

# X-ray spectroscopic method development for quantitative analysis of manganese ore in the Kalahari basin

by

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# Declaration

I, \_\_\_\_\_\_\_\_hereby declare that this dissertation which I submit for the qualification of <u>Masters of Technology Degree in Chemistry</u> to the Vaal University of Technology, Department of Chemistry. My work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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Co Supervisor Signature:	_Date:

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#### Abstract

Manganese is a crucial element in the manufacturing of steel, which in turn is an essential material in many industries including construction and transportation. Its use in the steel making process results in increased strength and resistance.

Manganese samples are analyzed quantitatively by volumetric titration techniques. These wet chemistry methods are simple, accurate, and are sufficiently detailed for ordinary personnel to follow with ease.

The research method used included the investigation of using secondary standard created from the current mining activities to match the matrix and mineralogy. The matrix matching standard has shown that the mineralogical effect and matrix effect can be controlled by creating the ore specific program. The matrix and mineralogical effect are the main sources of errors in wavelength dispersive X-ray fluorescence analysis with pressed powder pellets. No fundamental parameters corrections and empirical coefficient correction were made on the press pellets calibration lines. The fusion method was investigated as a universal method that can produce fused beads retaining all the elements of interest. The calibration lines were developed from certified reference material and the results were accurate, substantiating that the fusion method elimination the mineralogical effect, matrix effect and particle size effects.

Fusion and press pellet methods were compared with the traditional wet chemical method and the results shows no significant difference between the methods.

The new methods were tested against three proficiency schemes for manganese and the results were satisfactory, the z-score was below  $\pm 3$  for all the elements. The participants used different methods including traditional wet chemical analysis and Inductive coupled plasma (ICP). The press pellets method has shown a good correlation with a fusion method were certified reference material was used for calibrations.

The new methods were validated using different statistical methods. All the validation criteria were satisfactory. The calibration range for all the lines were satisfactory. The Limit of quantification (LOQ) values for Mn, Fe, CaO, SiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, and P were very low. The new methods for the analysis are therefore sensitive enough to give good results for the expected concentration ranges of each element. The statistical analysis performed between fusion and press pellets methods has proven that there was no significant difference between the methods. The conclusion made after the validation procedures was that the methods

developed for the analysis of manganese ore was fit for purpose of the analysis of the elements of interest for the Kalahari manganese ore.

The study confirmed that the newly developed press pellets methods can be used to analyse routine production samples based on the ore type or the area. Borates fusion method can be used for geological explorations, consignment and trade samples. The proposed XRF methods can replace the traditional wet chemical analysis which is time-consuming, toxic and labour-intensive.

# **Presentation and publications**

#### Presentations

National Laboratory Association (NLA) test and measurement 2016 conference and workshop: Oral presentation: Accuracy evaluation of matrix matching calibration of manganese ore on X-ray fluorescence

#### **Publications**

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# **Glossary of Terms**

AA	Atomic absorption
ADP	Ammonium-dihydrogen-phosphat
Al <sub>2</sub> O <sub>3</sub>	Aluminium oxide
Ве	Beryllium
CaO	Calcium oxide
CRM	Certified reference materials
E	Energy
EDDT	Ethylene - diamine-d- tartrate
EDXRF	Energy-Dispersive X-ray Fluorescence
Fe	Iron
FPC	Filled proportional detectors
Ge	Germanium
$H_2SO_4$	Sulphuric acid
HCl	Hydrochloric acid
Не	Helium
HgCl <sub>2</sub>	Mercuric chloride
ICP	Inductive coupled plasma
INAA	Instrumental neutron activation analysis
InSb	Indium antimonide
ISO	International standards organization
$K_2CrO_7$	Potassium dichromate

KMD	Kalahari manganese deposit
KMnO <sub>4</sub>	Potassium permanganate,
Kr	Krypton
LiF	Lithium fluoride
LiM	Lithium metaborate
LiT	lithium tetraborate
LOD	Limit of detection
LOI	Loss on ignition
Mg	Magnesium oxide
Mn	Manganese
Mn	Manganese
MnCl	Manganese chloride
MSDS	Materials safety sata sheet
Na	Sodium
$Na_2C_2O_4$	Sodium oxalate
NaI:Tl	Sodium iodide activated with thallium
Ne	Neon
Р	Phosphorus
PET	Pentaerythriltol
PHD	Pulse height distribution
PP	Press pellets
PPM	Parts per million
RAP	Rubidium-acid-phthalate

SEE	Standard error of estimate.
SHA	Sorbitol-hexaacetate
SiO <sub>2</sub>	Silicon dioxide
SnCl <sub>2</sub>	Stannous chloride
TAI	Tonnage accumulation index
ТАР	Thallium-acid-phthalate
U	Uranium
WDXRF	Wavelength-dispersive X-ray fluorescence
Xe	Xenon
XRF	X-ray fluorescence
Z	Atomic number

# Chapter 1

### Overview

#### 1.1. Introduction

X-ray fluorescence (XRF) spectrometry is now widely used as one of the most effective and efficient methods for elemental analysis. Its attractive features, such as the fact that most elements in the periodical table can be detected with detection limits that, depending upon the measurement conditions, are up to parts per million (ppm) levels and with linear calibration range up to 100%. The semi-quantitative analysis method makes it possible to determine the chemical composition of a sample rapidly and non-destructively. The capability of analysing solid samples accurately and its automatic operation make XRF a very useful tool in industrial process control in manufacturing factories, such as steel and cement factories [1-4].

XRF, being non-destructive having widely available artificial standards are widely available for many materials. The majority of XRF analysts choose to collect a set of artificial standards similar to their unknowns to create calibrations. Analyses are fast because little or no labour is required once calibrations are established. One reason people request new certified reference materials (CRMs) is that new materials require new artificial standards for new calibrations. A second reason is to obtain artificial standards for verification of method accuracy as part of their quality system. The artificial standards can be used to create calibration curves, with or without corrections for inter-element effects and matrix absorption. The process can be combined with fundamental parameters software that calculates the corrections from first principles with the advantage that it requires fewer artificial standards [5].

The accuracy of the XRF analysis depends mainly on factors such as the stability of the spectrometer, the quality of the certified reference materials (CRMs) or other 'standard samples' used for calibration, the homogeneity of the samples analysed, the effectiveness of the calibration of the matrix effect, particle size effect and mineralogical effect [3,6].

Production process usually require fast analyses and the choice of sample preparation routines have to find a balance between accuracy and speed. The pressed powder pellets for XRF method is significantly faster than most alternative methods, hence it is the preferred method in production [7]. The particle size effects, may influence the analysis results if not accounted for when establishing the sample preparation routines. The heterogeneity also causes problems in the bulk sampling [8].

The particle size effects are normally classified into three categories, i.e. grain size effects, inter-mineral effects and mineralogical effects. All these effects may be important if the effective path length of the measured radiation is in the range of the particle size of the sample. The effective path length for a given wavelength is defined as the path length that absorbs 99% of the initial radiation. If the particles are ground to less than one fifth of the effective path length the particle size effects normally become negligible [9]. However, this requires sub-micron particles if you are measuring light elements in a heavy matrix and that are normally not obtainable with the applied equipment [6].

The aim of this project is to develop a press pellet method that can be used to quantitatively analyse manganese samples from the mine samples. The origin of the problems will be discussed on the background of particle size effects and precaution to manage the problems will be suggested, grinding time, grinding vessel, grinding machine, cooling rate of the metal and choice of binder agent influence the analysis results.

#### **1.2.** Problem statement

Manganese samples are analyzed quantitative by a volumetric titration technique in most mines in the Kalahari region. Although these wet chemistry methods are simple, have a level of accuracy and are relatively cheap but exposes the operator to more risk.

During the wet chemical analysis process, various hazardous chemicals are used and expose the user to various risks. Exposure to hazardous chemicals is one of the biggest risks in any working environment, especially in Laboratories. Hazardous chemicals can cause harm when they enter the body in sufficient amounts via inhalation, ingestion, injection or skin absorption. Suitable control measures are implemented to minimise these exposures so as to safeguard the safety and health of laboratory analysts. To comply with environmental requirements, it is easier to eliminate the generation, handling and transportation of hazardous waste.

However, the most effective way of keeping hazards at bay is by eliminating the use of chemicals completely and substituting it with a better alternative which will not compromise the results of work to be carried out. The alternate technique requires the preparation of press pellet with a binder which will be discussed in this project and fusion beads which uses borates flux.

With better improved technology, many instruments are now available to replace the manual determination of manganese. However, the selection of instrument for analysis is a difficult task, as one must consider the cost, analytical capability of instrument, degree of accuracy and precision as well as simplicity of operating the instrument. In this study a comparison was made between Inductive coupled plasma (ICP) and X-rays fluorescence (XRF) to analyze production samples.

### **1.3.** Purpose of the study

The purpose of the study is to develop a quantitative method that will be used to analysed manganese ore sample in Kalahari basin using the X-ray fluorescence and to validate the method based on ISO 17025 method validation criteria.

# 1.4. Objectives

The specific objectives of the study are to:

- 1.4.1. Optimize the sample preparation process (,).
- 1.4.2. Optimize the operational setting for XRF spectrometer.
- 1.4.3. Generate data that assures the quality of the method used.
- 1.4.4. Validation of the analytical method according to ISO 17025.
- 1.4.5. Testing the methods by laboratory comparison technique.

# Chapter 2

#### Literature review

#### 2.1. Background of X-ray Fluorescence

The history of X-ray fluorescence dates back to the accidental discovery of X-rays in 1895 by the German physicist Wilhelm Conrad Roentgen. While studying cathode rays in a highvoltage, gaseous-discharge tube, Roentgen observed that even though the experimental tube was encased in a black cardboard box the barium-platinocyanide screen, which was lying adjacent to the experiment, emitted fluorescent light whenever the tube was in operation.

Roentgen's discovery of X-rays and their possible use in analytical chemistry went unnoticed until 1913. In 1913, H.G.J. Mosley showed the relationship between atomic number (Z) and the reciprocal of the wavelength  $(1/\lambda)$  for each spectral series of emission lines for each element. Today this relationship is expressed as equation 2.1

Equation 2.1: Mosley equation

$$\frac{c}{\lambda} = a (Z - s)^2$$
 2.1

Where:

a = is proportionality constant,

- s = is a constant dependent on a periodic series.
- Z = atomic number
- $\lambda$  = wavelength
- c = speed of light (2.99782108 m/s)

Mosley was also responsible for the construction of the early X-ray spectrometer. His design centred on a cold cathode tube where the air within the tube provided the electrons and the analyte which served as the tube target. The major problem experienced laid in the inefficiency of using electrons to create X-rays; nearly 99% of the energy was lost as heat [10-14].

Three types of Commercial X-ray Spectrometry were available to the analyst. From the 1950s to 1960s nearly all the X-ray spectrometers were wavelength dispersive spectrometers, such as those used initially at Berkeley, and by Shackley at Arizona State University. In a wavelength, dispersive spectrometer, a selected crystal separates the wavelengths of the fluorescence from the sample by diffraction, like grating spectrometers for visible light. The other X-ray spectrometer available at that time was the electron microprobe, which uses a focused electron beam to excite X-rays in a solid sample as small as 10 - 12 cm<sup>3</sup>. The first microprobe was built by R. Castaing in 1951 and became commercially available in 1958. By the early 1970s, energy dispersive spectrometers became available, which use Li drifted silicon or germanium detectors. The advantage of these instruments brought to the field was the ability to measure the entire spectrum simultaneously. With the help of computers, deconvolution methods can be performed to extract the net intensities of individual X-rays [10]. Conventional X-ray fluorescence analysis (XRFA) of bulk samples is carried out routinely in many laboratories using an X-ray tube as the energy source. Typically, the sample consists of a thin disc 1 cm across of glass or a pressed powder [15].

The relationship between the wavelength of electromagnetic radiation and its energy (E) is derived as follows.

Equation 2.2: The relationship between the wavelength of electromagnetic radiation and its energy

$$E = h \nu \qquad 2.2$$

Where:

*h* is the Planck constant (6.62  $10^{34}$  J.s);

v is the frequency expressed in Hertz.

For all wavelengths,

Equation 2.3: Duane-Hunt

$$\nu = \frac{c}{\lambda}$$
 2.3

where:

c = speed of light (2.99782108 m/s);

 $\lambda$ = wavelength (Å).

Thus, from Duane-Hunt equation 2.4,

Equation 2.4: Duane-Hunt equation

$$E = \frac{h c}{\lambda}$$
 2.4

 $E = 1.9863610 - 24 / \lambda$ 

where *E* is in Joule and  $\lambda$  in meters.

The conversion to angstroms and electron volts ( $1 \text{ eV} = 1.602110^{19} \text{ J}$ ) yields the Duane-Hunt equation:

$$E(eV) = \frac{12.396}{(\text{Å})\lambda}$$

#### 2.2. X-ray Fluorescence principles

X-ray fluorescence spectrometry is one of the most widely used instrumental routine of elemental analysis of rocks, cements, metallurgical samples, paint samples, and virtually any substance that can be adequately presented to the X-ray beam. The technique is capable of extremely good precision in a wide range of sample matrices and has a dynamic range from a few ppms up to 100%. Elements from Sodium (Na) to Uranium (U) are routinely determined using energy-dispersive X-ray fluorescence spectrometry (EDXRF) whereas application of wavelength-dispersive spectrometers (WDXRF) allows efficient determination of low-Z elements down to even Beryllium (Be). Although the samples can be analysed without treatment, high quality results can be ensured if appropriate sample preparation is applied. This may vary from simple cleaning and polishing of the sample (metals, alloys), powdering and pelletizing with or without binder (ceramics, minerals, ores, soils, etc.), fusing the sample with appropriate flux (ceramics, rocks, ores, etc.) to digestion with acids (metals, alloys) [16,17].

The accuracy of the XRF analysis depends mainly on factors such as the stability of the spectrometer, (I) the quality of the certified reference materials (CRMs), (II) other 'standard samples' used for calibration, (III) the homogeneity of the samples analysed, (IV) the effectiveness of the calibration of the matrix effect, (V) particle size effect and (VI)

mineralogical effect for pressed powder pellets. XRF spectrometers nowadays are so stable that the drift in 24 hour is less than 0.1%. Furthermore, there are many CRMs commercially available for different types of samples. The influences of heterogeneity, particle size and mineralogical effects can be reduced or even eliminated by a suitable sample preparation procedure, such as the glass fusion method [18].

#### 2.2.1. The origin of X-rays

Electromagnetic radiation can occur whenever electrically charged particles, particularly electrons, lose energy because of a change in their state of motion, e.g. upon deceleration, changing direction or moving to a lower energy level in the atomic shell. The deceleration of electrons and the transition from an energy level in the atomic shell to a lower one play an important part in the creation of X-rays in the field of X-ray analysis. To understand the processes in the atomic shell we must look at the Bohr's atomic model.

#### 2.2.2. Bohr's atomic model

Bohr's atomic model describes the structure of an atom as an atomic nucleus surrounded by electron shells.



Figure 2.1: Bohr's atomic model, shell model

Differences in the strength of the electrons bonds to the atomic nucleus are very clear depending on the area or level they occupy, i.e. they vary in their energy. This refers to energy levels or energy shells. This means that a clearly defined minimum amount of energy is

required to release an electron of the innermost shell from the atom. To release an electron of the second innermost shell from the atom, a clearly defined minimum amount of energy is required that is lower than that needed to release an innermost electron. An electron's bond within an atom is weaker, the farther away it is from the atom's nucleus. The minimum amount of energy required to releasing an electron from the atom, and thus the energy with which it is bound in the atom, is also referred to as the binding energy of the electron in the atom.

The binding energy of an electron in an atom is established mainly by determining the incident. It is for this reason that the term absorption edge is very often found in literature:

Energy level = binding energy = absorption edge

The individual shells are labelled with the letters K, L, M, N, the innermost shell being the K - shell, the second innermost the L-shell etc. The K - shell is occupied by 2 electrons. The L - shell has three sub levels and can contain up to 8 electrons. The M-shell has five sub-levels and can contain up to 18 electrons [19].

X-ray Fluorescence process example: Manganese atom (Mn = 25) in Figure 2.1 shows excitation x-ray, creating a vacancy.



Figure 2.2: An electron in the K shell is ejected from the atom by an external primary excitation X-ray creating a vacancy [20,21].



Figure 2.3: An electron from the L or M shell "jumps in" to fill the vacancy. In the process, it emits a characteristic X-ray unique to this element and in turn, produces a vacancy in the L or M shell [20,21].

The L Lines Auger "Electron"



Figure 2.4: When a vacancy is created in the L shell by either the primary excitation X-ray or by the previous event, an electron from the M or N shell "jumps in" to occupy the vacancy. In this process, it emits a characteristic X-ray unique to this element and in turn, produces a vacancy in the M or N shell [20,21].



Figure.2.5: production of K, L, M and N lines

The excitation energy from the inner atom is transferred to one of the outer electrons causing it to be ejected from the atom [20,21].

#### 2.2.3. Interaction of X-rays with a sample

When X-rays are directed into an object, some of the photons interact with the particles of the matter and their energy can be absorbed or scattered. This absorption and scattering is called attenuation. Other photons travel completely through the object without interacting with any of the materials particles. The number of photons transmitted through a material depends on the thickness, density and atomic number of the material, and the energy of the individual photons.

Even when they have the same energy, photons travel different distances within a material simply based on the probability of their encounter with one or more of the particles of the matter and the type of encounter that occur. Since the probability of an encounter increases with the distance travelled, the number of photons reaching a specific point within the matter decreases exponentially with distance travelled [22]. There are three main interactions when X-ray contacts the samples.

# 2.2.4. Coherent scattering

Coherent scattering (also known as classical scattering and Thompson scattering) may occur when a low-energy incident photon passes near an outer electron of an atom (which has a low binding energy). The incident photon interacts with the electron in the outer-shell by causing it to vibrate momentarily at the same frequency as the incoming photon. The incident photon then ceases to exist. The vibration causes the electron to radiate energy in the form of another X-ray photon with the same frequency and energy as in the incident photon [23,24].

# 2.2.5. Compton scattering

Compton scattering occurs when a photon interacts with an outer orbital electron, which receives kinetic energy and recoils from the point of impact. The incident photon is then deflected by its interaction and is scattered from the site of the collision. The energy of the scattered photon equals the energy of the incident photon minus the kinetic energy gained by the recoil electron plus its bonding energy.

### 2.2.6. Photoelectric absorption

Photoelectric absorption occurs when an incident photon collides with an inner-shell electron in an atom of the absorbing medium resulting in total absorption and the incident photon ceases to exist. The electron is ejected from its shell, resulting in ionization and becomes coil electron (photoelectron) [3]. If the X-rays photons has wavelength shorter than that of the iodine Kabsorption it may go under photoelectric absorption in the K shell of the iodine atom, expelling an iodine K electron and expending the remainder of its energy in imparting kinetic energy to the photoelectron [24]. The kinetic energy imparted to the recoil electron is equal to the energy of the incident photon minus that used to overcome the binding energy of the electron.

### 2.2.7. Secondary electron

Secondary electrons originate via interactions of primary electron with electrons in the solid. Most secondary electrons that leave the sample originate within a mean free path of their point of excitation, which is approximately 10 - 20 Å for metal. Secondary electrons are consequently very sensitive to surface conditions, composition, and crystal structure [25]. These secondary electrons give up their energy in the absorber by either of two processes:

Collisional interaction with other electrons, resulting in ionization or excitation of the affected atom, and

Radiative interactions, which produce Bremsstrahlung radiation resulting in the emission of low-energy X-ray photons. Secondary electrons eventually dissipate all their energy, mostly as heat by collisional interaction, and come to rest [5].



Figure 2.6: Three main interactions of X-ray and sample

The characteristic X-rays measured in X-ray fluorescence arise from transitions between the atomic energy levels. The name of each X-ray line corresponds to the upper and lower energy levels. The chart below illustrates the nomenclature. It is somewhat confusing, because three distinct naming systems are used for the atomic shells. Some authors refer to the energy levels (K, L1, L2, M1), some to the electron configuration (1s, 2p3/2), and some to the quantum numbers (2,0, $\frac{1}{2}$ ). The X-ray lines themselves were traditionally named using the "Siegbahn notation", developed years ago, by Manne Siegbahn [20,26].

The characteristic lines in X-ray emission spectra correspond to atomic electronic transitions where an electron jumps down to an unfilled level in one of the inner shells of an atom. Such a hole in an inner shell may have been produced by bombardment with electrons in an X-ray tube, by other particles as in PIXE, by other X-rays in X-ray fluorescence or by radioactive decay of the atom's nucleus [27,28].



Figure 2.7: X-ray Fluorescence line terminology labelling

### 2.2.8. Penetration depth

The X-rays Fluorescence is a surface technique. As fluorescent X-rays are significantly reduced within the sample there is a critical depth beyond which the X-ray cannot penetrate to be detected by the X-ray spectrometer. These depths differ between elements and depend on the X-ray photon energy and the samples compositions.

The depth distributions of the objective element in a series of samples must be constant to equalize the ratio of the fluorescent X-ray intensity to unit concentration. The depth profile reproducibility and the concentration consistency on the surface, homogeneity between samples produced in the same batch is also necessary for the sample preparation method [28].

### 2.2.9. Mineralogy

X-ray fluorescence analysis is a comparative technique and all matrix correction methods assume that the absorbed X-rays pass through a region of the sample that represents its average composition. Therefore, heterogeneous samples such as rocks must be finely ground prior to analysis. It is generally considered that it is not possible to grind beyond a grain size to avoid the particle size effects in pressed powder pellets and fusion. For pressed powder pellets, calculated attenuation coefficients may not be suitable for light elements because if attenuation occurs in discrete mineral phases then the results are not representative of the bulk composition of the sample [28].

The variation of chemical and mineralogical composition of the material to be analysed influences the measured intensities of characteristic x-rays of the determined elements. Two

approaches reducing XRF intensity data to elemental concentration are the empirical approach and the fundamental parameters (theoretical) approach.

Empirical methods require numerous standards within restricted compositional ranges can become complex if diverse suites of samples are to be analysed for many elements. The fundamental parameters method requires knowledge of physical constants such as mass absorption coefficients, jump ratios and fluorescence yields, but only single element independent standards to calculate the calibration constants for each element, making it an ideal approach to the analysis of geological samples [29].

#### 2.2.10. Matrix effects

The fluorescent X-ray count-rates observed in an analysis are not directly proportional to element concentration because of absorption-enhancement effects, which are due to the influence of all other elements in a sample. The matrix effects are caused largely by absorption and enhancement of both primary and fluorescent X-rays, with absorption being the dominant process. These effects must be corrected for major and trace elements to perform quantitative analysis [21].

In X-ray fluorescence analysis, the calculation of sample compositions is based on the general relationship between the concentration ( $C_i$ ) of the analyte *i* and the measured net intensity ( $I_i$ ), which is simply expressed by equation 2.5.

Equation 2.5: Matrix correction

$$C_i = K_i I_i. M_{is}$$
 2.5

Where  $C_i$  = concentration of analyte *i*,

 $K_i$  = calibration constant factor of *i*,

 $I_i$  = measured net intensity of *i* 

Mis= Factor correction

Factor for matrix effects of specimen "s" on *i*.

The concentration of the analyte *i* can be visualized as being equal to the product of three terms:

i. A calibration constant,

ii. The measured net intensity

iii. A factor that corrects for the effects of the matrix composition on the analyte intensity. These effects, mainly absorption and enhancement, are called the inter-element matrix effects, or simply matrix effects [30].

Eliminating the interelement effects has led numerous authors to propose diverse correction methods. These can be grouped into four procedures according to the empirical correction model employed [31,32]:

- i. Simple hyperbolic functions that relate the measured relative intensity with the analyte concentration (mass fraction), and into which correction factors are introduced; this method is developed for monochromatic excitation.
- ii. Algebraic functions equivalent to those mentioned above but at the right-hand side of the equation, instead of working with X-ray intensities, work with mass fraction.
- iii. The most representative of this third model is that of Claisse-Quintin, which is like the hyperbolic model but adds a quadratic term and a cross-product term for the elements other than the analyte, which, in many cases, are assumed to be insignificant. Another excellent algorithm which considers the dependence of the interaction coefficients on the concentration by the Claisse-Quintin equation.
- iv. The fourth model is basically represented by the Tertian formula which differs from the hyperbolic functions in that it considers the cross-product term as a function of the analyte instead of a function of the matrix elements.

Interelement corrections performed by means of dilution methods merit special mention because, owing to their specific application in complex matrices, they allow the overall elimination of the interferences. Nevertheless, a progressive dilution to eliminate these interelement effects is an insensitive procedure, which limits determination of elements found at low concentrations and presents serious difficulties in calculating the corresponding correction coefficient, which depends on the dilution ratio. Furthermore, the equation only becomes linear at very high dilutions [31].

Accuracy of the theoretical matrix correction methods, apart from their theoretical background, is determined by the uncertainties of atomic parameters (i.e., fluorescent yields, mass absorption coefficients, and transition probabilities), spectrometer geometry, and X-ray tube spectral distribution [32].


Figure 2.8: Typical X-ray fluorescence arrangement [3]

# 2.2.11. X-ray tubes

The signals of elements used in the X-ray fluorescence spectrometry are produced by excitation of electrons in the K or L shells with radiation from either radioisotope sources or X-ray tubes. The most frequently used radioisotopes are <sup>55</sup>Fe, <sup>109</sup>Cd, and <sup>241</sup>Am, while

The most common materials in the tubes are

- i. Rhodium,
- ii. Molybdenum,
- iii. Tungsten,
- iv. Copper.
- v. Chrome

An X-ray tube can be characterized by the kind of metal used as its anode, its input power, the voltage between the anode and cathode, the tube's current, and the degree of interference of the characteristic spectrum of the anode [33,34].

The general requirements to an X-ray source are:

- i. a sufficient photon flux over a wide spectral range,
- ii. a high stability of the photon flux, and
- iii. a low background spectrum.

Two designs of X-ray tube have evolved for use in modern instrumentation.

The side-window X-ray tube is designed with the filament biased at high negative potential and the anode (target) grounded. The mechanism of X-ray generation is as described above. However, a small fraction of electrons that strike the anode are backscattered out and impinge on the Beryllium (Be) exit window causing a heating effect. To avoid mechanical failure, the Beryllium (Be) window must be constructed of relatively thick foil (300-400 ppm). However, significant attenuation of low energy tube continuum then occurs within the Beryllium (Be) window so reducing excitation of the lightest elements, particularly Sodium (Na) and Magnesium (Mg). This deficiency can be offset in recently introduced tubes designed with a dual anode target [21].



Figure 2.9: Schematic cross-section through a side-window X-ray tube.

An alternative design is the end-window X-ray tube. Here, the filament is held at ground potential and the anode at high positive potential. Using this arrangement (known as reversed bias), the emission of backscattered electrons is suppressed, since these are attracted back into the anode. In consequence, the Beryllium (Be) exit window, which is no longer subjected to such a severe heating effect, may be constructed of thinner foil (exceptionally down to about 75 um). Improved excitation of lower atomic number elements is then observed due to the more

efficiently transmission of low energy continuum radiation. End-window tubes are normally designed to operate at up to a maximum of 75 kV [21].



Figure 2.10: Schematic cross-section through an end-window X-ray tube [5]

## 2.2.12. Collimators

The primary and secondary collimators are usually made of a series of parallel blades. The length and spacing of the blades determine the angular divergence admitted by the collimator. This angular divergence together with the crystal "rocking curve" (the width of the diffraction profile) determines the final resolution of the spectrum. One can improve the resolution by closing the collimators to minimise the divergence. But then, the photon flux across the collimator and hence the intensity decreases.

Thus, a compromise between the final resolution (necessary to avoid important spectral overlaps) and the sensitivity (related to the intensity) is made. Generally, the collimators are adopted in accordance with the crystal's intrinsic divergence, which varies from one type of crystal to another. Some of the crystals offer excellent resolution while others have a very wide diffraction profile. For this purpose, ARL's sequential spectrometers offer three types of collimators: fine, medium and coarse. The fine collimator is used for most of the heavy elements, medium for the mid-range elements and coarse for the light elements [35].

# 2.2.13. Analyser crystals

A crystal may be defined as a solid, composed of atoms arranged in a periodic pattern in three dimensions. In a crystal lattice, the plane in which atoms are in a row is called the crystal plane.

The planes are identified using miller indices. The interplanar spacing (the distance between any two adjacent planes of same type) is denoted as d. In XRF, we generally refer to the 2d values of the crystals since we will be using the 2d values [35,36].

In a wavelength, dispersive systems scintillation counters and LiF crystals for reflection at 200 lattice planes are used in most cases except for light elements below Ca, for which gas flow counters and special crystals are preferred.

Crystals which are employed in routine analysis; 2d-spacings, preferably use reflecting lattice planes, and the range of covered analyte elements (K - lines) are included as well [37,38].

Crystals	Plane	2d Å	Remarks
LiF	420	1.802	High resolution, high energy region
LiF	200	4.028	Standard crystal for Z >19
Ge	89	6.532	Low intensity second order reflection
PET	2	8.742	Pentaerythritol for Al to K
EDDT	20	8.808	Ethylene - diamine-d- tartrate for Al
ADP	101	10.64	Ammonium-dihydrogen-phosphate for Mg
SHA	110	13.98	Sorbitol-hexaacetate for Mg
RAP	1	26.1	Rubidium-acid-phthalate for Z<12
ТАР	1	25.7626	Thallium-acid-phthalate for Z<12
InSb	1	7.48	High intensity for Si only, high background.

Table 2.1: Commonly used analyzer crystals

$$n\lambda = 2d\sin\theta$$
 2.6

Where:

n = an integer (1, 2, 3...) called order of diffraction

d = Interplanar spacing of the crystal plane used (Angstroms)

 $\Theta$  = Bragg angle or diffraction angle (degrees)

 $\lambda$  = Wavelength of the spectral line (Angstroms)



Figure 2.11: Bragg diffraction from a crystal grating showing incident X-ray photons [35].

From this relationship that for a given crystal plane and for a given order of diffraction, each wavelength in the incident XRF spectrum is diffracted at a unique angle. The maximum wavelength a crystal plane can diffract is 2d itself (when sino takes the maximum value of 1). Therefore, one requires crystals or crystal planes with different 2d values to cover different wavelength ranges across the periodic table. Several crystals suitable for diffraction are available today. Some of them are inorganic (like Lithium fluoride (LiF)) while others are organic (like Pentaerythritol (PET)) in nature.

The advantage with these man-made structures is that one can try to optimize the combination of the light and heavy elements, the thickness of the layers, and the 2d spacing to get the best possible device for a given element. The result of these new developments is that we now have a family of multilayers allowing one to measure elements from Beryllium through Magnesium. We use essentially three or four types of these multilayers along with the natural crystals.

### 2.2.14. Detectors

The most important characteristics of a detector are efficiency, dead time, and energy resolution. Further properties to be taken into consideration are line shape (in solid-state detectors). Stability of response at higher count rates, and data related to the specific features of the detectors (for example the position resolution of position - sensitive detectors) [37].

In general, most X-ray detectors have an efficiency of between 50% and 90% depending on the wavelength that is measured with the detector. For this reason, very little improvement can be expected in the sensitivity of X-ray detectors. Improvements will take place in the form of:

- i. Improved energy resolution
- ii. More selective absorption
- iii. Elimination of escape peaks
- iv. Improved detector windows

For sequential X-ray spectrometers, it is often not possible to take full advantage of the optimal choice of detector, as detector selection is made as a compromise for a very large wavelength range. The trend in sequential spectrometers will be to include more than one gas proportional detector to allow optimal analysis of the range of elements which is at present measured with the gas flow detector.

In simultaneous spectrometers, it is possible to optimise the detector per element. For this reason, a wide range of gas detectors are used such as: He, Ne, Kr and Xe gas filled proportional detectors (FPC), in addition to scintillation detectors. By careful selection of detector window and gas it is possible to efficiently absorb the radiation of interest, while filtering crystal fluorescent radiation in the detector window and allowing higher order radiation to partially pass through the detector [38].

One of the most common gas fillings is the mixture of 90% Ar + 10% CH<sub>4</sub> called P10 gas. The purpose of methane addition is essentially to quench the phenomena of avalanche at one stage. The quench gas molecules also get ionized along with the Ar atoms. When they are dispersed in the detector's active volume, they contribute to the recombination of the electrons and ions when the avalanche proceeds in an uncontrolled manner [39].

Detectors used in most of the commercial spectrometers can be classified into two categories:

i. Gas filled proportional counters (FPC), for long to intermediate wavelengths

FPCs have a continuous flow of gas and the pressure inside the detector is regulated. They are generally closed with Aluminium coated thin polypropylene windows of the order of 1 - 2 microns thick. The purpose of such a thin window is essentially to increase the transmission of long wavelength X-rays.

Sealed detectors, referred to as exatrons and multitrons, have 25-200 micron beryllium (Be) windows. FPC's are used for light elements (from Beryllium through Copper in general) on a goniometer. Sealed detectors are employed in fixed channels although small size.

#### ii. Scintillation counters for short wavelengths.

Scintillation counters operate on an entirely different principle compared to the gas filled detectors. They consist of two essential parts: a scintillating material (called phosphor, usually a single crystal doped with an activator) and a photomultiplier. Scintillating crystals like NaI:T1 have an interesting property that when the X-ray photons are incident on such a crystal, they emit visible (in the present case, blue) light. Thus, they convert X-ray photons into visible photons [22,39-41].

### 2.3. Manganese elements

Manganese is the  $12^{\text{th}}$  most abundant element comprising about 0.10% of the earth's crust, with oxidation states existing in from -3 to +7. The common chemical forms of manganese dioxide found naturally are +2 and +4 [42].

Manganese is very like iron in its chemical properties. Both are commonly found in b2 and b3 valences with high spin states for the 3d electrons and with similar ionic radii. Mn and Fe b2 ions have radii 0.83 and 0.78 Å, while the b3 ions have 0.70 and 0.65 Å.

Manganese is commonly found substituted in small amounts in iron minerals. Manganese, however, also has access to a higher valence state, b4, which gives rise to a plethora of complex manganese oxide minerals. Both elements are mined from supergene enriched sedimentary deposits of a variety of ages. Iron, however, is dominantly hosted by Archean to earliest Paleoproterozoic rocks, whereas manganese ores are found in younger rocks as well [43].

The oxides and peroxides of manganese are used for manufacturing metal alloys to increase hardness and for enhancement of alloy to be corrosion resistance and as a de-sulphurizing, deoxidizing element in various industrial processes. Manganese plays an important role in steel production, preparation of dietary additives, chemical production, in battery cells industry. Manganese is added to steel for the following reasons: it is used as an alloying element to improve strength, toughness, and hardness; it is used for sulphur control whereby it combines with sulphur and controls the morphology of sulphides; and, lastly, it is used for oxygen removal. Manganese stabilizes the austenite in steel, although it is less potent than nickel. It lowers the temperature of austenite transformation into ferrite and improves the response of steel to quenching. The effect of manganese in forming austenite is improved by combining it with nitrogen, which is also an austenite-forming element [44-46]. Manganese (Mn) and iron (Fe) are close in the periodic table, with element numbers 25 and 26 and atomic weights of 55 and 56, they are mostly found in the same area.

Industrial manganese ores vary significantly in chemistry and mineralogy. It is well-known that the properties of a manganese ore have a large influence on the technology and efficiency of the production of manganese alloys. The melting and reduction behaviour of ores are defined by their chemistry, mineralogy and physical properties, which change as the ore is heated in a reducing atmosphere in a ferroalloy furnace [47].

### **2.3.1.** Manganese reserves resources of the world

The world's Mn reserves in terrestrial deposits have been variously estimated at 6.5 billion tons of ore (Brobst and Pratt, 1973), 630 million tons Mn (reserve) and 42 billion tons Mn (i.e., recoverable resource potential; Erickson, 1973), 1.62 billion tons Mn (Morgan, 1976), 1.76 billion tonnes (reserve) and 1.62 billion tonnes Mn (potential reserve; Bender, 1977; Hildebrandt et al., 1977). To this should be added the tonnage of Mn produced to-date (222 million tons to 1975). The "geological content" of Mn in strata-related deposits was calculated as 2043 tonnes Mn by Laznicka (1985b). The revised data resulting from the present study are expressed as the "geological content of Mn" (i.e., past production and reserves) as follows [48].

Mined "straight" Mn deposits: 8,727,958,000 t. In potentially mineable, terrestrial Mn accumulations: 9,179,500,000 t. In mined deposits where Mn is a co-product or by-product of another metal (this manganese, however, may not have been recovered): 589,806,000 t. In potentially mineable, terrestrial Mn co/by-product ores (or ores not recovered in the past): 41,921,000 t. Total: 17,907,458,000 t no. average or cut off grades are available for the

tabulation above. The Mn tonnages are included as listed in the literature and some "super lowgrade" deposits [48].

