0	0	0	100	0
CR-1077-ORE	14.75	0.36	39.18	26.16	9.96	0.23	0.005	0.008	5.48	1.01
CR-1001-ORE	14.67	0.41	40.68	27.21	9.74	0.25	0.003	0.004	4.01	0.90
CR-1049-ORE	15.60	0.72	38.74	25.81	10.26	0.27	0.005	0.206	5.96	0.79
CR-1061-ORE	12.66	0.39	44.06	21.33	11.41	0.23	0.005	0.005	7.91	0.48
CR-1069-ORE	14.82	0.14	45.93	26.35	9.70	0.23	0.004	0.004	1.15	0.67
CR-1081-ORE	13.59	1.12	39.59	23.25	11.72	0.25	0.005	0.013	8.45	0.57
CR-1046-CONC	14.52	0.38	38.89	26.65	10.96	0.23	0.005	0.006	6.17	0.92
CR-1054-CONC	15.28	0.19	42.09	28.23	9.34	0.24	0.005	0.008	2.13	1.10
CR-1058-CONC	11.42	1.15	34.56	21.20	12.58	0.28	0.010	0.875	13.16	0.57
CR-1070-CONC	14.90	0.15	45.91	26.27	9.62	0.22	0.004	0.004	1.02	0.68
CR-1074-CONC	14.67	0.17	45.47	26.06	9.83	0.24	0.003	0.005	1.63	0.67
CR-1078-CONC	14.40	0.15	46.18	26.12	9.79	0.24	0.003	0.004	1.05	0.63
CR-1082-CONC	14.90	0.17	45.51	25.82	9.95	0.23	0.003	0.004	1.48	0.68

Reference Material Preparation

For the benchtop and floor standing systems, pressed pellet preparation was used, but for the handheld, loose powder was poured into a sample cup fit with 4um thick polypropylene film.

The reference materials were sold as powders <70μm, and in the case of the handheld they were poured directly into a sample cup with a 4μm polypropylene film, without any further packing. The reason for this was that the preparation for the furnace tap plant samples had to be as simple as possible. These samples were going to be ground down to <75μm in a puck and ring mill next to the furnaces, and directly poured into a sample cup. Compacting is not advised as each operator would do it slightly different.

For the laboratory systems, each laboratory's routine methods were used, and the author is not commenting on the suitability of either method. For the EDX system, 18g sample (<75μm) was ground with 2g boric acid for 3 minutes. For the WDX system 11.7g sample (<75μm) and 1.3g of Sasol wax was ground for 15 seconds.

The different sample preparation methods would have no effect on the comparative results, as identical methods were followed on calibration reference materials and unknowns in each case. The loose powders would increase the uncertainty, but in this case where quick turnaround times with minimal operator input is the goal, the method is fit for purpose. For final product certification laboratory analysis was used on properly prepared samples where fine grinding and pressed pellet preparation minimises particle size and surface effects.

CALIBRATION

Handheld XRF spectrometers are usually factory calibrated using fundamental parameters for matrix correction, but these calibrations are not matrix specific. The best way to get accurate results is to calibrate with matrix matched certified reference materials. Here the instrument you choose is crucial, because most manufacturers have only "type standardisation" available in their software, where the user can measure a few standards, calculate a slope and intercept and apply a factor to values obtained with the factory calibration. Currently only the Bruker systems allows an end-user, upon acquiring EASYCAL™ software, to set up true calibrations as you would on a high power laboratory instrument.

There were three potential applications of interest – analysis of FeCr metal, FeCr slag and chromite ore. Comparison between the three instruments at this time could only be done for the chromite ore application, because the benchtop EDXRF used a fused bead preparation for the FeCr metal and FeCr slag applications. The chromite ore data only is thus presented.

The major and minor elements were calibrated on the three different instruments and calibration data compared. The calibration details and coefficients are presented in Table 4.

