

Combining XRF and XRD analyses and sample preparation to solve mineralogical problems

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ABSTRACT

X-ray Fluorescence Spectroscopy (XRF) has reached the stage where it is classified as a mature analytical technique. The theoretical principles are well understood. In addition modern instrumentation demonstrates enhanced generator and temperature stability. High sensitivity is possible even for light elements and effective matrix correction software is available to the modern day spectroscopist. Apart from its continued applications in research and development, XRF has become a routine process control tool.

X-ray Powder diffraction (XRD), on the other hand, has with minor exceptions as in the cement industry, largely remained a research tool, despite being an older analytical technique than XRF. XRD has progressed significantly in the past decade from a mainly qualitative technique for the identification of crystalline materials to a quantitative tool with the advance of more powerful software packages. This software has improved instrument control, but also quantification and structure determination using the Rietveld method. Consequently, XRD is rapidly entering the process control environment.

In this paper the authors demonstrate, with practical examples from different industrial applications, how combined XRF and XRD use can provide truly quantitative phase analyses. XRF is used to verify XRD data and visa versa.

The data obtained in this study clearly illustrate the value that can be added to either technique if XRF and XRD data are used together, and indicate some applications in routine process co.

Introduction

A research laboratory like the X-ray Analytical Facility of the University of Pretoria is exposed to a wide range of materials. Housed by the Geology Department, minerals and ores are routine matrices, but in collaboration with the Department of Metallurgy and Material Science and the Institute for Applied Materials as major users, the laboratory is exposed to many diverse material types. The laboratory is frequently approached by industry regarding problems that commercial laboratories cannot solve, or where high accuracy analysis on specialised matrices is needed. This creates some unique problems that can not always be solved by any single analytical technique and the combined use of XRD and XRF analysis proves an efficient way to solve problems.

X-ray Fluorescence Spectroscopy is used to determine the bulk chemical composition of a sample. Fundamental parameter software like UniQuant™ (Thermo Fisher Scientific Inc. 2006), enables the qualitative and quantitative analysis of an unknown sample with or without sample preparation. Elements from fluorine to uranium in the periodic table can be analysed with detection limits varying from 0.5 ppm for heavier elements like Mo to 100 ppm for the lightest element F. With the fundamental parameter approach, everything in the sample is analysed to enable accurate matrix corrections. The software allows for manual input of elements not determinable by XRF, like carbon, oxygen and hydrogen in different compounds and this data is then used in the matrix correction model. For higher accuracy, matrix matched calibration curves can be set up for specific matrices with specific sample

preparation protocols followed. Examples of calibrations used most often will be shown below.

X-ray Powder Diffraction is used to determine the crystalline phase(s) present in a sample. As each phase has a unique powder diffraction pattern, it is possible to distinguish between compounds as the diffraction method is sensitive to crystal structure and not just composition. The powder diffraction pattern for the spinel $MgAl_2O_4$ looks different from the powder pattern of periclase (MgO) and corundum (Al_2O_3) mixture although a chemical analysis may show identical results. It is also possible to distinguish between different polymorphic forms of the same compound. Additionally, the intensity of each component's pattern is proportional to the amount present.

Examples of problems encountered where the use of both techniques is of advantage include validation of results when XRF data do not add to $100 \pm 1.5\%$ without obvious reasons. XRD can confirm the phases present, e.g. carbonates that are not visible to XRF or a mixture of components with differing oxidation states. XRF determines total iron and / or titanium, but for matrix correction purposes adds stoichiometric amounts of oxygen according to the most common oxidation states. In the case of mixtures of hematite and magnetite or ilmenite and rutile, this could lead to erroneous results. The analysis of slag and refractory materials are other examples where additional XRD information is crucial to successful analysis. Slag samples often contain traces of metal. The XRF software either assigns oxygen or treats a sample as a metal, and consequently mixtures pose problems. In addition, sulphur and silicon are of the few elements that show a peak shift in XRF depending on

the oxidation state (Willis and Duncan 2008). If a system was set up using oxide materials and a sulphide or silicon metal is analysed, a peak shift will lead to erroneous results. XRD can easily be used to identify these problems.

Metal inclusions also pose serious risks to routine sample preparation procedures, as major element analysis is usually determined on fused lithium borate beads. Metals, exposed to platinum ware at elevated temperatures, form low melting ligands that react with the platinum laboratory ware (Lupon *et al.* 1997). Sulphide bearing materials have the same tendency.

In these cases XRD is used to identify possible deleterious elements in the sample and also to confirm that all metals and sulphides were oxidized during pre-treatment before fusion.

Analytical procedures

XRF

Bulk sample preparation consists of drying where necessary, crushing to 10mm, riffle splitting and milling in a tungsten carbide milling pot to ca. 80% below 75 μm . When Co and W analysis are specifically requested a carbon steel milling vessel is used. For XRD contamination from milling vessels is only a factor when material harder than that of the grinding medium is milled and here corundum as well as Si-carbides have been observed to be problematic.