# 2.4. Grade of Manganese (Mn) deposits

Mn deposits usually list average grades, a range of grades, or the grade of the shipping product (concentrate). In most cases, the quoted Figure is not further classified and the distribution of Mn grades within a deposit can be approximately visualized, if the ore deposit type is known. The average grade of the world's Mn ores mined in the 1970s as 35% Mn. The bulk of the "primary" Mn deposits, both sediment genic and hydrothermal, have a remarkably uniform grade throughout an orebody or, if the orebody is complex and composed of several ore layers/bands separated by a non-ore, throughout a band This uniformity is destroyed by supergene modification of "primary" orebodies caused by exposure or by groundwater. In the example representative of outcrops of Mn veins or Mn carbonate/gondite layers, the deposit is subdivided into the "primary" zone (often considered a protore) and the secondary, enriched zone. There, the enrichment factor rarely exceeds two to three, both zones have a relatively uniform grade distribution and the mutual contact tends to be sharp. Deposits and metal accumulations with tai =  $10^{10}$  and greater are designated as large deposits. Those with tai =  $10^{11}$  plus are giant deposits, and those with tai =  $10^{12}$  and more are supergiant deposits. The four largest Mn accumulations containing in excess of  $1 \times 10^9$  Mn are supergiant accumulations. The single largest presently mined Kalahari Mn Field has tai =  $4193 \times 10^9$ . [48].



Figure 2.12: Distribution of the world's Manganese-ore resources per continent

List of exceptionally large Mn localities that contain over 0.1% of the world's ore Mn						
	$(x10^{6})$	% of world's total	(x10 <sup>9</sup> )			
Supergiant						
Moanda Mn horizon	6500	36.3	6500			
Kalahari-Mamatwan type	4193	23.42	4193			
Molango Mn horizon	1500	8.38	1500			
Rapid creek Fe-Mn horizon	1162	6.5	1162			
Giant accumulations	4	<u> </u>				
Nikopol	940	5.25	940			
Chiatura	600	3.35	600			
Bol'shoi Tokmak	490	2.74	490			
Molango	465	2.6	465			
Moanda	275	1.54	275			
Groote eylandt	222	1.24	222			
Mezhdurechye	180	1	180			
Kalahari-Wessels type	175	0.98	175			
Leglier Fe-Mn	150	0.84	150			
Urucum	121	0.68	121			

Table 2.2: List of exceptionally large Mn localities that contain over 0.1% of the world's ore Manganese

Equation 2.7 : Tonnage accumulation index, (tai)

$$tai = \frac{M \times 10^6}{ck}$$
 2.7

Where:

M = ore metal content in a deposit, tonnes;

ck = average crustal abundance

#### 2.5. The Kalahari manganese field

The Kalahari manganese field, situated some 60 km to the northwest of Kuruman in the Northern Cape Province of South Africa, represents the world's largest manganese deposit. With some 13500 Mt of Mn ore at > 20% Mn and its wealth of beautiful and rare mineral specimens is sought after by mineral collectors. Its mineralogical diversity is unique geologically complex manganese deposits [49].

Based on mineral assemblage, Mn grade, texture and geochemical characteristics, the ores of the northern Kalahari manganese deposit (KMD) are broadly classified into least altered (LA), partially altered (PA) and advanced altered (AA) types. The LA ores are low grade (<40 wt.% Mn) Mn lutites, containing dolomite-group carbonates in significant proportions, with braunite [Mn<sup>2+</sup>Mn<sup>3+</sup> <sub>6</sub>SiO<sub>12</sub>] as the main Mn oxide mineral and serpentine as a common trace mineral. Ores of the PA type contain, additionally, hausmannite  $[Mn^{2+}(Mn^{3+}, Fe^{3+})_2O_4]$  as an important mineral, and comprise either braunite- hausmannite-calcite or hausmannite-calcite assemblages. They are fine to coarse grained, and display intermediate Mn grades (40 - 45 wt.% Mn). Advanced altered ores are oxide-dominated and mineralogical complex compared with LA and PA ores. The AA ores contain, as significant minerals, braunite, braunite II  $[Ca(Mn^{3+},Fe^{3+})_{14}SiO_{24}],$ hausmannite, bixbyite [(Mn,  $Fe_{2}O_{3}$ ], jacobsite  $[(Mn^{2+},Fe^{2+},Mg^{2+})(Fe^{3+},Mn^{3+})_2O_4$  [50].



Figure 2.13: (a)Locality of the KMD in South Africa. (b) The five erosional relics in which Mn ores are preserved; the largest is the Kalahari Manganese deposit, or KMD. (c) Detail of the KMD, in which current and previous mining operations are shown, together with structural features and the distribution of two major ore types in the basin. The study area is indicated by the shaded rectangle [50].

Two main ore types are present, namely low-grade primary sedimentary Mamatwan-type ore, with Mn contents of 20-38 wt.% and secondary high-grade Wessels-type ore containing 45 - 60 wt.% Mn. High-grade Wessels type ore represents an alteration product of low-grade sedimentary Mamatwan-type ore and it is economically the most sought after ore in the Kalahari deposit. However, it constitutes only about three per cent of the known reserves.

Wessels mine, like Nchwaneng mine, is an underground operation ideally suited for such a study. The room-and-pillar mining technique applied in both two mines provides excellent opportunities for sampling transitions between high-grade Wessels-type ore and low-grade Mamatwan-type ore in mined-out areas. Another advantage is that the structure of the area is well known because of mining operations [51].

Minerals	Chemical Formula
Barite	BaSO <sub>4</sub>
Braunite	$Mn^{2+}Mn^{3+}6SiO_{12}$
Calcite	CaCO <sub>3</sub>
Garnet(Andradite)	$Ca_3F_2Si_3O_{12}$
Hausmannite	Mn <sub>3</sub> O <sub>4</sub>
Hematite	Fe <sub>2</sub> O <sub>3</sub>
Jacobsite	Mn Fe <sub>2</sub> O <sub>4</sub>
Kutnohorite	Ca $(Mn, Mg)(CO_3)_2$
Mg calcite	(Ca, Mg)CO <sub>3</sub>
Mn calcite	(Ca,Mn)CO <sub>3</sub>
Rhodochrosite	MnCO <sub>3</sub>
Serpentine	(Mg, Fe) <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>

Table 2.3: List of major minerals and their chemical formula

# 2.6. Geological setting

Windblown Kalahari sands constitute the upper part of the Kalahari formation. These sands, in some areas referred to as hutton soils or sands are of pleistocene to recent age and occur as thin veneer across the calcretized sediments. Just below this erosional unconformity the carbonate-rich braunite lutite of the Hotazel formation is distinctly altered and enriched. The thickness of the zone of mesoscopically distinct supergene enrichment below the Kalahari formation varies between 1 m and 10 m. Invasion of calcrete along fractures and bedding planes is restricted to the immediate erosional contact with the Kalahari formation.

The degree of supergene alteration decreases away from the immediate sub out crop the highest grades of enrichment (up to 50 wt.% Mn) occur directly below the pre-Kalahari unconformity. However, the grade is not only determined by proximity to the unconformity, but also by the composition of the sedimentary protore. The primary ore bed is subdivided into different zones of different textural appearance and grade. Of these lithostratigraphic zones, the supergene-enriched equivalents of the M, C and N zones attain highest Mn grades [49,50,52].



Figure 2.14 : The lower manganese ore-body of the Hotazel Formation against the Kalahari unconformity [52].

# 2.7. Manganese ferroalloys

Several different types of manganese alloys have been developed and are being marketed [46]. These alloys may be divided into the following major categories:

- i. Ferromanganese FeMn, high carbon- (HC), medium carbon- (MC), and low-carbon (LC)
- ii. Silicomanganese SiMn (or ferrosilicomanganese FeSiMn)
- iii. Metallic manganese Mn
- iv. Nitrided manganese alloys (nitrided manganese MnN and silicomanganese SiMnN)

The number of alloy specifications is large. Some suppliers list more than 20 different products. The alloys vary in manganese, carbon, silicon, phosphorus, and nitrogen content. Because of the scarcity of low phosphorus manganese ores, many users, especially alloy steel manufacturers, will pay a premium for low phosphorus alloys [53, 54].

Alloy	Grade	Mn	С	Si	Р	S	N
HC-FeMn	78	78-82	7.5	1	0.05	0.03	
					<0.2-0.35		
	75	>75	<6-7	<4-6	0.05: 0.45	0.03	
	70	>70	7	6	0.06	0.03	
MC-FeMn	88	85-95	2	3	0.4	0.03	
	85C1	85	1-1.5	1	<0.1 - 0.3	0.03	
	75C2	75	1.5-2	2-2.25	<0.2 - 0.35	0.03	
LC-FeMn	90	95	0.2	1	0.07	0.05	
	85C0.5	85	0.5	2	<0.2 - 0.30	0.03	
FeSiMn	Si25	>60	0.5	25-35	0.05	0.01	
	Si22	>65	1	20-35	0.1	0.02	
	Si17	>65	2.5	15-20	0.1	0.02	
	Si12	>65	3.5	20-Oct	0.2	0.03	
FeSiMn	crude	bal	0.05-0.15	>27	0.05-0.07	0.02	
Metal Mn	998	99.8	0.04		0.003	0.003	
	997	99.7	0.06		0.05	0.1	
	965	96.5	0.1	0.8	0.05	0.05	
	95	95	0.2	1.8	0.07	0.05	
MnN	92N6	92	0.1		0.005	0.1	>6
	87N6	87	0.2	1.8	0.07	0.05	>6
	89N4	89	0.2	1.8	0.07	0.05	>4
	91N2	91	0.2	1.8	0.07	0.05	>2
SiMnN	7N	>60	3.5	9-17	0.1	0.02	>7
	5N	>60	3.5	9-17	0.1	0.02	>7

Table 2.4: Typical examples of alloy specifications for most commercially used manganese ferroalloys

# **2.8.** Press pellets (PP)

Traditionally, X-ray spectrometers are calibrated using reference materials (RMs) that have a similar matrix to the routine samples to be analysed. This means that most calibrations are

necessarily sample-type specific and dependent on the availability of these standards. However, most geologists are familiar with inductive coupled plasma (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. The composition of reference materials (RM) is determined by averaging analyses obtained by multiple techniques (ICP, instrumental neutron activation analysis (INAA), atomic absorption (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 [55].

It is well known that sample preparation is the source of the largest errors of XRFA. Most of the sample preparation methods in use nowadays were developed long ago. However, some new efficient variations of these methods and new techniques widening the possibilities of XRFA have recently been proposed. The simplest yet least accurate method of XRFA is the direct analyses of powders, in particular heterogeneous powders [56].

The use of pressed powders gives more accurate results. However, here, as in the first mentioned case, large errors are possible owing to differences in the granulometric and phase compositions of the substance under analysis and the reference materials. These errors can be minimized to a certain extent by pressing powders to a constant volume [56].

The best way to avoid the mineralogical effect is to fuse both the unknown samples and the calibration standards under the same conditions. When pressed powder pellets are used, the mineralogical composition of the calibration standards should be very similar to that of the unknown. However, in many cases where the pressed powder pellet method has to be used, a lack of suitable calibration reference exists [18].

Trace elements are analysed on pressed powder briquettes. Major element analyses are executed on fused beads, following a method adapted from H. Bennett and G. Oliver. 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 followed with specific sample preparation protocols [57].

Particle size effect could be significantly reduced or even avoided when the sample particle size is small enough: this can be achieved by means of crushing or other suitable methods. The mineralogical effect, on the other hand, relates to the occurrence of an element in different forms of mineralogical composition including valence, coordination, and crystal structure, i.e., properties that cannot be compensated by physical methods. An example is offered by chloritoid and chlorite compounds, which are composed primarily of Fe, Mg, Al, Si and O, but the behaviour of these elements in two minerals is different. The mineralogical effect leads to apparent errors in the results, especially for light elements [58].

During pulverizing, there are three major sources of contamination:

- i. The analyst's hand,
- ii. The previously pulverized sample, and
- iii. The crushing container.

Contamination from source (i) can be minimised if the rock and crushing container are handled only with plastic gloves. To minimise contamination from source (ii) two 100 mL aliquots of each sample are run separately and the first aliquot is discarded. Alternatively, a run of pure silica sand can be made between sample runs, to "clean" the container. This may introduce SiO<sub>2</sub> contamination but it will normally be a tiny fraction of the total SiO<sub>2</sub> in the rock.

Source (iii) cannot be eliminated, but prudent choice of grinding containers can reduce the contamination to elements that are not of great interest [58]. The sample is weighed together with the binder (if necessary) and pulverized in the pulverizing machine. Subsequently, the sample is pressed with 40-ton pressure for 10 seconds using suitable backing. (Boric acid or Aluminium cup). The backing absorbs stress and shock in the pressing process, and gives a smooth and nice pellet surface.

# 2.9. Fusion

Fusion is a chemical procedure in which a sample is transformed into a fused bead that has the required qualities for high accuracy in XRF analysis. It is homogeneous near the atomic level, flat, polished and with required infinite thickness regarding X-ray penetration.

Fusion techniques for sample preparation in X-ray fluorescence analyses are being more widely adopted for analysis of powdered materials when dealing with routine control analysis in the chemical, cement and steel industries as well as in numerous applications of geochemistry, where samples call for decomposition of the mineralogical components into practically homogeneous solutions and/or a dilution of the elements [59].

For obtaining optimum analysis results in emission spectroscopy, samples and standards must be excited under entirely identical conditions. To eliminate the influence of the latter on Spectro analytical results, samples are pre-treated by borate fusion mineralized calcination or roasting followed by fusion. For geological materials-which the present discussion will be chiefly confined to fusion with alkali metal borates has gained the greatest popularity. Fusion converts samples and standards to the glass state, thus reducing them to a common form. In the application of fusion techniques, the following variables must be considered [60, 61]:

- i. Sample type,
- ii. particle size,
- iii. fusing agent (flux),
- iv. sample-to-flux ratio,
- v. fusion temperature,
- vi. Fusion period.

Fusion into a glass bead eliminates particle size effects, minimizes matrix effects and does not dust the tube. Thus, by fusing the sample into a flat, homogeneous glass bead many inherent X-ray problems are solved or minimized. This type of specimen preparation technique is very well suited for X-ray analysis. Fusion, however, creates another problem. Volatile elements such as alkalis and sulphur may be lost during the high temperature fusion (about 1000 °C) modifying the flux/sample ratio and creating a most undesirable effect inaccurate result [62, 63].

#### 2.10. XRD and Mn ore composition

Quantitative phase analysis is frequently applied to the study of geologic materials in research and service laboratories, but also in quality control of mining operations. Understanding the properties of ore (minerals from which metals are extracted) and gangue (deleterious minerals that need to be separated from the ore) is of tremendous economic importance for the process mineralogy. The reason for this is simple. Physical properties that determine the processability of the material such as hardness, solubility, magnetism, or density are directly related to the crystal structure of the minerals and not to their chemical composition. Therefore, those properties directly influence beneficiation conditions such as the method of separation (gravity, magnetic washing or dissolution).

Recovery estimates in mining operations are typically based on chemical grade-estimates. Severe recovery losses may occur if the element of interest is located in one of the gangue minerals that are removed or not accessible during processing of the ore [64].

### 2.11. Sampling process

The process of taking a sample characterizing a complex, large system based on a small part hereof is, contrary to many beliefs, not an easy one, although the task specification could not be simpler: a sample is a portion, piece or segment representing a class or a larger whole (the lot). If the sample does in fact not represent what it is supposed to, erroneous deductions and conclusions will invariably follow no matter how precise the subsequent analysis. The goal of a sampling procedure is to extract a sample with the same properties as the lot where the sample came from a representative sample. The basic prerequisite for a representative sampling procedure is that all elements in a batch, container, or in a pipeline cross-section have the same probability of being selected, and that the elements selected are not altered in any way after the sample (or increment) has been taken. All elements that do not belong to the batch or sample container must have zero probability of being selected [65].

There are several sources of uncertainty in a mining project, some of which are listed in Figure 2.15. At the top left corner of this Figure is the long-term block model estimated using kriging and a diamond drill holes dataset. The short-term grade block model is obtained by re-

estimating the original long-term block model within certain regions of the deposit (or the entire deposit) after new assays are obtained from blast holes or channel samples. The reconciliation between the grades obtained by these two models measures the efficiency of the estimation methods combined with the quality of the new data incorporated. Next, the grades predicted by the short-term block model are reconciled with the grades declared from sampling the ore feeding the processing plant [66].



Figure 2.15: Simplified sketch of the multiple sampling and reconciliation stages at a mine site [66].

Correct sampling requires that there be little bias and that the sampling variance should also be small. Bias describes the average sampling error, while precision describes the scatter of sampling errors about their average, which is different and conceptually more complicated.

Sampling is biased if it is subject to errors that cannot be expected to balance out on average. Poorly designed, poorly maintained or poorly operated cross-stream cutters are susceptible to bias whereby large particles are under sampled. This occurs because the proportion of large particles which bounce off the edges of such cutters is larger than the proportion of small particles which bounce off the edges. The physical mechanisms associated with sampling bias are generally affected by material properties as well as being affected by cutter design and operation. Sample cutters and sampling procedures must be designed to be unbiased [67].

Preparation errors are non-selective operations without change of mass such as crushing, grinding, mixing, sample transfer, drying, etc. Typical errors include sample contamination, sample loss, moisture loss (from the moisture sample) and operator mistakes, such as mixing up sample labels. These errors can be eliminated using correct sampling equipment and practices. For example, sample cutters should be covered if necessary to prevent entry of extraneous material in the parked position and moisture samples should be prepared and weighed quickly to avoid change in moisture content. Care also needs to be taken to ensure that the finer particles are not lost in crushers/mills or during sample division due to excessive airflow in dust extraction systems installed in sample preparation laboratories [68].

# 2.12. Statistical method validation

There are two types of method validation techniques, namely:

- i. The inter-laboratory comparison techniques
- ii. The single laboratory techniques

The method will be validated based on the following minimum criteria for single laboratory techniques

- i. Linear regression
- ii. Limit of detection
- iii. Limit of quantification
- iv. Working range
- v. Accuracy
- vi. Precision
- vii. Reproducibility
- viii. Repeatability
- ix. Uncertainty of measurement

The following method validation techniques were also used:

i. Comparison of CRM

- ii. Inter-laboratory testing
- iii. Different method comparison

The analysis of variance (ANOVA) was used to evaluate the parameters of an analytical method during this validation phase, The ANOVA was computed using the Microsoft excel 2010 function.

### Linear regression line

Linearity indicates the ability of a method to produce the test results proportional to the concentration of the analyte within a given working range.

The object of regression is to establish the relationship in terms of a mathematical equation;

Equation for a straight line is: y = bx + a

- y = intensity (signal output) e.g. absorption intensity;
- b = gradient or slope of the line (y/x)
- x = the unknown sample concentration
- a = intercept on the y-axis

### Limit of detection (LOD)

It is the lowest concentration of analyte that can be detected and reliably distinguished from zero, but not necessarily quantified. The LOD represents the level below which we cannot be confident whether the analyte is actually present.

### Limit of quantification (LOQ)

It is the lowest concentration at which an analyte in the sample can be determined with the accuracy and precision required for the method in question. This value may be the lowest concentration in the standard curve.

## Working range

The working range of an analytical procedure is the interval between the upper and lower concentration of analyte in the sample for which it has been demonstrated that the analytical procedure has a suitable level of precision, accuracy and linearity. In the discussion, the working range is defined as the concentration range from the LOQ to the upper range of the calibration line.

### Sensitivity

The calibration sensitivity of the calibration curve,  $C_s$ , is the rate of change of the signal intensity with changes in the concentration of the analyte. The sensitivity of a method indicates how responsive a method is to small changes in the concentration of an analyte. A method is sensitive if b is not equal to zero. Where b is the slope of a regression line.

### Accuracy

The closeness of measured results to the true value. It can be expressed as a typical CRM's concentration that was analysed in a similar production range, compared with certificate true value. The accuracy can be validated by using t-test model at 95% or by percentage recovery.

### Precision

A measure of the scatter (spread) in the results obtained from multiple analyses of a homogeneous sample. The precision relative standard deviation (RSD) percentage should be 0.2% for major elements and < 5.0% for trace elements.

## Reproducibility

It is the value below which the absolute difference between multiple test results is obtained with the same method on sample samples, under the different condition or days.

## **Repeatability**

It is the value below which the absolute difference between multiple test results is obtained with the same method on sample samples, under the same condition.

### Uncertainty of measurement

The uncertainty is determined for each element applicable to this method and expressed as percentage. The parameters associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the analyte

# Chapter 3

# Experimental and analytical method

# **3.1.** Introduction

The experimental and analytical methodologies conducted in this research are discussed in this chapter. Sampling, sample preparations, instrumentation and method validation process are described in details. The chemicals and reagents used in manual titration are listed. All chemicals used in this experiment were handled according to the materials safety data sheet (MSDS) supplied by the manufactures.

# 3.2. Sampling

Without a sample, there can be no analysis. Without a proper representative sample, there should be no analysis or attempt to analyse. Sampling error cannot be corrected by analytical method precision and accuracy in the laboratory.

The samples were collected from different stream during explorations, mining and plant processing. The samples were reduced to 10 kg each for the experiment. The 10 kg of rock samples were first crushed using an 8 x 5 jaw crusher to obtain sample quantity with sizes of < 5 mm. After this, the samples were further crushed on 5 x 3 jaw crusher to obtain samples with sizes of < 3 mm. The samples were reduced using the rotary splitters.

# **3.3.** Sample preparation

Sample preparation is the source of the many errors in X-ray fluorescence (XRF) analysis. It is well known that inappropriate sample preparation can cause errors greater than 100% during an analysis. Incorrect results can cause a loss of revenue due to customer complaints, third party analysis and loss of the customer.

The required samples volume was taken for equipment optimization. To obtain good XRF results using the pressed powder technique, control of particle size is absolutely critical. Particle size was controlled by closely controlling grinding time and the mass of sample introduced to the pulverizer. Initially grinding times was determined by experimentally

constructing grinding curves. Control of mass was achieved by using scoops of a suitable volume as compared to weighing which will increase turnaround time.

# **3.4.** Secondary standard

Rock Samples were collected from the Kalahari basin, on the low grade and the high-grade area. A total of 40 samples were collected on each grade for secondary standard purpose. The standards were prepared in the controlled condition. The samples were splitted into four equal parts with the rotary splitters after pulverizing. Three out of four splits were distributed to three different ISO 17025 accredited laboratory to get consensus concentration which was used as true value for the calibration and the last portion was used for calibration.

# 3.5. XRD analysis

The samples were collected from different mines in the Kalahari basin. The Samples was prepared for XRD analysis using a back-loading preparation method. It was analysed with a PANalytical Empyrean diffractometer with pixcel detector and fixed slits with Ni filtered Cu-Kα radiation. The phases were identified using X'Pert high score plus software. The relative phase amounts (weight%) were estimated using the Rietveld method (High score software).

# **3.6.** Fusion pre-work method development

TheOx fusion machine was used for all fusion method development and test samples. The maximum operating temperature of the TheOx is up to 1200 °C. The can generate in 3.75 kW in the heating chamber. It has maximum of 6 positions to process the samples simultaneously. By achieving precise temperature control and monitoring to  $\pm 1$  °C, automatic agitation of the crucibles gives superior homogenization of the melt in less time.

The advantages of TheOx fusion machine are

- i. Repeatable inter position results at each fusion cycle and a superior homogenization of the melt solution.
- ii. Fully automated pouring, no handling of the hot crucible and moulds.
- iii. Safety door that locks automatically during the entire fusion process.
- iv. Six position that allow high through put of samples.
- v. Three different layers of refractory materials for maximum heat retention.

The Claisse 26 mL crucible and a 40 mm diameter, 1 mm thick mould composed of 95% Pt / 5% Au alloy were used.



Figure 3.1: The OX fusion machine

Non-roasted materials and in house standards were used to develop rapid fusion method for manganese ore and finished products.

Different sample to flux ratios were also evaluated (1:5, 1:10, 1:15 and 1:20). Different fusion temperatures were evaluated 950 °C, 1050 °C and 1150 °C. Different roasting time was also evaluated.

Four types of fluxes were selected to be tested,

- i. lithium metaborate (LiM),
- ii. lithium tetraborate (LiT),
- 49.75% lithium tetraborate (LiT), 49.75% lithium metaborate (LiM), containing integrated 0.50% LiBr non-wetting agent and sodium tetra-borate.
- iv. 50% lithium tetraborate (LiT), 50% lithium metaborate (LiM),

	Step	Step	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9
	1	2							
TYPE	Tran	Tran	Heat	Heat	Heat	Heat	Pour	Cool	Cool
Duration			0:06:00	0:06:00	0:04:00	0:01:00	0:00:19	0:01:15	0:03:30
Heat	1150	1150	1150	1150	1150	1150	-	-	-
R. speed			0	10	20	20	-	-	-
R.R Pos			0	10	30	30	-	-	-
R.F Pos				10	30	30	-	-	-
FAN								50	100

Table 3.1: The OX fusion program parameters, including pre-heating

# 3.7. Kalahari fusion method development

### Experimental procedure

The powder certified reference material was roasted at 1000 °C to determine the loss on ignition.

The certified reference material was roasted in duplicate and the average loss on ignition was used as true value because most of the CRM don't have the certified LOI value.

Determination of loss on ignition (LOI)

Apparatus:

- i. Electronic analytical balance
- ii. Crucible cups
- iii. Furnace
- iv. Scientific calculator
- Experimental procedure:

An empty crucible cup was accurately weighed on the calibrated analytical balance- the mass was recorded as  $M_1$ . 2.000 g of the sample was weighed into the crucible, the mass was recorded as  $M_2$ . The sample was roasted in a muffle furnace at a temperature of 1000 °C for 60

minutes. After roasting the sample was placed in a desiccator for 10 minutes to cool and weighed to get the final mass which was recorded as  $M_3$ .

Equation 3.1: LOI calculation

LOI(weight %) = 
$$\frac{(M2-M3)}{(M2-M1)} \times 100$$
 3.8

M<sub>1</sub> is the mass of the crucible, in grams;

M<sub>2</sub> is the mass of the crucible plus the dry test portion, in grams;

M<sub>3</sub> is the mass of the crucible plus test portion after ignition, in grams.

Preparation of fused glass beads

### Apparatus:

- i. Claisse TheOx fusion machine
- ii. Electronic analytical balance
- iii. Pt/Au 26 mL crucibles and 40 mm moulds
- iv. Ultrasonic bath
- v. Vortex mixer
- vi. The Ant automatic flux weighing machine

### Reagents:

- i. Lithium borate-flux
- ii. Roasted samples

## Experimental procedure

Roasted 0.5000 g of sample was accurately weighed into empty tared crucible. Approximately 10.000 g of flux was weighed into crucible using The Ant to a ration of 1:20. The flux and sample was mixed with a vortex mixer. The vortex speed was controlled to prevent any loss of sample and flux to maintain the correct flux to sample ratio. Variance of the flux to sample weight ratio causes error in the results. The mixture was fused in TheOx at 1150 °C. The fused glass bead was casted automatically into 40 mm Pt/Au moulds. The fused beads were rapidly cooled down by fans at the set speed to prevent cracking.

## **3.8.** X-ray fluorescence measurements

Thermo Fischer scientific advance 9900 series equipped with an end-window 3.6 kW Rh Xray tube operating at 70 kV of tube voltage and 120 mA of tube current. The detectors included a scintillation counter and a gas-flow proportional counter in which PR gas (90% Ar + 10% CH<sub>4</sub>) flowed at 50 cm<sup>3</sup> min<sup>-1</sup>. A measurement chamber in the spectrometer was regulated at a vacuum of several 8Pa to analyse the samples. The instrument is equipped with 7 monochromators (fixed channel) for simultaneous determination. The 29 mm mask was used. The rotation was used at all times to ensure that the entire sample is exposed to the X-rays. The automatic sample loader is a large capacity magazine, it loads standard cassettes or rings. The automatic sample loader being able to load the samples directly into the ARL 9900 series instrument using special sample supports. The collected data were processed by the QXAS program for qualitative and quantitative.

The spectrometer analytical conditions for the measurement of all the elements used for the analysis application are listed in Table 3.2.

Element	Mono/ Gonio	Collimator	Crystal	Detector	Counting Time (s)	Filter
Mn	Mono	0.25	LiF200	ExKrBe	30	on
Fe	Mono	0.25	LiF200	Sc	30	on
Са	Mono	0.60	LiF200	ExArBe	30	None
Mg	Mono	0.60	AX03	FPC	30	None
Si	Mono	0.60	PET	FPC	30	None
Al	Mono	0.60	PET	FPC	30	None
Р	Mono	0.60	Ge111	ExNeBe	30	None

Table 3.2: XRF	<sup>7</sup> spectrometer	hardware setti	ngs
----------------	---------------------------	----------------	-----

The current and voltage settings for elements are 50 kV and 50 mA

### Monochromators (Fixed channels)

High-throughput elemental analysis is ensured via fixed channels, each dedicated to the analysis of one element. The monochromators have been developed which optimizes the sensitivity and spectral background levels in order to obtain the lowest limits of detection. The special detectors ensure a wider linearity of response permitting to reach very high precision levels for major element analysis.



Monochromators equipped with flat crystals (Multilayers)

Figure 3.2: Monochromators (Fixed channels)

# **3.9.** Energy profile

The Pulse height distribution (PHD) is the electronic filter used to limit the pulse going through, only the pulses between the lower and the higher pulse height limit pass through to the counting to the detectors. The pulse height distribution window is made lower and upper levels. The pulse height is used to remove unwanted peaks coming from the electronic noise, low voltage, escape peaks, crystals reflections and background intensity.

The energy resolution of the X-ray detectors are calculated from the PHD according to the following equation

Equation 3.2: The energy resolution

$$R = \frac{FWHM}{V} \times 100\%$$
 3.2

R = Energy resolution

FWHM = full width at half maximum height

V = average pulse height

The energy resolution increases as the wavelength of the measured X-ray photon increase and the energy decreases.

## **3.10.** X-ray fluorescence calibration

### **3.10.1.** Calibration lines

The analytical applications used in this study, to determine major and trace element of manganese ore concentrations were optimized by using calibration curves comprising international certified reference materials, secondary matrix matching standard and long counting times.

### **3.10.2.** Press pellets method development

Pressed pellets were prepared from the pulverized samples according to the pulverizing criteria as indicated in Figure 4.1 - 4.3 and the prepared standards. About 30 g of sample was poured into label aluminium cup for extra support and pressed on the semi-automated press machine at 30 ton pressure and 10 seconds holding time.

Standard error of estimate (SEE).

The SEE expresses the quality of the correlation fit. By default, and according to the system parameter MVR:

Equation 3.3: Standard error of estimate.

$$SEE = \sqrt{\frac{\sum \Delta^2}{n-k}}$$
 3.3

Where

 $\Delta$  is the difference between the certified concentration and the calculated concentration

n is the number of samples

k is the number of parameters to calculate (i.e. number of polynomial(s) a0, a1, a2, a3 according to the degree of the base curve plus number of alpha coefficients to calculate (unfixed))

n - k is called "degrees of freedom".

If the system parameter is set to no, the formula uses n-2 instead of n-k.

The smaller the SEE value, the better the fit of results.

As this represents a measure of accuracy of the method, the SEE was used to judge the calibration line.

Instruments detection limit (LOD)

Detection limit is calculated with the following formula:

Equation 3.4: Instruments detection limit

$$LOD = 3 X \sqrt{\frac{-A0 \times A1}{t \times 1000}}$$
 3.4

where:

t is the count rate (in kcps/s) defined in the method.

It is important to notice that this value is only meaningful if the concentration range covers also the very low concentrations of the analyte.

This value is only calculated if A0 is negative and a linear regression with no matrix corrections has been performed.

Analysis of routine samples

A total of ten Wessels type ore samples were analysed under the same operating conditions as the routine samples. The final results will be compared with the consensus values.

#### 3.10.3. Kalahari fusion method

Accuracy and precision of the method depends on standard to produce a good calibration line. The international certified reference materials are used to develop the fusion method. Two sets of fused disks of each certified reference material (CRM) were prepared for the calibration curves of the XRF instrument and for the evaluation of fusion method. The first sets of CRM were used to develop the calibration curves on the XRF. The second sets were used as evaluations for the XRF and sample preparations. A total of 36 CRM were used to cover the concentration range of all elements according to the pre-knowledge of the Kalahari ore composition as discussed in chapter 2.

The loss on ignition (LOI) was accurately determined on all CRM according the described method prior to fusion process. The Manganese ore contain  $H_2O$ ,  $CO_2$  and other volatile elements. The LOI should be accounted in a fusion process. The manganese ore has different elements with deferent oxidation state like Mn and Fe. The final concentration was calculated after the LOI and was used as true value in the calibration line. The final results were adjusted for the LOI using the following formula:

Equation 3.5: Final concentration calculated from the LOI free base

$$C = Ci x \left(\frac{100 - LOI}{100}\right)$$
 3.5

Where

C = Final concentration

Ci = Measured concentration from calibration line

LOI = pre-determined LOI

### **3.11.** Traditional Mn and Fe determination

Titration is used to measure the grade of manganese and iron in manganese ore samples is a method that has been around for many years. The traditional titration of manganese is according to the Volhard manganese determination method. Manganese ore undergoes a decomposition reaction in concentrated hydrochloric acid (HCl) which results in a solution that is filtered to remove insoluble siliceous material. With the addition of HCl the solution is then heated until all the ore sample has dissolved. By adding zinc oxide emulsion to the solution increases its

pH. After re-heating to about 80 °C the solution is titrated against potassium permanganate standard solution. Iron is titrated based on the reduction of iron(III)  $[Fe^{3+}]$  to iron(II)  $[Fe^{2+}]$  in acid medium against Potassium dichromate standard solution. A small excess of Tin(II) chloride (SnCl<sub>2</sub>) is added for the complete reduction Fe<sup>3+</sup> to Fe<sup>2+</sup> and to prevent excess of SnCl<sub>2</sub> in the titration, mercury chloride is then added to neutralize the solution.

### **3.11.1.** Titration of manganese from manganese ore

The stoichiometric reaction for the titration of Mn is as follows:

Equation 3.6: The stoichiometric reaction for the titration of Mn is as follows:

$$2MnO_4^- + 3Mn^{+2} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$
 3.6

Concentrated HCl was added to the manganese ore. The solution then undergoes the following reaction:

Equation 3.7: Reaction after HCl

$$MnO_2 + 4H^+ + 4Cl^- \rightarrow Mn^{+2} + 2Cl^- + 2H_2O$$
 3.7

Zinc oxide emulsion was added and the solution was heated to about 80 °C and titrated against potassium permanganate standard solution.

#### Apparatus

- i. Electronic balance
- ii. 1000 mL and 500 mL Erlenmeyer flask
- iii. Hotplate
- iv. Daffert burette
- v. Funnel
- vi. Measuring cylinder
- vii. Calculator

#### Reagents

- i. Hydrochloric acid 30-32% concentrated, CP grade
- ii. Zinc oxide emulsion
- iii. Potassium permanganate, CP grade
- iv. Manganese chloride, CP grade
- v. Sodium oxalate, CP grade
- vi. Sulphuric acid 90%
- vii. Stannous chloride
- viii. Mercuric chloride
- ix. Potassium dichromate
- x. Diphenylamine indicator

#### Pre-task activities / preparations

Potassium permanganate stock solution (1.0 N KMnO<sub>4</sub>)

65.6 g KMnO<sub>4</sub> was measure into an 800 mL glass beaker and approximately 600 mL-deionised water was added into it. The solution was boiled slowly for 90 minutes and allowed to cool. The solution was transferred into a 2000 mL volumetric flask and diluted to the mark with deionised water.

Potassium permanganate work solution 0.1 N (KMnO<sub>4</sub>).

100 mL of the potassium permanganate stock solution was diluted into a 1000 mL volumetric flask with deionised water.

Standardization of KMnO4 work solution with sodium oxalate.

Pre-dried 0.3000 g ( $\pm 0.0005$  g) Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> ( $\pm 99.8\%$  pure) was weighed in triplicate into 400 mL squat beakers, 150 mL deionised water was added at 60 °C and 20 mL 1:1 H<sub>2</sub>SO<sub>4</sub>. The oxalate solution was titrated against KMnO<sub>4</sub> (0.1N) using the specified standardization program.