For the investigation into the effect of sample preparation the Bruker GeoMining Oxide Concentrates factory calibration was used for the slag analysis, and for the FeCr alloy the Bruker Alloy factory calibration: Multimatrix FP was used. For the Bruker GeoMining calibration, for Mg to Ca 15kV excitation was used, for Ti to Ga 30kV excitation and for the rest of the periodic table 50kV excitation was used. (Bruker Corporation, 2017). For the Alloy calibration for Mg to Cr 15kV no primary beam filter was used, and for Ti to Bi, 40kV with a TiAl primary beam filter was used, all under air atmosphere (Bruker Corporation, 2015).

Table 4: Chromate Ore Calibration details and coefficients.

Bruker S1Titan 600 Handheld XRF		**MgO**	**Al2O3**	**SiO2**	**P2O5**	**SO3**	**CaO**	**TiO2**	**Cr2O3**	**MnO**	**FeO**
R^2		0.81	0.95	0.95	0.90	0.99	0.99	0.99	0.98	0.53	0.95
RMS	**%**	0.35	0.27	0.85	7ppm	0.01	0.03	0.01	0.48	121ppm	0.47
Range min	**%**	9.34	11.42	1.02	30ppm	0.00	0.14	0.48	34.56	2210ppm	21.33
max	**%**	11.72	15.60	13.60	100ppm	0.88	1.15	0.92	46.18	2750ppm	28.23
Calibration points		11	12	11	10	10	11	11	11	12	9
Blank	**Intensity cps**	2	14	17	4	6	7	13	44	28	45
Q1046 conc.	**%**	**10.96**	**14.52**	**6.17**	**0.005**	**0.006**	**0.38**	**0.92**	**38.89**	**0.23**	**26.65**
Q1046	**Intensity cps**	6	40	67	5	9	108	178	6529	949	2855
measurement time	**seconds**	60	60	60	60	60	60	60	60	60	60
LLD	**%**	0.12	0.04	0.009	0.0001	0.00003	0.0004	0.0006	0.0007	0.00003	0.001
Matrix correction		Empirical matrix matched									
Overlap correction		AlKα	SiKα	AlKα	SKα	PKα			FeKα	CrKα	MnKα
Thermo Quant'X EDXRF											
R^2		0.99	0.98	0.99	0.57	0.77	0.99	0.98	0.99	0.97	0.99
RMS	**%**	0.23	0.64	0.26	69ppm	19ppm	0.01	0.03	0.37	0.01	0.67
Range min	**%**	0.00	0.00	1.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
max	**%**	11.72	15.60	8.45	0.01	0.88	1.15	1.01	46.18	0.28	28.23
Calibration points		13	14	11	8	10	13	13	13	13	13
Blank	**Intensity cps**	1	359	147	87	27	1	1.0	0.2	31	43
Q1046 conc.	**%**	**10.96**	**14.52**	**6.17**	**0.005**	**0.006**	**0.38**	**0.92**	**38.89**	**0.23**	**26.65**
Q1046	**Intensity cps**	3000	9290	10046	99	30	415	308	24729	559	15680
measurement time	**seconds**	30	30	30	30	30	30	30	30	30	30
LLD	**%**	0.004	0.03	0.008	0.0005	0.001	0.0008	0.003	0.007	0.002	0.01
Matrix correction		Empirical Alphas									
Overlap correction		Reference Spectra - Peak profiles									
Thermo ARL9900 WDXRF											
R^2		0.99	0.99	0.99	0.85	0.99	0.99	0.99	0.99	0.63	0.99
RMS	**%**	0.41	0.31	0.41	8ppm	0.002	0.04	0.01	0.47	0.01	0.35
Range min	**%**	0	0	0	0.001	0	0	0	0	0.221	0
max	**%**	11.41	15.6	13.16	0.005	0.21	1.15	0.92	46.18	0.275	27.21
Calibration points		11	11	10	12	11	12	12	12	12	12
Blank	**Intensity cps**	124	54	632	142	277	204	1115	350	1960	3804
Q1046 conc.	**%**	**10.96**	**14.52**	**6.17**	**0.005**	**0.006**	**0.38**	**0.92**	**38.89**	**0.23**	**26.65**
Q1046	**Intensity cps**	20454	52935	72362	211	345	3025	18084	324958	22974	946849
measurement time	**seconds**	40	20	40	40	40	40	40	40	40	40
background measurement time	**seconds**	20				20					
LLD	**%**	0.006	0.003	0.002	0.0002	0.0002	0.002	0.0016	0.002	0.0004	0.002
Matrix correction		Fundamental Parameters									
Overlap corrections		Interference samples								CrKβ	MnKβ
Background corrections		mathematical				mathematical					