Samples are dried at 110°C (Weight 1) and roasted at 1000°C (Weight 2), to determine the percentage loss on ignition (LOI) using the following equation:

$$\%LOI = \frac{\text{Weight}_1 - \text{Weight}_2}{\text{Weight}_1 - \text{Weight}_{\text{crucible}}} \times 100$$

Major element analyses are executed on fused beads, following a method adapted from H. Bennett and G. Oliver's proposed methods (1992). 1g pre-roasted sample is added to 6g of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) flux mixed in a 5% Au/Pt crucible and fused at 1000°C in a muffle furnace automated fluxer (Beadmaster F-M4). A mouldable crucible is used so that, on removal from the furnace, the bead is fast cooled in the crucible of which the bottom surface is analysed. This approach has the advantage, that should there be undissolved material, it is all retained in the bead which can be re-melted.

Trace elements are analysed on pressed powder briquettes, after an adaptation of the method described by Watson (1996), using a saturated solution of polyvinyl alcohol 40-88, as binder. The mixing of the sample and binder is accomplished in a plastic zip-lock bag. 20 g of 75 μm powder is mixed with a few drops of polyvinyl alcohol and pressed at a pressure of 20 ton/cm² for two minutes in collapsible aluminium holders for mechanical support, using a polished piston. The sample is then dried at 110°C before analysis.

Special sample preparation techniques have been developed for non-routine materials. Sulphide containing materials have to be prepared with special care as sulphides are not soluble in lithium borate fluxes and damage the platinum ware (Lupon *et al.* 1997). These samples have to be pre-oxidised while retaining the sulphur quantitatively as SO_4 . This is accomplished by using Lithium nitrate (LiNO_3). 0.5g of sample is thoroughly mixed with 3g of LiNO_3 and placed on a bed of (3g) $\text{Li}_2\text{B}_4\text{O}_7$ and covered with the remaining (3g) flux. This "sandwich" technique protects the platinum against un-oxidised sulphides and at the same time the flux lid helps to prevent the escape of any SO_2 gas. The mixing of sample and oxidant is crucial to facilitate complete oxidation. The pre-reaction is done at much lower temperatures than suggested in the literature (Sear L G, 1997), as it was found that sulphur is lost when oxidation reactions are executed at temperatures above the dissociation of LiNO_3 (600°C). A method was developed where the sample is pre-reacted for an hour in a muffle furnace at 500°C, above the melting temperature of LiNO_3 but below the dissociation temperature. The reaction was evaluated using Differential Scanning Calorimetry (DSC) and XRD to evaluate the reaction and confirm completion of the oxidation, before heating to 1000°C for the fusion to take place.

Metal bearing samples, like industrial refractory materials where a brick / metal interface exists, as well as modern refractory materials where metallic particles and graphite are added for increased strength, need special preparation. The same preparation methods are used for slag samples where metallic residues are often present. To prepare these samples for XRF analysis, a pre-oxidation step using nitric acid (HNO_3), is used as roasting was found to be ineffective. Roasting forms a oxidised layer on the outer surface of the particles, protecting the inside against further reaction and, when dissolved by the flux during fusion, the metallic residue is brought into direct contact with the platinum crucible. The method used is as follows: 1g sample is weighed directly into a platinum crucible and 5ml of a 50% aqueous HNO_3 solution is added. The mixture is heated slowly on a hot plate until all reaction ceases and dries. Then 6g of lithium tetraborate flux is added on top and fused at 1000°C as usual. As roasting could not be used to determine the loss or gain on ignition, the fused bead is weighed, and the difference in sample mass before and after oxidation is calculated.

The instrumentation used is an ARL 9400XP+ Wavelength dispersive XRF Spectrometer with a Rhodium tube, LiF200, LiF220, GER, AXO6 (a 50Å synthetic multilayer) and PET analysing crystals, with a flow proportional and scintillation detector. Data reduction is performed using three different software approaches: WINXRF using the COLA algorithm (Lachance and Claisse, 1980) with theoretical alphas deduced from fundamental parameters, for matrix correction of fused bead major elements as well as

Table 1. Instrumental parameters for Majors program.

Analyte	$^{\circ} 2\theta$	Crystal detector	Collimator ($^{\circ}$ divergence)	Time (s)	Interference	Highest conc. (%)	kV/mA
SiK α 1,2	109.01	PET FPC	0.6	20	-	100	30/80
TiK α 1,2	86.17	LiF200 FPC	0.15	20	-	3.77	50/50
AlK α 1,2	144.619	PET FPC	0.25	20	Br	100	30/80
FeK α 1,2	57.518	LiF200 FPC	0.15	20	Mn	50.00	50/50
MnK α 1,2	62.973	LiF200 FPC	0.25	20	Cr	0.35	50/50
MgK α 1,2	19.878	AX06 FPC	0.60	100	Zr2nd order PHS corrects	43.51	30/80
CaK α 1,2	113.086	LiF200 FPC	0.25	20	-	100.0	30/80
NaK α 1,2	23.993	AX06 FPC	0.60	100	Zn	5.84	30/80
KK α 1,2	136.637	LiF200 FPC	0.6	20	-	8.91	30/80
PK α 1,2	140.952	Ge111 FPC	0.60	20	Ca not relevant (Ge)	39.96	30/80
CrK α 1,2	69.354	LiF200 FPC	0.25	100	-	3.5	50/50
NiK α 1,2	48.667	LiF200 FPC	0.25	100 50+50	Yb Y2nd PHS, tube impurities	0.48	50/50
VK α 1,2	76.933	LiF200 FPC	0.25	100	Ti	0.09	50/50
ZrK α 1,2	32.038	LiF220 SC	0.15	20	Sr	0.1	50/50
SrK α 1,2	35.796	LiF220 SC	0.15	20		0.52	50/50
ZnK α 1,2	41.794	LiF200 SC	0.25	100		0.92	50/50
CuK α 1,2	45.030	LiF200 FPC	0.25	100 +50	Sr, tube impurity	0.7800	50/50
SK α 1,2	110.688	Ge111 FPC	0.60	100 50+50		0.4	30/80

