

Chemically pure synthetic standards for wide range analysis of oxides in geological material using wavelength dispersive X-ray fluorescence spectrometry

Olde Weghuis, M. S. ^[1], Ingham, M. N. ^[2]

1. PANalytical B.V., Almelo, The Netherlands

2. British Geological Survey, Keyworth, Nottingham, United Kingdom

ABSTRACT

X-ray fluorescence (XRF) spectrometry has always been considered to be a comparative method of analysis. Reference materials are required to calibrate the analytical system. This poster describes the use of a set of 'synthetic' oxide standards, made from commercially available high purity compounds, to calibrate a spectrometer for 21 major and minor oxides. The spectrometer software uses simple methods of background correction, and a fundamental parameter method of matrix correction. Sample preparation is by fusion in 66% lithium tetraborate, 34% lithium metaborate. The use of synthetic standards, made from traceable compounds, brings XRF significantly closer to being a primary rather than a comparative method. Reference materials were used to validate the method described and examples of accuracy for major constituents are given using ores and other minerals. This method has successfully been used to analyze a wide variety of minerals and ores, as validation data shows. A titanium process example clearly shows the benefits of highest accuracy analysis.

INTRODUCTION

Elemental analysis of rock, minerals and ores using X-ray spectrometry is regarded as one of the most powerful tools for the mining and industrial minerals industries. The standard technique utilizes wavelength dispersive X-ray fluorescence (WDXRF) spectrometry to characterize the element composition of geological materials. It delivers fast, precise and accurate analysis across a broad range of elements (Be-U), from trace amounts to one hundred percent. In contrast with alternative methods, WDXRF analysis requires only straightforward, essentially hazard-free sample preparation with no time-consuming chemical methods. Samples can be in almost any form: solid pieces, pressed powders, loose powders, and granules can all be placed directly into a spectrometer with little or no pre-treatment. Furthermore, analysis is non-destructive and very rapid, providing high throughput, accurate and precise analysis of minerals and ores. Low power, compact systems that are robust can be sited in the field, for on the spot analysis at the site of the exploration and mining activity.

Technological developments in spectrometer software, detector technology, optical components and analytical algorithms are ongoing, bringing a beneficial impact on ease of use as well as on the speed, detection limits and accuracy of analysis. Nevertheless, the need for good standards is often

underestimated and a bad calibration is in many cases the bottleneck for accurate and precise analysis.

Traditionally, X-ray spectrometers are calibrated using reference materials (RMs) that have a similar matrix to the routine samples to be analyzed. This means that most calibrations are necessarily sample-type specific and dependent on the availability of these standards. However, most geologists are familiar with ICP as an 'absolute' primary technique in which analytes are dissolved in a strong acid before analysis. To overcome mineralogical and particle-size effects that can have a negative impact on the reliability of a calibration in XRF analysis, ores and other mineralogical samples can also be dissolved in flux material by fusion. Dissolving synthetic powders with known absolute concentrations yields the 'perfect' standard, providing a calibration that is valid for a wide variety of geological sample types. Concentrations are traceable back to pure chemicals. As a result, XRF becomes a primary rather than a comparative secondary analytical method.

The composition of an RM is determined by averaging analyses obtained by multiple techniques (ICP, INAA, AA etc.) and is by definition secondary. The calibration process with expensive RMs results in a fairly limited selection of materials that are not widely available.

In this poster we describe and evaluate the use of synthetic standards for the analysis oxides across a wide concentration range in different types of geological material on a WDXRF

spectrometer. Validation data from these synthetic standards compared to Reference Materials of different geological type materials is presented.

METHODS

General

All analysis was carried out using a 2.4 kW Axios-Minerals WDXRF spectrometer (PANalytical).

Analysis of majors and minors

The setup

The standard set contains 20 synthetic oxide standards for the analysis of 21 oxides and is made from pure compounds. It is commercially available under the name WROXI (Wide Range OXide) from PANalytical. Each of the standards is prepared in a unique way. The standards are selected in a way that they are free from line-overlaps. The powders are packaged in bottles under nitrogen for fusion by the end-user before use.

A fundamental parameters (FP) algorithm, which is part of the Axios-Mineral's system software, calculates matrix corrections based on the theoretical laws governing the physics of X-rays. This enables accurate analyses over very wide ranges in concentration and in very different sample types. In addition, accurate analysis can be made outside the range of concentrations bracketed by the standards.

Table 1. Total measurement time (peak + backgrounds) on a 2.4 kW WDXRF spectrometer.