#### Procedure

 $0.3000 \text{ g} \pm 0.0002$  powdered manganese ore was weighed into a weighing boat. The sample was transferred into a clean 1000 mL erlenmeyer flask. 30 mL concentrated hydrochloric acid (HCl) was added into the sample. The sample boiled until pieces of manganese ore are no longer visible when the flask was held against a white background. 50 mL of zinc oxide emulsion and 400 mL boiling water was added to the dissolved sample. The flask was placed back on the hotplate to a boiling point. The sample was titrated with standardized potassium

permanganate (KMnO<sub>4</sub>). The flask turned vigorously from side to side during titration. The final potassium permanganate was recorded for the calculation of the manganese percentage.



Figure 3.3: Manganese sample with zinc oxide emulsion



Figure 3.4 The endpoint of the manganese titration

# 3.11.2. Titration of iron from manganese ore

The stoichiometric reaction for the titration of Fe against potassium dichromate  $(K_2Cr_2O_7)$  occurs as follows:

Equation 3.8: Fe against potassium dichromate

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + Fe^{3+} + 7H_2O$$
 3.8

The reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> with SnCl<sub>2</sub>, which is represented as follows:

Equation 3.9: Fe<sup>3+</sup> to Fe<sup>2+</sup> with SnCl<sub>2</sub>,

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$$
 3.9

SnCl<sub>2</sub> is then neutralized with mercury chloride and the reaction is as follows:

Equation 3.10: SnCl<sub>2</sub> neutralized with mercury chloride

$$2\text{HgCl}_2 + \text{Sn}^{2+} \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{Cl}^- + \text{Sn}^{4+}$$
 3.10

#### Procedure

 $0.3000 \text{ g} \pm 0.0002 \text{ g}$  sample was accurately weighed into a 500 mL erlenmeyer flask and 30 mL concentrated hydrochloric acid (HCl) was added to the sample, and heated until the sample has dissolved. Stannous Chloride was added to the solution drop by drop until the solution has decolourised. 5 mL of Mercuric Chloride solution was added to the sample after cooling. The sample was stirred and left to stand for 2 - 3 minutes. The solution was dilute with cold water to  $\pm$  200 mL, 25 mL Sulphous acid was added and few drops of Fe indicator. The sample was titrated with 0.04 N potassium dichromate solution until the purple colour becomes stable and the titration value was recorded. The total iron content was calculated as follows: % Fe = titre value x 0.6666666



Figure 3.5: Dissolved manganese sample for Fe determination

### **3.12.** Statistical method validation

Analytical method validation is a mandatory step to evaluate the ability of developed methods to provide accurate results for their routine application. Indeed, without results of adequate quality or reliability, the critical decisions that will be made during routine application of the method will be untrustworthy leading to either over or under estimations of effect of new drugs [69].

The statistical procedures used to compare two methods or laboratories. Schemes for evaluating comparison studies have been presented for clinical chemistry assays and analytical chemistry methods while examining the potential of the various statistical tests for determining errors in comparison studies concluded that linear regression probably provides the most useful information. More rigorous linear regression models which consider the effect of errors associated with both variables have recently been applied to the comparison of analytical methods [70].

The final goal of the validation of an analytical method is to ensure that every future measurement in routine analysis will be close enough to the unknown true value for the content of the analyte in the sample. Accordingly, the objectives of validation are not simply to obtain estimates of trueness or bias and precision but also to evaluate those risks that can be expressed by the measurement uncertainty associated with the result [71-72].

Precision may be considered at three levels: repeatability, intermediate precision and reproducibility. Repeatability expresses the precision evaluated under the same experimental conditions over a short time interval. Sometimes it is termed as intra-assay or within-run precision and refers to the "pure" random error associated with the assay measurement process. Intermediate precision applies to within-laboratory variations: different days, different analysts, different equipment and so forth. Intermediate precision is sometimes called between-run or inter-assay precision [72].

#### **3.13.** The inter-laboratory comparison techniques

Another technique to validation the method is by inter-laboratory tests. The validation of a Manganese ore determination on XRF is descried below. In order to validate the manganese ore determination method, the Kalahari inter-laboratory comparison scheme was used. The scheme is comprised of 21 chemical laboratories. The samples were prepared from the low grade Mamatwan type ore, high grade Wessels type ore and the Hotazel ore. The variation in the samples due to homogeneity was tested before distribution to the participating laboratory. The particle size was tested to determine the pulp of the samples and the sample pass the pulp criteria of 90% of the sample passing 75  $\mu$ m sieve on the wet screen.

The participating laboratory used the test method that they believe was technically appropriate. Participating laboratory treated the samples in the same way as they would treat a routine sample. All laboratory stated the method used on the reporting templates. The results of the inter-laboratory test were compiled in the predetermined calculation sheet agreed by the scheme participants.

The z-scores represent a measure of how far a result is from the (consensus) assigned value. The statistics of a normal distribution means that 95% of data points will lie between a z-score of -2 and +2. The z score is calculated using the following formula.

Equation 3.11: The z-score calculation

$$z = \frac{x - \mu}{\sigma}$$
 3.11

x =sample score

- $\mu$  = the sample mean
- $\sigma$  = the sample standard deviation

The basic performance categories

 $|Z| \leq 2$  Satisfactory

 $2 \leq |Z| \geq 3$  Questionable

 $|Z| \ge 3$  Unsatisfactory

### 3.14. Quality controls

XRF instruments are not absolutely stable. The XRF drift over a period due to mechanical wear, power fluctuations, changing of the gas, environmental condition, periodical maintenance and aging of electronic components.

A quality control samples were analysed each day for a period of six months. The results were checked to see if they are within the limit and recorded on the control charts. Drift corrections are only performed if the results are outside of the specified range. The results compared with previous results to check the amount of variations between the days.

### **3.15.** Drift monitoring samples

The drift monitoring samples were prepared from the same matrix with high and low concentration of all the analytes. The drift monitor intensities for the different analytes had high concentration so that counting errors are minimized within reasonable counting times for each element (e.g. 30 s). The high drift monitor concentration of each analyte was higher than the highest concentration of the analyte concentration range. Multiple drift monitoring standards were used since a single drift monitor sample didn't contain all the elements to be determined in the samples.

A drift monitor was homogeneous and with infinitely thickness with a flat and smooth surface for high reproducibility. The drift monitoring standards were always measured under the same conditions and production samples. The instruments showed a good stability of the six months period. The drift correction samples were analysed once a day, automated to start at seven am every day.

# Chapter 4

# **Results and Discussion**

# 4.1. Introduction

Results obtained from this study are presented and discussed in this chapter. These include sample preparations optimisation, particle size effect, mineralogical analysis by XRD, XRF calibrations.

# 4.2. Optimization of sample preparation equipment

X-ray fluorescence (XRF) intensity initially rises sharply with grinding time and then tends to level. The chosen grinding time is the level region in this case 240 seconds was chosen for high grade samples and 180 seconds for low grade samples. Grinding time was set by means of a timer connected to the pulverizer power supply. Control of mass was achieved by using scoops of a suitable volume as compared to weighing which will increase turnaround time.





Control of mass was achieved by using scoops of a suitable volume  $\pm 200$  g as compared to weighing which will increase turnaround time. The scoop was design in such way that it will take required volume of  $\pm 200$  g and was pulverized in 250 cc pot for 240 seconds on the high-grade ore to achieve the required particle size and 180 seconds on the low-grade ore. The selected criteria were 90% must pass 75 µm sieve.



Figure 4.2: Pulverizer weight setting graph



Figure 4.3 : Time settings on the pulverizer

From Figure 4.3, the particle size decreases sharply with the increase in grinding time and then tends to increase slowly. The chosen grinding time is at 180 seconds for low grade and 240

seconds for high grade respectively where 90% of the sample passes 75  $\mu$ m sieves. The low grade showed a decrease in particle size from 330 and 360 seconds due to over pulverizing and caking.



# Particle size effect on high grade ore

Figure 4.4: Particle size effect on Mn

In Figure 4.4, Mn showed a proportional increase in concentration with the decrease in particle size.



Figure 4.5: Particle size effect on Fe

In Figure 4.5, a proportional increase in concentration with the decrease in particle size of Fe was observed.



Figure 4.6: Particle size effect on CaO

CaO showed decrease in concentration with the decrease in particle size in Figure 4.6.







Figure 4.8: Particle size effect on SiO<sub>2</sub>

In Figure 4.8,  $SiO_2$  showed no change from the high particle size to the lower particle size, and there are no significant changes in concentration.



Figure 4.9: Particle size effect on Al<sub>2</sub>O<sub>3</sub>

Al<sub>2</sub>O<sub>3</sub> showed decrease in concentration with the decrease in particle size in Figure 4.9



Figure 4.10: Particle size effect on P

In Figure 4.10 P showed decrease in concentration with the decrease in particle size. P showed a sharp decrease a -45µm sieve.

# 4.3. XRD mineralogical results

Table 4.1: Kalahari manganese mineral compositions

Kalahari manganese M	Aineral Compositions
Bixbyite	(Mn,Fe) <sub>2</sub> O <sub>3</sub>
Manganite	MnO(OH)
Hematite	Fe <sub>2</sub> O <sub>3</sub>
Hausmannite	Mn <sub>3</sub> O <sub>4</sub>
Calcite	CaCO <sub>3</sub>
Andradite	Ca <sub>3</sub> Fe <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>
Cryptomelane	KMn <sub>6</sub> Mn <sub>2</sub> O <sub>16</sub>
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>
Jacobsite	(Mn,Fe, Mg)(Fe,Mn) <sub>2</sub> O <sub>4</sub>
Braunite 2	Ca(Mn,Fe) <sub>14</sub> SiO <sub>24</sub>
Braunite	Mn <sub>2</sub> Mn <sub>6</sub> SiO <sub>12</sub>
Rhodonite	MnSiO <sub>3</sub>
Birnessite	Mn <sub>8</sub> SiO <sub>15</sub> (OH) <sub>10</sub>
Quartz	SiO <sub>2</sub>
Kutnohorite	Ca(Mn,Mg,Fe <sup>2+</sup> (CO <sub>3</sub> ) <sub>2</sub>



Figure 4.11 : Jan 2014m11 3 (Mamatwan type ore)



Figure 4.12 : Khudumane round robin A fy15. (Mamatwan type ore)



Figure 4.13 : Assamang fy 15 A March (Mamatwan type ore)



Figure 4.14: UMK C round robin (Mamatwan type ore)



Figure 4.15: G8010 0921 (Wessels type ore)



Figure 4.16: W4L40 -1 15 Nov 12 (Wessels type ore)



Figure 4.17: HTZ Chips 01



Table 4.2 : Summary of data from XRD results.

Amorphous phases were not taken into consideration during quantification. Neltnerite and Braunite are part of a solid solution series and only Braunite 1 & 2 was used in calculations. The results obtained from the XRD analyses showed that sample in Figure 4.11 to 4.14 are similar, with minor differences in the intensity of some of the main peaks which indicated quantitative differences of the components. The XRD analysis also indicates that sample in Figure 4.15, and 4.16 are similar with minor differences in the intensity. Some of the main peaks indicate quantitative differences of the components. The XRD analysis also indicates that sample in Figure 4.15, and 4.16 are similar with minor differences in the intensity. Some of the main peaks indicate quantitative differences of the components. The XRD results of Figure 4.17 indicate Calcite and Kutnohorite to be the dominant constituents which is not consistent with the two patterns observed.

It was clear from the XRD results that there are two types of ore in the Kalahari basin and the Hotazel formation is the mixture of both low and high grade with the large portion being the high grade with additional Pyrite mineral. The results in Figure 4.11 to 4.14 represent low grade ore and from Figure 4.15 and 4.16 represents high grade ore. The ore in the current mining area do not differ significantly over the 2-year mining cycle.

#### 4.4. Fusion pre-work conclusion

It was determined that roasting of all samples and standard at the beginning of the fusion process is required for manganese ore when using analytical fusion method. The calibration curve indicated the two sets of samples types in the calibration line and this was due to the different composition of the ore. The samples containing high LOI was observed to be below the calibration line and the samples containing low LOI was observed to be below the calibration line.

In the first ratio of 1:5, the samples did not dissolve completely and amount of flux solution was not enough to cover the base on the casting mould. The final fused bead resulted in half moon shape bead as shown in Figure 4.18. The same observation was found in the 1:10 ratio.



Figure 4.18 : Half-moon shaped fused bead.

The samples were completely dissolved in the 1:15 ratio and the flux solution covered the base of the casting mould but the final fused bead was very thin and some of the fused beads cracked during the handling and removal from the fusion machine as shown in Figure 4.19.



Figure 4.19 : Cracked fused bead

1:20 sample to flux ratio at 1150 °C was considered to be the best because of the easy dissolution of the sample due to the more amount of flux present and the fused bead was more stable with accepted infinite thickness.

The Lithium borate flux has a melting point of 920 °C. Optimal fusion temperature should be higher than the melting point of the selected flux. The measured intensity of all elements at 1150 °C was higher than that of 950 °C and 1050 °C respectively.

The optimum temperature was 1150 °C, however a fusion temperature of 1150 °C is too high because both flux and alkali like K and Na may be lost from the melt during the fusion process.

The life of platinum crucible, moulds and the fusion rods will be compromised because of the high temperature.

The choice of the flux depends on the composition of the sample. The Manganese ore found at Kalahari is basic as it is high in Ca, Mg, K and Na oxides. Fluxes are classified based on their ability to react with these oxides. Thus, the flux chosen for this investigation is lithium borate as it reacts best with these basic oxides.

The fused beads of lithium metaborate (LiM) showed a concave upper surface and sample was sticking to the moulds making it difficult to remove during the experiments. The fused beads of lithium tetraborate (LiT) were having bubbles and concave upper surface with some residual samples left in the moulds.

The fused beads of 49.75% lithium tetraborate (LiT), 49.75% lithium metaborate (LiM), containing integrated 0.50% LiBr non-wetting agent and sodium tetra-borate was considered to be the best during the fusion cycles and easy removal of the fused beads. The LiBr non-wetting agent introduced interferences during calibration of Aluminium. The inter-elements correction was not successful due to the high concentration of the Br than Al.

The 50% lithium tetraborate (LiT), 50% lithium metaborate (LiM), flux was successful with a non-concave, non-sticking, no residual and no inter-elements interferences.

# 4.5. X-ray fluorescence calibration

# 4.6.1. Press pellets method development

It should be noted that, in the preparation of the press pellets with different proportions of sample and binder were made to test the influence of binder dilution on the sample. By increasing the binder, there was a noticeable decrease in the sample intensity with a significant increase in the background. The Manganese has binding properties without any binder, it was concluded that the press pellets will be prepared without any binder. A prepared pressed pellet without a binder is shown in the Figure 4.20.



Figure 4.20: Prepared pressed pellets



#### 4.6.1.1. Low grade press method

	Base Curve Parameters											
Eement/Lin	Intensity Low	Intensity High	A0	A1	A2	A3	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg		
Mn_m	0.8921727	438.5	-2.01E-2	9.92E-2	0.00000	0.00000	None	No	No	1		
				Re	gression St	atistics						
Bement/Lin	Bement/Lin SEE [%] R2 Samples Interfering BEC Q [cps/%] LOD (15.00 s)											
Mn_m	0.2916	0.9995	29	0	0.0201		10082	0.0011				

Figure 4.21: Mn calibration line

Figure 4.21 shows a Mn calibration line plotted without any correction. A total of 33 standards was used and 4 standards were removed from the calibration as outlier. The four standards had high percentage differences. Three standards were also removed to improve the correlation on the graph. The correlation coefficient is 0.9995 which indicates a good correlation between the given concentrations and intensities. The SEE is very low at 0.2916 which shows good agreement between the given and calculated values. The LOD calculated based on 15 second count is very low at 0.0011%. The calibration line was computed without any matrix correction.



				Base Curve P	arameters				
Element/Line	Intensity Low	Intensity High	A0	A1	A2	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg
Fe_m	4.4271	1,212.9241	-2.03E-1	1.20E-2	0.00000	None	No	No	1
				Regression	Statistics				
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q [cps/%]		LOD (15.00 s)	
Fe_m	0.0606	0.9995	30.0000	0.0000	0.2030	83,221		0.00121	

Figure 4.22: Fe calibration line

Figure 4.22 shows a Fe calibration line plotted without any correction. A total of 36 standards was used, no standard was removed from the calibration as outlier. Six standards were removed to improve the correlation on the graph. The correlation coefficient is 0.9995 which indicates a good correlation between the given concentrations and intensities. The SEE is very low at 0.0606 which shows good agreement between the given and calculated values. The LOD calculated based on 15 second count is very low at 0.00121%. The calibration line was computed without any matrix correction.



				Base Curve P	arameters				
Element/Line	Intensity Low	Intensity High	A0	A1	A2	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg
Ca_m	0.4798	701.9170	1.23E-1	4.20E-2	0.00000	None	No	No	1
				Regression	Statistics				
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q [cps/%]		LOD (15.00 s)	
Ca_m	0.0943	0.9996	25.0000	0.0000	0.0000	23,837		-	

#### Figure 4.23: CaO calibration line

Figure 4.24 shows a CaO calibration line plotted without any correction. A total of 35 standards was used and 10 standards were removed from the calibration as outlier. The standards had high percentage differences. One standard was also removed to improve the correlation on the graph. The correlation coefficient is 0.9996 which indicates a good correlation between the given concentrations and intensities. The SEE is very low at 0.0.0943 which shows good agreement between the given and calculated values. The LOD was not calculated because A0 shows positive value. The calibration line was computed without any matrix correction.



				Base Curve P	arameters				
Element/Line	Intensity Low	Intensity High	A0	Al	A2	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg
Mg_m	0.4745	101.3107	-2.43E-1	1.19E-1	0.00000	None	No	No	1
	-	-	-	Regression	Statistics	-		-	
Element/Line	Element/Line SEE [%] R2 Samples Interfering BEC Q [cps/%] LOD (15.00 s)								
Mg_m	0.0550	0.9991	32.0000	0.0000	0.2434	8,371.0992		0.00418	

Figure 4.24: MgO calibration line

Figure 4.25 shows MgO calibration line plotted without any correction. A total of 36 standards was used and 4 standards were removed to improve the correlation on the graph. The correlation coefficient is 0.9991 which indicates a good correlation between the given concentrations and intensities. The SEE is very low at 0.0550 which shows good agreement between the given and calculated concentration. The LOD calculated based on 15 second count is very low at 0.00418%. The calibration line was computed without matrix correction.



				Base Curve P	arameters					
Element/Line	Intensity Low	Intensity High	A0	A1	A2	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg	
Si_m	0.4068	170.4250	5.24E-2	5.97E-2	0.00000	None	No	No	1	
				Regression	Statistics					
Element/Line	Element/Line SEE [%] R2 Samples Interfering BEC Q [cps/%] LOD (15.00 s)									
Si_m	0.0507	0.9993	28.0000	0.0000	0.0000	16,747		-		

Figure 4.25: SiO<sub>2</sub> calibration line

Figure 4.26, without any corrections, clearly shows a perfect straight line. A total of 34 standards were used and 8 standards were also removed to improve the correlation on the graph. The correlation coefficient is 0.9993 which indicates a good correlation between the given concentrations and intensities. The SEE is very low at 0.0507 which shows good agreement between the given and calculated concentration. The LOD was not calculated because A0 shows positive value. The calibration line was computed without any matrix correction.



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				Base Curve P	arameters				
Element/Line	Intensity Low	Intensity High	A0	Al	A2	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg
Al_m	0.0636	12.3798	1.03E-2	8.22E-2	0.00000	None	No	No	1
				Regression	Statistics				
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q [cps/%]		LOD (15.00 s)	
Al_m	0.0106	0.9960	20.0000	0.0000	0.0000	12,161.7547		-	

Figure 4.26: Al<sub>2</sub>O<sub>3</sub> calibration line

In Figure 4.27, a total of 36 standards was used and no standard was removed from the calibration as outlier. Sixteen standards were removed to improve the correlation on the graph. The correlation coefficient is 0.9960 which indicates a good correlation between the given concentrations and intensities. The SEE is very low at 0.0106 which shows good agreement between the given and calculated values. The LOD was not calculated because A0 shows positive value. The calibration line was computed without any matrix correction.



				Base Curve P	arameters				
Element/Line	Intensity Low	Intensity High	A0	Al	A2	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg
P_m	0.1157	6.8301	-6.12E-4	1.83E-2	0.00000	None	No	No	1
				Regression	Statistics				
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q [cps/%]		LOD (15.00 s)	
P_m	0.0012	0.9980	26.0000	0.0000	0.0006	54,507		0.00008	

#### Figure 4.27: P calibration line

A total of 36 standards were used, five standards were removed from the calibration as outlier. Five standards were removed to improve the correlation on the graph. The correlation coefficient in Figure 4.27 is 0.9980 which indicates a good correlation between the given concentrations and intensities. The SEE is very low at 0.0012 which shows good agreement between the given and calculated concentration. The LOD calculated based on 15 second count is very low at 0.00008%. The calibration line was computed without any matrix correction.

# 4.6.1.2. High grade press pellets method



Base Curve Pa	rameters								
Element/Line	Intensity Low	Intensity High	A0	A1	A2	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg
Mn_mf	0.5153	719.0620	8.46E-1	10.00E-2	0.00000	None	No	1	0
Regression Sta	tistics		1					1	
Element/Line	SEE [%]	R2	Samples	Interfering Elements	BEC	Q [cps/%]		LOD (30.00 s)	
Mn_mf	0.2975	0.9994	25	0	-	10000.9		-	

Figure 4.28: High grade Mn calibration line





Base Curve Par	ameters								
Element/Line	Intensity Low	Intensity High	A0	A1	A2	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg
Fe_m	3.9359	1,660.1580	-8E-1	1.45E-2	0.00000	None	No	1	0
Regression Stat	istics								
Element/Line	SEE	R2	Samples	Interfering	BEC	Q [cps/%]		LOD	
	[%]			Elements				(30.00 s)	
Fe_m	0.2358	0.9984	22	0	0.8876			0.00340	

Figure 4.29: High grade Fe calibration line







Base Curve Para	ameters								
Element/Line	Intensity	Intensity	A0	A1	A2	Correction	Theo.	Poly.	Corr.
	Low	High					Alphas	Deg.	Deg
Ca_m	0.4821	332.1345	-1.99E-1	5.53E-2	0.00000	None	No	1	0
Regression Stati	istics			·					
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q [cps/%]		LOD	
				Elements				(30.00 s)	
Ca_m	0.0575	0.9997	23	0	0.1995	18095.4		0.00315	

Figure 4.30: High grade CaO calibration line





Base Curve Pa	rameters								
Element/Line	Intensity Low	Intensity High	A0	A1	A2	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg
Mg_m	0.5670	235.2461	-4.8E-1	8.4E-2	0.00000	None	No	1	0
Regression Sta	tistics	I		I	I	•		1	
Element/Line	SEE [%]	R2	Samples	Interfering Elements	BEC	Q [cps/%]		LOD (30.00 s)	
Mg_m	0.0783	0.9997	19	0	0.4884	11904.8		0.00608	

Figure 4.31: High grade MgO calibration line





Dasa Cumo Daramatara									
Dase Curve Farameters									
Element/Line	Intensity	Intensity	A0	A1	A2	Correction	Theo.	Poly. Deg.	Corr. Deg
	Low	High					Alphas		
Si_m	14.6802	418.83	7.76E-1	4.78E-2	0.000	None	No	1	0
Regression Statistics									
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q [cps/%]		LOD (30.00	
				Elements				s)	
Si_m	0.0337	0.9999	21	0	-	20909.6		-	

Figure 4.32: High grade SiO<sub>2</sub> calibration line





Page Curry Deventer									
base Cui ve Fai ameters									
Element/Line	Intensity	Intensity	A0	A1	A2	Correction	Theo.	Poly. Deg.	Corr. Deg
	Low	High					Alphas		
		8					F		
A1 m	0.1181	40 5734	5 E 2	1 26E 1	0.00	None	No	1	0
AI_III	0.1101	40.5754	-5.12-2	1.20E-1	0.00	None	NO	1	0
Regression Statistics									
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q [cps/%]		LOD (30.00	
				Elements				s)	
				Liemento				5)	
Al m	0.0302	0.0001	10	0	0.0528	7027.2		0.00245	
AI_III	0.0392	0.7771	17	U	0.0528	1921.2		0.00243	

Figure 4.33: High grade Al<sub>2</sub>O<sub>3</sub> calibration line







Base Curve Parameters									
Element/Line	Intensity Low	Intensity High	A0	A1	A2	Correction	Theo. Alphas	Poly. Deg.	Corr. Deg
P_m	0.0124	8.0047	-2.E-3	1.62E-2	0.00	None	No	1	0
Regression Statistics									
Element/Line	SEE [%]	R2	Samples	Interfering Elements	BEC	Q [cps/%]		LOD (30.00 s)	
P_m	0.0010	0.9983	20	0	0.0028	61821.0		0.00020	

Figure 4.34: High grade P calibration line

	$\mathbb{R}^2$	SEE	LOD	Samples
Mn	0.9994	0.2975	-	25
Fe	0.9984	0.2358	0.00340	22
CaO	0.9997	0.0575	0.00315	23
MgO	0.9997	0.0783	0.00608	19
SiO <sub>2</sub>	0.9999	0.0337	-	21
Al <sub>2</sub> O <sub>3</sub>	0.9991	0.0392	0.00245	19
Р	0.9983	0.0010	0.0002	20

Table 4.3: High grade method calibration summary

A total of 26 standards were used in the calibration lines from Figures 4.28 to 4.34. Some of the samples were removed from the calibration lines as outlier or to improve the correlation on the graph. The correlation coefficient for all elements is satisfactory. The lowest correlation was observed in P calibration line at 0.9983 as shown in Figure 4.34. The correlation coefficient is close to 1 which indicates a good correlation between the given concentrations and intensities. The SEE is very low for all elements which demonstrates good agreement between the given and calculated concentration. The SEE in Figures 4.28 and 4.29 are slightly higher than other elements because of the high concentration range. The instrument calculated LOD based on 30 second count was very low for all elements except for Figure 4.28 and 4.31 which was not calculated because the A0 is positive. The calibration lines were computed without any matrix correction.

#### Analysis of routine samples

A total of ten Wessels type ore samples were analysed under the same operating conditions as the routine samples. The final results obtained were in correlation with the consensus values.
### 4.6.2. Kalahari fusion method

A total of 36 certified reference materials were used in Figure 4.35 to 4.41 calibration lines. Some of the certified reference materials were removed from the calibration lines to improve the correlation on the graph. The correlation coefficient for all elements is satisfactory. The correlation coefficient is close to 1 which indicates a good correlation between the given concentrations and intensities in Figure 4.36 to 4.42. The SEE is very low for all elements which demonstrations good agreement between the given and calculated concentration. The SEE for Figure 4.45 is slightly higher than other elements. The instrument calculated LOD based on 20 second count is very low for all elements except for Mn in Figure 4.36 which was not calculated because the matrix correction was used in the calibration line.







Base Curve Parameters									
Element/Line	Intensity	Intensity	A0	A1	Correction	Theo.	Poly.	Corr.	
	Low	High				Alphas	Deg.	Deg	
Mn_mf	0.7552297	221.780	-2.21E-1	3.67E-1	COLA	Yes	Yes	1	
Regression Stat	istics								
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q	LOD	(20.00 s)	
				Elements		[cps/%]			
Mn_mf	0.199154	0.999928	22	1	-	-	-		
Matrix Correcti	on - COLA								
Interfering	Alpha 1	Alpha 2	Alpha 3						
Element									
Fe_mf	0.0004580	-0.00123	0.0140904						

Figure 4.35: Kalahari fusion Mn calibration line

Kalahari fusion with LOI





Base Curve	Parameters									
	•									
Element/L	Intensity	Intensity	A0	A1	Cori	rection	The	ю.	Poly.	Corr. Deg
ine	Low	High					Alp	has	Deg.	
Fe_mf	2.05330	550.565	-2.35E-1	1.23E-1	Non	e	No		No	1
	93									
Regression	Statistics									·
Element/	SEE [%]	R2	Samples	s Interfe	ering	BEC		Q [c	ps/%]	LOD (20.00
Line				Eleme	ents					s)
Fe_mf	0.103235	0.999955	19	0		0.2348	36	8158	8.67	0.00465

Figure 4.36: Kalahari fusion Fe calibration line

Kalahari fusion with LOI





Base Curve Par	rameters								
Element/Line	Intensity	Intensity	A0	A1	Correcti	on	Theo.	Poly.	Corr.
	Low	High					Alphas	Deg.	Deg
Ca_m	0.62340	60.610	-5.40E-1	6.63E-1	None		No	No	1
Regression Sta	tistics								
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q [	cps/%]	LOD	
				Elements				(20.00 s)	
Ca_m	0.04976	0.99998	18	0	0.5398	150	07.41	0.0164	

Figure 4.37: Kalahari fusion CaO calibration line





Base Curve Parameters										
Element/Line	Intensity	Intensity	A0	A1	Correc	tion	Theo.	Pol	y.	Corr.
	Low	High					Alphas	Deg	ç.	Deg
Mg_m	0.5736	12.998	-1.56	2.08	None		No	No		1
Regression Sta	tistics									
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q [0	cps/%]		LO	D
				Elements					(20	0.00 s)
Mg_m	0.058456	0.999935	14	0	1.556	480	.46		0.0	493

Figure 4.38: Kalahari fusion MgO calibration line



Base Curve Parameters									
Element/Line	Intensity	Intensity	A0	A1	Correction	Theo.	Poly.	Corr.	
	Low	High				Alphas	Deg.	Deg	
Si_m	0.0252686	121.335	-0.034	0.602	None	No	No	1	
Regression Sta	tistics					•	L	•	
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q		LOD	
				Elements		[cps/%]		(20.00 s)	
Si_m	0.245467	0.999779	20	0	0.0336	1661.85		0.0039	

Figure 4.39: Kalahari fusion SiO<sub>2</sub> calibration line

Kalahari fusion with LOI





Base Curve Parameters										
Element/Line	Intensity	Intensity	A0	A1	Correcti	on	Theo.	Poly.	Corr.	
	Low	High					Alphas	Deg.	Deg	
Al_m	0.3132	15.080	-0.415	1.390	None		No	No	1	
Regression Sta	tistics				•					
Element/Line	SEE [%]	R2	Samples	Interfering	BEC	Q [	cps/%]	LOD (20	0.00 s)	
				Elements						
Al_m	0.0972	0.999603	17	0	0.4145	721	.33	0.0208		

Figure 4.40: Kalahari fusion Al<sub>2</sub>O<sub>3</sub> calibration line

Kalahari fusion with LOI





Base Curve P	Base Curve Parameters										
Element/Li	Intensit	Intensity	A0	A1	Cor	rection	Theo.	Poly.	Corr. Deg		
ne	y Low	High					Alphas	Deg.			
P_m	0.2107	10.6857	-5.08E-	1.86E-1	Nor	ne	No	No	1		
			2								
Regression S	tatistics				•						
Element/Li	SEE [%]	R2	Samples	Interferi	ng	BEC	Q [cps/%	6]	LOD		
ne				Element	S				(20.00 s)		
P_m	0.00591	0.99976	21	0		0.0508	5388.04	87	0.0027		

Figure 4.41: Kalahari fusion P calibration line

# Kalahari fusion calibration summary

	$\mathbb{R}^2$	SEE	LOD	Samples
Mn	0.9999	0.1991		22
Fe	0.9999	0.1032	0.000456	19
CaO	0.9999	0.04976	0.0164	18
MgO	0.9999	0.0586	0.0493	14
SiO <sub>2</sub>	0.9998	0.2455	0.0039	20
Al <sub>2</sub> O <sub>3</sub>	0.9996	0.0972	0.0208	17
Р	0.99976	0.00591	0.0027	21

Table 4.4: Kalahari fusion calibration summary

### **Certified Reference Material (CRM) evaluation results**

A total of eighteen certified reference materials were analysed under the same operating conditions as the routine samples. The final results are compared with CRM true value.

	Mn	Fe	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Р	LOI
BAM 633-1	47.661	1.844	2.113	0.526	10.115	1.340	0.199	13.479
CMSI 1756(NCS HC13806)	10.093	12.711	22.647	21.474	21.500	3.514	0.059	
ECRM 609-1	0.394	30.046	6.586	1.602	17.876	2.252	0.745	18.102
ECRM 651-1	0.645	23.944	23.009	1.988	7.761	3.999	0.429	26.369
ECRM 678-1	0.180	59.997	5.485	0.853	3.482	0.231	1.958	
GBW 07222a (NCS DC	0.808	43.247	3.461	4.123	3.934	0.376	0.037	21.815
46005)								
GBW 07227	0.175	13.200	11.834	8.593	36.663	11.645	0.007	0.903
KZ 185-89	21.771	1.202	25.931	1.022	15.697	1.322	0.010	22.240
NCS DC11021	26.789	11.090	2.134	0.967	21.739	6.999	0.195	13.539
NCS DC28041	14.204	1.139	2.108	0.865	57.093	8.298	0.010	
NCS DC19001	0.418	32.394	6.524	5.983	20.624	8.103		0.100
NCS DC19002	0.398	27.225	7.652	6.290	25.417	10.489	0.007	0.037
NCS HC28803	0.794	1.012	36.508	10.200	32.105	16.732		
OREAS 73b	0.296	9.460	4.247	19.872	45.124	7.192	0.022	6.951
SMU 7-1-007(N-7-1-007)	0.698	0.666	31.697	20.978	39.207	6.126		0.470
DH 3911	4.409	16.343	50.141	1.650	9.013	0.909	1.485	0.158
VS 5403-90	0.372	62.209	0.747	0.536	7.310	0.686		0.904
VS R13/3	58.967	0.664	0.299	0.160	1.799	0.478	0.235	12.912

Table 4.5: Final CRM results after calibration

The T test was used to determine if there is no difference between the analysed CRM after calibration and the true value of the CRM. The test was used to see if the mean of the differences between the CRM analysis after calibration and the true value of the CRM deviates significantly from zero or not.

Equation 4.1: T-test

 $H_0: \mu_d = 0$ 

 $H_1{:}\;\mu_d\!\neq\!0$ 

$$t_{cal} = \frac{|d-0|}{\frac{s}{\sqrt{n}}}$$
 4.1

n = degrees of freedom

d = mean of differences within each pair of data

s = standard deviation

Table 4.6: Difference between CRM results and CRM true value

	Difference between CRM results and CRM true value								
	Mn	Fe	CaO	MgO	SiO2	Al2O3	Р		
BAM 633-1	-0.189	0.204	0.093	-0.054	-0.275	-0.301	0.029		
CMSI 1756(NCS HC13806)	-0.099	-0.399	-0.051	0.294	0.130	-0.486	0.005		
ECRM 609-1	-0.078	-0.474	-0.285	-0.398	1.125	-0.008	0.137		
ECRM 651-1	-0.323	0.093	0.409	0.258	0.361	-0.262	0.079		
ECRM 678-1	0.100	-0.753	0.000	-0.093	-0.219	-0.299	0.348		
GBW 07222a (NCS DC 46005)		-0.413	0.081	0.283	-0.056	-0.224	0.003		
GBW 07227	-0.013	-0.030	0.214	0.273	0.333	0.175	-0.005		
KZ 185-89	0.161	0.092	0.211	0.072	-0.373	-0.098	-0.005		
NCS DC11021	0.259	0.080	-0.176	0.193	-0.361	0.009	0.032		
NCS DC28041	-0.246	0.289	0.038	0.265	1.063	0.048	-0.001		
NCS DC19001	0.195	-0.576	0.144	-0.177	0.294	-0.157	-0.010		
NCS DC19002	0.193	-0.325	0.152	0.120	-0.053	0.199	-0.005		
NCS HC28803	0.190	0.092	0.248	0.280	0.285	-0.118	-0.008		
OREAS 73b	0.181	0.830	-0.161	0.306	0.434	0.068	-0.002		
SMU 7-1-007(N-7-1-007)	0.094	0.116	0.497	2.078	0.207	-0.074	0.000		
DH 3911	-0.011	-2.167	-0.359	0.110	0.433	-0.024	0.328		
VS 5403-90	0.210	-0.531	-0.143	-0.114	0.170	-0.044	0.000		
VS R13/3	0.087				-0.211		0.039		
mean	0.042	-0.228	0.054	0.217	0.183	-0.094	0.054		
Standard deviation	0.176	0.638	0.233	0.521	0.428	0.180	0.110		
T <sub>cal</sub>	0.981	-1.472	0.952	1.719	1.811	-2.149	2.066		
T <sub>crit</sub>	2.120	2.120	2.120	2.120	2.110	2.120	2.110		

The calculated t values of all elements were lower than the critical value, except  $t_{cal}$  of  $Al_2O_3$  which was 0.029 higher than the  $t_{crit}$  as indicated in Table 4.6. The null hypothesis that the methods do not differ was accepted. It was concluded that the Kalahari fusion method agree with the results of the CRM true values, except for  $Al_2O_3$ . The  $Al_2O_3$  result indicated that there was a negative bias on the results. The error can be attributed to the dilution on the fused beads method. The final results obtained were in correlation with the certified values.