PET - Peta-erythritol

LiF - Lithium fluoride

Ge - Germanium

FPC - Flow proportional Counter

SC - Scintillation Counter

AX06 - Layered synthetic microstructure

powder majors and trace element analysis of Cl, Co, Cr, V, Sc and S. The Rhodium Compton peak ratio method (Feather and Willis, 1976) is used for the other trace elements.

The XRF Spectrometer is calibrated with certified reference materials, specpure oxides and some in-house standards, e.g. Specpure Al_2O_3 , AGV-1, BCR-1, BE-N, BHVO-1, BR, Specpure $CaCO_3$, Specpure CaO, DR-N, FeCa (in-house), FeSi (in-house), GA, GS-N, GSP-1, Specpure SiO_2 , JB-1, JG-1, Lithium tetraborate blank, MA-N, Mica-Fe, Mica-Mg, MRG-1, NIM-D (SARM 6), NIM-

G (SARM1), NIM-N (SARM4), NIM-P (SARM5), NIM-S (SARM2), PCC-1, SARM8, SARM9, SARM32, SARM34, SARM39, SARM40, SARM42, SARM44, SARM45, SARM46, SARM47, SARM49, SY-2, SY-3, UB-N, UREM3, UREM4, UREM7, W-2 (Govindaraju, K. 1984).

Background and overlap corrections were calculated on a set of interference standards and stored in the calibration according to a method proposed by Willis and Duncan (1993).

Tables 1 to 4 show the instrumental parameters for the three analytical approaches:

Table 2. Instrumental parameters for Trace elements

Analyte	$^{\circ} 2\theta$	Crystal detector	Collimator ($^{\circ}$ divergence)	Time (s)	Interference	Highest conc. (%)	kV/mA
CuK α 1,2	45.030	LiF200 SC	0.25	20 10+10	Sr, tube impurity	0.7800	50/50
NiK α 1,2	48.667	LiF2000 SC	25	20 10+10	Yb Y2nd PHS, tube impurities	0.26	50/50
ClK α 1,2	92.76	Ge111 FPC	0.60	100 50+50		0.1161	30/80
CoK α 1,2	52.8	LiF200 FPC	0.25	100 +50		0.0267	50/50
ScK α 1,2	97.72	LiF200 FPC	0.15	100 50+50		0.0064	50/50
FK α 1,2	37.236	AX06 FPC	0.60	100 50+50		2.85	30/80
BaL α 1,2	87.17	LiF200 FPC	0.15	100 50+50		0.45	50/50
LaL α 1,2	82.95	LiF200 FPC	0.15	100 50+50		0.27	50/50
CeL α 1,2	79.010	LiF200 FPC	0.15	100 +50		0.27	50/50
CsL α 1,2	91.823	LiF200 FPC	0.15	100 50+50		0.02	50/50
GaK α 1,2	38.917	LiF200 SC	0.25	20 10+10		0.0095	50/50
MoK α 1,2	28.843	LiF220 SC	0.15	40 20+20	Zr, U	0.0330	50/50
NbK α 1,2	30.378	LiF220 SC	0.15	20 20+20	Y, Th	0.0270	50/50
PbL α 1,2	40.379	LiF220 SC	0.15	20 10+10		2.82	50/50
RbK α 1,2	37.929	LiF220 SC	0.15	20 10+10	U	0.2200	50/50
SrK α 1,2	35.793	LiF220 SC	0.15	20 10+10		0.1600	50/50
ThL α 1,2	39.227	LiF220 SC	0.15	40 10+10		0.0150	50/50
UL α 1,2	37.295	LiF220 SC	0.15	40 20+20		0.0080	50/50
YK α 1,2	33.839	LiF220 SC	0.15	20 10+10	Rb, Th	0.0143	50/50
ZnK α 1,2	41.799	LiF200 SC	0.25	20 10+10	Tube impurities	0.9083	50/50
ZrK α 1,2	32.032	LiF220 SC	0.15	20 10+10	Sr,Th, tube impurities	0.0943	50/50
AsK α 1,2	43.5500	LiF200 SC	0.15	40 10+10	Ba and Rh	0.0121	50/50
WL α 1,2	43.001	LiF200 SC	0.15	20 10+10		0.0450	50/50

PET – Peta-erythritol

LiF – Lithium fluoride

Ge – Germanium

FPC – Flow proportional Counter

SC – Scintillation Counter

AX06 – Layered synthetic microstructure

Table 3. Instrumental parameters for corrections

Analyte	2θ	Crystal detector	Collimator ($^\circ$ divergence)	Time	Interference	kV/mA
RhK α compton	26.345	LiF220 SC	0.15	20	Feather Willis correction	50/50
RhK α compton	18.549	LiF200 SC	0.15	20	Feather Willis correction	50/50
RhK α	24.899	LiF220 SC	0.15	20	Tube impurities correction	50/50
RhK α	17.563	LiF200 SC	0.15	20	Tube impurities correction	50/50

Table 4. Instrumental parameters for UniQuant.