Compound	Total time (s)
Na ₂ O	72
MgO	42
Al ₂ O ₃	36
SiO ₂	36
P ₂ O ₅	12
SO ₃	24
K ₂ O	16
CaO	20
TiO ₂	16
V ₂ O ₅	16
Cr ₂ O ₃	16
Mn ₃ O ₄	16
Fe ₂ O ₂	16
NiO	12
CuO	12
ZnO	12
SrO	56
ZrO ₂	28
BaO	48
HfO ₂	26
PbO	8
Total Application	540

Preparation of standards & samples

The standards and reference materials (RMs) illustrated in the figures and tables were prepared as fusions using 1.0 g of

sample fused in 10.0 g flux (66% lithium tetraborate, 34% lithium metaborate) and cast into 40 mm diameter fused beads. 15-200 mg of Lil has been used as a releasing agent. Fusion temperature was between 1150 and 1200 °C depending on composition. Loss on Ignition (LOI) is accurately determined separately.

Measurement conditions

40 mm fused beads were measured using 37 mm cups (opening) and a 37 mm collimator mask. Single unshared backgrounds were used for all channels except Zn, Cu, Ni, Mg and Na, for which two background positions were used. One of the Na background positions was shared with Mg. K α lines were measured for all elements except Pb (L β 1), Ba and Zr (L α 1). The measurement program takes approximately nine minutes, with measurement times for individual oxides ranging from 8 seconds for PbO to 72 seconds for Na₂O.

RESULTS

Accuracy

An overview plot for a number of oxides is shown in Figure 1, along with plots for individual oxides: Al₂O₃, P₂O₅, K₂O, TiO₂, Mn₃O₄, and Fe₂O₃ (Figure 2 A-F). Table 2 shows a comparison of certified and measured values for 14 Reference Materials (RMs) of widely varying composition. The absolute and relative accuracy of the WROXI method is also reported for a range of oxides (Table 2). For all comparisons between certified and measured values, the RMs were measured as routine samples against the WROXI calibration. The combination of WROXI standards and the Fundamental Parameter calibration model enables accurate extrapolation of calibrations outside the range in the standards. For example, high Al₂O₃ and high Fe₂O₃ RMs have been analyzed successfully with WROXI (Figure 2 A and F).

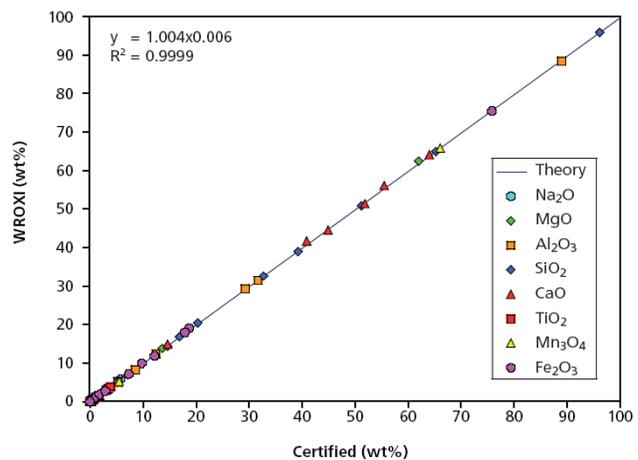


Figure 1: Accuracy overview: comparison of certified and measured values for 8 oxides in the wide variety of RMs listed in Table 2.