# 4.6. Statistical method validation

# 4.7.1. Low grade press pellets method

Low grade method regression lines

Table 4.7: Mn	linearity and	regression
---------------	---------------	------------

Summary output

Regression Statistic	S				
Multiple R	0.99973				
R Square	0.99946				
Adjusted R Square	0.99944				
Standard Error	0.2916				
Observations	29.0000				
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	435268.0	435268.0	50382	1.05158E-45
Residual	27	233.3	8.6		
Total	28	435501.3			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	0.36099	1.42884	0.25264	0.80246	-2.57075
X Variable 1	10.07673	0.04489	224.46039	0.00000	9.98462

### F-test for significance of linearity

 $F_{calc} > 50382$ 

 $F_{crit} = 1.882$ 

Since  $F_{calc} > F_{crit}$ , linearity/regression is proven to be significant.

#### T-test for significance of linearity

 $H_o (r = 0)$ , and there's no linear relation between x and y.

 $H_1$  (r > 0), and there's a significant linearity.

Equation 4.2: Two tailed test

$$t_{cal} = r \sqrt{\frac{n-2}{1-r^2}}$$
 4.2

 $t_{calc} = 224.460$ 

 $t_{crit} = 2.048$ 

 $t_{calc} > t_{crit}$ , therefore reject H<sub>o</sub> and it points out to a significant linearity.

 $t_{calc} > t_{crit}$  then there is significant linearity between x and y.

#### Regression parameters

Slope (b) = 10.077

Intercept (a) = 0.3610

Equation 4.3: Regression line

Line: 
$$y = bx + a$$
 4.3

Y = 10.077x + 0.3610

Calibration uncertainty

Random calibration uncertainty  $(S_{y/x}) = 0.2916$ .

Uncertainty in the slope  $(S_b) = 0.0449$ .

Uncertainty in the intercept  $(S_a) = 1.4288$ .

Total calibration uncertainty is the combination of individual calibration uncertainty.

Equation 4.4: Calibration uncertainty

$$U = \sqrt{(Sy/x)^2 + (Sa)^2 + (Sb)^2}$$
 4.4

U = 1.459

 $S_b < S_a$  therefore the range of standards is wide enough.

 $S_a/S_b = 31.828$ 

The confidence interval (CI) for slope (b) and intercept

 $T_{crit} = 2.05$ 

Equation 4.5: Confidence interval

$$b = b \pm t \cdot sb \tag{4.5}$$

 $b = b + t \cdot sb$  : 95% CI of b = 10.1688

 $b = b - t \cdot sb$  : 95% CI of b = 9.9846

95% CI of b : 10.169 < b < 9.9846

$$a = a \pm t \cdot s_a$$

 $a = a + t \cdot s_a$  95% CI of a = 3.2927

 $a = a - t \cdot s_a$  95% CI of a = -2.5708

95% CI of a: 3.2927 < a < -2.5708

#### Calibration sensitivity

b = 10.077

b not equal 0, therefore calibration sensitivity is satisfactory.

Limit of detection (LOD)

Equation 4.6: Limit of detection (LOD)

$$X_{\text{LOD}} = \frac{3\text{Ss/y}}{b}$$
 4.6

 $X_{\rm LOD} = 0.0868$ 

Limit of quantification (LOQ)

Equation 4.7: Limit of quantification (LOQ)

$$X_{LOQ} = \frac{(10Ss/y)}{b}$$
 4.7

 $X_{\text{LOQ}} = 0.2894$ 

The LOD and LOQ unit's is percentages.

Therefore, this method can only detect Mn > 0.0868, and quantify Mn > 0.2894.

Table 4.8	8. Summary	of Mn low	grade method	validation
1 4010 4.0	5. Summary		grade memou	vanuation

Conclusion	Description		Mn
	Observations (n)	Number of standards	29
		analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9997
Sy/x very low indicate	Standard error (Sy/x)	Random calibration	0.2916
good precision and		uncertainty	
accuracy			
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.0449
precision	Error (Sb)		
	Intercept Standard Error	Uncertainty in intercept	1.4288
	(Sa)		
linear regression	Regression line ( $y=bx + a$ )	Y=10.077x +	
			0.3610
Calibration line intercept	Intercept (a)	Calibration line intercept	0.3610
Since Slope is > 1 thus is	X Variable 1 (b)	Calibration line slope	10.0767
sensitive to the analyte			
LOD	Lowest distinguishable sig	0.0868	
LOQ	LOQ > lowest calibration	standard	0.2894
Analytical working	Max	Highest CRM	43.0250
range	Min	LOD	0.0868

Summary output					
Regression Statistics					
Multiple R	0.9997				
R Square	0.9995				
Adjusted R Square	0.9994				
Standard Error	0.0606	-			
Observations	30	_			
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	1337286.5	1337286.5	52625.9	2.161E-47
Residual	28	711.5	25.4		
Total	29	1337998.0			
	Coefficients	Standard Error	t Stat	P-value	Lower 95%
Intercept	17.1303	2.1261	8.0571	0.0000	12.7751
X Variable 1	83.1771	0.3626	229.4033	0.0000	82.4344

Table 4.9: Fe linearity /regression, CI, sensitivity, LOD and LOQ

### F-test for significance of linearity

 $F_{calc} > 52626$ 

 $F_{crit} = 1.861$ 

Since  $F_{calc} > F_{crit}$ , linearity/regression is proven to be significant.

## T-test for significance of linearity

 $H_o (r = 0)$ , and there's no linear relation between x and y.

 $H_1$  (r > 0), and there's a significant linearity.

Equation 4.8: Two tailed test

$$t_{cal} = r \sqrt{\frac{n-2}{1-r^2}}$$
 4.8

 $t_{calc} = 229.403$ 

 $t_{crit} = 2.045$ 

t<sub>calc</sub> > t<sub>crit</sub>, therefore reject Ho and it points out to a significant linearity.

 $t_{calc} > t_{crit}$  then there is significant linearity between x and y.

#### **Regression parameters**

Slope (b) = 83.177

Intercept (a) = 17.1303

Therefore, Regression Line: y = bx + a

Y = 83.177x + 17.1300

Calibration uncertainty

Random calibration uncertainty  $(S_{y/x}) = 0.0606$ 

Uncertainty in the slope  $(S_b) = 0.3626$ 

Uncertainty in the intercept  $(S_a) = 2.1261$ 

Total calibration uncertainty is the combination of individual calibration uncertainty.

$$U = \sqrt{(Sy/x)^2 + (Sa)^2 + (Sb)^2}$$

U = 2.158

 $S_b < S_A$ , therefore the range of standards is wide enough.

$$S_a/S_b = 5.864$$

#### The confidence interval (CI) for slope (b) and intercept

Where t is the two-tailed t critical value at the required significance level (typically  $\alpha = 0.05$ ) with degrees of freedom = n-2 for the number of standards used in the regression.

 $T_{crit} = 2.05$   $b = b \pm t \cdot sb$   $b = b + t \cdot sb$  95% CI of b = 83.9199  $b = b - t \cdot sb$  95% CI of b = 82.4344 95% CI of b: 83.920 < b < 82.434  $a = a \pm t \cdot sa$   $a = a + t \cdot sa$  95% CI of a = 21.4855  $a = a - t \cdot sa$  95% CI of a = 12.775195% CI of a = 12.7751

Calibration sensitivity

b = 83.177

b not equal 0, therefore calibration sensitivity is satisfactory.

Limit of detection (LOD)

$$X_{LOD} = \frac{3Ss/y}{b}$$

 $X_{\text{LOD}} = 0.0022$ 

Limit of quantification (LOQ)

$$X_{LOQ} = \frac{(10Ss/y)}{b}$$

 $X_{\text{LOQ}} = 0.0073$ 

The LOD and LOQ unit's is percentages.

Therefore, this method can only detect Fe > 0.0022 and quantify Fe > 0.0073.

Table 4.10: Summary of Fe low grade validation	ł
--	---

Conclusion	Description	Fe	
	Observations (n)	Number of standards	30
		analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9997
Sy/x very low indicate good	Standard error (Sy/x)	Random calibration	0.0606
precision and accuracy		uncertainty	
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.3626
precision	Error (Sb)		
	Intercept Standard Error	Uncertainty in	2.1261
	(Sa)	intercept	
linear regression	Regression line (y= bx +	Y=83.177x +	
		17.1300	
Calibration line intercept	Intercept (a)	Calibration line	17.1303
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line slope	83.1771
sensitive to the analyte			
LOD	D Lowest distinguishable signal		0.0022
LOQ	LOQ > lowest calibration	0.0073	
Analytical working range	Max	Highest CRM	12.0000
	Min	LOD	0.0022

Summary output					
Regression Statistics					
Multiple R	0.99980				
R Square	0.99959				
Adjusted R Square	0.99957				
Standard Error	0.09432				
Observations	25				
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	284831.144	284831.144	56374	1.72539E-40
Residual	23	116.209	5.053		
Total	24	284947.353			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	-2.8029	1.5044	-1.8632	0.0753	-5.9150
X Variable 1	23.8270	0.1004	237.4316	0.0000	23.6194

Table 4.11: CaO linearity /regression, CI, sensitivity, LOD and LOQ

## F-test for Significance of Linearity

 $F_{calc} > 56374$ 

 $F_{crit} = 1.984$ 

Since  $F_{calc} > F_{crit}$ , linearity/regression is proven to be significant

T-test for Significance of linearity

 $H_o(r=0)$  and there's no linear relation between x and y

 $H_1$  (r >0) and there's a significant linearity

Two tailed test

$$t_{cal} = r \sqrt{\frac{n-2}{1-r^2}}$$

 $t_{calc} = 237.432$ 

 $t_{crit} = 2.064$ 

t<sub>calc</sub> > t<sub>crit</sub>, therefore reject Ho and it points out to a significant linearity.

 $t_{calc} > t_{crit}$  then there is significant linearity between x and y.

#### **Regression parameters**

Slope (b) = 23.827

Intercept (a) = -2.8029

Therefore, Regression Line: y = bx + a

Y = 23.827x - 2.8029

Calibration uncertainty

Random calibration uncertainty  $(S_{y/x}) = 0.0943$ 

Uncertainty in the slope  $(S_b) = 0.1004$ 

Uncertainty in the intercept  $(S_a) = 1.5044$ 

Total calibration uncertainty is the combination of individual calibration uncertainty.

$$U = \sqrt{(Sy/x)^2 + (Sa)^2 + (Sb)^2}$$

U = 1.511

 $S_b < S_a$ , therefore the range of standards is wide enough.

$$S_a/S_b = 14.991$$

### The confidence interval (CI) for slope (b) and intercept

Where t is the two-tailed t critical value at the required significance level (typically  $\alpha = 0.05$ ) with degrees of freedom = n-2 for the number of standards used in the regression.

$$T_{crit} = 2.07$$
  

$$b = b \pm t \cdot sb$$
  

$$b = b + t \cdot sb$$
  

$$95\% \text{ CI of } b = 24.0346$$
  

$$b = b - t \cdot sb$$
  

$$95\% \text{ CI of } b = 23.6194$$
  

$$95\% \text{ CI of } b: 24.035 < b < 23.619$$
  

$$a = a \pm t \cdot sa$$
  

$$a = a \pm t \cdot sa$$
  

$$95\% \text{ CI of } a = 0.3092$$
  

$$a = a - t \cdot sa$$
  

$$95\% \text{ CI of } a = -5.9150$$
  

$$95\% \text{ CI of } a: 0.3092 < a < -5.9150$$

Calibration sensitivity

b = 1.000

b = 1.000 not equal 0, therefore calibration sensitivity is satisfactory.

Limit of detection (LOD)

$$X_{LOD} = \frac{3Ss/y}{b}$$

 $X_{\rm LOD} = 0.0119$ 

Limit of quantification (LOQ)

$$X_{LOQ} = \frac{(10Ss/y)}{b}$$

 $X_{\text{LOQ}} = 0.0396$ 

The LOD and LOQ unit's is percentages.

Therefore, this method can only detect CaO > 0.0119, and quantify CaO > 0.0396.

Table 4.12:	Summary	of CaO	low	grade	method	validation

Conclusion	Description		CaO
	Observations (n)	Number of	25
		standards	
		analysed	
It shows a linear trend	Multiple R (r)	Regression	0.9998
		value	
Sy/x very low indicate good	Standard error (Sy/x)	Random	0.0943
precision and accuracy		calibration	
		uncertainty	
Sb < Sa Good general precision	X Variable 1 Standard	Uncertainty in	0.1004
	Error (Sb)	slope	
	Intercept Standard Error	Uncertainty in	1.5044
	(Sa)	intercept	
linear regression	Regression line ( $y=bx + b$	a)	Y= 2.827x - 2.8029
Calibration line intercept	Intercept (a)	Calibration	-2.8029
		line intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration	23.8270
sensitive to the analyte		line slope	
LOD	Lowest distinguishable si	ignal	0.0119
LOQ	LOQ > lowest calibration	n standard	0.0396
Analytical working range	Max	Highest CRM	24.6570
	Min	LOD	0.0119

Summary output					
Regression Statistics					
Multiple R	0.9994				
R Square	0.9989				
Adjusted R Square	0.9986				
Standard Error	0.0566				
Observations	32				
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	13.9939	13.9939	4361.88	1.5E-08
Residual	5	0.01604	0.00321		
Total	6	14.0099			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	0.0347	0.0396	0.8773	0.4205	-0.0670
X Variable 1	0.9878	0.0150	66.0446	0.0000	0.9494

Table 4.13: MgO Linearity /regression, CI, sensitivity, LOD and LOQ

## F-test for significance of linearity

 $F_{calc} > 34437$ 

 $F_{crit} = 1.822$ 

Since  $F_{calc} > F_{crit}$ , linearity/regression is proven to be significant.

T-test for significance of linearity

 $H_o (r = 0)$ , and there's no linear relation between x and y.

 $H_1$  (r > 0), and there's a significant linearity.

Two tailed test

$$t_{cal} = r \sqrt{\frac{n-2}{1-r^2}}$$

 $t_{calc} = 185.572$ 

 $t_{\rm crit} = 2.040$ 

t<sub>calc</sub> > t<sub>crit</sub>, therefore reject Ho and it points out to a significant linearity.

 $t_{calc} > t_{crit}$  then there is significant linearity between x and y.

#### **Regression parameters**

Slope (b) = 8.364

Intercept (a) = 2.0666

Therefore, Regression Line: y = bx + a

Y = 8.364x + 2.0666

Calibration uncertainty

Random calibration uncertainty  $(S_{y/x}) = 0.0550$ .

Uncertainty in the slope  $(S_b) = 0.0451$ .

Uncertainty in the intercept  $(S_a) = 0.1951$ .

Total calibration uncertainty is the combination of individual calibration uncertainty.

$$U = \sqrt{(Sy/x)^2 + (Sa)^2 + (Sb)^2}$$

U = 0.208

 $S_b < Sa$ , therefore the range of standards is wide enough.

$$S_a/S_b = 4.328$$

### The confidence interval (CI) for slope (b) and intercept

Where t is the two-tailed t critical value at the required significance level (typically  $\alpha = 0.05$ ) with degrees of freedom = n-2 for the number of standards used in the regression.

 $t_{crit} = 2.04$   $b = b \pm t \cdot sb$   $b = b + t \cdot sb$  95% CI of b = 8.4559  $b = b - t \cdot sb$  95% CI of b = 8.2718 95% CI of b: 8.456 < b < 8.272  $a = a \pm t \cdot sa$   $a = a + t \cdot sa$  95% CI of a = 2.4650  $a = a - t \cdot sa$  95% CI of a = 1.668295% CI of a: 2.4650 < a < 1.6682

**Calibration sensitivity** 

b = 8.364

b not equal 0, therefore calibration sensitivity is satisfactory.

Limit of detection (LOD)

$$X_{LOD} = \frac{3\text{Ss/y}}{\text{b}}$$

 $X_{\text{LOD}} = 0.0197$ 

Limit of quantification (LOQ)

$$X_{LOQ} = \frac{(10\text{Ss/y})}{\text{b}}$$

 $X_{LOQ} = 0.0658$ 

The LOD and LOQ unit's is percentages.

Therefore, this method can only detect MgO > 0.0197, and quantify MgO > 0.0658.

Conclusion	Description		MgO
	Observations (n)	Number of	32
		standards analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9996
Sy/x very low indicate good	Standard error	Random	0.0550
precision and accuracy	(Sy/x)	calibration	
		uncertainty	
Sb < Sa Good general	X Variable 1	Uncertainty in	0.0451
precision	Standard Error (Sb)	slope	
	Intercept Standard	Uncertainty in	0.1951
	Error (Sa)	intercept	
linear regression	Regression line (y= b	x + a)	Y = 8.364x + 2.0666
Calibration line intercept	Intercept (a)	Calibration	2.0666
		line intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration	8.3638
sensitive to the analyte		line slope	
LOD	Lowest distinguishab	ole signal	0.0197
LOQ	LOQ > lowest calibra	ation standard	0.0658
Analytical working range	Max	Highest CRM	9.8630
	Min	LOD	0.0197

Table 4.14: Low grade MgO validation summary

SiO <sub>2</sub> summary output	t	]			
Regression Statistics		-			
Multiple R	0.9996				
R Square	0.9993	-			
Adjusted R Square	0.9992	-			
Standard Error	0.0507	-			
Observations	28	-			
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	25705.07	25705	35710	2.48E-42
Residual	26	18.72	0.71983		
Total	27	25723.79			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	-0.8233	0.4251	-1.9367	0.0637	-1.6971
X Variable 1	16.7345	0.0886	188.9710	0.0000	16.5525

Table 4.15: SiO<sub>2</sub> linearity /regression, CI, sensitivity, LOD and LOQ

## F-test for Significance of linearity

 $F_{calc} > 35710$ 

 $F_{crit} = 1.905$ 

Since  $F_{calc} > F_{crit}$ , linearity/regression is proven to be significant.

T-test for significance of linearity

 $H_o (r = 0)$ , and there's no linear relation between x and y.

 $H_1$  (r > 0), and there's a significant linearity.

Two tailed test

$$t_{cal} = r \sqrt{\frac{n-2}{1-r^2}}$$

 $t_{calc} = 188.971$ 

 $t_{crit} = 2.052$ 

t<sub>calc</sub> > t<sub>crit</sub>, therefore reject H<sub>o</sub> and it points out to a significant linearity.

 $t_{calc} > t_{crit}$  then there is significant linearity between x and y.

#### **Regression parameters**

Slope (b) = 16.734

Intercept (a) = -0.8233

Therefore, Regression Line: y = bx + a

Y = 16.734 - 0.8233

Calibration uncertainty

Random calibration uncertainty  $(S_{y/x}) = 0.0507$ 

Uncertainty in the slope  $(S_b) = 0.0886$ 

Uncertainty in the intercept  $(S_a) = 0.4251$ 

Total calibration uncertainty is the combination of individual calibration uncertainty.

$$U = \sqrt{(Sy/x)^2 + (Sa)^2 + (Sb)^2}$$

U = 0.437

 $S_b < S_a$ , therefore the range of standards is wide enough.

$$S_a/S_b = 4.800$$

### The confidence interval (CI) for slope (b) and intercept

Where t is the two-tailed t critical value at the required significance level (typically  $\alpha = 0.05$ ) with degrees of freedom = n-2 for the number of standards used in the regression.

 $t_{crit} = 2.06$   $b = b \pm t \cdot sb$   $b = b + t \cdot sb$  95% CI of b = 6.9165  $b = b - t \cdot sb$  95% CI of b = 16.5525 95% CI of b: 16.917 < b < 16.552  $a = a \pm t \cdot sa$   $a = a + t \cdot sa$  95% CI of a = 0.0505  $a = a - t \cdot sa$  95% CI of a = -1.697195% CI of a: 0.0505 < a < -1.6971

Calibration sensitivity

b = 16.734

b not equal 0, therefore calibration sensitivity is satisfactory.

Limit of detection (LOD)

$$X_{LOD} = \frac{3\text{Ss/y}}{\text{b}}$$

 $X_{\text{LOD}} = 0.0091$ 

Limit of quantification (LOQ)

$$X_{LOQ} = \frac{(10Ss/y)}{b}$$

 $X_{LOQ} = 0.0303$ 

The LOD and LOQ unit's is percentages.

Therefore, this method can only detect  $SiO_2 > 0.0091$ , and quantify  $SiO_2 > 0.0303$ .

Table 4.16: Summary of SiO <sub>2</sub> low grade method validation	n
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Conclusion	Description	SiO <sub>2</sub>	
	Observations (n)	Number of	28
		standards analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9996
Sy/x very low indicate	Standard error (Sy/x)	Random calibration	0.0507
good precision and		uncertainty	
accuracy			
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.0886
precision	Error (Sb)		
	Intercept Standard Error	Uncertainty in	0.4251
	(Sa)	intercept	
linear regression	Regression line (y= bx +	Y= 16.734 - 0.8233	
-			
Calibration line	Intercept (a)	Calibration line	-0.8233
Calibration line intercept	Intercept (a)	Calibration line intercept	-0.8233
CalibrationlineinterceptSince Slope is > 1 thus	Intercept (a) X Variable 1 (b)	CalibrationlineinterceptCalibrationline	-0.8233 16.7345
CalibrationlineinterceptSince Slope is > 1 thusis sensitive to the	Intercept (a) X Variable 1 (b)	CalibrationlineinterceptCalibrationlineslope	-0.8233 16.7345
CalibrationlineinterceptSince Slope is > 1 thusis sensitive to theanalyte	Intercept (a) X Variable 1 (b)	CalibrationlineinterceptCalibrationlineslope	-0.8233 16.7345
CalibrationlineinterceptSince Slope is > 1 thusis sensitive to theanalyteLOD	Intercept (a) X Variable 1 (b) Lowest distinguishable s	CalibrationlineinterceptCalibrationlineslopeignal	-0.8233 16.7345 0.0091
CalibrationlineinterceptSince Slope is > 1 thusis sensitive to theanalyteLODLOQ	Intercept (a) X Variable 1 (b) Lowest distinguishable s LOQ > lowest calibration	Calibration line intercept Calibration line slope ignal n standard	-0.8233 16.7345 0.0091 0.0303
CalibrationlineinterceptSince Slope is > 1 thusis sensitive to theanalyteLODLOQAnalyticalworking	Intercept (a) X Variable 1 (b) Lowest distinguishable s LOQ > lowest calibration Max	Calibration line intercept Calibration line slope ignal n standard Highest CRM	-0.8233 16.7345 0.0091 0.0303 8.5320
CalibrationlineinterceptSince Slope is > 1 thusis sensitive to theanalyteLODLOQAnalyticalworkingrange	Intercept (a) X Variable 1 (b) Lowest distinguishable s LOQ > lowest calibration Max	CalibrationlineinterceptlineCalibrationlineslopelineignallinen standardlineHighest CRMline	-0.8233 16.7345 0.0091 0.0303 8.5320

Al <sub>2</sub> O <sub>3</sub> summary output	ıt	]			
Regression Statistics		1			
Multiple R	0.9980	1			
R Square	0.9960				
Adjusted R Square	0.9958				
Standard Error	0.0106	-			
Observations	20	-			
		-			
ANOVA		-			
	df	SS	MS	F	Significance F
Regression	1	74.87	75	4484	4.851E-23
Residual	18	0.30	0.01670		
Total	19	75.17			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	-0.1120	0.0581	-1.9283	0.0697	-0.2340
X Variable 1	12.1131	0.1809	66.9595	0.0000	11.7331

Table 4.17: Al<sub>2</sub>O<sub>3</sub> linearity /regression, CI, sensitivity, LOD and LOQ.

# F-test for significance of linearity

 $F_{calc} > 4484$ 

 $F_{crit} = 2.168$ 

Since  $F_{calc} > F_{crit}$ , linearity/regression is proven to be significant.

T-test for significance of linearity

 $H_o (r = 0)$ , and there's no linear relation between x and y.

 $H_1$  (r > 0), and there's a significant linearity.

Two tailed test

$$t_{cal} = r_{\sqrt{\frac{n-2}{1-r^2}}}$$

 $t_{calc} = 66.959$ 

 $t_{crit} = 2.093$ 

 $t_{calc} > t_{crit}$ , therefore reject  $H_0$  and it points out to a significant linearity.

 $t_{calc} > t_{crit}$  then there is significant linearity between x and y.

#### **Regression parameters**

Slope (b) = 12.113

Intercept (a) = -0.1120

Therefore, Regression Line: y = bx + a

Y = 12.113x - 0.1120

Calibration uncertainty

Random calibration uncertainty  $(S_{y/x}) = 0.0106$ 

Uncertainty in the slope  $(S_b) = 0.1809$ 

Uncertainty in the intercept  $(S_a) = 0.0581$ 

Total calibration uncertainty is the combination of individual calibration uncertainty.

$$U = \sqrt{(Sy/x)^2 + (Sa)^2 + (Sb)^2}$$

U = 0.190

 $S_b < S_a$  therefore the range of standards is wide enough.

$$S_a/S_b = 0.321$$

### The confidence interval (CI) for slope (b) and intercept

Where t is the two-tailed t critical value at the required significance level (typically  $\alpha = 0.05$ ) with degrees of freedom = n-2 for the number of standards used in the regression.

 $t_{crit} = 2.10$   $b = b \pm t \cdot sb$   $b = b + t \cdot sb$  95% CI of b = 12.4932  $b = b - t \cdot sb$  95% CI of b = 11.7331 95% CI of b : 12.493 < b < 11.733  $a = a \pm t \cdot sa$   $a = a \pm t \cdot sa$  95% CI of a = 0.0100  $a = a - t \cdot sa$  95% CI of a = -0.234095% CI of a : 0.0100 < a < -0.2340

Calibration sensitivity

b = 12.113

b not equal 0, therefore calibration sensitivity is satisfactory.

Limit of detection (LOD)

$$X_{LOD} = \frac{3\text{Ss/y}}{\text{b}}$$

 $X_{\text{LOD}} = 0.0026$ 

Limit of quantification (LOQ)

$$X_{LOQ} = \frac{(10Ss/y)}{b}$$

 $X_{\text{LOQ}} = 0.0088$ 

The LOD and LOQ unit's is percentages.

Therefore, this method can only detect  $Al_2O_3 > 0.0026$ , and quantify  $Al_2O_3 > 0.0088$ .

Conclusion	Description	Al <sub>2</sub> O <sub>3</sub>	
	Observations (n)	Number of	20
		standards	
		analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9980
Sy/x very low indicate	Standard error (Sy/x)	Random	0.0106
good precision and	calibration		
accuracy		uncertainty	
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in	0.1809
precision	Error (Sb)	slope	
	Intercept Standard Error	Uncertainty in	0.0581
	(Sa) intercept		
linear regression	Regression line $(y=bx + a)$		Y= 12.113x - 0.1120
Calibration line	Intercept (a)	Calibration line	-0.1120
intercept	intercept		
Since Slope is > 1 thus is	X Variable 1 (b)	Calibration line	12.1131
sensitive to the analyte		slope	
LOD	Lowest distinguishable sig	0.0026	
LOQ	LOQ > lowest calibration s	0.0088	
Analytical working	Max	Highest CRM	0.8420
range	Min	LOD	0.0026

Table 4.18: Summary of Al<sub>2</sub>O<sub>3</sub> low grade method validation
P Summary output					
Regression Statistics		-			
Multiple R	0.998975	-			
R Square	0.997950	_			
Adjusted R Square	0.997865	_			
Standard Error	0.001245	-			
Observations	26	_			
		-			
ANOVA		-			
	df	SS	MS	F	Significance F
Regression	1	53.73	54	11685	8.87385E-34
Residual	24	0.11	0.00460		
Total	25	53.84			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	0.0381	0.0250	1.5229	0.1409	-0.0135
X Variable 1	54.3949	0.5032	108.0962	0.0000	53.3563

## Table 4.19: P linearity /regression, CI, sensitivity, LOD and LOQ

### F-test for significance of linearity

F<sub>calc</sub> > 11685

 $F_{crit} = 1.955$ 

Since  $F_{calc} > F_{crit}$ , linearity/regression is proven to be significant.

T-test for significance of linearity

 $H_o (r = 0)$ , and there's no linear relation between x and y.

 $H_1$  (r > 0), and there's a significant linearity.

Two tailed test

$$t_{cal} = r_{\sqrt{\frac{n-2}{1-r^2}}}$$

 $t_{calc} = 108.096$ 

 $t_{crit} = 2.060$ 

 $t_{calc} > t_{crit}$ , therefore reject  $H_0$  and it points out to a significant linearity.

 $t_{calc} > t_{crit}$  then there is significant linearity between x and y.

#### **Regression parameters**

Slope (b) = 54.395

Intercept (a) = 0.0381

Therefore, regression Line: y = bx + a

Y = 54.395x + 0.0381

Calibration uncertainty

Random calibration uncertainty  $(S_{y/x}) = 0.0012$ 

Uncertainty in the slope  $(S_b) = 0.5032$ 

Uncertainty in the intercept  $(S_a) = 0.0250$ 

Total calibration uncertainty is the combination of individual calibration uncertainty.

$$U = \sqrt{(Sy/x)^2 + (Sa)^2 + (Sb)^2}$$

U = 0.003

 $S_b > S_a$ , therefore the range of standards are not wide enough.

$$S_a/S_b = 0.504$$

#### The confidence interval (CI) for slope (b) and intercept

Where t is the two-tailed t critical value at the required significance level (typically  $\alpha = 0.05$ ) with degrees of freedom = n-2 for the number of standards used in the regression.

 $t_{crit} = 2.06$   $b = b \pm t \cdot sb$   $b = b + t \cdot sb$  95% CI of b = 55.4334  $b = b - t \cdot sb$  95% CI of b = 53.3563 95% CI of b : 55.433 < b < 53.356  $a = a \pm t \cdot sa$   $a = a \pm t \cdot sa$  95% CI of a = 0.0897  $a = a - t \cdot sa$  95% CI of a = -0.013595% CI of a : 0.0897 < a < -0.0135

**Calibration sensitivity** 

b = 1.000

b not equal 0, therefore calibration sensitivity is satisfactory.

Limit of detection (LOD)

$$X_{LOD} = \frac{3\text{Ss/y}}{\text{b}}$$

 $X_{LOD} = 0.0001$ 

Limit of quantification (LOQ)

$$X_{LOQ} = \frac{(10Ss/y)}{b}$$

 $X_{\text{LOQ}} = 0.0002$ 

The LOD and LOQ unit's is percentages.

Therefore, this method can only detect P > 0.0001 and quantify P > 0.0002.

Table 4.20: Summary of P low grade method validation	n
--	---

Conclusion	Description		Р
	Observations (n) Number of standards		26
		analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9990
Sy/x very low indicate	Standard error $(Sy/x)$	Random calibration	0.0012
good precision and		uncertainty	
accuracy			
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.5032
precision	Error (Sb)		
	Intercept Standard	Uncertainty in	0.0250
	Error (Sa)	intercept	
linear regression	Regression line (y= bx	+ a)	Y=54.395x + 0.0381
Calibration line intercept	Intercept (a)	Calibration line	0.0381
		intercept	
Since Slope is > 1 thus is	X Variable 1 (b)	Calibration line	54.3949
sensitive to the analyte		slope	
LOD	Lowest distinguishable	0.0001	
LOQ	LOQ > lowest calibrati	0.0002	
Analytical working range	Max	Highest CRM	0.1026
	Min	LOD	0.0001

## 4.7.1.1. Low grade press pellets accuracy

To test accuracy of the method 10 replicates of the Sarm 17 which is a low grade type ore was used. The mean, standard deviation and the RSD was calculated from the obtained results.

Sample	name	Mn	Fe	CaO	MgO	SiO2	Al2O3	Р
number								
1	SARM 17	38.81	4.28	14.40	3.04	4.67	0.239	0.0179
2	SARM 17	38.82	4.24	14.40	3.02	4.67	0.239	0.0181
3	SARM 17	38.78	4.29	14.40	3.03	4.67	0.239	0.0183
4	SARM 17	38.80	4.27	14.40	3.03	4.67	0.241	0.0181
5	SARM 17	38.81	4.26	14.39	3.03	4.97	0.240	0.0180
6	SARM 17	38.79	4.27	14.39	3.02	4.67	0.239	0.0179
7	SARM 17	38.81	4.29	14.40	3.03	4.67	0.238	0.0179
8	SARM 17	38.82	4.32	14.41	3.03	4.68	0.240	0.0181
9	SARM 17	38.81	4.37	14.40	3.03	4.68	0.241	0.0179
10	SARM 17	38.82	4.28	14.40	3.04	4.68	0.240	0.0179
Mean		38.81	4.29	14.40	3.03	4.70	0.240	0.0180
SD		0.0116	0.0362	0.0052	0.0052	0.0944	0.0009	0.0001
RSD		0.0298	0.8441	0.0361	0.1733	2.0057	0.3812	0.7609
True Value		38.81	4.27	14.40	3.03	4.69	0.240	0.018
Tcalc		-1.26	1.28	-0.83	-0.40	0.47	-1.48	0.22
Tcrit		2.262	2.262	2.262	2.262	2.262	2.262	2.262
Comment		t <sub>calc</sub> <						
		t <sub>crit</sub>						
Uncertainty		0.0037	0.0114	0.0016	0.0017	0.0298	0.0003	0.0000

Table 4.21: Low grade accuracy test results

The mean of a set of results obtained from Table 4.21 shows that the analysis of a certified reference material (CRM) is not significantly different from a certified value of the material. Therefore, the method has proven to be accurate. All results showed the  $t_{calc} < t_{crit}$  at a 95% confidence limit, and there was no statistical difference between the mean values ant the true value. The calculated RSD was below 1% for all elements except SiO<sub>2</sub> which was 2% and still fell within the upper side of the acceptable limit of 2%. The Q test was used to determine if there were outliers on the obtained results. The results fell within the expected random error and were retained. The SiO<sub>2</sub> accuracy can be improved by preparing more standards at the high concentration range once available from the ore body to match the matrix. The  $t_{cal}$  of all

elements were less than the  $t_{crit}$ . This indicates that the mean of a set of results obtained from the analysis of a certified reference material (CRM) was not significantly different from a certified value of the material. Therefore, the method can produce accurate results.

#### 4.7.1.2. Low grade press pellets Method Precision

The in-house standard was used to test the method precision. 10 replicates of the same samples were prepared and analysed.

	Mn	Fe	CaO	MgO	SiO2	Al2O3	Р
RR1 -1	39.323	4.244	13.060	3.066	4.695	0.219	0.0197
RR1 -2	39.363	4.250	13.056	3.064	4.696	0.216	0.0195
RR1 -3	39.344	4.206	13.057	3.062	4.701	0.218	0.0196
RR1 -4	39.359	4.206	13.057	3.061	4.696	0.220	0.0197
RR1 -5	39.362	4.223	13.060	3.066	4.700	0.217	0.0196
RR1 -6	39.350	4.197	13.061	3.063	4.696	0.219	0.0195
RR1 -7	39.341	4.234	13.061	3.062	4.698	0.216	0.0197
RR1 -8	39.316	4.271	13.059	3.074	4.700	0.219	0.0195
RR1 -9	39.345	4.205	13.064	3.076	4.697	0.217	0.0197
RR1 -10	39.324	4.289	13.052	3.079	4.700	0.217	0.0194
SD	0.0169	0.0307	0.0033	0.0068	0.0022	0.0015	0.0001
Mean	39.34	4.23	13.06	3.07	4.70	0.22	0.02
RSD (< 1.0%)	0.0429	0.7260	0.0251	0.2214	0.0477	0.6732	0.0056
Uncertainty	0.0053	0.0097	0.0010	0.0021	0.0007	0.0005	0.0000

Table 4.22: Low grade precision test results

The precision standard deviation was calculated from 10 measurements of different pellets of the same sample as shown in Table 4.22. The RSD was used to evaluate the precision of the method and all elements were within the 1% criteria as prescribed by the ISO 17025 method validation criteria. The standard deviations are very low indicating slight deviation between obtained results. The% RSD of less than 1% supports the statement that the analytical method is capable of giving repeatable results and indicates good precision across all elements.

### 4.7.1.3. Low grade press pellets Instruments Precision

The sample was prepared from the low grade CRM Sarm 138. The same sample was analysed 10 times on the XRF.