Crystal	2d Crystal	Collimator ($^\circ$ divergence)	Detector	X-Ray tube anode	Tube setting KV	Tube setting mA	Primary beam filter
LiF220	2.8480	0.15	SC	Rh	60	40	0.25Cu
LiF420	1.8000	0.15	SC	Rh	60	40	
LiF220	2.8480	0.15	FPC	Rh	40	60	
GE111	6.5320	0.15	FPC	Rh	40	60	
AX06	55.400	0.60	FPC	Rh	30	80	

AX06 – Layered synthetic microstructure

As part of ongoing quality control, a blank and two certified reference materials are analysed with each batch of samples. Each tenth sample is run in duplicate and clients are encouraged to include their own standards and duplicates in batches. The laboratory participates in the International Association for Geoanalysts' GeoPT proficiency test (Thompson *et al.*, 1997) where geological materials are analysed three times a year, and results reported after statistical treatment with "z" values for each element from each laboratory. To evaluate sample preparation errors, an in-house standard is submitted monthly with a batch of unknowns and prepared in the same manner as unknowns. Reported standard deviations are expressed as the standard deviation of a calibration curve, set up

with an average of 20-30 standards, as this method best approximates the entire calibration range. Limits of Quantification were also calculated from calibration standards. (Table 5)

XRD

At the X-ray Analytical Facility at the University of Pretoria samples are analysed using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits each set at between 5 and 15 mm, depending on the sample holder used. The samples are scanned at the required 2θ angle ranges. The radiation can be Fe-filtered CoK α , Ni-filtered CuK α or Mn-filtered FeK α radiation depending on the chemical composition of the samples analyzed in order

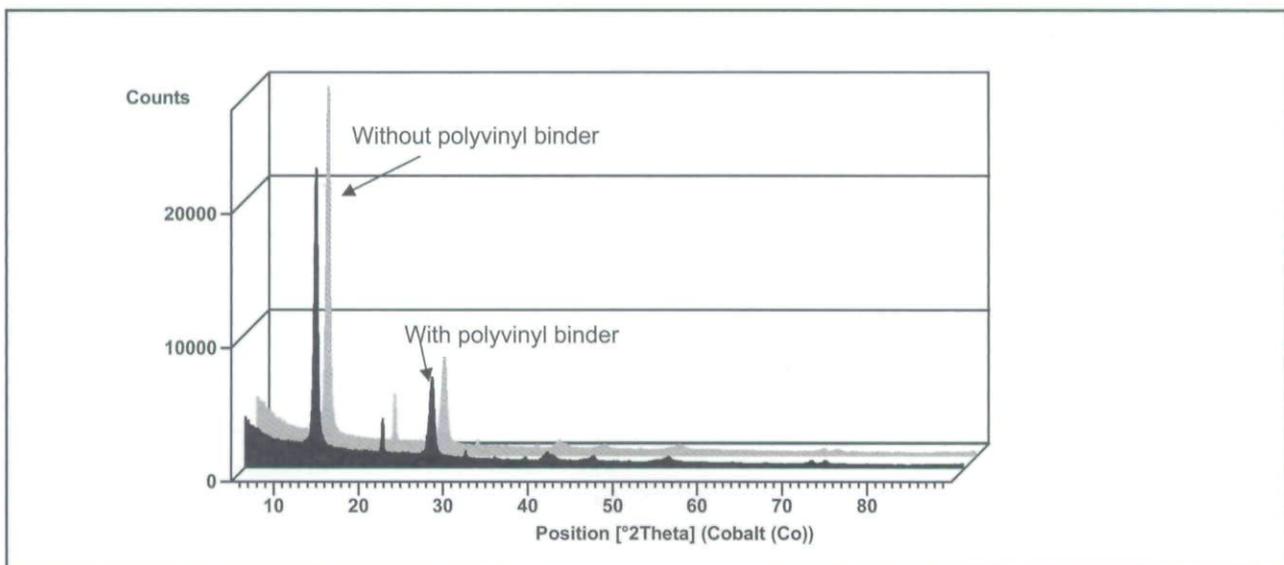
**Figure 1.** Effect of polyvinyl alcohol binder on XRD scans of pressed powder briquettes

Table 5. Standard deviation and Limit of Quantification.

	std dev.(%)	LOQ.(%)
SiO ₂	0.4	0.02
TiO ₂	0.03	0.0032
Al ₂ O ₃	0.3	0.01
Fe ₂ O ₃	0.3	0.0097
MnO	0.0065	0.0013
MgO	0.1	0.0118
CaO	0.07	0.01
Na ₂ O	0.11	0.0265
K ₂ O	0.06	0.005
P ₂ O ₅	0.08	0.01
Cr ₂ O ₃	0.0053	0.0006
NiO	0.01	0.0013
V ₂ O ₅	0.0018	0.0008
ZrO ₂	0.005	0.0009
CuO	0.0037	0.0003
	std dev.(ppm)	LOQ.(ppm)
As	10	3
Cu	3	2
Ga	2	2
Mo	1	1
Nb	3	2
Ni	6	3
Pb	3	3
Rb	4	2
Sr	4	3
Th	2	3
U	2	3
W	10	6
Y	4	3
Zn	4	4
Zr	6	10
Ba	14	5
Ce	14	6
Cl	100	11
Co	6	3
Cr	40	15
F	500	100
La	24	5
S	300	40
Sc	5	1
V	10	1

to eliminate fluorescence which would cause, high background and poor peak to background ratio. The phases are identified using PANalytical X'Pert Highscore plus software.

