CHEMICALLY PURE SYNTHETIC STANDARDS FOR WIDE RANGE ANALYSIS OF OXIDES IN GEOLOGICAL MATERIAL USING WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY

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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 work 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 the validation data shows. A titanium process example clearly shows the benefits of highest accuracy analysis.

Advantages of X-Ray Fluorescence Spectrometry

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.

- Fast, high throughput
- Precise and accurate analysis
- Broad range of elements (Be-U)
- Traces, minor and major elemental concentrations
- Hazard-free sample preparation
- No time-consuming chemical methods
- Different sample types:
  - Solid pieces
  - Pressed powders
  - Loose powders
  - Granules
  - Filters and more...

Importance of standards

The need for **good standards** is often underestimated and the availability of good standards for the calibration is in many cases the bottleneck for accurate and precise analysis.

Traditionally, XRF spectrometers are calibrated using reference materials (RMs) with similar matrix to the routine samples. The resulting calibrations are then sample-type specific and the availability of these in-type standards is often limited. The composition of an RM is determined by averaging analyses obtained by multiple techniques (ICP, INAA, AA etc.) and is by definition secondary.

Difficulties with in-type RMs:

- In-type standards are scarce and expensive
- Mineralogical and particle-size effects in pressed powders have a negative impact on the reliability of the calibration
- Multiple calibrations are needed

Solution to these difficulties:

- Use of synthetic powders with known absolute concentrations
- Dissolve with flux material by fusion to overcome mineralogical and particle size effects

Fusion of synthetic pure chemicals results in the 'perfect' standards:

- One single calibration is valid for a wide variety of geological sample types
- Concentrations are traceable back to pure chemicals
- Constituents can be chosen, free from interfering elements

In this work we describe and evaluate the use of synthetic standards for the analysis of 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.

General

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

Analysis of majors and minors

The setup

- Oxides covered and their concentration ranges are given in table 1.
- The standards are made from high purity compounds and chosen so that they are free from line-overlaps.
- The set comprises 20 standards for the analysis of 21 oxides.
- The set-up suite contains an application template and a standards concentration file.
- The set is developed by PANalytical in cooperation with the British Geological Survey.
- The standards are packaged under nitrogen in bottles and have to be fused according to the end-user's fusion recipe.

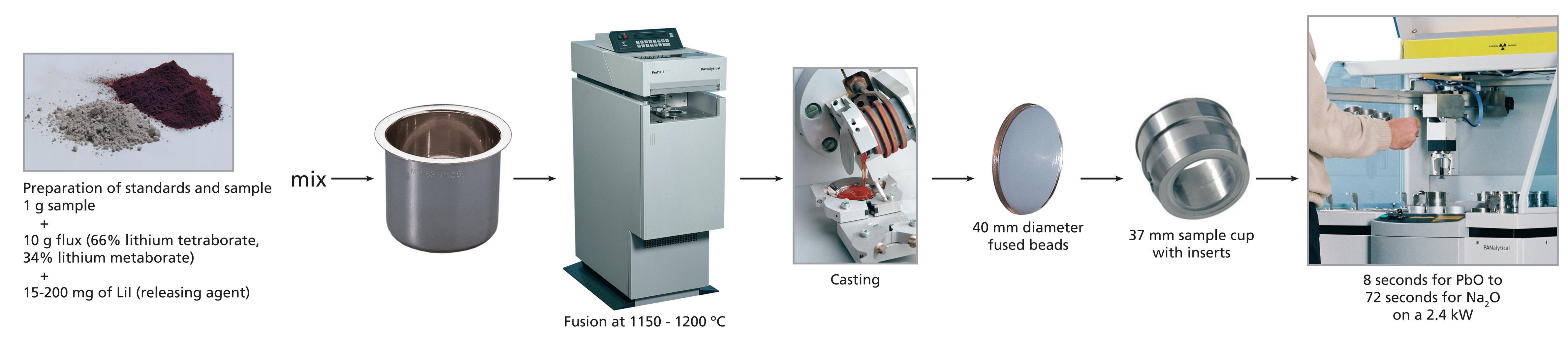
Data handling

- The SuperQ software contains a Fundamental Parameter (FP) method to correct for matrix effects.
- The analytical range can be extended outside the calibrated concentration range bracketed by the standards as a result of the FP-model and the excellent linearity of the XRF-spectrometer.