	Mn	Fe	CaO	MgO	SiO2	Al2O3	Р
Sarm 138 -1	37.434	5.738	12.988	3.999	6.081	0.228	0.0203
Sarm 138 -2	37.427	5.742	12.993	4.006	6.083	0.228	0.0203
Sarm 138 -3	37.416	5.743	12.993	4.004	6.086	0.228	0.0203
Sarm 138 -4	37.436	5.742	12.985	4.005	6.085	0.228	0.0203
Sarm 138 -5	37.436	5.742	12.985	4.005	6.085	0.229	0.0204
Sarm 138 -6	37.444	5.742	12.990	4.006	6.087	0.228	0.0203
Sarm 138 -7	37.454	5.744	12.990	4.009	6.085	0.228	0.0203
Sarm 138 -8	37.449	5.742	12.995	4.008	6.083	0.228	0.0203
Sarm 138 -9	37.434	5.738	12.988	3.999	6.081	0.228	0.0203
Sarm 138 -10	37.447	5.745	12.992	4.014	6.084	0.228	0.0203
SD	0.0113	0.0022	0.0033	0.0047	0.0021	0.0003	0.000032
Mean	37.44	5.74	12.99	4.005	6.08	0.23	0.0203
RSD (< 0.2%)	0.0303	0.0376	0.0251	0.1164	0.0339	0.1433	0.1557
Uncertainty	0.003588	0.000683	0.001031	0.001474	0.000653	0.000103	0.000010

 Table 4.23: Low grade instruments precision results

From Table 4.23, the precision standard deviation was calculated from 10 measurements of the same pellets from the same sample. RSD is less than 0.2% which means the instrument is capable of producing good precision.

**4.7.1.4.** Low grade press pellets method uncertainty of measurement 10 different Press pellet samples were prepared from the same Sample. The same samples were analysed 10 times under the same conditions.

Table 4.24:	Reproducib	ility test for	measurements	uncertainty
		<i></i>		

SID1	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
NCS DC 28044-1	36.323	6.972	3.232	1.304	17.430	2.782	0.1381
NCS DC 28044-2	36.314	6.967	3.228	1.305	17.440	2.784	0.1383
NCS DC 28044-3	36.286	6.969	3.232	1.303	17.440	2.780	0.1380
NCS DC 28044-4	36.352	6.971	3.232	1.305	17.436	2.778	0.1381
NCS DC 28044-5	36.332	6.970	3.233	1.302	17.442	2.780	0.1379
NCS DC 28044-6	36.304	6.965	3.230	1.302	17.434	2.778	0.1376
NCS DC 28044-7	36.313	6.969	3.232	1.302	17.436	2.782	0.1377
NCS DC 28044-8	36.305	6.969	3.228	1.302	17.416	2.774	0.1376
NCS DC 28044-9	36.322	6.969	3.229	1.300	17.389	2.773	0.1376
NCS DC 28044-10	36.282	6.964	3.227	1.299	17.401	2.779	0.1369
Average	36.313	6.968	3.230	1.302	17.426	2.779	0.1378
Standard deviation	0.021	0.002	0.002	0.002	0.018	0.004	0.0004
RSD	0.058	0.033	0.066	0.144	0.105	0.127	0.288
Uncertainty	0.009	0.001	0.001	0.001	0.007	0.001	0.00016
% Inst. Repeatability	0.058	0.033	0.066	0.144	0.105	0.127	0.288
% Inst. Total. (U)	0.009	0.001	0.001	0.001	0.007	0.001	0.0002
% Total Instrument	0.012	<u>I</u>		1	1	J	1
(U)							

Table 4.25: Repeatability test for measurements uncertainty

SID1	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
PE-FY 14 COMP 10	37.490	4.047	15.929	2.847	4.162	0.178	0.02
PE-FY 14 COMP 9	37.597	4.148	15.810	2.857	4.172	0.182	0.02
PE-FY 14 COMP 8	37.562	4.097	15.807	2.845	4.158	0.177	0.02
PE-FY 14 COMP 7	37.588	4.143	15.762	2.847	4.168	0.174	0.02
PE-FY 14 COMP 6	37.626	4.082	15.795	2.850	4.164	0.178	0.02
PE-FY 14 COMP 5	37.523	4.105	15.871	2.850	4.159	0.179	0.02
PE-FY 14 COMP 4	37.576	4.057	15.774	2.843	4.161	0.180	0.02
PE-FY 14 COMP 3	37.594	4.106	15.738	2.849	4.169	0.190	0.02
PE-FY 14 COMP 2	37.562	4.092	15.775	2.843	4.168	0.176	0.02
PE-FY 14 COMP 1	37.705	4.033	15.718	2.854	4.181	0.179	0.02
Average	37.582	4.091	15.798	2.848	4.166	0.179	0.02
Std. Deviation	0.058	0.038	0.063	0.005	0.007	0.004	0.000
RSD	0.155	0.930	0.396	0.158	0.167	2.329	1.045
Uncertainty	0.018	0.012	0.020	0.001	0.002	0.001	0.000
Repeatability	0.155	0.930	0.396	0.158	0.167	2.329	1.045
(U)	0.018	0.012	0.020	0.001	0.002	0.001	0.000
% Total (U)	0.030			1	1	1	1

Eight different analysts were given the same sample to prepare and analysed under the same conditions.

Table 4.26: Analyst comparison results

Analyst	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
Analyst 1	39.419	4.217	13.056	2.883	4.749	0.206	0.0192
Analyst 2	39.387	4.216	13.056	2.886	4.741	0.209	0.0192
Analyst 3	39.430	4.210	13.035	2.863	4.751	0.220	0.0192
Analyst 4	39.402	4.217	13.054	2.902	4.734	0.205	0.0192
Analyst 5	39.424	4.217	13.063	2.929	4.731	0.202	0.0191
Analyst 6	39.443	4.210	13.051	2.953	4.711	0.197	0.0192
Analyst 7	39.424	4.214	13.050	2.951	4.713	0.196	0.0191
Analyst 8	39.447	4.221	13.091	2.907	4.726	0.204	0.0192
Average	39.422	4.215	13.057	2.909	4.732	0.205	0.019
Std.	0.020	0.004	0.016	0.033	0.015	0.008	0.000
RSD	0.050	0.090	0.122	1.123	0.318	3.688	0.241
Uncertainty	0.008	0.002	0.007	0.013	0.006	0.003	0.000
% Inst. Repeatability	0.050	0.090	0.122	1.123	0.318	3.688	0.241
% Analyst	0.008	0.002	0.007	0.013	0.006	0.003	0.000
Total. (U)							
% Total	0.018						
Analyst (U)							

Therefore total % uncertainty for low grade press pellets based on the whole step from Table 4.24 to 4.26 of analysis is 0.324%.

	-					0	
Table 4 27+1 ow	grade press	nellets	method	total	uncertainty	v of measur	ement
1 doie 4.27. Low	grade press	penets	memou	ioiai	uncertaint	y or measur	omont

Parameters	Uncertainty (%)
Low grade method	0.012
Calibration	0.321
Instrumentation	0.030
Analyst	0.018
Total (U)	0.324

## 4.7.1.5. Accuracy test using recovery

To test for accuracy the recovery method was also used. Two CRMs and one secondary standard were in the same conditions as the routine samples and analysed. The acceptable mean percentage recovery is within 90 to 110% of the true value.

 Table 4.28: Instruments results

Instrument results							
CRM Name	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
RR1	39.3621	4.2232	13.0604	3.0664	4.7003	0.2172	0.0196
Sarm 138	37.4341	5.7383	12.988	3.9985	6.081	0.2176	0.0183
SARM 17	38.813	4.2761	14.4006	3.0374	4.6734	0.2389	0.0179

Table 4.29: Standard true value

True value							
Name	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
RR1	39.4	4.2	13.11	3.11	4.65	0.22	0.02
Sarm 138	37.5	5.74	13.01	3.81	6.06	0.198	0.0175
SARM 17	38.81	4.27	14.4	3.03	4.69	0.24	0.018

The mean recovery is within 90 to 110% of the true value which is acceptable level.

Recovery							
Name	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
RR1	100.096	99.451	100.380	101.422	98.930	101.289	102.041
Sarm 138	100.176	100.030	100.169	95.286	99.655	90.993	95.628
SARM 17	99.992	99.857	99.996	99.756	100.355	100.460	100.559

Table 4.30: Low grade press pellets mean recovery

All elements recovery was between the acceptable range which indicates the method was capable of producing accurate and precise results as shown in Table 4.30. The method was found to be produce accurate results when compared to the known values.

# 4.7.2. High grade press pellets method

High grade press pellets method regression lines

Table 4.31: Mn linearity and regression

Mn summary output					
Regression Statistics					
Multiple R	0.99972				
R Square	0.99944				
Adjusted R Square	0.99941				
Standard Error	0.2975				
Observations	25.0000				
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	360028.5	360028.5	40697	7.30326E-39
Residual	23	203.5	8.8		
Total	24	360232.0			
	Coefficients	Standard Error	t Stat	P-value	Lower 95%
Intercept	-8.22527	2.13021	-3.86125	0.00079	-12.63195
X Variable 1	9.99529	0.04955	201.73565	0.00000	9.89280

#### Mn linearity /regression, CI, sensitivity, LOD and LOQ

#### F-test for significance of linearity

 $F_{calc} > 40697$ 

 $F_{crit} = 1.984$ 

Since  $F_{calc} > F_{crit}$ , linearity/regression is proven to be significant.

#### T-test for significance of linearity

 $H_o (r = 0)$ , and there's no linear relation between x and y.

 $H_1$  (r > 0), and there's a significant linearity.

Two tailed test

 $t_{calc} = 201.736$ 

 $t_{crit} = 2.064$ 

 $t_{calc} > t_{crit}$ , therefore reject  $H_0$  and it points out to a significant linearity.

 $t_{calc} > t_{crit}$  then there is significant linearity between x and y.

#### Regression parameters

Slope (b) = 9.995

Intercept (a) = -8.2253

Therefore, Regression Line: y = bx + a

Y = 9.995x - 8.2253

#### Calibration uncertainty

Random calibration uncertainty  $(S_{y/x}) = 0.2975$ 

Uncertainty in the Slope  $(S_b) = 0.0495$ 

Uncertainty in the Intercept  $(S_a) = 2.1302$ 

Total calibration uncertainty is the combination of individual calibration uncertainty.

$$U = \sqrt{(Sy/x)^2 + (Sa)^2 + (Sb)^2}$$

U = 2.151

 $S_b < S_a$ , therefore the range of standards is wide enough.

$$S_a/S_b = 42.994$$

#### The confidence interval (CI) for slope (b) and intercept

Where t is the two-tailed t critical value at the required significance level (typically  $\alpha = 0.05$ ) with degrees of freedom = n-2 for the number of standards used in the regression.

 $T_{crit} = 2.10$  $b = b \pm t \cdot sb$  $b = b + t \cdot sb$ 95% CI of b = 10.0978  $b = b - t \cdot sb$ 95% CI of b = 9.8928 95% CI of b: 10.098 < b < 9.893  $a = a \pm t \cdot sa$  $a = a + t \cdot sa$ 95% CI of a = -3.8186  $a = a - t \cdot sa$ 95% CI of a = -12.6319 95% CI of a: -3.8186 < a < -12.6319 Calibration sensitivity b = 9.995

b not equal 0, therefore calibration sensitivity is satisfactory.

Limit of detection (LOD)

$$X_{LOD} = \frac{3\text{Ss/y}}{b}$$
$$X_{LOD} = 0.0893$$
$$\underline{\text{Limit of quantification (LOQ)}}$$
$$X_{LOQ} = \frac{(10\text{Ss/y})}{b}$$

 $X_{\text{LOQ}} = 0.2976$ 

The LOD and LOQ units are percentages.

Therefore, this method can only detect  $Al_2O_3 > 0.0893$ , and quantify  $Al_2O_3 > 0.2976$ .

Table 4 32	High	orade Mn	regression	summary
1 auto 4.52.	rngn	graue win	regression	summar y

Conclusion	Description		Mn
	Observations (n)	Number of	25
		standards analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9997
Sy/x very low indicate good	Standard error (Sy/x)	Random	0.2975
precision and accuracy		calibration	
		uncertainty	
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in	0.0495
precision	Error (Sb)	slope	
	Intercept Standard Error	Uncertainty in	2.1302
	(Sa)	intercept	
linear regression	Regression line (y= bx +	a)	Y=9.995x -
			8.2253
Calibration line intercept	Intercept (a)	Calibration line	-8.2253
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line	9.9953
sensitive to the analyte		slope	
LOD	Lowest distinguishable s	0.0893	
LOQ	LOQ > lowest calibratio	0.2976	
Analytical working range	Max	Highest CRM	60.6430
	Min	LOD	0.0893

Summary output		]			
Regression Statistics		_			
Multiple R	0.9992	_			
R Square	0.9984	_			
Adjusted R Square	0.9983	_			
Standard Error	0.2358	_			
Observations	22	_			
		-			
ANOVA		-			
	df	SS	MS	F	Significance F
Regression	1	3220488.9	3220488.9	12211.8	2.408E-29
Residual	20	5274.4	263.7		
Total	21	3225763.3			
	Coefficients	Standard Error	t Stat	P-value	Lower 95%
Intercept	62.5043	8.1165	7.7009	0.0000	45.5736
X Variable 1	68.8081	0.6227	110.5072	0.0000	67.5093

Table 4.33: Fe linearity /regression, CI, sensitivity, LOD and LOQ

Table 4.34: High grade Fe regression summary

Conclusion	Description		Fe
	Observations (n)	Number of	22
		standards	
		analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9992
Sy/x very low indicate good	Standard error (Sy/x)	Random	0.2358
precision and accuracy		calibration	
		uncertainty	
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in	0.6227
precision	Error (Sb)	slope	
	Intercept Standard	Uncertainty in	8.1165
	Error (Sa)	intercept	
linear regression	Regression line (y= bx +	Y=68.808x	
			+62.5043
Calibration line intercept	Intercept (a)	Calibration line	62.5043
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line	68.8081
sensitive to the analyte		slope	
LOD	Lowest distinguishable s	0.0103	
LOQ	LOQ > lowest calibratio	0.0343	
Analytical working range	Max	Highest CRM	19.2600
	Min	LOD	0.0103

Summary output					
Regression Statistics					
Multiple R	0.9998				
R Square	0.9997				
Adjusted R Square	0.9997				
Standard Error	0.0575				
Observations	23	-			
		-			
ANOVA		J			
	df	SS	MS	F	Significance F
Regression	1	71439	71439	66049	3.2284E-38
Residual	21	23	1		
Total	22	71461			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	3.6547	0.5911	6.1830	0.000004	2.4254
X Variable 1	18.0897	0.0704	256.9999	3.2284E-38	17.9433

# Table 4.35: CaO linearity /regression, CI, sensitivity, LOD and LOQ

Table 4.36: High grade CaO regression summary

Conclusion	Description		CaO
	Observations (n)	Number of	23
		standards	
		analysed	
It shows a linear trend	Multiple R (r)	Regression	0.9998
		value	
Sy/x very low indicate good	Standard error (Sy/x)	Random	0.0575
precision and accuracy		calibration	
		uncertainty	
Sb < Sa Good general	X Variable 1 Standard	Uncertainty	0.0704
precision	Error (Sb)	in slope	
	Intercept Standard Error	Uncertainty	0.5911
	(Sa)	in intercept	
linear regression	Regression line (y= bx +	a)	Y = 18.090x + 3.6547
Calibration line intercept	Intercept (a)	Calibration	3.6547
		line intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration	18.0897
sensitive to the analyte		line slope	
LOD	Lowest distinguishable s	ignal	0.0095
LOQ	LOQ > lowest calibratio	n standard	0.0318
Analytical working range	Max	Highest	15.0910
		CRM	
	Min	LOD	0.0095

Summary output					
Regression Statistics					
Multiple R	0.9999				
R Square	0.9997				
Adjusted R Square	0.9997				
Standard Error	0.0783				
Observations	19				
		_			
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	49386	49386	56801	2.1187E-31
Residual	17	15	1		
Total	18	49401			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	5.8258	0.2631	22.1463	0.000000	5.2708
X Variable 1	11.9013	0.0499	238.3296	2.1187E-31	11.7959

Table 4.37: MgO linearity /regression, CI, sensitivity, LOD and LOQ

Table 4-38+	High	orade MoO	regression	summary
10010 1.50.	ingn	Sidde Migo	10510551011	Summary

Conclusion	Description		MgO
	Observations (n)	Number of	19
		standards analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9999
Sy/x very low indicate	Standard error (Sy/x)	Random	0.0783
good precision and		calibration	
accuracy		uncertainty	
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in	0.0499
precision	Error (Sb)	slope	
	Intercept Standard Error	Uncertainty in	0.2631
	(Sa)	intercept	
linear regression	Regression line $(y = bx + a)$	)	Y= 11.901x +5.8258
Calibration line intercept	Intercept (a)	Calibration line	5.8258
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line	11.9013
sensitive to the analyte		slope	
LOD	Lowest distinguishable sig	0.0197	
LOQ	LOQ > lowest calibration	standard	0.0658
Analytical working range	Max	Highest CRM	16.0667
	Min	LOD	0.0197

Summary output					
Regression Statistics					
Multiple R	1.0000				
R Square	0.9999	-			
Adjusted R Square	0.9999	-			
Standard Error	0.0337				
Observations	21				
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	113598	113598	228621	3.112E-40
Residual	19	9	0		
Total	20	113607			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	-16.2179	0.3129	-51.8295	0.000000	-16.8729
X Variable 1	20.9079	0.0437	478.1438	3.11224E-40	20.8164

Table 4.39: SiO<sub>2</sub> linearity /regression, CI, sensitivity, LOD and LOQ

Table 4.40:	High	grade	SiO <sub>2</sub>	regression	summary
1 4010 1.10.	1 ngn	Since	0102	10510551011	Summary

Conclusion	Description		SiO <sub>2</sub>
	Observations (n)	Number of	21
		standards analysed	
It shows a linear trend	Multiple R (r)	Regression value	1.0000
Sy/x very low indicate	Standard error (Sy/x)	Random calibration	0.0337
good precision and		uncertainty	
accuracy			
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.0437
precision	Error (Sb)		
	Intercept Standard Error	Uncertainty in	0.3129
	(Sa)	intercept	
linear regression	Regression line ( $y=bx + a$	Y= 20.980 -	
			16.2179
Calibration line intercept	Intercept (a)	Calibration line	-16.2179
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line	20.9079
sensitive to the analyte		slope	
LOD	Lowest distinguishable sig	0.0048	
LOQ	LOQ > lowest calibration	standard	0.0161
Analytical working range	Max	Highest CRM	17.4561
	Min	LOD	0.0048

Summary output					
Regression Statistics		-			
Multiple R	0.9996	-			
R Square	0.9991	-			
Adjusted R Square	0.9991	-			
Standard Error	0.0392	-			
Observations	19	-			
ANOVA		-			
	df	SS	MS	F	Significance F
Regression	1	1856	1856	19256	2.07594E-27
Residual	17	2	0		
Total	18	1857			
	Coefficients	Standard Error	t Stat	P-value	Lower 95%
Intercept	0.4265	0.0969	4.4032	0.000389	0.2221
X Variable 1	7.9202	0.0571	138.7667	2.0764E-27	7.7998

# Table 4.41: Al<sub>2</sub>O<sub>3</sub> linearity /regression, CI, sensitivity, LOD and LOQ

Conclusion	Description		Al <sub>2</sub> O <sub>3</sub>
	Observations (n)	Number of standards	19
		analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9996
Sy/x very low indicate	Standard error (Sy/x)	Random calibration	0.0392
good precision and		uncertainty	
accuracy			
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.0571
precision	Error (Sb)		
	Intercept Standard Error	Uncertainty in intercept	0.0969
	(Sa)		
linear regression	Regression line ( $y=bx + a$ )		Y= 7.920x +
			0.4265
Calibration line intercept	Intercept (a)	Calibration line	0.4265
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line slope	7.9202
sensitive to the analyte			
LOD	Lowest distinguishable sig	0.0148	
LOQ	LOQ > lowest calibration s	standard	0.0495
Analytical working range	Max	Highest CRM	4.1950
	Min	LOD	0.0148

Table 4.42: High grade  $Al_2O_3$  regression summary

Summary output					
Regression Statistics					
Multiple R	0.9996	-			
R Square	0.9991				
Adjusted R Square	0.9991				
Standard Error	0.0010	-			
Observations	19	-			
		-			
ANOVA		-			
	df	SS	MS	F	Significance F
Regression	1	1856	1856	19256	2.07594E-27
Residual	17	2	0		
Total	18	1857			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	0.4265	0.0969	4.4032	0.000389	0.2221
X Variable 1	7.9202	0.0571	138.7667	2.07594E-27	7.7998

# Table 4.43: P linearity /regression, CI, sensitivity, LOD and LOQ

Table 4.44: High grade P regression summary

Conclusion	Description		Р
	Observations (n)	Number of standards	19
		analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.9996
Sy/x very low indicate	Standard error (Sy/x)	Random calibration	0.0010
good precision and		uncertainty	
accuracy			
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.0571
precision	Error (Sb)		
	Intercept Standard Error	Uncertainty in	0.0969
	(Sa)	intercept	
linear regression	Regression line $(y=bx + a)$		Y=7.920x + 0.4265
Calibration line	Intercept (a)	Calibration line	0.4265
intercept		intercept	
Since Slope is > 1 thus	X Variable 1 (b)	Calibration line	7.9202
is sensitive to the		slope	
analyte			
LOD	Lowest distinguishable sig	0.0004	
LOQ	LOQ > lowest calibration s	standard	0.0012
Analytical working	Max	Highest CRM	4.1950
range	Min	LOD	0.0004

#### 4.7.2.1. High grade press pellets accuracy

Table 4.45: High grade press pellets accuracy test

Name	Mn	Fe	CaO	MgO	SiO2	Al2O3	Р
AMIS 402-1	43.71	15.09	5.71	0.49	4.21	0.402	0.0413
AMIS 402-2	43.37	15.42	5.65	0.50	4.22	0.417	0.0449
AMIS 402-3	44.18	15.87	5.69	0.57	4.17	0.328	0.0420
AMIS 402-4	44.28	15.67	5.69	0.47	4.37	0.378	0.0420
AMIS 402-5	43.98	15.09	5.29	0.49	4.23	0.383	0.0460
AMIS 402-6	43.90	15.34	5.33	0.57	4.34	0.427	0.0420
AMIS 402-7	43.81	15.45	5.69	0.58	4.37	0.386	0.0408
AMIS 402-8	44.10	15.40	5.58	0.53	4.21	0.410	0.0600
AMIS 402-9	44.08	15.49	5.67	0.59	4.35	0.350	0.0457
AMIS 402-10	44.10	15.60	5.63	0.54	4.36	0.395	0.0440
Mean	43.95	15.44	5.59	0.53	4.28	0.39	0.0449
SD	0.2655	0.2416	0.1538	0.0418	0.0806	0.0302	0.0056
RSD	0.6042	1.5647	2.7504	7.8553	1.8807	7.8030	12.5598
True Value	43.97	15.47	5.70	0.54	4.31	0.380	0.044
Tcalc	-0.21	-0.37	-2.10	-0.53	-0.98	0.75	0.65
Tcrit	2.262	2.262	2.262	2.262	2.262	2.262	2.262
Comment	$t_{calc} < t_{crit}$						
Uncertainty	0.0840	0.0764	0.0486	0.0132	0.0255	0.0096	0.0018

The mean of a set of results obtained from Table 4.45 indicates that the analysis of a certified reference material (CRM) is not significantly different from a certified value of the material. Therefore, the method has been proven to be accurate. All results showed the  $t_{calc} < t_{crit}$  at a 95% confidence limit, there is no statistical difference between the mean values of Amis 402 and the true value. The calculated RSD was below 1% for Mn only. The RSD of all other elements were higher than 1%. There were no outliers according to the Q test on the obtained results. The results fell within the expected random error and were retained. The  $t_{cal}$  of all elements were less than the  $t_{crit}$  which means that mean of a set of results obtained from the analysis of a certified reference material (CRM) are not significantly different from a certified value of the material therefore the method can produce accurate results.

### 4.7.2.2. High grade press pellets method precision

The in-house standard was used to test method precision. 10 replicates of the same samples were prepared and analysed.

	Mn	Fe	CaO	MgO	SiO2	Al2O3	Р
W4L40 1	44.360	13.140	6.750	0.785	4.740	0.371	0.0330
W4L40 2	44.270	13.060	6.730	0.788	4.730	0.373	0.0340
W4L40 3	44.290	13.170	6.760	0.791	4.760	0.374	0.0350
W4L404	44.320	13.110	6.740	0.789	4.770	0.373	0.0340
W4L40 5	44.250	13.070	6.720	0.785	4.740	0.372	0.0340
W4L40 6	44.130	13.100	6.720	0.787	4.740	0.371	0.0330
W4L407	44.230	13.070	6.720	0.783	4.740	0.372	0.0330
W4L40 8	44.250	13.070	6.720	0.781	4.740	0.372	0.0340
W4L409	44.250	13.090	6.740	0.803	4.730	0.372	0.0340
W4L40 10	44.230	13.070	6.750	0.774	4.730	0.370	0.0340
SD	0.0611	0.0360	0.0151	0.0075	0.0132	0.0012	0.0006
Mean	44.26	13.10	6.74	0.79	4.74	0.37	0.03
RSD (<	0.1380	0.2747	0.2241	0.9517	0.2776	0.3104	0.0187
1.0%)							
Uncertainty	0.0193	0.0114	0.0048	0.0024	0.0042	0.0004	0.0002

Table 4.46: High grade precision results

The method precision standard deviation in Table 4.46 was calculated from 10 measurements of different pellets of the same sample. The RSD was used to evaluate the precision of the method and all elements were within the 1% criteria as prescribed by the ISO 17025 method validation criteria. The standard deviations are very low indicating minor deviation between obtained results. The % RSD of less than 1% which supports the statement that the analytical method is capable of giving repeatable results and indicates good precision across all elements.

### 4.7.2.3. High grade press pellets instruments precision

The sample was prepared from the Wessels type ore. The sample was analysed 10 times on the XRF.

	Mn	Fe	CaO	MgO	SiO2	Al2O3	Р
WES-4 1	43.380	13.050	7.010	0.987	5.850	0.426	0.0350
WES-4 2	43.370	13.060	7.010	0.985	5.850	0.427	0.0350
WES-4 3	43.380	13.050	7.010	0.988	5.840	0.427	0.0350
WES-4 4	43.380	13.060	7.010	0.991	5.840	0.425	0.0350
WES-4 5	43.390	13.050	7.010	0.990	5.850	0.426	0.0350
WES-4 6	43.370	13.060	7.000	0.987	5.850	0.426	0.0350
WES-4 7	43.350	13.060	7.010	0.988	5.840	0.426	0.0350
WES-4 8	43.370	13.060	7.010	0.991	5.840	0.426	0.0350
WES-4 9	43.370	13.060	7.010	0.987	5.850	0.426	0.0350
WES-4 10	43.350	13.070	7.010	0.989	5.840	0.427	0.0350
SD	0.0129	0.0063	0.0032	0.0019	0.0053	0.0006	0.000000
Mean	43.37	13.06	7.01	0.988	5.85	0.43	0.0350
RSD (< 0.2%)	0.0297	0.0484	0.0451	0.1970	0.0902	0.1484	0.0000
Uncertainty	0.004069	0.002000	0.001000	0.000616	0.001667	0.000200	0.000000

Table 4.47: High grade instrument precision results

The precision standard deviation in Table 4.47 was calculated from 10 measurements of the same pellets from the same sample. RSD is less than 0.2% which means the instrument is capable of producing good precision.

4.7.2.4.	High grade press pellets method uncertainty of measuremen
Table 4.48: Hi	h grade press pellets method measurement uncertainty

Parameters	Uncertainty (%)
High grade method	0.029
Calibration	0.395
Instrument	0.005
Analyst	0.032
Total (U)	0.398

Therefore total % uncertainty in Table 4.48 for high grade press pellets method based on the whole step of analysis is 0.398%.

### 4.7.2.5. Accuracy test using recovery

The precision of the high grade press pellets method was determined by the mean percentage recovery of each element in the three standards. The acceptable mean percentage recovery is within 90 to 110% of the true value.

Instruments results								
CRM Name	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P	
Sarm 135	43.109	15.998	6.3821	0.43	4.411	0.313	0.02675	
Sarm 136	46.240	10.200	7.550	0.740	3.800	0.290	0.02547	
AMIS 402	44.051	15.329	5.539	0.591	4.297	0.361	0.047	

Table 4.49: Standards results

Table 4.50: CRM true value

CRM true value							
CRM Name	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
Sarm 135	42.500	16.600	6.320	0.463	4.210	0.293	0.026
Sarm 136	46.900	10.370	7.130	0.739	3.890	0.271	0.026
AMIS 402	43.970	15.471	5.700	0.540	4.310	0.380	0.044

 Table 4.51: High grade press pellets mean recovery

Percentage recovery								
CRM Name	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P	
Sarm 135	101.433	96.373	100.983	92.873	104.774	106.826	104.902	
Sarm 136	98.593	98.361	105.891	100.135	97.686	107.011	97.586	
AMIS 402	100.185	99.080	97.180	109.450	99.693	95.016	108.395	

All elements recovery is between the acceptable range which indicates the method was capable of producing accurate and precise results. The method was found to produce accurate results when compared to the known values of the CRM.

## 4.7.3. Kalahari fusion method

Kalahari fusion method regression lines

Table 4.52: Mn linearity /regression, CI, sensitivity, LOD and LOQ

Summary outpu	t					
Regression Stati	stics					
Multiple R		0.999968469				
R Square		0.999936938				
Adjusted R Squ	are	0.999933785				
Standard Error		0.199154177				
Observations		22				
ANOVA						
	df	SS	MS	F	Significance F	
Regression	1	81161.59	81162	317129	1.7557E-43	
Residual	20	5.12	0.25593			
Total	21	81166.71				
	Coefficients	Standard	t Stat	P-value	Lower 95%	Upper 95%
		Error				
Intercept	0.4816	0.1395	3.4533	0.002512	0.190703	0.772559
X Variable 1	2.7205	0.0048	563.1421	1.8E-43	2.7E+00	2.7E+00

Conclusion	Description		Mn
	Observations (n)	Number of standards	22
		analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.99997
Sy/x very low indicate good	Standard error (Sy/x)	Random calibration	0.1992
precision and accuracy		uncertainty	
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.0048
precision	Error (Sb)		
	Intercept Standard Error	Uncertainty in	0.1395
	(Sa)	intercept	
linear regression	Regression line (y= bx +	Y=2.721x+0.4816	
Calibration line intercept	Intercept (a)	Calibration line	0.4816
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line slope	2.7205
sensitive to the analyte			
LOD	Lowest distinguishable s	0.2196	
LOQ	LOQ > lowest calibration	0.7320	
Analytical working range	Max	Highest CRM	67.5605
	Min	LOD	0.2196

Table 4.53: Kalahari fusion method Mn regression summary

Summary output					
Regression Statistics	3				
Multiple R	0.999977582	-			
R Square	0.999955164	-			
Adjusted R Square	0.999952527	-			
Standard Error	0.103234707	-			
Observations	19	-			
		-			
ANOVA		-			
	df	SS	MS	F	Significance F
Regression	1	268951.54	268952	379143	2.0853E-38
Residual	17	12.06	0.70937		
Total	18	268963.60			
	Coefficients	Standard Error	t Stat	P-value	Lower 95%
Intercept	1.9214	0.2700	7.1172	0.000002	1.351793
X Variable 1	8.1583	0.0132	615.75	2.1E-38	8.1863

# Table 4.54: Fe linearity /regression, CI, sensitivity, LOD and LOQ

Table 4 55.	Valahami	function	E.		011 /00 /00 0 /// X
1 able 4 35	Kalanari	Inston	ге	regression	summary
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Conclusion	Description		Fe		
	Observations (n)	Number of standards	19		
		analysed			
It shows a linear trend	Multiple R (r)	Regression value	0.99998		
Sy/x very low indicate	Standard error (Sy/x)	Random calibration	0.1032		
good precision and		uncertainty			
accuracy					
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.0132		
precision	Error (Sb)				
	Intercept Standard	Uncertainty in	0.2700		
	Error (Sa)	intercept			
linear regression	Regression line (y= bx +	- a)	Y=8.158x- 1.9214		
Calibration line intercept	Intercept (a)	Calibration line	1.9214		
		intercept			
Since Slope is > 1 thus is	X Variable 1 (b)	Calibration line	8.1583		
sensitive to the analyte		slope			
LOD	Lowest distinguishable	0.0380			
LOQ	LOQ > lowest calibration	0.1265			
Analytical working range	Max	Highest CRM	55.7524		
	Min	LOD	0.0380		
Summary output					
-----------------------	--------------	----------	---------	----------	----------------
Regression Statistics	3	-			
Multiple R	0.99998981	-			
R Square	0.99997962	-			
Adjusted R Square	0.999978347	-			
Standard Error	0.049764398	-			
Observations	18	-			
		-			
ANOVA		-			
	df	SS	MS	F	Significance F
Regression	1	4417.81	4418	785080	5.84358E-39
Residual	16	0.09	0.00563		
Total	17	4417.90			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	0.8140	0.0231	35.304	0.000000	0.7651
X Variable 1	1 5074	0.0017	886.048	5 8E 20	1 504

Table 4.56: CaO linearity /regression, CI, sensitivity, LOD and LOQ

Conclusion	Description		CaO
	Observations (n)	Number of standards	18
		analysed	
It shows a linear trend	Multiple R (r)	0.99999	
Sy/x very low indicate	Standard error (Sy/x)	Random calibration	0.0498
good precision and		uncertainty	
accuracy			
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.0017
precision	Error (Sb)		
	Intercept Standard	0.0231	
	Error (Sa)		
linear regression	Regression line (y= bx +	y=1.507x+ 0.8140	
Calibration line intercept	Intercept (a)	Calibration line	0.8140
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line slope	1.5074
sensitive to the analyte			
LOD	Lowest distinguishable	0.0990	
LOQ	LOQ > lowest calibration	0.3301	
Analytical working range	Max	Highest CRM	32.9574
	Min	LOD	0.0990

Table 4.57: Kalahari fusion CaO regression summary

# Table 4.58: MgO linearity /regression, CI, sensitivity, LOD and LOQ

# Summary output

Regression Statistics	8				
Multiple R	0.999967429				
R Square	0.999934859	-			
Adjusted R Square	0.999929431	-			
Standard Error	0.058455673	-			
Observations	14				
		-			
ANOVA		-			
	df	SS	MS	F	Significance F
Regression	1	145.29	145	184205	1.72361E-26
Residual	12	0.01	0.00079		
Total	13	145.30			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	0.7476	0.0092	80.8909	8.5E-18	0.727424
X Variable 1	0.4804	0.0011	429.1907	1.7E-26	0.4780

Table 4.59: Kalahari fusion MgO regression summary

Conclusion	Description		MgO		
	Observations (n)	Number of	14		
		standards analysed			
It shows a linear trend	Multiple R (r)	Regression value	0.99997		
Sy/x very low indicate	Standard error (Sy/x)	Random	0.0585		
good precision and		calibration			
accuracy		uncertainty			
Sb < Sa Good general	X Variable 1	Uncertainty in	0.0011		
precision	Standard Error (Sb)	slope			
	Intercept Standard	Uncertainty in	0.0092		
	Error (Sa)	intercept			
linear regression	Regression line (y= bx	Regression line $(y=bx + a)$			
Calibration line	Intercept (a)	Calibration line	0.7476		
intercept		intercept			
Since Slope is > 1 thus	X Variable 1 (b)	Calibration line	0.4804		
is sensitive to the		slope			
analyte					
LOD	Lowest distinguishabl	0.3650			
LOQ	LOQ > lowest calibra	tion standard	1.2167		
Analytical working	Max	Highest CRM	20.9700		
range	Min	LOD	0.3650		

Summary output					
Regression Statistics	3	-			
Multiple R	0.99988966	-			
R Square	0.999779333	-			
Adjusted R Square	0.999767073	-			
Standard Error	0.245467234	-			
Observations	20	-			
		-			
ANOVA		-			
	df	SS	MS	F	Significance F
Regression	1	13567.93	13568	81553	2.30125E-34
Residual	18	2.99	0.16637		
Total	19	13570.92			
	Coefficients	Standard Error	t Stat	P-value	Lower 95%
Intercept	0.0620	0.1328	0.4665	0.64645	-0.2171
X Variable 1	1.6615	0.0058	285.574	2.3E-34	1.6493

Table 4.60: SiO<sub>2</sub> linearity /regression, CI, sensitivity, LOD and LOQ

Table 4.61:	Kalahari	fusion	SiO <sub>2</sub>	regression	summarv
14010 1.01.	1 Sulullul I	rabion	0102	regression	Summary