When required, relative phase amounts are estimated by the Rietveld method using either the Autoquan - BGMN Rietveld Program (Kleeberg and Bergmann, 1998; 2002, Kleeberg *et al.*, 2000) or topas from Bruker AXS employing the fundamental parameter approach or PANalytical X'Pert Highscore plus software.

Various sample preparation methods are employed. For routine analysis on powders a back loading preparation method is used. Front Loading onto a zero background Silicon sample disc is used when the

sample amount is too small for the routine samples holders. Solid sample fragments which cannot be powdered (*e.g.* metals and plastics) are mounted in a sample cup. In certain instances it is possible to use the same powder briquettes prepared for XRF analysis. The effect of the additional polyvinyl binder was investigated and found to be negligible (Figure 1).

For routine phase identification a particle size of less than 50 µm is required, which is achieved by milling in a tungsten carbide or carbon steel milling vessel using a swing mill or even by hand grinding in an agate mortar and pestle. For quantitative phase analysis, the preferred particle size is below 10 µm and that is reached by wet grinding for between five and ten minutes using ethanol in a McCrone micronizing mill (Klug and Alexander, 1974; Buhrke *et al.*, 1998). When the determination of amorphous content is required, a known amount of a standard, usually 15 or 20% Si (Aldrich 99% pure), is added to a milled sample and the sample and standard are homogenized in a McCrone micronizing mill.

In order to test the reproducibility of phase quantification using Rietveld analysis the analysis of iron ore sinters, as discussed below, is used as an example. Three tests were performed:

1. The same sample mount was analyzed ten times to test the reproducibility of the instrument and method.
2. To test the reproducibility of sample packing and sample presentation to the beam the same sub-sample was remounted ten times and re-analysed.
3. The homogeneity and representativeness of sub-samples was tested by taking ten different sub-samples and repeating the sample preparation and mounting procedure. In each case 16.6 weight per cent Si powder (Aldrich, 99% purity) for verification of results was added. The results are presented in Table 6.

Case studies

Iron Ore Sintners

Iron ore sinters are important feedstock materials for the steel industry. As a result of increased quality requirements, the chemistry and the phase composition of sinters are of importance. Historically point counting was used in the analysis of these sinters. Quantitative X-ray powder diffraction analysis, however, is another method for determination of the relative quantities of phases present in sinters. Although no observations on textural features can be made, it is fast and can easily be adapted for process control.

Minerals typically present in the sinters are magnetite, hematite, magnesioferrite, periclase, di-calcium silicate, glass and silico ferrites of calcium and aluminium. The latter phases are abbreviated as SFCA, of which three varieties have been described depending on the molar ratio of cations to oxygen: SFCA (M₁₄O₂₀), SFCA-I (M₂₀O₂₈) and SFCA-II (M₂₆O₃₆) (M=Ca, Fe, Al and Si). The four sinter samples used in this example were obtained from Mittal Steel SA. 20% Si powder (Aldrich,

Table 6. Representativeness of XRD preparation

	C2S	Hematite	Magnetite	SFCA I	SFCA	SFCAII	Silicon
Identical sample mount							
Mean	9.30	8.91	23.81	3.54	15.31	22.46	16.22
Standard Deviation	0.54	0.16	0.51	0.98	1.54	1.37	0.26
Same subsample - Different sample mount							
Mean	9.35	9.01	23.80	3.25	15.56	22.46	16.17
Standard Deviation	0.49	0.23	0.57	0.61	1.28	1.46	0.36
Different subsamples							
Mean	9.16	9.04	23.76	3.53	15.54	22.35	16.19
Standard Deviation	0.54	0.43	0.52	0.97	1.69	1.37	0.43

Table 7. Quantitative XRD data of Iron Ore Sinters used in the study.

	C2S	Hematite	Magnetite	SFCA	SFCA II	Silicon
Sinter 1	7.47	11.02	34.10	13.17	13.67	20.56
Sinter 2	5.66	21.93	29.39	12.69	8.75	21.58
Sinter 3	6.08	12.17	33.24	14.37	13.32	20.83
Sinter 4	6.02	19.82	32.26	10.63	9.82	21.45

Table 8. XRF data on Sinter samples (weight %).

	Sinter 1	Sinter 2	Sinter 3	Sinter 4
SiO ₂	4.21	4.51	4.63	4.2
TiO ₂	0.09	0.09	0.08	0.09
Al ₂ O ₃	1.24	1.27	1.32	1.23
Fe ₂ O ₃	61.3	57.28	57.68	60.9
MnO	86	0.96	0.78	0.91
MgO	2.7	2.84	2.9	2.68
CaO	9.07	9.07	10.51	8.64
Na ₂ O	<0.005	<0.005	<0.005	<0.005
K ₂ O	0.13	0.14	0.13	0.13
P ₂ O ₅	0.1	0.1	0.12	0.1
Cr ₂ O ₃	0.02	0.02	0.02	0.02
NiO	<0.01	<0.01	<0.01	<0.01
V ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ZrO ₂	<0.01	<0.01	<0.01	<0.01
LOI	19.41	23.09	21.94	20.35
Total	99.15	99.37	100.11	99.25

99% purity) for determination of amorphous content as well as verification of results was added. More detailed XRD results are shown in de Villiers and Verryn (2007).