WROXI Standards: oxides and their concentration ranges (wt %)						
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O
0 - 58	0 - 78	0 - 78	0 - 80	0 - 40	0 - 59	0 - 40
CaO	TiO_2	V_2O_5	Cr_2O_3	Mn_3O_4	Fe_2O_3	NiO
0 - 80	0 - 40	0 - 10	0 - 10	0 - 80	0 - 81	0 - 12
CuO	ZnO	SrO	ZrO_2	BaO	HfO_2	PbO
0 - 8	0 - 10	0 - 20	0 - 43	0 - 43	0 - 10	0 - 10

Table 1. The 21 oxides present in WROXI and their calibrated concentration ranges

Sample preparation and measurement of standards and routine samples



Accuracy

Several Reference Materials (RMs) of widely varying composition and sample type, were analysed using the WROXI calibration. The measured concentrations were compared to the values on the certificates. An overview graph is shown in figure 1, illustrating the excellent correlation. More detailed validation data are given in figure 2A-F.

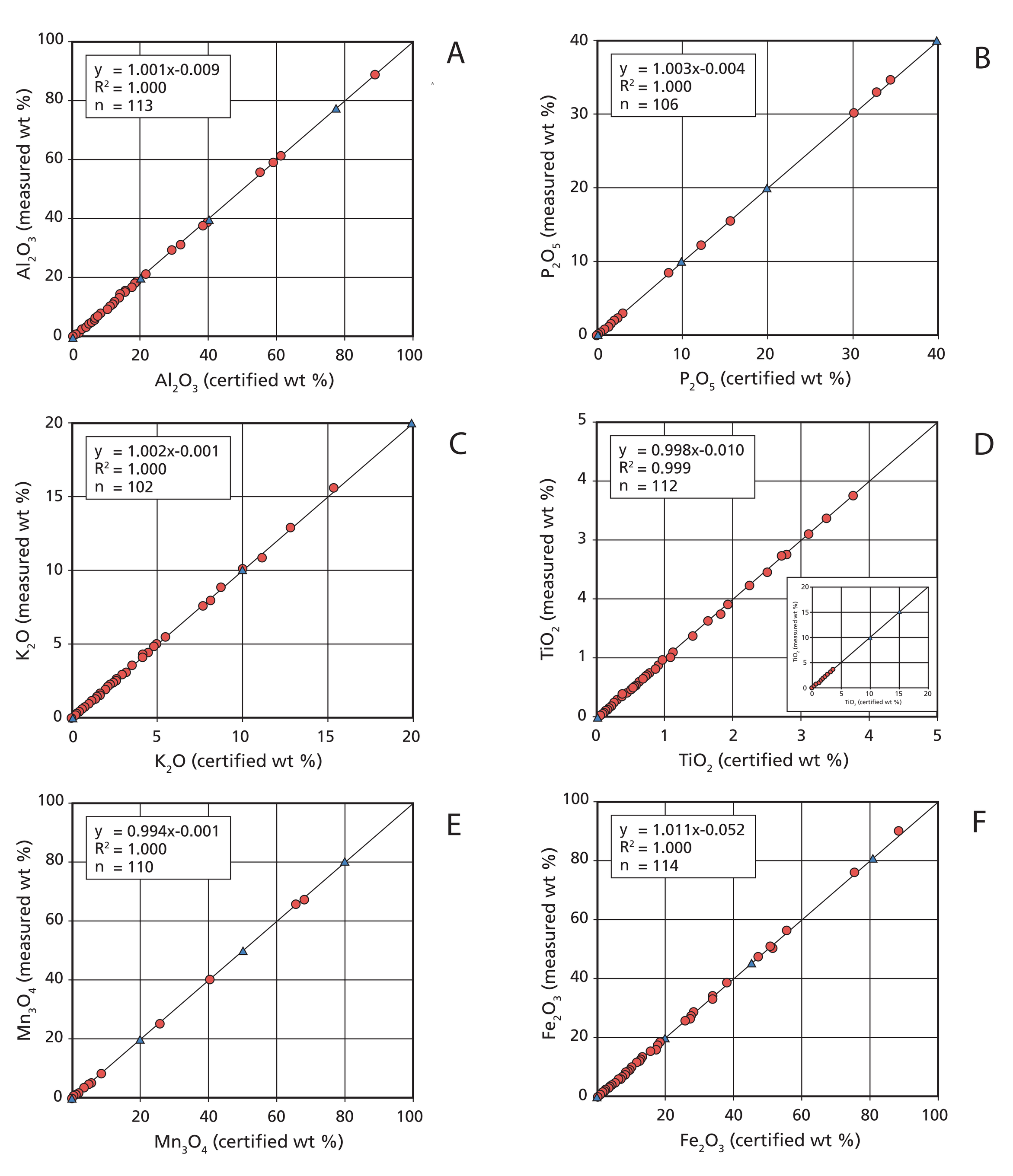


Figure 2. Accuracy verification: comparison of certified and measured values for the WROXI standards (▲) and a large number (n) of RMs (●). The regression values y, x and R2 are for the RMs only