Conclusion	Description		SiO <sub>2</sub>
	Observations (n)	Number of standards	20
		analysed	
It shows a linear trend	Multiple R (r)	0.99989	
Sy/x very low indicate good	Standard error (Sy/x)	Random calibration	0.2455
precision and accuracy			
Sb < Sa Good general	X Variable 1 Standard	0.0058	
precision	Error (Sb)		
	Intercept Standard Error	0.1328	
	(Sa)	intercept	
linear regression	Regression line (y= bx +	Y=1.661x+0.062	
Calibration line intercept	Intercept (a)	Calibration line	0.0620
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line slope	1.6615
sensitive to the analyte			
LOD	Lowest distinguishable s	0.4432	
LOQ	LOQ > lowest calibratio	n standard	1.4774
Analytical working range	Max	60.3250	

Table / 6/2. Al. (), Incority regression ('Legnestivity I ()) and	
1 a U C + 0 L. $A D C 3 m C a m C 4 D C 5 0 0 1. C1. SCH SH V H V. LOD and$	LUU

Summary output					
Regression Statistics	8				
Multiple R	0.999801637				
R Square	0.999603312				
Adjusted R Square	0.999576867				
Standard Error	0.097171802				
Observations	17				
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	185.63	186	37798	6.23881E-27
Residual	15	0.07	0.00491		
Total	16	185.70			
	Coefficients	Standard Error	t Stat	P-value	Lower 95%
Intercept	0.3006	0.0267	11.2505	1.0E-08	0.2437
X Variable 1	0.7210	0.0037	194.4174	6.2E-27	0.7131

Conclusion	Description		Al <sub>2</sub> O <sub>3</sub>
	Observations (n)	Number of standards	17
		analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.99980
Sy/x very low indicate good	Standard error (Sy/x)	Random calibration	0.0972
precision and accuracy		uncertainty	
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.0037
precision	Error (Sb)		
	Intercept Standard Error	Uncertainty in	0.0267
	(Sa)	intercept	
linear regression	Regression line (y= bx +	Y=0.721x+ 0.3006	
Calibration line intercept	Intercept (a)	Calibration line	0.3006
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line slope	0.7210
sensitive to the analyte			
LOD	Lowest distinguishable s	0.4043	
LOQ	LOQ > lowest calibration	n standard	1.3477
Analytical working range	Max	Highest CRM	17.0072
	Min	LOD	0.4043

# Table 4.63: Kalahari fusion $Al_2O_3$ regression summary

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Table 4.64: P	linearity	/regression,	CI,	sensitivity	, LOD	and LOQ

Summary output					
Regression Statistics					
Multiple R	0.999877811				
R Square	0.999755637	-			
Adjusted R Square	0.999742776				
Standard Error	0.005911469	_			
Observations	21	-			
		-			
ANOVA					
	df	SS	MS	F	Significance F
Regression	1	78.84	79	77734	8.77468E-36
Residual	19	0.02	0.00101		
Total	20	78.86			
	Coefficients	Standard	t Stat	P-value	Lower 95%
		Error			
Intercept	0.2742	0.0080	34.157	1.6E-18	0.2574
X Variable 1	5.3867	0.0193	278.809	8.8E-36	5.3463

	1		1
Conclusion	Description		Р
	Observations (n)	Number of standards	21
		analysed	
It shows a linear trend	Multiple R (r)	Regression value	0.99988
Sy/x very low indicate good	Standard error (Sy/x)	Random calibration	0.0059
precision and accuracy		uncertainty	
Sb < Sa Good general	X Variable 1 Standard	Uncertainty in slope	0.0193
precision	Error (Sb)		
	Intercept Standard Error	Uncertainty in	0.0080
	(Sa)	intercept	
linear regression	Regression line $(y = bx + b)$	a)	Y=5.387 + 0.2742
Calibration line intercept	Intercept (a)	Calibration line	0.2742
		intercept	
Since Slope is $> 1$ thus is	X Variable 1 (b)	Calibration line slope	5.3867
sensitive to the analyte			
LOD	Lowest distinguishable s	0.0033	
LOQ	LOQ > lowest calibratio	n standard	0.0110
Analytical working range	Max	Highest CRM	1.6100
	Min	LOD	0.0033

Table 4.65: Kalahari fusion P regression summary

### 4.7.3.1. Kalahari fusion accuracy

10 replicates of the CRM were prepared to test the accuracy of Kalahari fusion method. The mean, standard deviation and the RSD were calculated from the obtained results. The T test was used to determine the accuracy.

name	Mn	Fe	CaO	MgO	SiO2	A12O3	Р
Sarm 137 - 1	49.189	9.772	5.603	0.592	5.595	0.242	0.028
Sarm 137 - 2	49.184	9.673	5.650	0.573	5.572	0.237	0.027
Sarm 137 - 3	49.112	9.882	5.556	0.616	5.562	0.254	0.027
Sarm 137 - 4	49.128	9.891	5.698	0.580	5.581	0.268	0.028
Sarm 137 - 5	49.151	9.801	5.666	0.572	5.558	0.243	0.027
Sarm 137 - 6	49.099	9.887	5.556	0.562	5.554	0.250	0.027
Sarm 137 - 7	49.134	9.859	5.547	0.576	5.610	0.261	0.025
Sarm 137 - 8	49.124	9.869	5.694	0.584	5.577	0.245	0.027
Sarm 137 - 9	49.127	9.709	5.657	0.573	5.581	0.261	0.028
Sarm 137 - 10	49.358	9.8674	5.6206	0.5974	5.548	0.235	0.027
Mean	49.16	9.82	5.62	0.58	5.57	0.250	0.0271
SD	0.0752	0.0789	0.0573	0.0158	0.0193	0.0110	0.0007
RSD	0.1529	0.8039	1.0185	2.7039	0.3468	4.4178	2.7429
True Value	49.20	9.83	5.61	0.58	5.56	0.253	0.027
T <sub>calc</sub>	-1.58	-0.35	0.76	0.30	2.12	-0.95	1.57
T <sub>crit</sub>	2.262	2.262	2.262	2.262	2.262	2.262	2.262
Comment	$t_{calc} < t_{crit}$						
Uncertainty	0.0238	0.0250	0.0181	0.0050	0.0061	0.0035	0.0002

Table 4.66: Kalahari fusion method accuracy results

The mean of a set of results in Table 4.66, obtained from the analysis of a certified reference material (CRM) is not significantly different from a certified value of the material. Therefore, the method has proven to be accurate. All results showed the  $t_{calc} < t_{crit}$  at a 95% confidence limit, there was no statistical difference between the mean values of Sarm 137 and the true value. The calculated RSD was below 1% for Mn, Fe, CaO and SiO<sub>2</sub> except MgO, Al<sub>2</sub>O<sub>3</sub> and P which were higher than 2%. The Q test was used to determine if there were outliers in the obtained results. The results fell within the expected random error and were retained. The  $t_{cal}$  of all elements were less than the  $t_{crit}$ , which means the mean of a set of results obtained from the analysis of a certified reference material (CRM) is not significantly different from a certified value of the material. Therefore, the method can produce accurate results. The higher

RSD may be associated to several factors affecting the accuracy of fusion like the inferior sensitivity and high dilution of trace elements on fused beads.

### 4.7.3.2. Kalahari fusion method precision

The in-house standards were used to test method precision. 10 replicates of the same sample were prepared and analysed.

	3.6	-	<b>a</b> a	14.0	a: 0 0	110.00	<b>D</b>
	Mn	Fe	CaO	MgO	SiO2	Al2O3	Р
BAM 633-1	47.810	1.678	2.111	0.560	10.300	1.645	0.1754
BAM 633-2	47.822	1.677	2.106	0.564	10.345	1.653	0.1750
BAM 633-3	47.815	1.680	2.087	0.562	10.327	1.615	0.1754
BAM 633-4	47.839	1.680	2.113	0.557	10.317	1.641	0.1753
BAM 633-5	47.807	1.681	2.100	0.560	10.326	1.652	0.1739
BAM 633-6	47.829	1.681	2.093	0.560	10.336	1.657	0.1744
BAM 633-7	47.785	1.674	2.090	0.565	10.300	1.651	0.1749
BAM 633-8	47.804	1.672	2.090	0.566	10.304	1.653	0.1746
BAM 633-9	47.848	1.671	2.096	0.555	10.281	1.661	0.1758
BAM 633-10	47.801	1.676	2.077	0.568	10.328	1.621	0.1748
SD	0.0187	0.0039	0.0114	0.0042	0.0198	0.0153	0.0006
Mean	47.82	1.68	2.10	0.56	10.32	1.64	0.17
RSD (<	0.0391	0.2303	0.5436	0.7393	0.1916	0.9274	0.0032
1.0%)							
Uncertainty	0.0059	0.0012	0.0036	0.0013	0.0063	0.0048	0.0002

Table 4.67: Kalahari fusion method precision results

RSD was used to evaluate the precision of the method as indicated in table 4.67 and all elements were within the 1% criteria as prescribed by the ISO 17025 method validation criteria. The % RSD of less than 1% supports the statement that the analytical method was capable of giving repeatable results and indicates good precision across all elements. The results proved excellent precision despite the wide range of concentration.

#### 4.7.3.3. Kalahari fusion instruments precision

The sample was analysed 10 times on the XRF without changing the position. This also referred as repeatability.

	Mn	Fe	CaO	MgO	SiO2	A12O3	Р
NCS DC 11021	26.556	11.131	2.328	0.7482	22.125	7.049	0.1739
NCS DC 11021	26.549	11.129	2.332	0.7451	22.167	7.043	0.1742
NCS DC 11021	26.559	11.149	2.324	0.7478	22.200	7.048	0.1735
NCS DC 11021	26.554	11.143	2.329	0.7481	22.169	7.067	0.1745
NCS DC 11021	26.559	11.147	2.324	0.7473	22.167	7.041	0.1744
NCS DC 11021	26.572	11.167	2.338	0.7452	22.167	7.018	0.1746
NCS DC 11021	26.555	11.140	2.324	0.7468	22.156	7.066	0.1740
NCS DC 11021	26.578	11.162	2.325	0.7455	22.156	7.049	0.1744
NCS DC 11021	26.540	11.141	2.326	0.7460	22.165	7.043	0.1740
NCS DC 11021	26.556	11.131	2.328	0.7492	22.125	7.056	0.1739
SD	0.0108	0.0126	0.0044	0.0014	0.0217	0.0140	0.000335
Mean	26.56	11.14	2.33	0.747	22.16	7.05	0.1741
RSD (< 0.2%)	0.0405	0.1133	0.1887	0.1907	0.0980	0.1991	0.1923
Uncertainty	0.003401	0.003994	0.001389	0.000450	0.006864	0.004437	0.000106

Table 4.68: Kalahari fusion instruments precision results

RSD from Table 4.68 was less than 0.2% on all elements which indicates that the instrument is capable of reproducing the same results. The instrument is then deemed precise. The statistical data indicates that the precision of analytical result for all elements were satisfactory.

#### 4.7.3.4. Kalahari fusion method uncertainty of measurement

10 different Press pellet samples were prepared from the same sample.

Parameters	Uncertainty (%)
Balance	0.001
LOI	0.081
Sample weighing	0.002
Flux weighing	0.000
Fused bead	0.014
Fusion	0.036
Calibration	0.357
Instrument	0.028
Analyst	0.087
Total (U)	0.379

Table 4.69: Kalahari fusion budget for combined measurements uncertainties

Therefore, total % uncertainty for Kalahari fusion method based on the whole step of analysis as indicated in Table 4.69 was 0.378%. The method was fit for purpose based on the validated parameters.

#### 4.7.3.5. Kalahari fusion Accuracy test using recovery

The precision of the Kalahari method was determined by the mean percentage recovery of each element in the three standards. The acceptable mean percentage recovery is within 90 to 110% of the true value.

Kalahari fusion CRM results obtained from the instruments

Table 4.70: Kalahari fusion CRM results

Instruments results							
CRM Name	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
MO203	49.617	9.454	5.313	0.630	4.829	0.360	0.033
NCS DC 11022	30.570	10.376	1.722	0.671	18.609	6.790	0.143
NCS DC 47006	32.586	11.657	0.075	0.113	14.914	8.355	0.209

True Value							
CRM Name	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
MO203	50.000	9.570	5.315	0.628	4.990	0.350	0.035
NCS DC 11022	29.480	10.220	1.820	0.650	19.840	6.490	0.150
NCS DC 47006	32.540	11.240	0.083	0.110	14.500	8.550	0.207

Table 4.71: CRM true value from the certificates

Table 4.72: Kalahari fusion CRM percentage recovery

Percentage recovery								
CRM Name	% Mn	% Fe	% CaO	% MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P	
MO203	99.234	98.792	99.964	100.355	96.783	102.911	94.886	
NCS DC 11022	103.696	101.525	94.598	103.283	93.794	104.620	95.427	
NCS DC 47006	100.142	103.708	90.241	102.582	102.855	97.713	100.870	

The method was fit for purpose based on the validated parameters from Table 4.70 to 4.72. The recoveries of all elements were within the acceptable limits except CaO on NCS DC 47006 which was on the border of acceptable range. CRM were within the acceptable range and hence method was found accurate.

# 4.7. **Results comparison**



# 4.8.1. Comparison of low grade method, Kalahari fusion and wet chemical analyses

Figure 4.42: Comparison of Mn on low grade method, Kalahari fusion and wet chemical analyses



Figure 4.43: Comparison of Mn on low grade method, Kalahari fusion and wet chemical analyses



Figure 4.44: The absolute difference between the Mn of low grade method, Kalahari fusion and wet chemical



Figure 4.45: The absolute difference between the Fe of low grade method, Kalahari fusion and wet chemical

The F-test was used to determine if there is a significant difference between the methods.

Table 4.73: The F-test

	Low grade PP		Kalahari Fusi	Kalahari Fusion		
	% Mn	% Fe	% Mn	% Fe	% Mn	% Fe
M1F-04	35.9	4.6	36.0	4.7	36.1	4.5
GL34	40.2	3.8	40.2	3.8	40.1	3.7
KMD 16	37.8	4.2	37.9	4.3	37.6	4.3
TSH -1	37.5	4.2	37.2	4.2	37.4	4.0
M1L	38.6	4.5	38.9	4.4	38.7	4.3
M1F-12	30.5	4.8	30.2	4.8	30.3	4.8
GL 33	41.0	4.9	41.1	5.0	41.2	4.8
GL20	39.7	4.6	39.6	4.8	39.7	4.5
TC	32.8	7.8	32.9	7.9	33.0	7.8
UM F	28.7	4.1	28.6	4.2	28.0	4.1
Mean	36.263	4.749	36.265	4.809	36.210	4.680
SD	4.023	1.059	4.099	1.094	4.176	1.090

# 4.8.2. Comparison between Mn of low grade and wet chemical method

Equation 4.9: F-test

$$F = \frac{S_1^2}{S_2^2}$$
 4.9

 $H_0:S_1 = S_2$ . Accept the null hypothesis

 $H_1:S_1 \neq S_2$ : Reject the null hypothesis

 $S_{low grade} = 36.263$ 

 $S_{wet chem} = 36.210$ 

 $F_{calc} = 1.00291$ 

 $F_{crit} = 4.025994$ 

 $F_{cal} < F_{crit}$ , therefore it was concluded with 95% confidence that there was no significant difference in precision. The null hypothesis that  $S_1 = S_2$  is accepted. The null hypothesis was not rejected and the differences between the two data sets are due to chance variation or random error.

# 4.8.3. Comparison between Mn of Kalahari fusion and wet chem method

F-test

$$\mathbf{F} = \frac{S_1^2}{S_2^2}$$

 $H_0:S_1 = S_2$  Accept the null hypothesis

 $H_1{:}S_1\neq S_2$ 

 $S_{Kalahari fusion} = 36.265$ 

 $S_{wet chem} = 36.210$ 

 $F_{calc} = 1.003066$ 

$$F_{crit} = 4.025994$$

 $F_{cal} < F_{crit}$ , therefore it was concluded with 95% confidence that there was no significant difference in precision. The null hypothesis that  $S_1 = S_2$  was accepted. The null hypothesis was not rejected and the differences between the two data sets are due to chance variation or random error. According to the F - test there was no significant statistical difference between the precision of the three methods as shown in Figure 4.42 to 4.45.

The correlations between low grade and wet chemical was 0.9973 on Mn and 0.9944 on Fe which indicates good correlation between the two methods. The correlation between Kalahari fusion and wet chemical was 0.9972 on Mn and 0.9949 Fe which indicates good correlations between the two methods.

# 4.8.4. Comparison of high grade method, Kalahari fusion and wet chemical analyses

The following Figures 4.46 to 4.49 shows comparative results for the percentages of Manganese for different samples against developed method and traditional wet chemical analysis.



Figure 4.46: Comparison of Mn on high grade method, Kalahari fusion and wet chemical analyses.



Figure 4.47: Comparison of Fe on high grade method, Kalahari fusion and wet chemical analyses.



Figure 4.48: The absolute difference between the Mn of high grade method, Kalahari fusion and wet chemical.



Figure 4.49: The absolute difference between the Fe of high grade method, Kalahari fusion and wet chemical.

	high grade p	ress pellet	Kalahari fus	ion	Wet chemica	al
Sample ID	% Mn	% Fe	% Mn	% Fe	% Mn	% Fe
W-14	36.38	15.45	36.32	15.22	36.40	15.10
СВ	39.84	8.44	39.55	8.31	39.70	8.40
WB-7	42.36	15.55	42.49	15.46	42.30	15.60
WL-04	50.56	15.50	49.93	15.79	49.80	15.80
WC	43.11	13.68	43.09	13.71	43.00	13.50
WL-06	44.91	13.81	45.25	13.82	45.25	13.80
CB-251	52.85	10.79	52.71	10.91	52.50	11.00
CB-356	56.55	7.80	56.72	8.05	56.40	7.90
RR 11	45.67	12.98	45.93	12.83	45.60	13
WL-02	47.08	12.58	46.98	12.51	46.80	12.60
Average	45.93	12.66	45.90	12.66	45.78	12.67
SD	6.09	2.82	6.08	2.79	5.97	2.79

Table 4.74: Comparison between Mn and Fe of high grade and wet chemical.

Comparison between Mn and Fe of high grade and wet chemical

F-test

$$\mathbf{F} = \frac{S_1^2}{S_2^2}$$

 $H_0:S_1 = S_2$  Accept the null hypothesis

 $H_1:S_1 \neq S_2$ : Reject the null hypothesis

Table 4.75: Summary of F test calculation

	Mn	Fe
Shigh grade	45.93	12.58
S wet chem	46.80	12.60
Fcal	1.0068	0.9980
Fcrit	4.0260	4.0260

 $F_{cal} < F_{crit}$  for both Mn and Fe. Therefore, it is concluded with 95% confidence that there was no significant difference in precision between the two methods, the null hypothesis that  $S_1 = S_2$  was accepted. The null hypothesis was accepted and the differences between the two data sets are due to random error.



4.8.5. Correlation of Kalahari fusion method and low grade PP method

Figure 4.50: Comparison of Mn between Kalahari fusion and low grade method

From Figure 4.50, the correlation coefficient of 0.9962 indicated a good comparison between the Kalahari fusion and Low grade press pellets method.



Figure 4.51: Comparison of Fe between Kalahari fusion and low grade pp method

The correlation coefficient from Figure 4.51 of 0.9970 indicated a good comparison between the Kalahari fusion and Low grade press pellets method.



Figure 4.52: Comparison of CaO between Kalahari fusion and low grade pp method

Figure 4.52 indicated a good comparison between the Kalahari fusion and low grade press pellets method. The correlation coefficient was 0.9914.





The correlation coefficient of 0.9830 indicated a poor comparison between the Kalahari fusion and low grade press pellets method as indicated in Figure 4.53. The correlation can be improved by adding more secondary standard.



Figure 4.54: Comparison of SiO<sub>2</sub> between Kalahari and low grade pp method

The correlation coefficient of 0.9908 in Figure 4.54 indicated a good comparison between the Kalahari fusion and low grade press pellets method.



Figure 4.55: Comparison of Al<sub>2</sub>O<sub>3</sub> between Kalahari fusion and low grade pp method

The correlation coefficient of 0.9950 in Figure 4.55 indicated a good comparison between the Kalahari fusion and low grade press pellets method.



Figure 4.56: Comparison of P between Kalahari fusion and low grade pp method

The correlation coefficient of 0.9250 in Figure 4.56 indicated a poor comparison between the Kalahari fusion and Low grade press pellets method. The poor correction can be attributed to a lower concentration of P in the manganese ore and a 20:1 high dilution ratio in Kalahari fusion method.

Name	Correlation
% Mn	0.9962
% Fe	0.9970
% CaO	0.9914
% MgO	0.9830
% SiO <sub>2</sub>	0.9908
% Al <sub>2</sub> O <sub>3</sub>	0.9950
% P	0.9250

4.8.6. Correlation of Kalahari fusion method and high grade method



Figure 4.57: Comparison of Mn between Kalahari fusion and high grade method



Figure 4.58: Comparison of Fe between Kalahari fusion and high grade method



Figure 4.59: Comparison of CaO between Kalahari fusion and high grade method



Figure 4.60: Comparison of MgO between Kalahari fusion and high grade method



Figure 4.61: Comparison of SiO<sub>2</sub> between Kalahari fusion and high grade method



Figure 4.62: Comparison of Al<sub>2</sub>O<sub>3</sub> between Kalahari fusion and high grade method



Figure 4.63: Comparison of P between Kalahari fusion and high grade method

# 4.8.7. Low grade press pellet inter-laboratory comparison results.

	Low grade	Consensus true	Consensus	Relative	Z-score
	PP	value	Standard	percentage	
			deviation	difference	
% Mn	33.700	33.765	0.143	0.065	-0.456
% Fe	5.260	5.300	0.051	0.040	-0.785
% SiO <sub>2</sub>	5.410	5.400	0.116	-0.010	0.086
% CaO	18.760	18.280	0.595	-0.481	0.808
% MgO	2.970	2.960	0.094	-0.010	0.106
% Al <sub>2</sub> O <sub>3</sub>	0.210	0.219	0.037	0.009	-0.228
% P	0.022	0.019	0.001	-0.003	2.167

Table 4.77: Low grade press pellet inter-laboratory comparison results.

All elements in Table 4.77 showed lower relative percentage difference between low grade and consensus true value. CaO showed high relative percentage difference but still within the tolerance limit. All elements compared very well with the consensus results. The z-score of all elements was less than 2 which was satisfactory except P, which was between 2 and 3 and it's questionable according to the evaluation criteria. P results are 0.003% higher than the

consensus results and was questionable based on the z- score criteria. P was the most difficult elements to determine because of low concentration in the samples.

# 4.8.8. High grade press pellet inter-laboratory comparison results.

	High grade	Consensus true	Consensus	Relative	Z-score
	PP	value	Standard	percentage	
			deviation	difference	
% Mn	48.700	48.200	0.251	-0.500	1.991
% Fe	10.600	10.300	0.146	-0.300	2.057
% SiO <sub>2</sub>	7.200	7.195	0.455	-0.005	0.011
% CaO	4.700	5.075	0.167	0.375	-2.242
% MgO	0.450	0.600	0.079	0.150	-1.910
% Al <sub>2</sub> O <sub>3</sub>	0.279	0.290	0.050	0.011	-0.221
% P	0.032	0.032	0.002	0.000	0.000

Table 4.78: High grade press pellet inter-laboratory comparison results.

All elements showed in Table 4.78 indicate lower relative percentage difference between high grade and consensus true value. CaO and Fe showed high relative percentage difference but still within the tolerance limit. All elements compared very well with the consensus results. The z-score of all elements was less than 2 which is satisfactory except CaO and Fe which was between 2 and 3 and it's questionable according to the evaluation criteria. Fe results were 0.300% higher than the consensus results. CaO results are 0.375% lower than the consensus results.

# 4.8.9. Kalahari fusion inter-laboratory comparison results.

	Kalahari	Consensus true	Consensus	Relative	Z-score
	Fusion	value	Standard	percentage	
			deviation	difference	
% Mn	48.500	48.200	0.251	0.300	1.195
% Fe	10.300	10.300	0.146	0.000	0.000
% SiO2	6.900	7.195	0.455	-0.295	-0.649
% CaO	5.300	5.075	0.167	0.225	1.345
% MgO	0.600	0.600	0.079	0.000	0.000
% Al <sub>2</sub> O <sub>3</sub>	0.240	0.290	0.050	-0.050	-1.006
% P	0.029	0.032	0.002	-0.003	-1.604

Table 4.79: High grade type ore comparison from Kalahari fusion

All elements in Table 4.79 showed lower relative percentage difference when compared with the consensus results. Mn showed high relative percentage difference but still within the tolerance limit. All elements compared very well with the consensus results. The z-score of all elements was less than 2 which indicate satisfactory results.

Table 4.80 : Low grade tyre ore comparison from Kalahari fusion

	Kalahari	Consensus true	Consensus	Relative	Z-score
	Fusion	value	Standard	percentage	
			deviation	difference	
% Mn	33.600	33.765	0.143	-0.165	-1.158
% Fe	5.280	5.300	0.051	-0.020	-0.393
% SiO <sub>2</sub>	5.430	5.400	0.116	0.030	0.259
% CaO	19.040	18.280	0.595	0.761	1.279
% MgO	2.960	2.960	0.094	0.000	0.000
% Al <sub>2</sub> O <sub>3</sub>	0.227	0.219	0.037	0.009	0.228
% P	0.020	0.019	0.001	0.001	0.765

All elements in Table 4.56 showed lower relative percentage difference between low grade press pellet and Kalahari fusion. Mn showed lower relative percentage difference but still within the tolerance limit. All elements compared very well with the consensus results. The z-score of all elements was less than 2 which indicates satisfactory.

### 4.8. Quality controls

XRF instruments are not absolutely stable. The XRF drift over a period of time due to mechanical wear, power fluctuations, changing of the gas, environmental condition, periodical maintenance and aging of electronical components. Quality control samples were analysed each day for a period of six months. The results were checked to see if they are within the limit and recorded on the control charts. Drift corrections are only performed if the results are outside of the specified range. The results compared with previous results to check the amount of variations between the days.

### **4.9.1.** Control charts

A quality control charts are used for proactive, actions are taken before the process is out of control using the standard deviations. The operating, warning and action limit are calculated based on the one, two and three times standard deviations.

Quality control samples (QC)

40.50 40.00 39.50 39.00 38.50 Low grade RR1 Mn chart 40.50 40.00 aninus 2SD minus 3SD plus 3SD plus 2SD True Value

Sep

Oct

Nov

Low grade press pellet RR1 quality control samples results over six months.

Aug

Figure 4.64: Low grade Mn Qc chart

Jun

Jul



Figure 4.65: Low grade Fe Qc chart

High grade press pellet Wes 6 quality control samples results over six months



Figure 4.66: High grade Mn Qc chart





Kalahari Fusion MO196 quality control samples result over six months



Figure 4.68: Kalahari fusion Mn QC charts



Figure 4.69: Kalahari fusion Fe QC charts

The instrumental drift was found to be insignificant as indicated in Figure 4.64 to 4.69. It was also found by repeated measurements of the QC sample over a period of time, the variation was within the control limits.

# Chapter 5

### **Conclusion and Recommendations**

#### 5.1. Conclusion

The main objective of this research was to develop a quantitative method that can be used to analyse Kalahari manganese ore samples and validation. The following conclusion were drawn from this research project.

### 5.1.1. Sample preparation

Special attention must be taken to ensure that no changes of qualitative composition occur during, sampling, sample reduction and sample preparation of the sample. The samples for analysis must be representative of the original bulk. It is important that all samples and standards have the same average particle size and particle size distribution in order for all the particle size effects to cancel each other out. The quality control pulp must be performed regularly to monitor the sample preparation setting parameters.

### 5.1.2. Press pellets methods

A press pellet is the simplest accurate method of analysing the samples on the XRF. The use of pressed powders gives more accurate and precise results. As mentioned in other literature, large errors are possible due to differences in the particle size and mineralogical composition of the ore for the analysis and the calibration standard. These errors can be minimized to be insignificant by press pellets method under the constant pressure and a constant volume with a matrix matching secondary standard. The matrix matching techniques is hard to meet, it requires an extensive knowledge of the ore composition of the current active mining area. The press pellets methods have the advantage of simple and quick preparation and, as the technique is non-destructive, samples can be recovered for further study. The calibration lines for all elements showed good correlations and covered the wide range of concentration.

The results have indicated that matrix matching between standards and the samples can yield accurate and precise results without any matrix corrections and the use of theoretical alphas. The accuracy of the pressed powder pellets method can be improved by continuously
improving the calibration range as the mining continues. The press pellets analysis compared very well with the wet chemical and fusion method. The press pellets method is fast and sample preparation is also simple. This method will be more suitable for day to day production samples.

#### 5.1.2.1. Low grade press pellets method conclusion

All calibration line showed a perfect linear regression. The T and F test has indicated the good linear relation between concentration and intensities. The standard error of the regression was very small which indicates the perfect relation between the concentrations of the analyte. The calibration slope was not equal to zero which indicated the good calibration sensitivity. The intercept standard error ( $S_a$ ) and variable standard error ( $S_b$ ) were less than standard error (Sy/x) and that points to good general precision in the regression, except for P calibration. The matrix matching standard proved to be accurate and reliable. The method requires more standards covering a wide range of P. The calibration can be upgraded to increase the compositional range of P by adding new standards to the calibration as they become available. The method is fit for purpose based on the validated parameters.

#### 5.1.2.2. High grade press pellets method conclusion

All calibration line showed a perfect linear regression. The T and F test has indicated the good linear relation between concentration and intensities. The standard error of the regression was very low which indicate the perfect relation between the concentrations of the analyte. The calibration slope was not equal to zero which indicated the good calibration sensitivity. The intercept standard error ( $S_a$ ) and variable standard error ( $S_b$ ) were less than standard error (Sy/x) that points to good general precision in the regression. The method is fit for purpose based on the validated parameters.

#### 5.1.3. Kalahari Fusion

All calibration line showed a perfect linear regression. The T and F test has indicated the good linear relation between concentration and intensities. The standard error of the regression was very small which indicate the perfect relation between the concentrations of the analyte. The calibration slope was not equal to zero which indicate the good calibration sensitivity. The intercept standard error  $S_a$  and variable standard error  $(S_b)$  were less than standard error (Sy/x) that points to good general precision in the regression, except for P calibration and  $S_a$  of Fe. The method is fit for purpose based on the validated parameters.

The higher accuracy of the fused beads when compared to the pressed powder results were because of the reduced matrix effects as well as the elimination of the mineralogical effects on the fused beads. The CRM recovery was well within the tolerance limit which proves the method was accurate and precise. The inter-laboratory comparison has showed very good correlation with consensus and the z-score was satisfactory. The results have indicated a successful fusion method. The total method uncertainty for fusion was very low at 0.379% for all the steps. The fusion method will be suitable for the forward prospecting or exploration work since is the new area for mining.

#### 5.1.4. Statistical method validation

The calibration lines were validated with routine samples, certified reference material (CRM) and in house standard. The validation was performed on all elements with a wide concentration range that can cover the known concentration of the current ore body. All the elements and oxides were recovered and showed very good comparisons with consensus values. The precision and accuracy was evaluated on an absolute concentration base by calculating the difference between the results of the analysed elements for the duplicates preparations of selected CRM and secondary standard. The precision determined from the secondary standard indicated well homogeneous samples. The Phosphorus showed a systematic error due to lower concentration in the ore body. The method was validated and deem fit for purpose.

### 5.1.5. Summary

The study has demonstrated that the mineralogical effect, which is one of the main sources of errors in X-ray fluorescence analysis with pressed powder pellets, can be corrected by closely matching the calibration standard to the unknown samples. The results clearly confirm the methods are capable of producing overall high quality of analytical results for Kalahari manganese ore with optimised sample preparation. The methods are fully validated according to the stated parameters.

The quality of the XRF results are satisfactory, the manual titration technique can be replaced with XRF analysis. The XRF analysis will reduce the turnaround time, save money and eliminate the hazard associated with chemical analysis.

### 5.2. Recommendations

- Fusion cycle time can be improved if the loss on ignition (LOI) can be eliminated from the process to develop rapid fusion method for final products.
- The use of releasing agents must be investigated for the sample with high content of Fe. The moulds life span can be increased.
- Investigate the use of binding agents for high iron samples or ferruginized ore.
- Register the manganese fusion method with international standard organization (ISO) body.

#### References

- 1. Lobster, M. (2008). *An introduction to XRF spectrometer. [course notes]* (2nd ed.). Pretoria: University of Pretoria.
- 2. Willis, J. P., & Duncan, A. R. (2008). Understanding XRF spectrometry: Basic concepts and instrumentation PANalytical BV, 1-93
- 3. Willis, J. P., Turner, K., & Pritchard, G. (2011). *XRF in the workplace: A guide to practical XRF spectrometry*. Australia: PANalytical, 1-85.
- 4. Bruker Corporation. An overview of XRF basics., www.bruker.com /01/06/2014
- Willis, J., & Duncan, A. (2008). Understanding XRF spectrometry, volume 2: Quantitative analysis and special sample preparation and presentation methods. (2nd ed., ) PANalytical BV,20-140.
- Willis, J. P., Feather, C., & Spice, E. (2010). *Elementary XRF: Practical, hands-on XRF spectrometry [course notes]*. Stellenbosch: The Spectroscopic Society of South Africa.
- Eivindson, T., & Mikkelsen, O. (2001). Problems by using pressed powder pellets for XRF analysis of ferrosilicon alloys, advances in X-ray analysis. *JCPDS-International Centre for Diffraction Data*, 44, 409-418.
- 8. Willis, J. P. (2011). *Theory and practice of XRF spectrometry [course notes]*. Cape Town: University of Cape Town.
- Anzelmo, J., Seyfarth, A., & Arias, L. (2001). Approaching a universal sample preparation method for XRF analysis of powder materials. *Adv.X-ray Anal*, 44, 368-373.
- Shackley, M. S. (2011). An introduction to X-ray fluorescence (XRF) analysis in archaeology. In M. S. Shackley (Ed.), *X-ray fluorescence spectrometry (XRF) in* geoarchaeology (1st ed., pp. 7-30) Springer-Verlag New York.
- 11. Rousseau, R. M., Willis, J. P., & Duncan, A. R. (1996). Practical XRF calibration procedures for major and trace elements. *X-ray Spectrometry*, *25*(4), 179-189.
- 12. ISO/IEC 17025. (2005). General requirements for the competence of testing and calibration laboratories (2nd ed.). Pretoria: SANS.
- 13. Streli, C., P Wobrauschek, P., & Kregsamer, P. (1999). X-ray fluorescence spectroscopy, application. *Academic Press*, *1*, 2478 2487.

- 14. Bounakla, M., & Tahir, M. X-ray fluorescence analytical techniques. *National Center* for Energy Sciences and Nuclear Techniques (CNESTEN), Rabat, Morocco, 1, 1-73.
- Lu, F., Smith, J. V., Sutton, S. R., Rivers, M. L., & Davis, A. M. (1989). Synchrotron X-ray fluorescence analysis of rock-forming minerals: 1. comparison with other techniques; 2. white-beam energy-dispersive procedure for feldspars. *Chemical Geology*, 75(1-2), 123-143.
- Sitko, R., & Zawisza, B. (2012). Quantification in X-ray fluorescence spectrometry. In S. K. Sharma (Ed.), *X-ray spectroscopy* (1st ed., pp. 137-150). Poland: InTech.
- Mori, P. E., Reeves, S., Correia, C. T., & Haukka, M. (1999). Development of A fused glass disc XRF facility and comparison with the pressed powder pellet technique at Instituto de Geociencias, Sao Paulo University. *Brazilian Journal of Geology*, 29(3), 441-446.
- Shan, H. Z., Zhuo, S. J., Shen, R. X., & Sheng, C. (2008). Mineralogical effect correction in wavelength dispersive X-ray florescence analysis of pressed powder pellets. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 63(5), 612-616.
- 19. Schlotz, R., & Uhlig, S. (2002). *Introduction to X-ray fluorescence analysis (XRF)* (1st ed.). Karsruhe, Germany: Bruker Advanced X-ray Solutions.
- 20. http://www.amptek.com/xrf/ 2015 02/10/2015.
- Potts, P. J., & Webb, P. C. (1992). X-ray fluorescence spectrometry. *Journal of Geochemical Exploration*, 44(1), 251-296.
- 22. Janssens, K. (2013). X-ray based methods of analysis. In K. Janssens (Ed.), Modern methods for analysing archaeological and historical glass (1st ed., pp. 79-128) John Wiley & Sons Ltd.
- Goaz, P. W., & Pharoah, M. J. (1999). Production of X-rays and interactions of X-rays with matter. In N. Serman (Ed.), (1st ed., pp. 11-20)
- 24. Bertin, E. P. (2013). Properties of X-rays. In E. P. Bertin (Ed.), *Introduction to X-ray spectrometric analysis* (3rd ed., pp. 59-178). USA: Springer US.
- 25. Kite, J., & Dennison, J. R. (2003). Secondary electron production and transport mechanisms by measurement of angle-energy resolved cross sections of secondary and backscattered electrons. *All Physics*, *1*, 1-6.
- Jenkins, R. (2000). X-ray techniques: Overview. International Centre for Diffraction Data, 1, 13269-13288.