DISCUSSION/RESULTS

Evaluation of the calibrations performed on the three instruments was done by comparing the correlation coefficients, the RMS, intensities for blank and reference material and limit of detection (LLD). The calibration statistics, countrates for a blank and reference material Q1046, and limit of detection (LLD) are shown in Table 4.

The correlation coefficient, expressed as R^2, is comparable for all three instruments; because the same set of reference materials were used and uncertainties regarding accuracy should thus be similar. For the handheld calibration the linear fit is in general slightly worse, but this can be expected as loose powders were used. For the EDXRF P_2O_5 and SO_3 had a larger data scatter (R^2 value) than the other two instruments, which could be ascribed to non-optimal peak deconvolution showing larger scatter for samples with higher Si concentrations, and although the handheld is an energy dispersive spectrometer too, the peak deconvolution algorithms work better around P and S, as a matter of fact, P on the handheld had the lowest RMS across the calibration curve (7ppm)

The Root Mean Square (RMS) values, expressing the average deviation from the calibration line, is very similar for all three instruments.

The most significant difference amongst the calibrations is due to counting statistics. When one considers the intensities obtained from the different instruments, in this case measured on a reference material Q1046, the effect of the power difference between the instruments can clearly be seen. For Mg the 4W S1Titan800 only measured 6 cps, where the 50W Quant'X measured 3000 cps and the 4.2 kW ARL9900 measured 20454 cps. For a heavier element like Fe the 4W S1Titan800 only measured 2855 cps, where the 50W Quant'X measured 15680 cps and the 4.2 kW ARL9900 measured 946849 cps.

Uncertainty due to counting statistics is proportional to the count rate (Willis and Duncan, 2002):

$$S_I = \sqrt{\frac{I}{T}},$$

Where S_I = Standard deviation of the count rate

I = Intensity; count rate (cps)

T = counting time

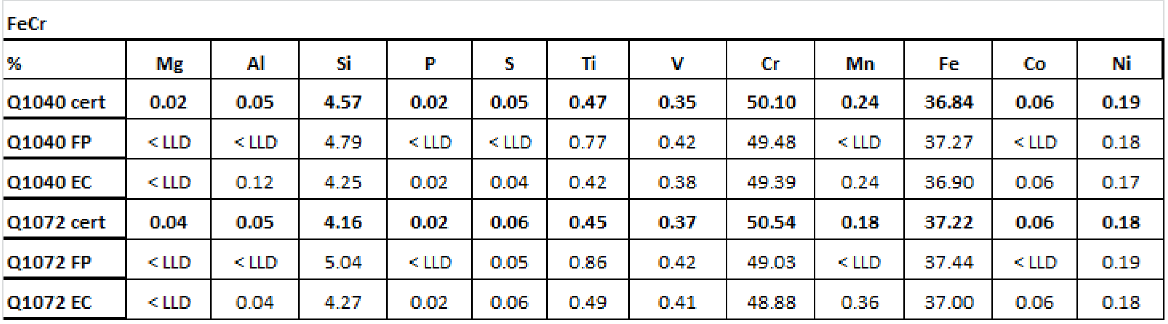
Higher count rates would naturally lead to lower uncertainty, but also lower detection limits. This is more pronounced for light elements where the fluorescence yield is already low.

This effect is further exacerbated by the fact that the handheld spectrometer does not normally operate under vacuum, and long wavelength, light elements are easily absorbed by an air path. To obtain the same Limits of Detection and Counting Statistical Uncertainty, we need to analyse for much longer on a low power handheld system. In this case the measurement times were arbitrarily selected by the individual laboratories according to their internal protocols. The handheld spectrometer actually performed much better than expected and similar to the high power system for most elements, which proves that it could produce the same results if calibrated properly. (Note that most handheld spectrometers cannot be calibrated by the end user, only type standardisation is possible.)