CRM	Type	Na_2O (wt %)		MgO (wt %)		Al2O3 (wt %)		SiO_2 (wt %)		P_2O_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_2O (wt %)		CaO (wt %)		TiO_2 (wt %)		Cr_2O_3 (wt %)		Mn_3O_4 (wt %)		Fe_2O_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

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

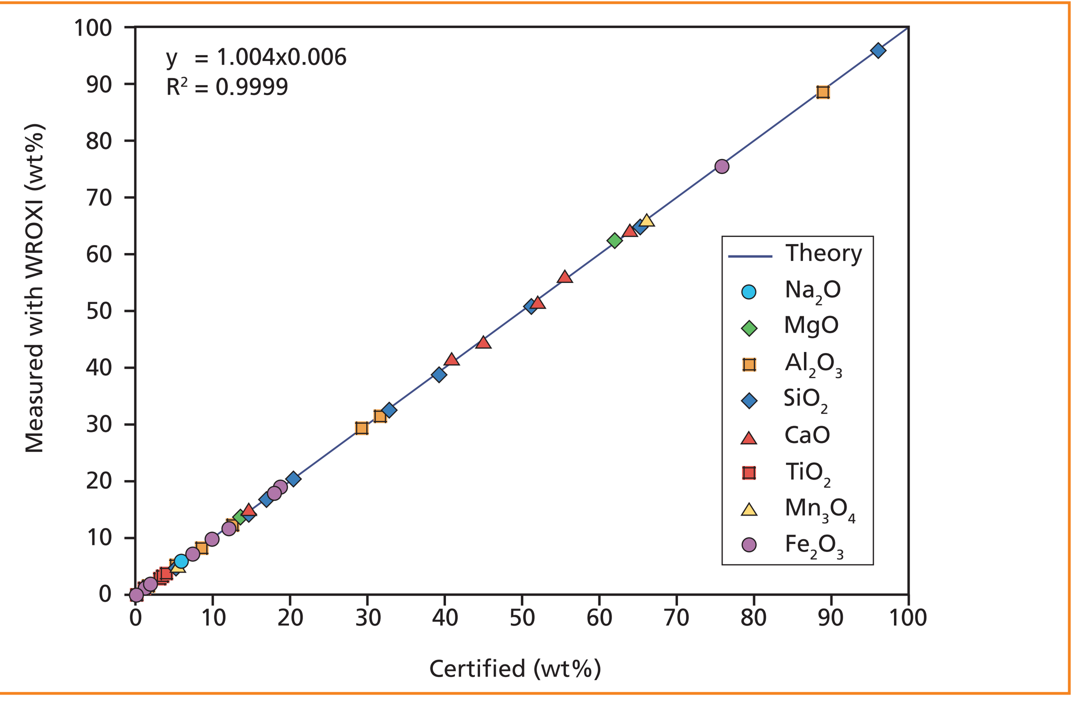


Figure 1. Accuracy overview: comparison of certified and measured values for 8 oxides in the wide variety of RMs listed in Table 2

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.

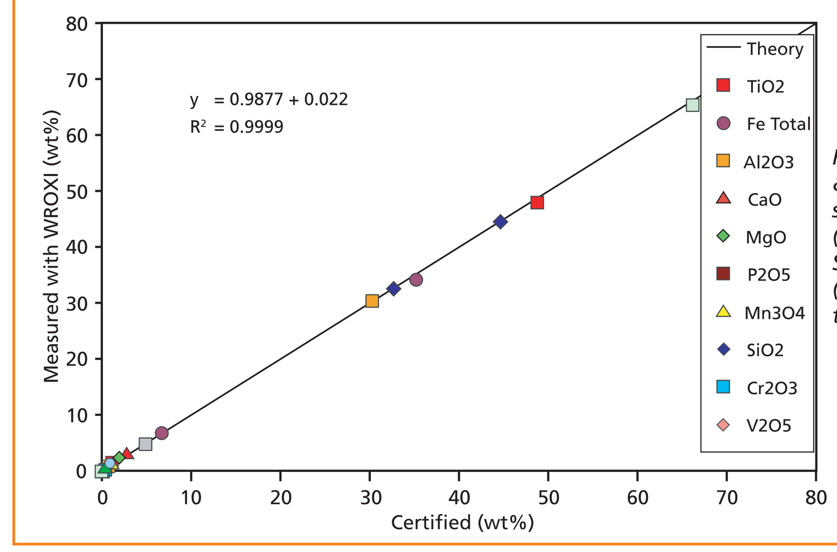


Figure 3. Courtesy Rio Tinto Fer & Titane. Validation of synthetic standards by external standards (Brammer 3701 (coke ashes) SARM 59 (ilmenite), BCS 388 (zircon) in the analysis of the titanium oxide process.

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.