- 27. Jenkins, R., Manne, R., Robin, R., & Senemaud, C. (1991). Nomenclature, symbols, units and their usage in spectrochemical analysis-VIII. nomenclature system for X-ray spectroscopy (recommendations 1991). *Pure and Applied Chemistry*, *63*(5), 735-746.
- 28. Brouwer, P. (2010). *Theory of XRF: Getting acquainted with the principles* (3rd ed.) PANalytical BV, 7-58.
- 29. Lankosz, M., Węgrzynek, D., Rybińska-Gracek, M., & Marchut, A. (1986). Correction of interelement effects in X-ray fluorescence analysis of iron ore. *International Journal* of Radiation Applications and Instrumentation Part A .Applied Radiation and Isotopes, 37(12), 1205-1207.
- 30. Rousseau, R. M. (2006). Corrections for matrix effects in X-ray fluorescence analysis-A tutorial. *Spectrochimica Acta Part B: Atomic Spectroscopy*, *61*(7), 759-777.
- 31. Reig, F. B., Carbó, T. D., Peris Martinez, V., & Adelantado, J. V. G. (1988). Limit dilution method: Determination of correction factors for resolving matrix effects in Xray fluorescence analysis. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 43(6), 811-818.
- 32. Sitko, R. (2008). Study on the influence of X-ray tube spectral distribution on the analysis of bulk samples and thin films: Fundamental parameters method and theoretical coefficient algorithms. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 63(11), 1297-1302.
- 33. Al-Merey, R., Karajou, J., & Issa, H. (2005). X-ray fluorescence analysis of geological samples: Exploring the effect of sample thickness on the accuracy of results. *Applied Radiation and Isotopes*, 62(3), 501-508.
- 34. Couture, R. A., Smith, M. S., & Dymek, R. F. (1993). X-ray fluorescence analysis of silicate rocks using fused glass discs and a side-window rh source tube: Accuracy, precision and reproducibility. *Chemical Geology*, 110(4), 315-328.
- 35. Thermo Fisher Scientific. (2013). *The optical emission and X-ray fluorescence analysis* (1.7.1.1728 ed.). switzerland: Thermo Fisher Scientific.
- 36. Chen,Z. W., Gibson, W. M. and Huang,H. (2008). High definition X-ray fluorescence: Principles and techniques. *X-ray Optics and Instrumentation*, 2008(1), 1-10.
- 37. Mantler, M. (1987). Recent methods and applications of X-ray fluorescence analysis. *Pergamon Journals Ltd*, *14*, 213-261.
- Kikkert, J. N. (1983). X-ray spectrometry in the eighties. Spectrochimica Acta Part B: Atomic Spectroscopy, 38(11), 1497-1508.

- 39. Willis, J.P , Feather, C.E and Turner K. (2014). Guidelines for XRF analysis setting up programmes for WDXRF and EDXRF. (1st ed., ) James Willis Consultants, 51-91.
- 40. Slaughter, M. (2013). X-ray analysis in mineral exploration. In J. G. Morse (Ed.), *Nuclear methods in mineral exploration and production* (7th ed., pp. 37-49) Elsevier.
- 41. Scholtze, F. (2007). Handbook of practical X-ray fluorescence analysis. In B. Beckhoff,
  B. Kanngießer, N. Langhoff, R. Wedell & H. Wolff (Eds.), *X-ray detectors and XRF detection channels* (1st ed., pp. 199-227). Berlin Heidelberg: Springer.
- 42. Das, A. P., Sukla, L. B., & Pradhan, N. (2012). Microbial recovery of manganese using staphylococcus epidermidis. *International Journal of Nonferrous Metallurgy*, *1*, 9-12.
- 43. Maynard, J. B. (2014). 9.11 manganiferous sediments, rocks, and ores. In H. D. Holland, & K. K. Turekian (Eds.), *Treatise on geochemistry* (2nd ed., pp. 327-349). Oxford: Elsevier.
- 44. Das, A. P., Sukla, L. B., Pradhan, N., & Nayak, S. (2011). Manganese biomining: A review. *Bioresource Technology*, 102(16), 7381-7387.
- 45. Magnuson, J. K., & Lasure, L. L. (2004). Organic acid production by filamentous fungi. Advances in fungal biotechnology for industry, agriculture, and medicine (pp. 307-340) Springer.
- 46. Matricardi, L. R., & Downing, J. (1995). Manganese and manganese alloys. *Kirk-Othmer Encyclopedia of Chemical Technology*, 15(4), 963-990.
- Sorensen, B., Gaal, S., Ringdalen, E., Tangstad, M., Kononov, R., & Ostrovski, O. (2010). Phase compositions of manganese ores and their change in the process of calcination. *International Journal of Mineral Processing*, 94(3–4), 101-110.
- 48. Laznicka, P. (1992). Manganese deposits in the global lithogenetic system: Quantitative approach. *Ore Geology Reviews*, 7(4), 279-356.
- Gutzmer, J., & Beukes, N. J. (1996). Mineral paragenesis of the kalahari managanese field, south africa. *Ore Geology Reviews*, 11(6), 405-428.
- Chetty, D., & Gutzmer, J. (2012). REE redistribution during hydrothermal alteration of ores of the kalahari manganese deposit. *Ore Geology Reviews*, 47, 126-135.
- 51. Beukes N J, Burger A M and Gutzmer J. (1995). Fault-controlled hydrothermal alteration of palaeoproterozoic manganese ore in wessels mine, kalahari manganese field . *South African Journal of Geology*, *98*(4), 430-451.
- 52. Gutzmer, J., Du Plooy, A. P., & Beukes, N. J. (2012). Timing of supergene enrichment of low-grade sedimentary manganese ores in the kalahari manganese field, south africa. *Ore Geology Reviews*, 47, 136-153.

- Olsen, S. E., Olsen, S., Tangstad, M., & Lindstad, T. (2007). *Production of manganese ferroalloys* (1st ed.). Trondheim, Norway: Tapir Akademisk Forlag, 11-73.
- Tangstad, M. (2013). Chapter 7 manganese ferroalloys technology. In M. Gasik (Ed.), Handbook of ferroalloys (pp. 221-266). Oxford: Butterworth-Heinemann.
- 55. Olde Weghuis, M. S., & Ingham, M. N. (2007). Chemically pure synthetic standards for wide range analysis of oxides in geological material using wavelength dispersive X-ray fluorescence spectrometry. *Geochemical Case Histories & Geochemical Exploration Methods*, 85, 1003-1006.
- 56. Demir, F., Budak, G., Baydaş, E., & Şahin, Y. (2006). Standard deviations of the error effects in preparing pellet samples for WDXRF spectroscopy. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 243(2), 423-428.
- Loubser, M., & Verryn, S. (2008). Combining XRF and XRD analyses and sample preparation to solve mineralogical problems. South African Journal of Geology, 111(2-3), 229-238.
- La Tour, T. E. (1989). Analysis of rocks using X-ray fluorescence spectrometry. . *The Rigaku Journal*, 6(1), 3-6.
- Sinaldi, F. F., & Aguzzi, P. E. (1967). A simple technique for casting glass disks for X-ray fluorescence analysis. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 23(1), 15-18.
- 60. Maessen, F. J. M. J., & Boumans, P. W. J. M. (1968). Critical examination of the borate fusion technique for spectrochemical trace analysis of geological materials using the d.c. arc. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 23(11), 739-749.
- 61. Yamada, Y. (2010). X-ray fluorescence analysis by fusion bead method for ore and rocks. *The Rigaku Journal*, 26(2), 15-22.
- 62. Broton, D. J. (1999). Lithium based borate fusion of gypsum/high sulfate samples: A new approach. *Advances in X-ray Analysis (AXA)-the Proceedings of the Denver X-ray Conferences. Denver, Colorado, USA*, pp. 868-972.
- 63. Hettipathirana, T., Grey, N., & Naidu, R. (2003). Elimination of analytical error due to the use of catch weights with loss-eliminated alphas in X-ray fluorescence spectrometric analysis of limestone using borate fusions. *Spectrochimica Acta Part B: Atomic Spectroscopy*, *58*(1), 85-95.
- 64. Knorr, K. (2014). Accuracy in quantitative X-ray mineralogy No. 79). Karlsruhe, Germany: Bruker AXS.

- Esbensen, K. H., Friis-Petersen, H. H., Petersen, L., Holm-Nielsen, J. B., & Mortensen,
   P. P. (2007). Representative process sampling in practice: Variographic analysis and estimation of total sampling errors (TSE). *Chemometrics and Intelligent Laboratory Systems*, 88(1), 41-59.
- 66. Marques, D. M., & Costa, J. F. C. (2014). Choosing a proper sampling interval for the ore feeding a processing plant: A geostatistical solution. *International Journal of Mineral Processing*, 131, 31-42.
- Holmes, R. J. (2004). Correct sampling and measurement the foundation of accurate metallurgical accounting. *Chemometrics and Intelligent Laboratory Systems*, 74(1), 71-83.
- 68. Holmes, R. J., & Robinson, G. K. (2004). Codifying the principles of sampling into mineral standards. *Chemometrics and Intelligent Laboratory Systems*, 74(1), 231-236.
- 69. Rozet, E., Marini, R., Ziemons, E., Boulanger, B., & Hubert, P. (2011). Advances in validation, risk and uncertainty assessment of bioanalytical methods. *Journal of Pharmaceutical and Biomedical Analysis*, 55(4), 848-858.
- Gilbert, M. T., Barinov-Colligon, I., & Miksic, J. R. (1995). Cross-validation of bioanalytical methods between laboratories. *Journal of Pharmaceutical and Biomedical Analysis*, 13(4), 385-394.
- 71. González, A. G., & Herrador, M. Á. (2007). A practical guide to analytical method validation, including measurement uncertainty and accuracy profiles. *TrAC Trends in Analytical Chemistry*, 26(3), 227-238.
- 72. González, A. G., Herrador, M. Á., & Asuero, A. G. (2010). Intra-laboratory assessment of method accuracy (trueness and precision) by using validation standards. *Talanta*, 82(5), 1995-1998.

# Appendix

# Table A.1: Certified reference material (CRM) list used in fusion calibration

Standard ID	% Mn	% Fe	%	%	%	% Al <sub>2</sub> O <sub>3</sub>	% P
			CaO	MgO	SIO <sub>2</sub>		
BAM 633-1	47.850	1.640	2.020	0.580	10.390	1.640	0.170
BCS No.176/2	47.500	6.860	0.090	0.040	2.530	5.200	0.087
CMSI 1756 (NCS HC13806)	10.192	13.110	22.698	21.180	21.370	4.000	0.055
ECRM 609-1	0.472	30.520	6.870	2.000	16.751	2.260	0.608
ECRM 651-1	0.968	23.850	22.600	1.730	7.400	4.260	0.350
ECRM 678-1	0.080	60.750	5.485	0.945	3.701	0.529	1.610
GBW 07222a (NCS DC46005)	0.000	43.660	3.380	3.840	3.990	0.600	0.034
GBW 07227	0.187	13.230	11.620	8.320	36.330	11.470	0.012
KZ 185-89	21.610	1.110	25.720	0.950	16.070	1.420	0.014
MO196	49.580	9.630	5.175	0.582	4.930	0.370	0.030
NCS DC 11019	18.360	8.890	12.830	0.611	21.940	5.660	0.202
NCS DC 11020	22.310	9.660	2.360	1.720	28.110	7.690	0.171
NCS DC 11021	26.530	11.010	2.310	0.774	22.100	6.990	0.163
NCS DC 11023	35.540	10.250	2.340	0.780	13.030	3.800	0.105
NCS DC 19001	0.223	32.970	6.380	6.160	20.330	8.260	0.010
NCS DC 19002	0.204	27.550	7.500	6.170	25.470	10.290	0.012
NCS DC 28041	14.450	0.850	2.070	0.600	56.030	8.250	0.011
NCS DC 28042	22.180	10.620	6.200	3.140	24.730	2.800	0.074
NCS DC 28043	30.990	10.680	1.150	0.700	17.300	6.400	0.171
NCS DC 28044	36.310	6.900	3.300	1.290	17.700	2.080	0.105
NCS DC 28045	44.970	2.750	0.195	0.182	16.000	2.350	0.230
NCS DC 47004	45.390	1.220	1.060	0.640	16.160	2.200	0.054
NCS DC 47007	25.000	20.990	0.051	0.100	10.460	8.970	0.275
NCS DC 47009	15.740	2.070	19.780	3.820	15.820	2.490	0.061
NCS HC28803	0.604	0.920	36.260	9.920	31.820	16.850	0.008
OREAS 73b	0.115	8.630	4.407	19.566	44.690	7.123	0.024

Sarm 135	42.500	16.600	6.320	0.463	4.210	0.293	0.026
Sarm 136	46.900	10.370	7.130	0.739	3.890	0.271	0.026
Sarm 137	49.200	9.830	5.610	0.581	5.560	0.253	0.027
SARM 16	49.170	11.480	4.700	0.760	5.040	0.300	0.033
SARM 17	38.810	4.270	14.400	3.030	4.690	0.240	0.018
SMU 7-1-007 (N-7-1-007)	0.604	0.550	31.200	18.900	39.000	6.200	0.000
SX 3911 (DH 3911)	4.420	18.510	50.500	1.540	8.580	0.933	1.157
VS 5403-90	0.162	62.740	0.890	0.650	7.140	0.730	0.000
VS R13/3	58.880	0.000	0.000	0.000	2.010	0.000	0.196

Standard ID	% Mn	% Fe	% CaO	% MgO	% SIO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
BAM 633-1	55.260	1.894	2.333	0.670	11.999	1.894	0.196
BCS No.176/2	55.774	8.055	0.106	0.047	2.971	6.106	0.102
CMSI 1756 (NCS	10.192	13.110	22.698	21.180	21.370	4.000	0.055
HC13806)							
ECRM 609-1	0.574	37.144	8.361	2.434	20.386	2.750	0.740
ECRM 651-1	1.310	32.266	30.575	2.341	10.011	5.763	0.474
ECRM 678-1	0.080	60.750	5.485	0.945	3.701	0.529	1.610
GBW 07222a (NCS	0.000	55.752	4.316	4.904	5.095	0.766	0.043
DC46005)							
GBW 07227	0.190	13.398	11.768	8.426	36.791	11.616	0.012
KZ 185-89	27.691	1.422	32.957	1.217	20.592	1.820	0.018
MO196	52.044	10.109	5.432	0.611	5.175	0.388	0.031
NCS DC 11019	22.497	10.893	15.721	0.749	26.884	6.935	0.248
NCS DC 11020	25.740	11.145	2.723	1.984	32.432	8.872	0.197
NCS DC 11021	30.706	12.743	2.674	0.896	25.578	8.090	0.189
NCS DC 11023	41.039	11.836	2.702	0.901	15.046	4.388	0.121
NCS DC 19001	0.223	32.986	6.383	6.163	20.340	8.264	0.010
NCS DC 19002	0.204	27.555	7.501	6.171	25.475	10.292	0.012
NCS DC 28041	15.558	0.915	2.229	0.646	60.325	8.882	0.012
NCS DC 28042	26.510	12.693	7.410	3.753	29.557	3.347	0.088
NCS DC 28043	36.562	12.600	1.357	0.826	20.410	7.551	0.202
NCS DC 28044	42.417	8.060	3.855	1.507	20.677	2.430	0.123
NCS DC 28045	51.072	3.123	0.221	0.207	18.171	2.669	0.261
NCS DC 47004	52.887	1.422	1.235	0.746	18.829	2.563	0.063
NCS DC 47007	29.545	24.806	0.060	0.118	12.362	10.601	0.325
NCS DC 47009	22.577	2.969	28.371	5.479	22.691	3.572	0.087
NCS HC28803	0.604	0.920	36.260	9.920	31.820	16.850	0.008
OREAS 73b	0.123	9.250	4.724	20.970	47.898	7.635	0.026
Sarm 135	44.059	17.209	6.552	0.480	4.364	0.304	0.026
Sarm 136	50.051	11.067	7.609	0.789	4.151	0.289	0.028

Table A.2: Certified reference material (CRM) list after LOI conversion

Sarm 137	51.754	10.340	5.901	0.611	5.849	0.266	0.028
SARM 16	51.098	11.930	4.884	0.790	5.238	0.312	0.034
SARM 17	46.680	5.136	17.320	3.644	5.641	0.289	0.022
SMU 7-1-007 (N-7-1-007)	0.606	0.552	31.315	18.970	39.144	6.223	0.000
SX 3911 (DH 3911)	4.423	18.525	50.540	1.541	8.587	0.934	1.157
VS 5403-90	0.163	63.219	0.897	0.655	7.194	0.736	0.000
VS R13/3	67.560	0.000	0.000	0.000	2.306	0.000	0.225

	% Mn	% Fe	% CaO	% MgO	% SIO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
BLANK	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SARM17	38.810	4.2700	14.4000	3.0300	4.6900	0.2400	0.0180
ES 5	38.400	5.5000	13.9380	3.8730	4.6450	0.2300	0.0230
ES 4	33.700	4.3000	14.9210	3.9640	5.6350	0.2360	0.0230
ES 33	30.667	4.3000	15.2390	6.7140	4.6660	0.2960	0.0230
ES 32	17.050	6.8000	15.7500	4.0350	4.5200	0.2460	0.0210
ES 31	12.548	7.7000	24.6570	3.7180	6.7170	0.2910	0.0230
ES 30	7.431	10.5000	19.7690	8.6500	4.7500	0.3510	0.0270
ES 3	34.000	4.5000	14.5410	3.3920	4.0840	0.2720	0.0200
ES 29	8.679	8.3000	15.6950	3.5420	2.6170	0.2850	0.0240
ES 28	37.300	4.3000	12.3010	3.5350	4.9590	0.2620	0.0671
ES 20	32.100	4.4000	14.6280	3.6880	4.6950	0.2520	0.0710
ES 19	6.000	12.0000	14.9790	9.8630	3.6620	0.2610	0.0517
ES 15	35.800	6.5000	10.3660	4.1550	3.0240	0.5400	0.1026
ES 13	36.700	10.1000	14.6690	3.8730	4.9140	0.2680	0.0292
ES 10	24.615	8.9000	17.4380	4.1580	5.4040	0.2500	0.0600
EL 9	38.100	4.3000	14.5370	2.9888	4.5600	0.1740	0.0180
EL 8	38.000	4.0000	14.6550	3.5740	4.4580	0.1860	0.0200
EL 6	38.900	2.9000	14.9380	2.8230	3.3260	0.1810	0.0190
EL 4	43.025	1.7000	7.9510	1.8540	1.6130	0.2430	0.0220
EL 3	38.900	3.9000	14.2320	3.2570	1.2460	0.1900	0.0200
EL 23	37.800	4.4000	13.1980	3.9690	4.5260	0.2820	0.0200
EL 22	37.100	4.0000	14.4110	4.1330	4.6960	0.2300	0.0210
EL 2	40.800	3.8000	8.9190	1.7950	5.6780	0.2150	0.0200
EL 19	35.200	4.2000	20.9010	3.7220	8.5320	0.2650	0.0920
EL 18	36.600	4.0000	14.9680	5.2920	4.5080	0.2640	0.0460
EL 17	21.882	4.5000	17.8160	4.0070	4.7760	0.2960	0.0690
EL 16	26.538	5.2000	14.8510	3.5100	4.7380	0.2860	0.0748
EL 15	20.300	5.3000	14.2960	4.3330	2.3880	0.1960	0.0874
EL 14	39.300	4.4000	14.5500	5.8660	4.5400	0.2470	0.0506

Table A. 3: Low grade secondary standard consensus value

EL 13	38.500	4.4000	14.2850	3.6530	4.5620	0.2600	0.0391
EL 11	38.100	4.6000	13.2540	2.3330	4.7240	0.2160	0.0840
EL 1	39.400	4.1000	13.5420	4.3670	7.8940	0.8420	0.0220
RR1	39.400	4.2100	13.2400	3.1100	4.6500	0.2200	0.0200
EL 5	42.059	4.5000	13.2060	2.8620	6.3520	0.1720	0.0230

	% Mn	% Fe	% CaO	% MgO	% SIO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% P
BLANK	0.000	0.000	0.000	0.000	0.000	0.000	0.000
FD 998	37.396	18.200	8.736	1.217	4.462	0.300	0.044
FD 997	39.040	17.530	7.962	2.539	5.458	0.952	0.044
FD 980	34.872	16.130	6.383	11.197	9.897	1.659	0.025
FD 972	38.594	17.760	8.644	0.723	5.434	2.720	0.032
FD 960	38.396	19.076	7.736	0.000	3.093	0.450	0.030
FD 952	37.187	19.260	8.580	0.137	1.723	0.431	0.026
FD 951	37.128	18.760	8.541	8.135	1.667	0.406	0.025
FD 25	40.102	17.060	6.153	2.471	6.693	2.188	0.031
FD 23	57.001	5.200	5.874	0.000	2.173	0.235	0.017
FD 22	53.679	6.500	15.091	0.158	6.889	0.227	0.104
FD 211	58.361	5.900	4.255	6.120	5.676	0.181	0.024
FD 205	60.643	4.870	4.293	0.262	4.582	0.293	0.023
FD 16	47.637	6.930	12.700	0.174	3.144	0.098	0.040
FD 141	35.883	5.670	6.238	16.067	17.456	0.548	0.017
FD 14	45.948	10.000	5.974	0.599	3.661	0.225	0.050
FD 131	36.943	13.890	10.237	1.301	12.485	2.933	0.062
FD 122	35.637	14.670	10.587	0.227	11.980	2.099	0.041
FD 12	24.705	11.030	4.160	0.070	2.958	2.424	0.066
FD 118	52.650	6.970	6.454	0.309	7.271	3.672	0.076
FD 11	39.653	11.430	10.204	4.380	7.299	4.195	0.038
FD 07	49.700	6.500	7.071	0.471	7.074	0.551	0.021
FD 06	47.893	9.770	7.332	1.524	5.846	1.026	0.026
FD 04	35.540	16.530	10.963	1.778	4.901	1.351	0.039
FD 02	52.016	2.900	7.355	0.679	8.148	0.669	0.018
SARM	49.170	11.480	4.700	0.760	5.040	0.300	0.033
16							

Table A. 4: High grade secondary standard consensus value

### Kalahari Fusion energy profile

Figure A 1: Mn energy profile



				File ir	iforma	tion					
				Energy Pro	file Pa	rametere					
Element/Line	Gonio	Crystal	Detector	Collimator	KX.	mA.	PBF/ PBD	Mask	Rotation	AGC	Туре
Mn_mf		LIF200	ExkrBe		50	50	None	629 mm	Yes	Yes	Norm
				Energy	Profile	e data					
	PHD			F	aram [	Step]		Cour	it.Time [8]		Count Rate
Threshol	d	Window	S	tart	End		Inc.	Inc.	Global		[kcps]
40		70		20	150		2	2	20		180.50





Figure A. 3: Ca energy profile

Energy Profile





File Information														
Energy Profile Parameters														
⊟ement/Line	Gonio	Crystal	Det	ector	Collim ato r	kV	m /	4	PBF/ PBD	,	Mask	Rotatio n	AGC	Туре
Ca_m		LiF200	Ex,	ArBe		<b>3</b> 0	<b>8</b> 0	)	None	ø	29 mm	Yes	Yes	Norm
					Energy	Profil	e data	l.						
	PHD				P	aram	[Step]				Count.	Time [s]	0	Count Rate
Threshold		Window		St	art	Enc	1	I	Inc.		Inc.	Globa		[kcps]
40		66		2	20	150	ט		2		2	20		66.16

Figure A. 4: Mg energy profile



	File Information												
	Energy Profile Parameters												
Element/Line	Gonio	Crystal	Deteo	tor Col	lim ato	kV	mA	PBF/		Mask	Rotatio	AGC	Туре
		-			r			PBD			n		
								100					
Ma m		AX06	FP	2		30	80	None		ø29 mm	Yes	Yes	Norm
				l i i i i i i i i i i i i i i i i i i i	nergy	Profile	data						
	PHD				P	aram [	Sten1			Count	Time [s]		Count Rate
Threshold		Window		Start		End		Inc.		Inc.	Globa		[kcps]
30		81		20		150		2	1	2	20		12.36
								-		-			

# Energy Profile



### Figure A. 5: Si energy profile

#### Energy Profile





File Information											
Energy Profile Parameters											
Element/Line	Gonio	Crystal	Detecto	r Collimato r	kV	m A	PBF/ PBD	Mask	Rotatio n	AGC	Туре
Si_m		InSb	Ex Ne Be		30	80	None	ø29 mm	Yes	Yes	Norm
				Energy	Profile d	ata					
	PHD			P	aram [St	ep]		Cour	nt.Tim e [s]	С	Count Rate
Threshold		Window		Start	End		Inc.	Inc.	Globa		[kcps]
30		90		20	150		2	2	20		109.10

### Figure A. 6: Al energy profile

#### Energy Profile



File Information											
Energy Profile Parameters											
Ele me nt/Line	Gonio	Crystal	Detecto	r Collimato r	kV	mA	PBF/ PBD	Mas k	Rotatio n	AGC	Туре
Al_m		PET	ExNeBe	•	30	80	None	ø29 mm	Yes	Yes	Norm
				Energy	Profile	e data					
	PHD			P	aram [	[Step]		Cour	nt.Time [s]	С	ount Rate
Threshold		Window		Start	End		Inc.	Inc.	Globa	I	[kcps]
35		75		20	150		2	2	20		9.66

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Figure A. 7 : P energy profile



Low grade calibration MVR sample list

MVR Sample	List					
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative
Name			Conc.	Conc.	Diff.	Diff.[%]
BLANK	1	0.892	0.000	0.068	0.068	6.8E+12
SARM17	1	394.992	38.810	39.157	0.347	0.89514
ES 4	1	338.056	33.700	33.510	-0.190	0.56338
ES 33	1	311.308	30.667	30.857	0.190	0.621
ES 32	1	174.125	17.050	17.251	0.201	1.17627
ES 31	1	127.978	12.548	12.673	0.125	0.99871
ES 30	1	78.537	7.431	7.770	0.339	4.56254
ES 3	1	339.116	34.000	33.615	-0.385	1.13152
ES 29	1	85.941	8.679	8.504	-0.175	2.01548
ES 28	1	377.865	37.300	37.459	0.159	0.42523
ES 20	1	319.818	32.100	31.701	-0.399	1.2423
ES 19	1	58.624	6.000	5.795	-0.205	3.42363
ES 15	1	357.811	35.800	35.470	-0.330	0.92311
ES 13	1	365.747	36.700	36.257	-0.443	1.20789
ES 10	1	244.441	24.615	24.225	-0.390	1.58621
EL 9	1	384.250	38.100	38.092	-0.008	0.02132
EL 8	1	381.324	38.000	37.802	-0.198	0.52191
EL 6	1	396.758	38.900	39.333	0.433	1.1119
EL 4	1	438.489	43.025	43.472	0.447	1.03806
EL 23	1	381.955	37.800	37.864	0.064	0.17007
EL 22	1	371.303	37.100	36.808	-0.292	0.7877
EL 2	1	415.996	40.800	41.241	0.441	1.08012
EL 19	1	354.640	35.200	35.155	-0.045	0.12765
EL 17	1	219.163	21.882	21.718	-0.165	0.75247
EL 16	1	271.692	26.538	26.928	0.389	1.467
EL 15	1	207.951	20.300	20.606	0.306	1.50587
EL 13	1	386.321	38.500	38.297	-0.203	0.52638
RR1	1	398.390	39.400	39.494	0.094	0.23959

# Table A. 5: Low grade Mn MVR sample list

EL 5	1	422.486	42.059	41.884	-0.174	0.41487
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### Table A. 6: Low grade Fe MVR sample list

MVR Sample	e List					
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative
Name			Conc.	Conc.	Diff.	Diff.[%]
BLANK	1.00	5.53	0.00	-0.14	-0.14	
SARM17	1.00	375.12	4.27	4.30	0.03	0.81
ES 5	1.00	478.97	5.50	5.55	0.05	0.95
ES 4	1.00	364.03	4.30	4.17	-0.13	2.99
ES 32	1.00	589.50	6.80	6.88	0.08	1.18
ES 31	1.00	663.47	7.70	7.77	0.07	0.90
ES 30	1.00	881.33	10.50	10.39	-0.11	1.08
ES 3	1.00	396.91	4.50	4.57	0.07	1.47
ES 29	1.00	710.20	8.30	8.33	0.03	0.37
ES 28	1.00	369.25	4.30	4.23	-0.07	1.54
ES 20	1.00	383.01	4.40	4.40	0.00	0.02
ES 19	1.00	1010.77	12.00	11.94	-0.06	0.48
ES 15	1.00	558.64	6.50	6.51	0.01	0.15
ES 13	1.00	857.32	10.10	10.10	0.00	0.01
ES 10	1.00	754.84	8.90	8.87	-0.03	0.37
EL 8	1.00	348.36	4.00	3.98	-0.02	0.43
EL 6	1.00	258.11	2.90	2.90	0.00	0.05
EL 4	1.00	160.91	1.70	1.73	0.03	1.79
EL 3	1.00	336.41	3.90	3.84	-0.06	1.56
EL 23	1.00	381.65	4.40	4.38	-0.02	0.39
EL 22	1.00	349.40	4.00	4.00	0.00	0.11
EL 2	1.00	333.26	3.80	3.80	0.00	0.04
EL 19	1.00	374.49	4.20	4.30	0.10	2.31

EL 18	1.00	355.31	4.00	4.07	0.07	1.66
EL 16	1.00	449.92	5.20	5.20	0.00	0.06
EL 15	1.00	461.02	5.30	5.34	0.04	0.69
EL 14	1.00	383.78	4.40	4.41	0.01	0.19
EL 13	1.00	381.63	4.40	4.38	-0.02	0.39
EL 1	1.00	358.03	4.10	4.10	0.00	0.02
RR1	1.00	372.96	4.21	4.28	0.07	1.63

Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative
Name			Conc.	Conc.	Diff.	Diff.[%]
BLANK	1.00	0.5998	0.0000	0.1486	0.1486	
SARM17	1.00	342.1546	14.4000	14.4775	0.0775	0.5382
ES 5	1.00	326.4351	13.9380	13.8180	-0.1200	0.8607
ES 4	1.00	356.2963	14.9210	15.0708	0.1498	1.0038
ES 32	1.00	371.4565	15.7500	15.7068	-0.0432	0.2745
ES 31	1.00	584.9308	24.6570	24.6624	0.0054	0.0221
ES 30	1.00	470.2029	19.7690	19.8494	0.0804	0.4066
ES 29	1.00	371.1112	15.6950	15.6923	-0.0027	0.0173
ES 20	1.00	341.4685	14.6280	14.4487	-0.1793	1.2257
ES 15	1.00	246.8126	10.3660	10.4777	0.1117	1.0776
ES 10	1.00	412.1886	17.4380	17.4156	-0.0224	0.1287
EL 8	1.00	342.1571	14.6550	14.4776	-0.1774	1.2105
EL 6	1.00	355.7417	14.9380	15.0475	0.1095	0.7330
EL 4	1.00	184.3254	7.9510	7.8562	-0.0948	1.1918
EL 3	1.00	336.9816	14.2320	14.2605	0.0285	0.2001
EL 2	1.00	207.0895	8.9190	8.8112	-0.1078	1.2082
EL 19	1.00	497.7079	20.9010	21.0033	0.1023	0.4893
EL 17	1.00	421.1747	17.8160	17.7925	-0.0235	0.1316
EL 16	1.00	352.7265	14.8510	14.9210	0.0700	0.4714
EL 15	1.00	337.4251	14.2960	14.2791	-0.0169	0.1183
EL 13	1.00	337.8377	14.2850	14.2964	0.0114	0.0798
EL 11	1.00	312.0803	13.2540	13.2158	-0.0382	0.2881
EL 1	1.00	318.5713	13.5420	13.4881	-0.0539	0.3978
RR1	1.00	312.8708	13.2400	13.2490	0.0090	0.0678
EL 5	1.00	311.2731	13.2060	13.1820	-0.0240	0.1821

# Table A. 7: Low grade CaO MVR sample list

MVR Sample List									
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative			
Name			Conc.	Conc.	Diff.	Diff.[%]			
BLANK	1.00	0.5932	0.0000	-0.1726	-0.1726				
SARM17	1.00	27.7210	3.0300	3.0681	0.0381	1.2560			
ES 5	1.00	34.6667	3.8730	3.8978	0.0248	0.6401			
ES 4	1.00	35.3416	3.9640	3.9784	0.0144	0.3634			
ES 33	1.00	58.1262	6.7140	6.7002	-0.0138	0.2052			
ES 31	1.00	33.1487	3.7180	3.7165	-0.0015	0.0416			
ES 30	1.00	73.6560	8.6500	8.5554	-0.0946	1.0937			
ES 3	1.00	30.5357	3.3920	3.4043	0.0123	0.3627			
ES 29	1.00	32.0743	3.5420	3.5881	0.0461	1.3014			
ES 28	1.00	31.7928	3.5350	3.5545	0.0195	0.5510			
ES 20	1.00	33.4761	3.6880	3.7556	0.0676	1.8318			
ES 19	1.00	84.4256	9.8630	9.8419	-0.0211	0.2138			
ES 13	1.00	34.8994	3.8730	3.9256	0.0526	1.3576			
ES 10	1.00	36.6783	4.1580	4.1381	-0.0199	0.4787			
EL 9	1.00	27.8006	2.9888	3.0776	0.0888	2.9701			
EL 6	1.00	25.8543	2.8230	2.8451	0.0221	0.7819			
EL 4	1.00	17.8556	1.8540	1.8896	0.0356	1.9178			
EL 3	1.00	29.5992	3.2570	3.2924	0.0354	1.0879			
EL 23	1.00	35.2919	3.9690	3.9725	0.0035	0.0876			
EL 22	1.00	36.4414	4.1330	4.1098	-0.0232	0.5617			
EL 2	1.00	17.2632	1.7950	1.8188	0.0238	1.3252			
EL 19	1.00	33.3656	3.7220	3.7424	0.0204	0.5472			
EL 18	1.00	46.3021	5.2920	5.2877	-0.0043	0.0807			
EL 17	1.00	35.8766	4.0070	4.0423	0.0353	0.8814			
EL 16	1.00	31.5699	3.5100	3.5278	0.0178	0.5084			
EL 15	1.00	37.8907	4.3330	4.2829	-0.0501	1.1556			
EL 14	1.00	51.1252	5.8660	5.8639	-0.0021	0.0359			
EL 13	1.00	32.7849	3.6530	3.6730	0.0200	0.5472			

# Table A. 8: Low grade MgO MVR sample list

EL 11	1.00	20.4943	2.3330	2.2048	-0.1282	5.4962
EL 1	1.00	38.5966	4.3670	4.3672	0.0002	0.0056
RR1	1.00	27.4863	3.1100	3.0400	-0.0700	2.2501
EL 5	1.00	26.1907	2.8620	2.8853	0.0233	0.8125