THE EFFECT OF MATRIX MATCHED CALIBRATION ON THE HANDHELD SPECTROMETER.

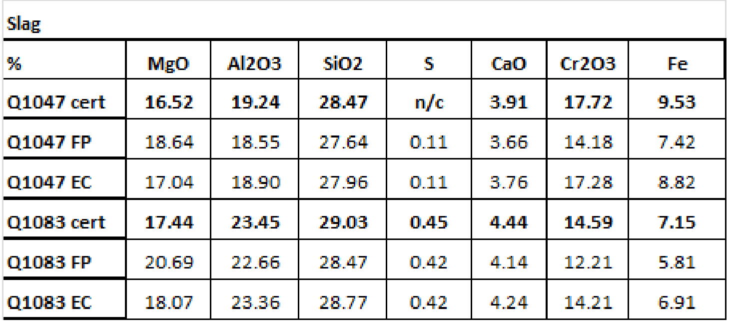
As explained above, most handheld spectrometers can only be operated with the Fundamental Parameter factory calibrations, with the possibility of adding a type standardisation to optimise for a specific matrix or sample preparation. With the Bruker handheld spectrometers there is the possibility to acquire EASYCAL™ Software, which is a concise package of the standard Bruker EDX software, adapted for the handheld spectrometer setup. This enables the customer to set up applications from scratch and execute matrix matched calibrations. To illustrate the improvement on data due to a matrix matched calibration, the following table shows the analysis results of two reference materials a FeCr metal and a FeCr slag, comparing the certified values (QXXXX cert), to the values obtained with the factory calibration (QXXXX FP) which is a wide range Fundamental Parameter calibration (Bruker Corporation, 2015, 2017), and lastly to values obtained the EASYCAL empirical calibration (QXXXX EC), as described above.

Table 5: FP Factory Calibration and EASYCAL Empirical Calibration results compared (weight %)



FeCr

%	Mg	Al	Si	P	S	Ti	V	Cr	Mn	Fe	Co	Ni
Q1040 cert	**0.02**	**0.05**	**4.57**	**0.02**	**0.05**	**0.47**	**0.35**	**50.10**	**0.24**	**36.84**	**0.06**	**0.19**
Q1040 FP	< LLD	< LLD	4.79	< LLD	< LLD	0.77	0.42	49.48	< LLD	37.27	< LLD	0.18
Q1040 EC	< LLD	0.12	4.25	0.02	0.04	0.42	0.38	49.39	0.24	36.90	0.06	0.17
Q1072 cert	**0.04**	**0.05**	**4.16**	**0.02**	**0.06**	**0.45**	**0.37**	**50.54**	**0.18**	**37.22**	**0.06**	**0.18**
Q1072 FP	< LLD	< LLD	5.04	< LLD	0.05	0.86	0.42	49.03	< LLD	37.44	< LLD	0.19
Q1072 EC	< LLD	0.04	4.27	0.02	0.06	0.49	0.41	48.88	0.36	37.00	0.06	0.18



Slag

%	MgO	Al2O3	SiO2	S	CaO	Cr2O3	Fe
Q1047 cert	**16.52**	**19.24**	**28.47**	**n/c**	**3.91**	**17.72**	**9.53**
Q1047 FP	18.64	18.55	27.64	0.11	3.66	14.18	7.42
Q1047 EC	17.04	18.90	27.96	0.11	3.76	17.28	8.82
Q1083 cert	**17.44**	**23.45**	**29.03**	**0.45**	**4.44**	**14.59**	**7.15**
Q1083 FP	20.69	22.66	28.47	0.42	4.14	12.21	5.81
Q1083 EC	18.07	23.36	28.77	0.42	4.24	14.21	6.91

THE EFFECT OF SAMPLE PREPARATION

After confirming that handheld equipment had the ability to perform on par with high power systems, it was necessary to evaluate other factors that could influence the data accuracy. A large determining factor of accuracy of laboratory analysis is the extensive sample preparation steps performed before analysis: crushing, splitting, milling, splitting again, preparation of fused glass beads (which remove any mineralogical and particle size effects), or pressing of pellets from finely powdered samples which all minimise inhomogeneity, particle size and surface effects.