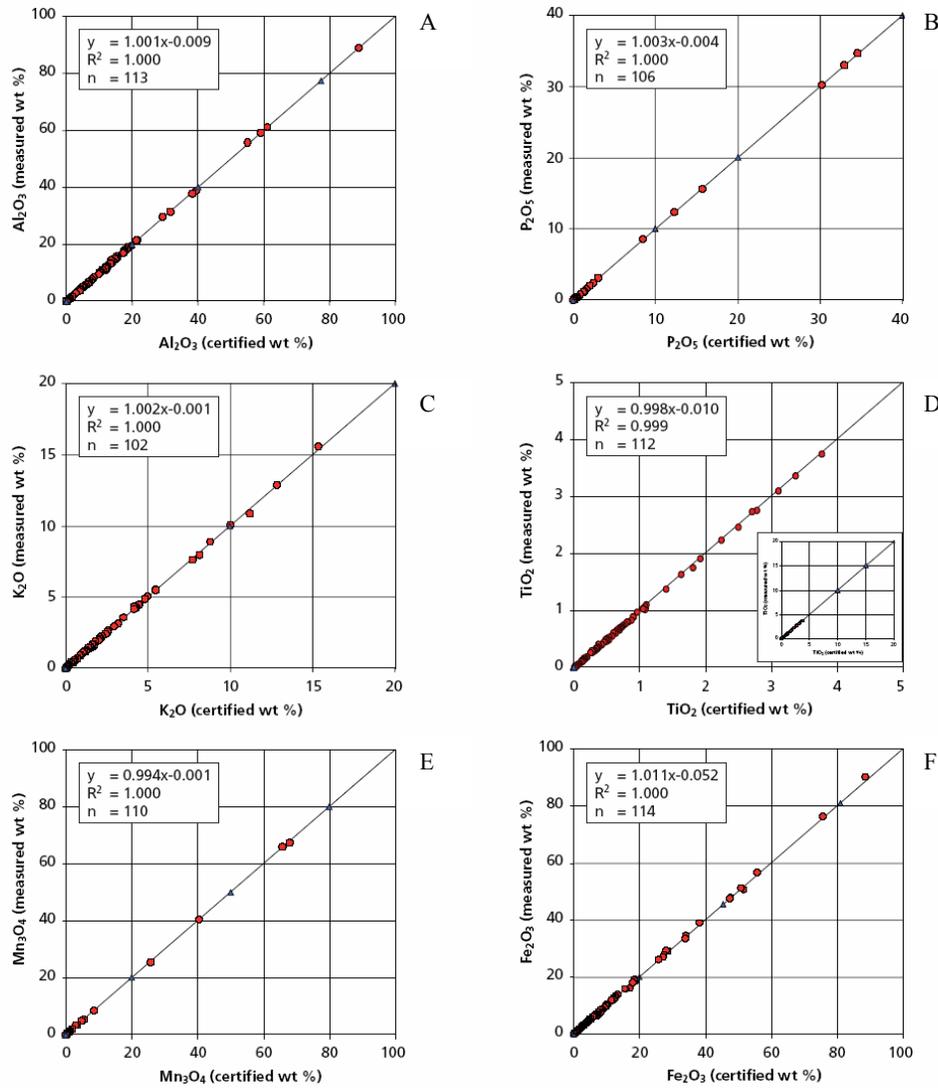


Figure 2: Accuracy verification: comparison of certified and measured values for the WROXI standards and a large number (n) of RMs. The regression values y, x and R2 are for the RMs only.

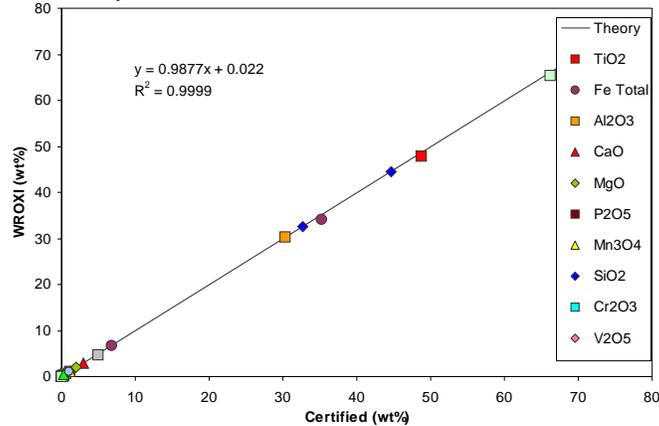


Figure 3: Courtesy Rio Tinto Fer & Titane. Validation of synthetic standards by external standards (Brammer 3701 (coke ashes) SARM 59 (ilmenite), BCS 388 (zircon) in the analysis of the titanium oxide process.

Synthetic standards in practice - Titanium processing

The titanium enrichment process generates several by-products. Some of these have commercial value, others do not. A wide variety of materials need to be analyzed during the process. Minerals such as zircon ($ZrSiO_4$), sillimanite (Al_2SiO_5), spinel ($MgAl_2O_4$) and quartz (SiO_2) are analyzed alongside regular raw materials for TiO_2 or Ti production: slags, coals, rutiles and ilmenites, for example. Figure 3 shows the validation of the synthetic standards by Rio Tinto Fer & Titane.

CONCLUSION

Data presented here supports the successful synthesis and use of a well-selected set of synthetic standards. The WROXI standards correlated well with all different Reference Materials tested over

a wide concentration range. The fact that WROXI standards are chemically pure and traceable offers important support for compliance with company operating procedures and relevant legislation.

REFERENCES

Giles, H.I., Hurley, P.W. and Webster, H. W. M., 1995, Simple approach to the analysis of oxides, silicates and carbonates using X-ray fluorescence spectrometry, X-ray spectrometry, Vol 24, 205, 218, John Wiley and sons, Ltd.

Table 2: Analytical accuracy: comparison of certified and measured values for twelve major and minor oxides in fourteen RMs of various types.