These results are a first approximation and minor phases were ignored, recalculation including minor phases can improve the results. Ignoring the added Si, these results are in good agreement with the results obtained by XRF, and in this case the analytical totals are acceptable. From the XRD results we obtain information about the oxidation states of most of the Fe in the sample (Tables 7 and 8).

Analysis of Fly Ash and other glass containing materials

At our laboratory samples containing glassy or amorphous materials are routinely analyzed and quantified after addition of between 15 and 20% Si

Table 9. Combining XRD and XRF results to calculate an approximate composition of the amorphous component in Fly Ashes.

	1	2	3	4
XRD				
Amorphous	67.84	63.64	68.41	63.81
Calcite	0.26	0.34	0.3	0.26
Hematite	0.46	0.77	0.73	0.72
Mullite	23.91	21.46	20.52	21.88
Quartz	7.54	13.79	10.04	13.32
XRF				
CaO	1.47	0.83	0.89	1.19
SiO ₂	60.9	62.3	62.3	56.8
Fe ₂ O ₃	4.23	4.24	4.25	4.65
Al ₂ O ₃	29.8	28.9	28.9	33.9
MgO	0.47	0.56	0.64	0.57
TiO ₂	0.29	0.29	0.3	0.31
Mn ₂ O ₃	0.22	0.22	0.22	0.24
K ₂ O	0.93	1.13	1.17	0.9
Composition of amorphous component				
CaO	1.21	0.49	0.59	0.93
SiO ₂	43.796	39.926	44.052	34.728
Fe ₂ O ₃	4.046	3.932	3.958	4.362
Al ₂ O ₃	15.454	16.024	16.588	20.772
MgO	0.47	0.56	0.64	0.57
TiO ₂	0.29	0.29	0.3	0.31
Mn ₂ O ₃	0.22	0.22	0.22	0.24
K ₂ O	0.93	1.13	1.17	0.9

powder as described above. Other methods as well as the use of other spike materials have been described by Ward and French (2005). After spiking, the phases are identified and then quantified, using the Rietveld method defining Si as a standard, which is then used to calculate the amount of amorphous material.

Combining XRD and XRF results, an approximate composition of the amorphous component(s) can be