With a "point and shoot" handheld instrument - this is often exactly what is done in the field - untrained field assistants, with no understanding of homogeneity or representative sampling (not even to talk about surface effects and the influence of moisture or sample bags), indiscriminately point and shoot and collect masses of data. Which often have no value - apart from really damaging the reputation of the technique.

The original purpose of this investigation was to see if a handheld XRF spectrometer could provide analytical results of adequate accuracy and precision to use it directly adjacent to the furnaces for tap control with as little sample preparation as possible, at a FeCr smelter.

The following tables present direct analysis using the handheld instrument on the FeCr metal and FeCr slag ingots, without any sample preparation. The factory calibration as described in the Calibration section was used with a default setting of 60 seconds for each analytical condition. The instrument was mounted in a stand and the roughly 8x4x4cm^3 ingot was repositioned after every analysis to analyse a fresh flat surface. The average and standard deviation for each set was calculated and the laboratory result, from a calibrated bench top EDXRF, for a homogenised, prepared pressed pellet sample reported too.

Table 6: Handheld spot measurements on a FeCr metal ingot using the factory calibration (weight %)

FeCr metal ingot %	Mg	Al	Si	P	S	Ti	V	Cr	Mn	Fe	Total:
Spot 1	0.64	<LLD	3.71	<LLD	0.11	0.61	0.34	49.6	0.15	43.7	98.8
Spot 2	0.41	<LLD	3.97	<LLD	0.03	0.61	0.35	49.6	0.22	43.6	98.8
Spot 3	0.65	<LLD	3.93	<LLD	0.06	0.58	0.31	49.2	0.10	44.0	98.8
Spot 4	0.49	<LLD	3.14	<LLD	<LLD	0.74	0.39	57.7	<LLD	36.8	99.2
Spot 5	<LLD	<LLD	3.79	<LLD	<LLD	0.62	0.35	51.0	<LLD	43.4	99.2
Spot 6	0.56	<LLD	3.06	<LLD	<LLD	0.74	0.40	58.2	<LLD	36.3	99.2
Spot 7	<LLD	<LLD	3.80	<LLD	<LLD	0.6	0.33	50.8	<LLD	43.6	99.2
Spot 8	0.35	<LLD	4.05	<LLD	<LLD	0.6	0.33	49.8	0.11	43.6	98.9
Spot 9	0.68	<LLD	3.86	<LLD	<LLD	0.6	0.35	49.3	0.14	43.7	98.7
avg	0.5		3.7		0.06	0.6	0.3	51.7	0.1	42.1	99.0
sdev	0.1		0.4		0.04	0.06	0.03	3.6	0.05	3.2	0.2
Laboratory result			4.50	0.02	0.03			50.60		36.30	98.05

Table 7: Handheld spot measurements on a FeCr Slag ingot using the factory calibration (weight %)

Slag ingot %	MgO	Al_2O_3	SiO_2	S	K_2O	CaO	Ti	V	Cr_2O_3	Mn	Fe
Spot 1	15.47	16.44	25.62	0.18	0.24	2.13	0.33	0.06	12.36	0.14	3.4
Spot 2	20.26	19.05	38.86	0.47	0.36	3.13	0.40	0.03	7.58	0.30	2.3
Spot 3	21.86	18.44	35.05	0.19	0.40	2.88	0.38	0.03	7.67	0.31	2.3
Spot 4	20.65	19.78	31.42	0.16	0.25	2.28	0.41	0.07	16.56	0.17	4.3
Spot 5	19.73	19.14	29.67	0.16	0.22	2.16	0.37	0.09	17.09	0.17	4.3
Spot 6	12.80	12.20	22.63	0.13	0.20	1.70	0.26	0.05	12.96	0.13	3.3
Spot 7	14.05	14.03	27.07	0.14	0.20	1.96	0.32	0.05	12.90	0.15	3.3
Spot 8	13.72	13.55	25.46	0.15	0.20	1.84	0.30	0.04	11.97	0.13	3.0
Spot 9	21.37	20.64	37.05	0.20	0.33	2.69	0.46	0.06	13.14	0.18	3.3
avg	17.8	17.03	30.3	0.2	0.3	2.3	0.4	0.05	12.5	0.2	3.3
sdev	3.7	3.1	5.7	0.1	0.08	0.5	0.06	0.02	3.3	0.07	0.7
Laboratory results	19.9	22.7	27.9	0.1		2.5			18.4		6.6