CRM	Type	Na ₂ O (wt %)		MgO (wt %)		Al ₂ O ₃ (wt %)		SiO ₂ (wt %)		P ₂ O ₅ (wt %)		SO ₃ (wt %)	
		Cert.	Meas.	Cert.	Meas.	Cert.	Meas.	Cert.	Meas.	Cert.	Meas.	Cert.	Meas.
BCR32	Phosphate		0.77	0.4	0.39	0.55	0.52	2.09	2.09	32.98	32.71	1.84	1.85
BCS174/1	Slag		0.17	7.13	7.04	1.72	1.73	14.69	14.37	12.30	12.40	0.40	0.40
BCS176/2	Manganese Ore	0.11	0.13	0.04	0.03	5.20	5.29	2.53	2.59	0.20	0.20	0.04	0.14
BCS276	Silica Brick	0.06	0.06	0.06	0.04	0.85	0.89	95.90	96.08		0.03	0.01	0.14
BCS348	Ball Clay	0.34	0.34	0.31	0.29	31.59	31.44	51.13	50.91	0.07	0.08		0.13
BCS370	Magnesite	0.06	0.02	61.8	62.48	12.3	12.38	3.01	2.96				
BCS393	Limestone	0.05	0.00	0.15	0.15	0.12	0.16	0.70	0.68	0.01	0.01	0.02	0.10
BCS394	Bauxite	0.02	0.04	0.12	0.13	88.80	88.74	4.98	4.94	0.22	0.23		0.13
FER-1	Iron Ore	0.01	0.01	0.28	0.25	0.50	0.54	16.92	16.84	2.44	2.45	0.62	0.51
GBW03109	Gypsum	0.018	0.011	1.02	1.04	0.016	0.071	0.27	0.24		0.036	55.63	55.17
GSS-7	Soil	0.07	0.07	0.26	0.20	29.26	29.40	32.69	32.56	0.26	0.27	0.06	0.14
MRG-1	Gabbro	0.74	0.73	13.55	13.84	8.47	8.41	39.12	39.14	0.08	0.07	0.15	0.21
NBS89	Lead-Barium Glass	5.70	5.85	0.03	0.04	0.18	0.17	65.15	65.12	0.23	0.23	0.03	0.03
NIST1880a	Cement	0.19	0.19	1.72	1.69	5.18	5.12	20.31	20.38	0.22	0.22	3.25	3.18

CRM	Type	K ₂ O (wt %)		CaO (wt %)		TiO ₂ (wt %)		Cr ₂ O ₃ (wt %)		Mn ₂ O ₃ (wt %)		Fe ₂ O ₃ (wt %)	
		Cert.	Meas.	Cert.	Meas.	Cert.	Meas.	Cert.	Meas.	Cert.	Meas.	Cert.	Meas.
BCR32	Phosphate		0.08	51.76	51.46	0.03	0.03	0.04	0.04	0.00	0.01	0.23	0.24
BCS174/1	Slag		0.03	44.83	44.52	0.70	0.69	0.26	0.24	5.49	5.31	12.10	12.04
BCS176/2	Manganese Ore	1.30	1.26	0.09	0.13	0.30	0.28	0.01	0.01	65.91	65.84	9.81	10.06
BCS276	Silica Brick	0.14	0.12	1.75	1.70	0.17	0.16	0.02	0.02	0.16	0.16	0.79	0.78
BCS348	Ball Clay	2.33	2.23	0.17	0.18	1.08	1.08	0.16	0.01		0.00	1.04	1.05
BCS370	Magnesite	0.03	0.02	1.54	1.59	0.13	0.11	13.40	13.53	0.12	0.12	7.23	7.18
BCS393	Limestone	0.02	0.01	55.40	56.13	0.01	0.01	0.00	0.00	0.01	0.01	0.05	0.06
BCS394	Bauxite	0.02	0.02	0.08	0.10	3.11	3.09	0.08	0.08		0.00	1.90	1.92
FER-1	Iron Ore	0.01	0.01	3.31	3.27	0.03	0.02	0.00	0.00	0.23	0.23	75.72	75.65
GBW03109	Gypsum	0.02	0.01	40.70	41.95	0.00	0.00		0.00		0.00	0.02	0.03
GSS-7	Soil	0.20	0.19	0.16	0.14	3.37	3.36	0.06	0.06	0.25	0.26	18.76	19.02
MRG-1	Gabbro	0.18	0.18	14.70	14.83	3.77	3.77	0.06	0.07	0.18	0.19	17.94	18.14
NBS89	Lead-Barium Glass	8.40	8.49	0.21	0.23	0.01	0.01		0.01	0.10	0.09	0.05	0.06
NIST1880a	Cement	0.92	0.92	63.83	64.23	0.25	0.26	0.01	0.00	0.12	0.12	2.81	2.80