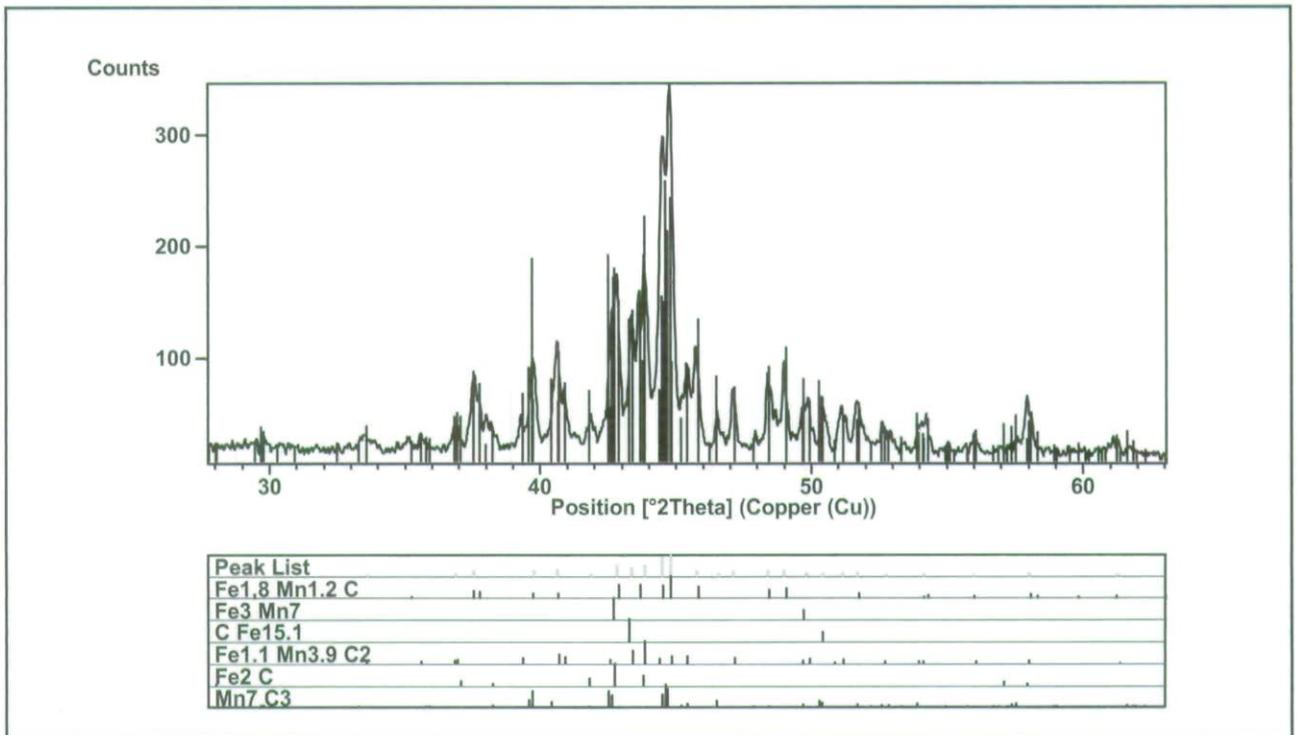


Figure 2. XRD scan of original FeMn sample

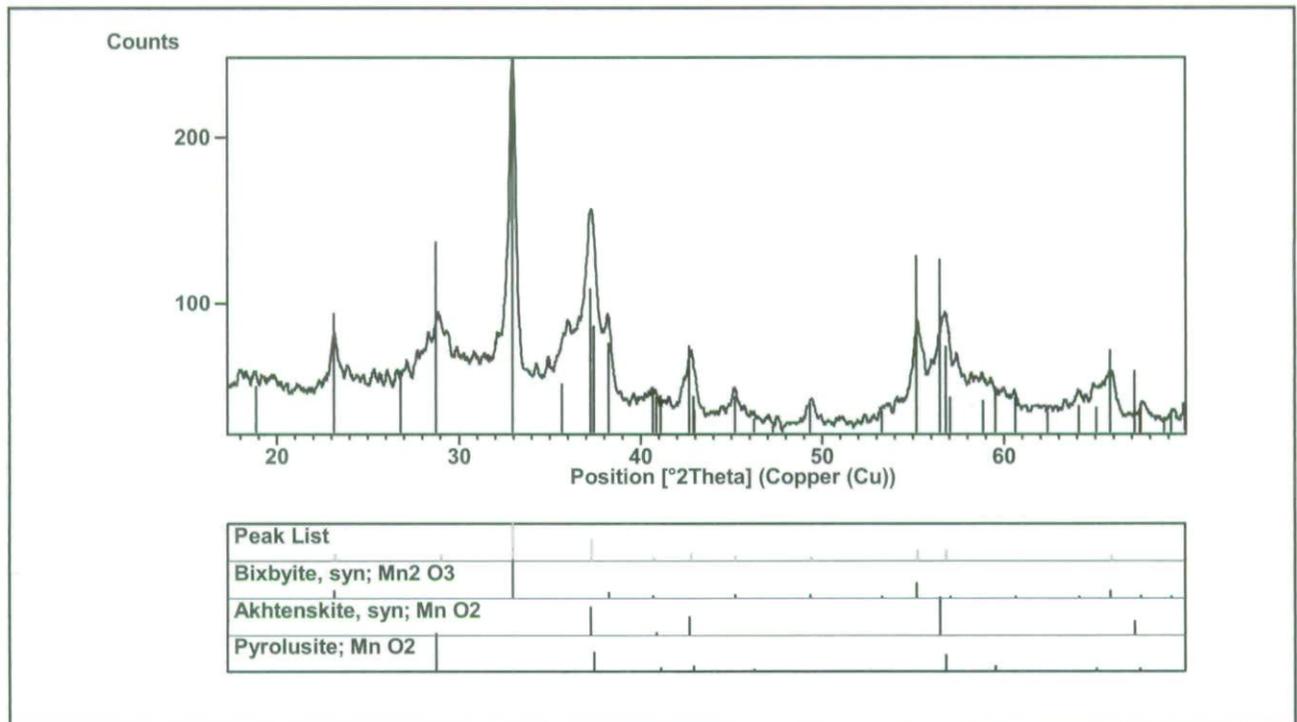


Figure 3. XRD scan of FeMn sample after oxidation with HNO_3

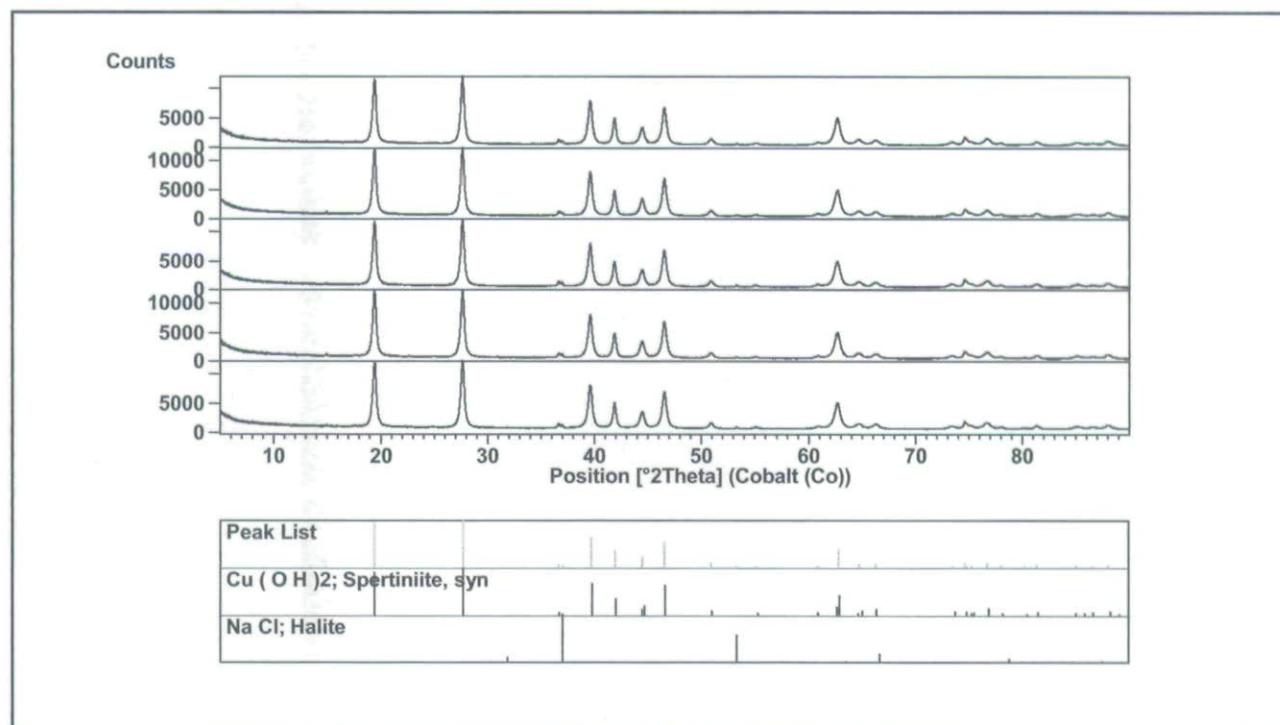
calculated as shown in Table 9. The calculations are performed under the assumption that the phases detected have an ideal composition. Care should be taken when dealing with samples where phases may deviate from ideal compositions or show solid solution between 2 or more elements. It would then be advisable to obtain chemical compositions of the individual phases which should be used in the calculations.

Analyses of Ferro Manganese samples

Ferro Manganese samples that are submitted for analysis usually require fusion preparation methods due to the influence mineralogical effects have on the accuracy of powder briquette methods. Samples are prepared according to the methods described earlier in this paper, and to evaluate the oxidation step, XRD diffractograms were recorded before and after the oxidation step (Figures 2 and 3). It can clearly be seen that the

Table 10. FeMn fused bead reproducibility.

%	FeMn fused 1	FeMn fused 2	FeMn fused 3	Avg.	Std. dev.
MnO	80.96	80.96	81.10	81.01	0.08
Fe ₂ O ₃	17.27	17.27	16.70	17.08	0.32
SiO ₂	0.21	0.21	0.24	0.22	0.02
P ₂ O ₅	0.10	0.10	0.11	0.10	0.01
SO ₃	0.06	0.06	0.12	0.08	0.03
CaO	0.05	0.05	0.06	0.06	0.005
Cr ₂ O ₃	0.05	0.05	0.03	0.05	0.01
Total	98.70	98.70	98.36		

**Figure 4.** XRD scans of Cu(OH)₂ containing samples.

ferromanganese metal phases and ferromanganese carbide phases were oxidised to manganese oxide and ferromanganese oxide phases. Consideration of the results in table 10 shows good reproducibility.

Analyses of Copper salts

XRF is routinely used for the quantitative analysis of elements between fluorine and uranium on the periodic table of the elements. Oxygen and hydrogen cannot be determined as their characteristic x-ray photon wavelengths are long and are easily absorbed by air and anything else in the optical pathway. Fluorescence yields for these elements are too low