The standard deviations on the major elements for the data presented in Tables 6 and 7 were quite large when compared to the laboratory analysis, which was generated on prepared samples, on a calibrated EDXRF system in the quality control laboratory. The precision and accuracy was found to be not adequate for using data generated this way as a process control tool. For the metal analysis, using the factory calibration, there is no option to correct for unanalysed elements, and the 6 wt% Carbon in the sample is basically ignored and results normalised. The uncertainty was a combination of the lack of sample preparation and the uncertainty associated with the factory calibration versus a custom matrix matched reference material calibration and the normalisation as mentioned above.

Subsequently very basic sample preparation was done by crushing the 8x4x4cm^3 ingot with a crude mortar and pestle setup, pouring the sample into a sample cup with polypropylene film and analysing it. The following tables (8 and 9) present results after rudimentary sample preparation:

Table 8: FeCr metal after basic preparation (weight %)

FeCr Metal %	Mg	Al	Si	P	S	Ti	V	Cr	Mn	Fe	C
FeCr 23516 a	< LLD	< LLD	4.50	0.02	0.03	0.29	0.26	51.02	< LLD	36.91	
FeCr 23516 b	< LLD	< LLD	4.52	0.02	0.03	0.29	0.26	51.00	< LLD	36.92	
FeCr 23516 c	< LLD	0.05	4.50	0.02	0.03	0.29	0.27	51.57	< LLD	36.48	
Laboratory			**4.70**	**0.02**	**0.04**			**50.00**		**36.50**	**6.30**

Table 9: FeCr slag after basic preparation (weight (%)

FeCr Slag %	MgO	Al_2O_3	SiO_2	S	CaO	Cr_2O_3	Fe
F2 23516 slag a	20.82	22.27	29.21	0.17	3.21	17.94	6.32
F2 23516 slag b	20.47	22.29	29.58	0.16	3.18	17.98	6.36
F2 23516 slag c	20.51	23.00	29.57	0.16	3.19	17.98	6.35
Laboratory	**19.60**	**22.60**	**27.00**	**0.14**	**2.50**	**19.40**	**7.00**

The samples were not homogenous and the repeatability not good on the ingots as is, BUT, when slag and metal samples were crudely ground in a mortar pestle setup, the results were much improved and compared better to the laboratory results.

CONCLUSION

For the above FeCr project - after an EASYCAL™ calibration with certified reference materials, and some degree of sample preparation, results comparable to laboratory results were obtained. The fact that the relative standard deviation of calibration curve (RMS) and fitting factor (R^2) was similar, independent to the power of the XRF system, proves that bigger is not necessarily better! The optimal setup of each instrument, and inherent limitations in the specific matrix and spectrum processing software had a larger effect than the power of the system. Sample preparation also proved to be a huge contributing factor and this is an aspect often neglected when handheld spectrometers are used. The other factor that needs to be considered is that for a lower power system, much longer analysis times are necessary, making the instrument unsuitable when a high sample throughput is necessary.

For this specific FeCr smelter project, the final proposal was to use rudimentary sample preparation (crushing with a crude mortar and pestle setup) and pouring material into a sample cup), analysing them directly with the handheld spectrometer next to the furnaces. This provided the plant with very quick feedback of an adequate quality to regulate their process effectively. Composite samples were then collected and sent to the quality control laboratory for final verification of the results.

Handheld XRF instruments are a very exciting development, and are an excellent screening tool in the field and complimentary tool to laboratory analysis, which makes sampling and selection of samples to submit to the laboratory, a much more informed process. In theory, they can do what a laboratory instrument can do, (with longer measurement times), and thus be used for process control, assuming the same level of sample preparation is done as in the laboratory - and this is usually the determining factor.

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