to produce enough photons to be detected. Oxygen is usually assigned in stoichiometric quantities to enable accurate matrix corrections. Hydrogen cannot be determined at all. This could lead to erroneous results where these elements are present. Consider the following Copper salts submitted to the laboratory for analysis. The samples were analysed as pressed powder briquettes (Table 10). As the pressed powder program is calibrated for oxides Cu will be expressed as CuO. CuSO₄ would

be eliminated as a possible composition due to the low S concentrations, (CuO + SO₃ = CuSO₄). The analytical totals were very low and a wavelength scan revealed no additional elements. A XRD scan was obtained to determine the phases present and the results shown in Figure 4. From this data the major phase was identified as Cu(OH)₂ (Spertiniite), explaining the low analytical totals as a 21% hydroxide content constituted the difference.

Table 11. XRF Copper salt results (in weight %).

%	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
CuO	34.76	33.04	32.89	34.65	34.39
Na ₂ O	30.10	31.66	32.04	30.67	31.34
Cl	12.53	12.56	12.22	12.07	11.77
CaO	0.31	0.34	0.32	0.32	0.29
SiO ₂	0.08	0.04	0.02	0.06	0.08
P ₂ O ₅	0.04	0.07	0.05	0.03	0.08
SO ₃	0.03	0.04	0.05	0.05	0.06
Fe ₂ O ₃	0.01	0.02	0.02	0.02	0.03
ZnO	0.01	0.02	0.02	0.02	0.02
Total	77.87	77.79	77.64	77.89	78.06

Conclusion

From the above case studies it is clear that a research facility dealing with a wide range of mineralogical samples can hardly function with XRF or XRD instrumentation exclusively. Combined the techniques complement each other and bring a new dimension to the data mining that can be performed. XRF and XRD analysis are each used extensively for the confirmation of results obtained by the other technique. Both techniques are also used to elucidate problems encountered. XRD is an essential tool in method development for XRF sample preparation and XRF results are important for the verification of qualitative as well as quantitative results obtained by XRD analysis.

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