MVR Sample List							
Sample Name	Weight	Intensity	Given	Calcul.	Absolute	Relative	
			Conc.	Conc.	Diff.	Diff.[%]	
BLANK	1.00	0.508	0.000	0.083	0.083		
SARM17	1.00	77.581	4.690	4.685	-0.005	0.107	
ES 5	1.00	77.999	4.645	4.710	0.065	1.399	
ES 4	1.00	94.191	5.635	5.677	0.042	0.743	
ES 33	1.00	78.009	4.666	4.711	0.045	0.955	
ES 32	1.00	74.415	4.520	4.496	-0.024	0.531	
ES 31	1.00	112.695	6.717	6.782	0.065	0.965	
ES 30	1.00	78.862	4.750	4.761	0.011	0.242	
ES 3	1.00	65.805	4.084	3.982	-0.102	2.502	
ES 29	1.00	43.542	2.617	2.652	0.035	1.354	
ES 28	1.00	80.782	4.959	4.876	-0.083	1.670	
ES 20	1.00	78.081	4.695	4.715	0.020	0.423	
ES 19	1.00	59.452	3.662	3.602	-0.060	1.625	
ES 15	1.00	49.529	3.024	3.010	-0.014	0.466	
ES 13	1.00	81.677	4.914	4.930	0.016	0.318	
ES 10	1.00	88.594	5.404	5.343	-0.061	1.136	
EL 9	1.00	74.832	4.560	4.521	-0.039	0.859	
EL 6	1.00	55.074	3.326	3.341	0.015	0.453	
EL 4	1.00	24.674	1.613	1.526	-0.087	5.407	
EL 3	1.00	20.243	1.246	1.261	0.015	1.219	
EL 2	1.00	93.136	5.678	5.614	-0.064	1.129	
EL 19	1.00	142.021	8.532	8.533	0.001	0.011	
EL 15	1.00	39.280	2.388	2.398	0.010	0.417	
EL 14	1.00	76.398	4.540	4.614	0.074	1.638	
EL 11	1.00	78.433	4.724	4.736	0.012	0.252	
EL 1	1.00	131.247	7.894	7.890	-0.004	0.056	
RR1	1.00	77.117	4.650	4.657	0.007	0.157	
EL 5	1.00	105.964	6.352	6.380	0.028	0.439	

# Table A. 9: Low grade SiO<sub>2</sub> MVR sample list

MVR Sample List								
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative		
Name			Conc.	Conc.	Diff.	Diff.[%]		
BLANK	1.00	0.0796	0.0000	0.0169	0.0169			
SARM17	1.00	2.6509	0.2400	0.2283	-0.0117	4.8773		
ES 5	1.00	2.7613	0.2300	0.2374	0.0074	3.2039		
ES 4	1.00	2.7201	0.2360	0.2340	-0.0020	0.8547		
ES 33	1.00	3.3649	0.2960	0.2870	-0.0090	3.0398		
ES 30	1.00	3.9765	0.3510	0.3373	-0.0137	3.9049		
ES 3	1.00	3.2350	0.2720	0.2763	0.0043	1.5874		
ES 29	1.00	3.3407	0.2850	0.2850	0.0000	0.0036		
ES 20	1.00	2.9076	0.2520	0.2494	-0.0026	1.0315		
ES 19	1.00	2.9450	0.2610	0.2525	-0.0085	3.2658		
ES 15	1.00	6.2883	0.5400	0.5274	-0.0126	2.3368		
ES 10	1.00	2.8195	0.2500	0.2422	-0.0078	3.1372		
EL 8	1.00	2.2978	0.1860	0.1993	0.0133	7.1276		
EL 22	1.00	2.5304	0.2300	0.2184	-0.0116	5.0488		
EL 19	1.00	3.1536	0.2650	0.2696	0.0046	1.7458		
EL 15	1.00	2.3433	0.1960	0.2030	0.0070	3.5724		
EL 14	1.00	2.7824	0.2470	0.2391	-0.0079	3.1966		
EL 1	1.00	10.3165	0.8420	0.8586	0.0166	1.9712		
RR1	1.00	2.5698	0.2200	0.2216	0.0016	0.7370		
EL 5	1.00	2.1591	0.1720	0.1879	0.0159	9.2166		

Table A. 10: Low grade Al<sub>2</sub>O<sub>3</sub> MVR sample list

MVR Sample List								
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative		
Name			Conc.	Conc.	Diff.	Diff.[%]		
BLANK	1.00	0.1446	0.0000	0.0020	0.0020			
ES 4	1.00	1.2840	0.0230	0.0229	-0.0001	0.2400		
ES 31	1.00	1.2899	0.0230	0.0231	0.0001	0.2255		
ES 30	1.00	1.3930	0.0270	0.0249	-0.0021	7.6129		
ES 29	1.00	1.3627	0.0240	0.0244	0.0004	1.6198		
ES 28	1.00	3.7457	0.0671	0.0681	0.0010	1.4637		
ES 20	1.00	4.0064	0.0710	0.0729	0.0019	2.7341		
ES 19	1.00	2.9624	0.0517	0.0537	0.0021	3.9903		
ES 15	1.00	5.6917	0.1026	0.1038	0.0012	1.1831		
ES 13	1.00	1.6382	0.0292	0.0294	0.0002	0.7844		
ES 10	1.00	3.2523	0.0600	0.0591	-0.0009	1.5158		
EL 9	1.00	1.0688	0.0180	0.0190	0.0010	5.5365		
EL 8	1.00	1.1290	0.0200	0.0201	0.0001	0.5017		
EL 6	1.00	1.1132	0.0190	0.0198	0.0008	4.2698		
EL 4	1.00	1.2151	0.0220	0.0217	-0.0003	1.4552		
EL 23	1.00	1.1437	0.0200	0.0204	0.0004	1.8528		
EL 22	1.00	1.1629	0.0210	0.0207	-0.0003	1.3197		
EL 18	1.00	2.4635	0.0460	0.0446	-0.0014	3.0783		
EL 17	1.00	3.7322	0.0690	0.0679	-0.0011	1.6524		
EL 16	1.00	4.0421	0.0748	0.0735	-0.0013	1.6778		
EL 15	1.00	4.7104	0.0874	0.0858	-0.0016	1.8225		
EL 14	1.00	2.6934	0.0506	0.0488	-0.0018	3.5526		
EL 13	1.00	2.0814	0.0391	0.0376	-0.0015	3.9029		
EL 11	1.00	4.6950	0.0840	0.0855	0.0015	1.8146		
EL 1	1.00	1.2240	0.0220	0.0218	-0.0002	0.7137		
EL 5	1.00	1.2756	0.0230	0.0228	-0.0002	0.9095		

# Table A. 11: Low grade P MVR sample list

### High grade calibration MVR sample list

MVR Sample List								
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative		
Name			Conc.	Conc.	Diff.	Diff.[%]		
BLANK	1.00	0.6441	0.0000	0.9102	0.9102			
FD 998	1.00	363.5423	37.3960	37.1966	-0.1994	0.5333		
FD 997	1.00	379.4227	39.0400	38.7845	-0.2555	0.6545		
FD 980	1.00	337.5105	34.8720	34.5936	-0.2784	0.7982		
FD 972	1.00	375.9031	38.5940	38.4325	-0.1615	0.4184		
FD 960	1.00	373.8572	38.3960	38.2280	-0.1680	0.4376		
FD 952	1.00	361.3885	37.1870	36.9812	-0.2058	0.5534		
FD 951	1.00	360.7790	37.1280	36.9203	-0.2077	0.5595		
FD 25	1.00	390.4290	40.1020	39.8850	-0.2170	0.5411		
FD 23	1.00	562.5751	57.0010	57.0980	0.0970	0.1701		
FD 211	1.00	578.7781	58.3610	58.7181	0.3571	0.6119		
FD 205	1.00	599.2183	60.6430	60.7620	0.1190	0.1962		
FD 16	1.00	469.1857	47.6370	47.7599	0.1229	0.2580		
FD 141	1.00	347.9391	35.8830	35.6364	-0.2466	0.6872		
FD 14	1.00	450.7355	45.9480	45.9151	-0.0329	0.0717		
FD 131	1.00	358.8717	36.9430	36.7296	-0.2134	0.5777		
FD 122	1.00	345.4052	35.6370	35.3830	-0.2540	0.7126		
FD 12	1.00	237.7929	24.7050	24.6228	-0.0822	0.3326		
FD 118	1.00	520.0942	52.6500	52.8503	0.2003	0.3804		
FD 11	1.00	386.8238	39.6530	39.5245	-0.1285	0.3240		
FD 07	1.00	490.4891	49.7000	49.8901	0.1901	0.3824		
FD 06	1.00	471.8244	47.8930	48.0238	0.1308	0.2730		
FD 04	1.00	344.3999	35.5400	35.2825	-0.2575	0.7245		
FD 02	1.00	516.4151	52.0160	52.4824	0.4664	0.8967		
SARM 16	1.00	486.4345	49.1700	49.4846	0.3146	0.6399		

Table A. 12: Low grade Mn MVR sample list

MVR Samp	le List					
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative Diff.[%]
Name			Conc.	Conc.	Diff.	
BLANK	1.00	4.9199	0.0000	-0.8162	-0.8162	
FD 997	1.00	1271.8110	17.5300	17.5656	0.0356	0.2031
FD 980	1.00	1175.4033	16.1300	16.1668	0.0368	0.2280
FD 972	1.00	1277.4820	17.7600	17.6479	-0.1121	0.6313
FD 960	1.00	1360.1837	19.0760	18.8478	-0.2282	1.1961
FD 952	1.00	1383.4650	19.2600	19.1856	-0.0744	0.3861
FD 951	1.00	1350.1610	18.7600	18.7024	-0.0576	0.3070
FD 25	1.00	1236.0787	17.0600	17.0471	-0.0129	0.0754
FD 23	1.00	438.1081	5.2000	5.4691	0.2691	5.1743
FD 22	1.00	521.0973	6.5000	6.6732	0.1732	2.6644
FD 16	1.00	554.6545	6.9300	7.1601	0.2301	3.3201
FD 14	1.00	759.6417	10.0000	10.1343	0.1343	1.3432
FD 131	1.00	1014.0110	13.8900	13.8251	-0.0649	0.4674
FD 122	1.00	1055.7953	14.6700	14.4313	-0.2387	1.6269
FD 12	1.00	826.5392	11.0300	11.1050	0.0750	0.6797
FD 118	1.00	554.7637	6.9700	7.1617	0.1917	2.7499
FD 11	1.00	854.1846	11.4300	11.5061	0.0761	0.6657
FD 07	1.00	528.1410	6.5000	6.7754	0.2754	4.2367
FD 06	1.00	741.5749	9.7700	9.8722	0.1022	1.0459
FD 04	1.00	1200.3203	16.5300	16.5283	-0.0017	0.0102
FD 02	1.00	262.5699	2.9000	2.9221	0.0221	0.7624
SARM 16	1.00	851.3660	11.4800	11.4652	-0.0148	0.1290

# Table A. 13: Low grade Fe MVR sample list

MVR San	nple List					
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative Diff.[%]
Name			Conc.	Conc.	Diff.	
BLANK	1.00	0.6026	0.0000	-0.1662	-0.1662	
FD 998	1.00	161.3591	8.7360	8.7176	-0.0184	0.2103
FD 997	1.00	147.6624	7.9620	7.9607	-0.0013	0.0162
FD 980	1.00	119.5650	6.3830	6.4080	0.0250	0.3913
FD 972	1.00	159.7752	8.6440	8.6301	-0.0139	0.1608
FD 960	1.00	143.5713	7.7360	7.7346	-0.0014	0.0177
FD 952	1.00	158.6529	8.5800	8.5681	-0.0119	0.1390
FD 951	1.00	157.9333	8.5410	8.5283	-0.0127	0.1486
FD 25	1.00	115.5849	6.1530	6.1880	0.0350	0.5693
FD 22	1.00	276.7787	15.0910	15.0960	0.0050	0.0332
FD 211	1.00	81.8786	4.2550	4.3253	0.0703	1.6529
FD 205	1.00	82.5955	4.2930	4.3650	0.0720	1.6761
FD 16	1.00	234.5740	12.7000	12.7637	0.0637	0.5013
FD 141	1.00	117.6098	6.2380	6.2999	0.0619	0.9928
FD 131	1.00	187.8432	10.2370	10.1812	-0.0558	0.5450
FD 122	1.00	194.0394	10.5870	10.5236	-0.0634	0.5987
FD 12	1.00	80.2998	4.1600	4.2381	0.0781	1.8770
FD 118	1.00	120.8315	6.4540	6.4780	0.0240	0.3714
FD 11	1.00	187.2122	10.2040	10.1463	-0.0577	0.5651
FD 07	1.00	131.7833	7.0706	7.0832	0.0126	0.1787
FD 06	1.00	136.4373	7.3320	7.3404	0.0084	0.1143
FD 04	1.00	200.8984	10.9630	10.9027	-0.0603	0.5503
FD 02	1.00	136.8323	7.3553	7.3622	0.0069	0.0943

# Table A. 14: Low grade CaO MVR sample list

MVR Sample List						
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative Diff.[%]
Name			Conc.	Conc.	Diff.	
BLAN	0.00	0.7088	0.0000	-0.4289	-0.4289	0.0000
К						
FD 998	1.00	19.9786	1.2170	1.1897	-0.0272	2.2386
FD 997	1.00	35.6576	2.5394	2.5068	-0.0327	1.2858
FD 980	1.00	138.3033	11.1971	11.1290	-0.0681	0.6079
FD 972	1.00	14.1235	0.7231	0.6979	-0.0252	3.4880
FD 960	1.00	5.2683	0.0000	-0.0459	-0.0459	0.0000
FD 952	1.00	7.4064	0.1370	0.1337	-0.0033	2.4213
FD 951	1.00	103.4356	8.1350	8.2001	0.0651	0.8003
FD 25	1.00	34.8495	2.4713	2.4389	-0.0324	1.3100
FD 211	1.00	81.9089	6.1200	6.3919	0.2719	4.4422
FD 205	1.00	8.5254	0.2620	0.2277	-0.0343	13.0982
FD 16	1.00	7.6094	0.1737	0.1507	-0.0230	13.2258
FD 141	1.00	196.0384	16.0667	15.9787	-0.0880	0.5477
FD 12	1.00	6.4354	0.0700	0.0521	-0.0179	25.5402
FD 118	1.00	9.6325	0.3090	0.3207	0.0117	3.7785
FD 11	1.00	58.3791	4.3800	4.4154	0.0354	0.8075
FD 07	1.00	11.6628	0.4710	0.4912	0.0202	4.2935
FD 06	1.00	23.6143	1.5236	1.4951	-0.0285	1.8704
FD 04	1.00	26.6356	1.7785	1.7489	-0.0295	1.6610
FD 02	1.00	14.5145	0.6790	0.7308	0.0518	7.6236

# Table A. 15: Low grade MgO MVR sample list

MVR Sample List						
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative Diff.[%]
Name			Conc.	Conc.	Diff.	
FD 998	1.00	76.9076	4.4620	4.4542	-0.0078	0.1740
FD 997	1.00	97.8669	5.4580	5.4566	-0.0014	0.0255
FD 980	1.00	190.7022	9.8973	9.8964	-0.0008	0.0084
FD 972	1.00	97.2489	5.4340	5.4271	-0.0069	0.1278
FD 960	1.00	47.9052	3.0930	3.0672	-0.0258	0.8342
FD 951	1.00	18.3503	1.6670	1.6537	-0.0133	0.7956
FD 25	1.00	123.8620	6.6930	6.6998	0.0068	0.1019
FD 23	1.00	28.9051	2.1726	2.1585	-0.0141	0.6480
FD 22	1.00	127.7029	6.8895	6.8835	-0.0060	0.0869
FD 211	1.00	102.7926	5.6760	5.6922	0.0162	0.2850
FD 205	1.00	80.0808	4.5820	4.6060	0.0240	0.5236
FD 141	1.00	349.0261	17.4561	17.4683	0.0121	0.0695
FD 14	1.00	60.0746	3.6607	3.6492	-0.0115	0.3148
FD 131	1.00	243.9730	12.4850	12.4441	-0.0409	0.3275
FD 12	1.00	45.3486	2.9577	2.9449	-0.0127	0.4305
FD 118	1.00	134.2009	7.2710	7.1943	-0.0767	1.0552
FD 07	1.00	131.0103	7.0740	7.0417	-0.0323	0.4568
FD 06	1.00	107.2753	5.8460	5.9066	0.0606	1.0360
FD 04	1.00	86.6239	4.9010	4.9189	0.0179	0.3655
FD 02	1.00	155.1409	8.1480	8.1957	0.0477	0.5858
SARM 16	1.00	90.5130	5.0400	5.1049	0.0649	1.2878

Table A. 16: Low grade SiO<sub>2</sub> MVR sample list

MVR Sample List						
Sample	Weight	Intensity	Given	Calcul.	Absolute	Relative Diff.[%]
Name			Conc.	Conc.	Diff.	
BLANK	1.00	0.1477	0.0000	-0.0342	-0.0342	
FD 960	1.00	4.0976	0.4501	0.4641	0.0140	3.1161
FD 952	1.00	3.9544	0.4305	0.4461	0.0156	3.6140
FD 951	1.00	3.7718	0.4055	0.4230	0.0175	4.3214
FD 22	1.00	2.4669	0.2267	0.2584	0.0317	13.9888
FD 211	1.00	2.1319	0.1808	0.2162	0.0354	19.5534
FD 205	1.00	3.0285	0.2930	0.3293	0.0363	12.3743
FD 16	1.00	1.5250	0.0976	0.1396	0.0420	43.0223
FD 141	1.00	4.6167	0.5480	0.5296	-0.0184	3.3566
FD 131	1.00	23.6323	2.9330	2.9284	-0.0046	0.1572
FD 122	1.00	16.8161	2.0987	2.0685	-0.0302	1.4372
FD 12	1.00	20.0382	2.4240	2.4750	0.0510	2.1040
FD 118	1.00	29.5914	3.6720	3.6801	0.0081	0.2212
FD 11	1.00	33.8112	4.1950	4.2124	0.0174	0.4158
FD 07	1.00	4.6864	0.5510	0.5384	-0.0126	2.2868
FD 06	1.00	8.0046	1.0260	0.9570	-0.0690	6.7266
FD 04	1.00	10.4198	1.3510	1.2617	-0.0893	6.6130
FD 02	1.00	5.4518	0.6690	0.6349	-0.0341	5.0898
SARM 16	1.00	2.9817	0.3000	0.3233	0.0233	7.7824

# Table A. 17: Low grade Al<sub>2</sub>O<sub>3</sub> MVR sample list

MVR Sample List						
Sample	Weigh	Intensity	Given	Calcul.	Absolute	Relative Diff.[%]
Name	t		Conc.	Conc.	Diff.	
BLANK	1.00	0.0155	0.0000	-0.0026	-0.0026	0.0000
FD 998	1.00	2.9167	0.0440	0.0443	0.0003	0.7865
FD 997	1.00	2.8448	0.0440	0.0432	-0.0008	1.8541
FD 980	1.00	1.7432	0.0250	0.0254	0.0004	1.4572
FD 972	1.00	2.1587	0.0320	0.0321	0.0001	0.2671
FD 960	1.00	2.0718	0.0300	0.0307	0.0007	2.2682
FD 952	1.00	1.8138	0.0260	0.0265	0.0005	1.9466
FD 22	1.00	6.6706	0.1040	0.1051	0.0011	1.0272
FD 211	1.00	1.7200	0.0240	0.0250	0.0010	4.1250
FD 205	1.00	1.6402	0.0230	0.0237	0.0007	3.0341
FD 16	1.00	2.6563	0.0399	0.0401	0.0002	0.5898
FD 141	1.00	1.2639	0.0170	0.0176	0.0006	3.5989
FD 14	1.00	3.2152	0.0495	0.0492	-0.0003	0.6547
FD 12	1.00	4.1705	0.0660	0.0646	-0.0014	2.0798
FD 118	1.00	4.7552	0.0760	0.0741	-0.0019	2.5190
FD 11	1.00	2.5215	0.0376	0.0380	0.0004	0.9404
FD 06	1.00	1.7926	0.0260	0.0262	0.0002	0.6314
FD 04	1.00	2.5964	0.0390	0.0392	0.0002	0.4253
FD 02	1.00	1.3266	0.0180	0.0186	0.0006	3.4739
SARM 16	1.00	2.2224	0.0330	0.0331	0.0001	0.3499

Table A. 18: Low grade P MVR sample list
# Kalahari fusion calibration MVR sample list

MVR Sample List									
Sample Name	Weight	Intensity	Given	Calcul.	Absolute	Relative Diff.[%]			
			Conc.	Conc.	Diff.				
BLANK	1.00	0.695	0.000	0.401	0.401				
BCS No.176/2	1.00	151.678	55.774	55.616	-0.158	0.283			
CMSI 1756 (NCS HC13806)	1.00	28.142	10.192	10.156	-0.036	0.355			
ECRM 609-1	1.00	2.106	0.574	0.556	-0.018	3.168			
ECRM 651-1	1.00	4.035	1.310	1.270	-0.040	3.031			
ECRM 678-1	1.00	1.490	0.080	0.325	0.245	306.681			
GBW 07227	1.00	1.300	0.190	0.257	0.068	35.567			
MO196	1.00	142.475	52.044	52.266	0.222	0.427			
NCS DC 11019	1.00	61.723	22.497	22.523	0.026	0.116			
NCS DC 19001	1.00	1.038	0.223	0.161	-0.062	27.764			
NCS DC 19002	1.00	0.953	0.204	0.130	-0.075	36.573			
NCS DC 28042	1.00	71.984	26.510	26.319	-0.190	0.718			
NCS DC 28043	1.00	98.622	36.562	36.140	-0.422	1.154			
NCS DC 28044	1.00	115.820	42.417	42.415	-0.001	0.003			
NCS DC 28045	1.00	139.947	51.072	51.197	0.125	0.245			
NCS DC 47007	1.00	81.432	29.545	29.885	0.339	1.149			

## Table A. 19: Kalahari fusion Mn MVR sample list

NCS HC 28803	1.00	1.979	0.604	0.505	-0.099	16.339
OREAS 73b	1.00	1.158	0.123	0.205	0.081	66.076
SMU 7-1-007 (N-7-1- 007)	1.00	2.073	0.606	0.540	-0.067	10.975
SX 3911 (DH 3911)	1.00	11.673	4.423	4.088	-0.335	7.573
VS 5403-90	1.00	0.944	0.163	0.125	-0.038	23.400
VS R13/3	1.00	184.816	67.560	67.589	0.029	0.043

MVR Sample List									
Sample Name	Weight	Intensity	Given	Calcul.	Absolute	Relative			
			Conc.	Conc.	Diff.	Diff.[%]			
BLANK	1.00	2.567	0.000	0.080	0.080				
BAM 633-1	1.00	17.911	1.894	1.960	0.066	3.511			
ECRM 609-1	1.00	304.764	37.144	37.120	-0.024	0.065			
GBW 07222a (NCS	1.00	458.804	55.752	56.000	0.248	0.445			
DC46005)									
GBW 07227	1.00	110.817	13.398	13.348	-0.050	0.374			
KZ 185-89	1.00	13.061	1.422	1.366	-0.056	3.958			
MO196	1.00	84.713	10.109	10.148	0.040	0.393			
NCS DC 11019	1.00	90.204	10.893	10.821	-0.072	0.660			
NCS DC 11021	1.00	106.446	12.743	12.812	0.069	0.544			
NCS DC 19001	1.00	269.072	32.986	32.745	-0.241	0.732			
NCS DC 19002	1.00	226.190	27.555	27.489	-0.066	0.240			
NCS DC 28041	1.00	9.577	0.915	0.939	0.024	2.601			
NCS DC 28044	1.00	67.932	8.060	8.092	0.031	0.386			
NCS DC 28045	1.00	28.027	3.123	3.200	0.077	2.471			
NCS DC 47004	1.00	13.785	1.422	1.455	0.033	2.341			
NCS DC 47007	1.00	203.180	24.806	24.669	-0.138	0.554			
Sarm 136	1.00	92.093	11.067	11.053	-0.014	0.124			
SARM 16	1.00	99.055	11.930	11.906	-0.024	0.201			
SARM 17	1.00	43.952	5.136	5.152	0.016	0.320			

# Table A. 20: Kalahari fusion Fe MVR sample list

MVR Sample List									
Sample Name	Weight	Intensity	Given	Calcul.	Absolute	Relative			
			Conc.	Conc.	Diff.	Diff.[%]			
BLANK	1.00	0.779	0.000	-0.023	-0.023				
ECRM 678-1	1.00	9.130	5.485	5.517	0.032	0.589			
GBW 07222a (NCS	1.00	7.372	4.316	4.351	0.035	0.803			
DC46005)									
GBW 07227	1.00	18.515	11.768	11.743	-0.025	0.211			
KZ 185-89	1.00	50.509	32.957	32.967	0.010	0.029			
NCS DC 11023	1.00	4.960	2.702	2.751	0.049	1.804			
NCS DC 19001	1.00	10.480	6.383	6.412	0.029	0.456			
NCS DC 19002	1.00	12.141	7.501	7.515	0.013	0.177			
NCS DC 28043	1.00	2.758	1.357	1.290	-0.067	4.933			
NCS DC 28044	1.00	6.593	3.855	3.834	-0.021	0.552			
NCS DC 28045	1.00	1.027	0.221	0.142	-0.080	36.088			
NCS DC 47004	1.00	2.621	1.235	1.199	-0.036	2.945			
NCS DC 47007	1.00	0.822	0.060	0.006	-0.055	90.475			
NCS DC 47009	1.00	43.536	28.371	28.342	-0.030	0.105			
Sarm 135	1.00	10.741	6.552	6.585	0.034	0.512			
Sarm 136	1.00	12.419	7.609	7.699	0.090	1.183			
SARM 16	1.00	8.293	4.884	4.962	0.077	1.584			
SMU 7-1-007 (N-7-1-	1.00	47.970	31.315	31.283	-0.032	0.103			
007)									

# Table A. 21: Kalahari fusion CaO MVR sample list

MVR Sample List									
Sample Name	Weight	Intensity	Given	Calcul.	Absolute	Relative Diff.[%]			
			Conc.	Conc.	Diff.				
BLANK	1.00	0.717	0.000	-0.063	-0.063				
GBW 07227	1.00	4.864	8.426	8.568	0.142	1.689			
NCS DC 11019	1.00	1.131	0.749	0.799	0.050	6.613			
NCS DC 11020	1.00	1.707	1.984	1.997	0.013	0.630			
NCS DC 11021	1.00	1.163	0.896	0.865	-0.031	3.456			
NCS DC 11023	1.00	1.180	0.901	0.900	-0.001	0.164			
NCS DC 19001	1.00	3.699	6.163	6.144	-0.019	0.306			
NCS DC 19002	1.00	3.703	6.171	6.151	-0.020	0.326			
NCS DC 28041	1.00	1.075	0.646	0.682	0.036	5.621			
NCS DC 28043	1.00	1.128	0.826	0.793	-0.033	4.024			
NCS DC 47007	1.00	0.822	0.118	0.155	0.037	31.167			
OREAS 73b	1.00	10.831	20.970	20.988	0.018	0.086			
Sarm 137	1.00	1.015	0.611	0.556	-0.055	8.973			
SMU 7-1-007 (N-7-1-	1.00	9.827	18.970	18.897	-0.073	0.383			
007)									

# Table A. 22: Kalahari fusion MgO MVR sample list

MVR Sample List									
Sample Name	Weight	Intensity	Given		Absolute	Relative Diff.[%]			
			Conc.	Calcul.	Diff.				
				Conc.					
BCS No.176/2	1.00	5.090	2.971	3.029	0.059	1.978			
BLANK	1.00	0.032	0.000	-0.015	-0.015				
CMSI 1756 (NCS	1.00	34.578	21.370	20.773	-0.597	2.792			
HC13806)									
ECRM 609-1	1.00	33.696	20.386	20.242	-0.144	0.706			
ECRM 651-1	1.00	16.919	10.011	10.147	0.136	1.358			
ECRM 678-1	1.00	6.627	3.701	3.954	0.253	6.840			
GBW 07222a (NCS	1.00	8.703	5.095	5.203	0.108	2.123			
DC46005)									
GBW 07227	1.00	60.532	36.791	36.391	-0.400	1.089			
MO196	1.00	8.743	5.175	5.227	0.052	1.009			
NCS DC 11021	1.00	42.151	25.578	25.330	-0.248	0.971			
NCS DC 11023	1.00	24.978	15.046	14.997	-0.049	0.328			
NCS DC 19001	1.00	33.426	20.340	20.080	-0.260	1.277			
NCS DC 28041	1.00	101.113	60.325	60.810	0.485	0.804			
NCS DC 47007	1.00	20.659	12.362	12.398	0.036	0.290			
NCS DC 47009	1.00	37.727	22.691	22.668	-0.023	0.103			
OREAS 73b	1.00	79.886	47.898	48.037	0.139	0.289			
Sarm 136	1.00	7.130	4.151	4.257	0.106	2.547			
SARM 16	1.00	8.897	5.238	5.320	0.082	1.575			
SARM 17	1.00	9.714	5.641	5.812	0.171	3.027			
VS 5403-90	1.00	12.195	7.194	7.305	0.110	1.530			

# Table A. 23: Kalahari fusion SiO<sub>2</sub> MVR sample list

MVR Sample List									
Sample Name	Weight	Intensity	Given	Calcul.	Absolute	Relative			
			Conc.	Conc.	Diff.	Diff.[%]			
BLANK	1.00	0.391	0.000	0.128	0.128				
BAM 633-1	1.00	1.663	1.894	1.891	-0.003	0.146			
CMSI 1756 (NCS	1.00	3.108	4.000	3.894	-0.106	2.651			
HC13806)									
ECRM 651-1	1.00	4.558	5.763	5.904	0.141	2.454			
ECRM 678-1	1.00	0.706	0.529	0.564	0.035	6.561			
GBW 07222a (NCS	1.00	0.863	0.766	0.781	0.015	2.017			
DC46005)									
GBW 07227	1.00	8.727	11.616	11.684	0.068	0.584			
NCS DC 11021	1.00	6.018	8.090	7.928	-0.162	1.999			
NCS DC 11023	1.00	3.451	4.388	4.369	-0.019	0.426			
NCS DC 19001	1.00	6.173	8.264	8.144	-0.120	1.453			
NCS DC 19002	1.00	7.666	10.292	10.213	-0.079	0.771			
NCS DC 28041	1.00	6.705	8.882	8.880	-0.002	0.021			
NCS DC 28045	1.00	2.193	2.669	2.626	-0.043	1.611			
NCS DC 47004	1.00	2.169	2.563	2.593	0.030	1.161			
NCS HC 28803	1.00	12.567	16.850	17.007	0.157	0.933			
OREAS 73b	1.00	5.735	7.635	7.536	-0.099	1.300			
Sarm 135	1.00	0.560	0.304	0.362	0.058	19.154			

# Table A. 24: Kalahari fusion Al<sub>2</sub>O<sub>3</sub> MVR sample list

Sample Name	Weight	Intensity	Given	Calcul.	Absolute	Relative
			Conc.	Conc.	Diff.	Diff.[%]
BAM 633-1	1.00	1.322	0.196	0.194	-0.002	0.933
BCS No.176/2	1.00	0.776	0.102	0.093	-0.009	8.723
BLANK	1.00	0.263	0.000	-0.002	-0.002	
ECRM 609-1	1.00	4.342	0.740	0.755	0.015	2.025
ECRM 651-1	1.00	2.864	0.474	0.481	0.007	1.539
ECRM 678-1	1.00	8.905	1.610	1.602	-0.008	0.506
GBW 07222a (NCS	1.00	0.512	0.043	0.044	0.001	1.857
DC46005)						
KZ 185-89	1.00	0.385	0.018	0.021	0.003	14.618
MO196	1.00	0.443	0.031	0.031	0.000	0.310
NCS DC 11020	1.00	1.356	0.197	0.201	0.004	1.801
NCS DC 11021	1.00	1.321	0.189	0.194	0.006	2.984
NCS DC 19001	1.00	0.327	0.010	0.010	0.000	1.710
NCS DC 19002	1.00	0.352	0.012	0.014	0.002	20.733
NCS DC 28042	1.00	0.718	0.088	0.082	-0.006	6.888
NCS DC 28045	1.00	1.625	0.261	0.251	-0.010	3.968
NCS DC 47004	1.00	0.592	0.063	0.059	-0.004	6.172
Sarm 135	1.00	0.414	0.026	0.026	0.000	1.850
Sarm 136	1.00	0.423	0.028	0.028	0.000	0.451
Sarm 137	1.00	0.435	0.028	0.030	0.002	6.610
SARM 17	1.00	0.387	0.022	0.021	-0.001	2.761
VS R13/3	1.00	1.504	0.225	0.228	0.003	1.525

# Table A. 25: Kalahari fusion P MVR sample list

[LOG			[Flux	[Sample	Sample ID	Mass of
THEANT]	[Duration]	[Precision]	mass]	mass]		fused bead
LOG	82	0.0018	10.0035	0.0000	Blank	9.8429
THEANT						
LOG	90	0.0018	9.9980	0.4999	BAM 633-1	10.3867
THEANT						
LOG	95	0.0018	9.9972	0.4999	BCS No.176/2	10.2349
THEANT						
LOG	133	0.0018	9.9910	0.4996	CMSI 1756 (NCS	10.3785
THEANT					HC13806)	
LOG	135	0.0018	10.0094	0.5005	ECRM 609-1	10.4102
THEANT						
LOG	101	0.0018	10.0006	0.5001	ECRM 651-1	10.2969
THEANT						
LOG	97	0.0018	10.0069	0.5004	ECRM 678-1	10.3000
THEANT						
LOG	84	0.0018	9.9964	0.4999	GBW 07222a (NCS	10.3824
THEANT					DC46005)	
LOG	157	0.0018	10.0007	0.5001	GBW 07227	10.262
THEANT						
LOG	98	0.0018	10.0110	0.5006	KZ 185-89	10.3727
THEANT						
LOG	92	0.0018	10.0273	0.5014	MO196	10.3491
THEANT						
LOG	135	0.0018	9.9965	0.4998	NCS DC 11019	10.3867
THEANT						
LOG	136	0.0018	10.0027	0.5002	NCS DC 11020	10.3985
THEANT						
LOG	93	0.0018	9.9967	0.4999	NCS DC 11021	10.2991
THEANT						

Table A. 26: Determination of the total mass of a sample, flux prior to fusion and fused bead

LOG	88	0.0018	9.9928	0.4997	NCS DC 11023	10.4155
THEANT						
LOG	122	0.0018	10.0107	0.5006	NCS DC 19001	10.1934
THEANT						
LOG	93	0.0018	9.9946	0.4998	NCS DC 19002	10.2140
THEANT						
LOG	91	0.0018	9.9948	0.4998	NCS DC 28041	10.2087
THEANT						
LOG	87	0.0018	10.0210	0.5011	NCS DC 28042	10.3078
THEANT						
LOG	99	0.0018	10.0046	0.5003	NCS DC 28043	10.4184
THEANT						
LOG	125	0.0018	9.9986	0.5000	NCS DC 28044	10.2854
THEANT						
LOG	92	0.0018	10.0034	0.5002	NCS DC 28045	10.3650
THEANT						
LOG	128	0.0018	10.0106	0.5006	NCS DC 47004	10.3652
THEANT						
LOG	96	0.0018	9.9933	0.4997	NCS DC 47007	10.1985
THEANT						
LOG	83	0.0018	9.9996	0.5000	NCS DC 47009	10.3954
THEANT						
LOG	76	0.0018	10.0029	0.5002	NCS HC28803	10.2896
THEANT						
LOG	135	0.0018	10.0044	0.5003	OREAS 73b	10.3678
THEANT						
LOG	85	0.0018	10.0009	0.5001	Sarm 135	10.2689
THEANT						
LOG	130	0.0018	9.9991	0.5000	Sarm 136	10.3452
THEANT						
LOG	83	0.0018	10.0009	0.5001	Sarm 137	10.2161
THEANT						

LOG	91	0.0018	9.9972	0.4999	SARM 16	10.2136
THEANT						
LOG	89	0.0018	10.0001	0.5000	SARM 17	10.2011
THEANT						
LOG	127	0.0018	10.0028	0.5002	SMU 7-1-007 (N-7-	10.4264
THEANT					1-007)	
LOG	127	0.0018	10.0028	0.5002	SX 3911 (DH 3911)	10.3514
THEANT						
LOG	84	0.0018	9.9987	0.5000	VS 5403-90	10.4158
THEANT						
LOG	129	0.0018	9.9989	0.5000	VS R13/3	10.4264
THEANT						
Average	105.222	0.0018	10.0020	0.5001		10.3242
Standard			0.00752	0.00038		0.07771
deviation						

Manganese ore round ro							
Stockpile A							
LAB ID	%Mn	%Fe	%SiO <sub>2</sub>	%CaO	%MgO	%Al <sub>2</sub> O <sub>3</sub>	%P
1	34.03	5.20			2.79	0.240	0.019
2	33.60	5.28	5.43	19.04	2.96	0.227	
Low grade PP	33.70	5.26	5.41	18.76	2.97	0.210	0.022
4	33.70		5.40		2.97	0.281	
5	33.77	5.30	5.36	17.71	2.90		
7	33.64	5.33	5.36	17.94		0.210	
10	33.60	5.23	5.26	18.73	2.79	0.153	0.020
12	33.90		5.33	18.03	2.83	0.200	0.018
13							
14	33.85	5.36	5.64	18.26	3.08	0.168	
16	33.88	5.32	5.56	17.80	3.01	0.237	0.019
18				19.55	2.90	0.240	0.018
19	33.90	5.30		18.30	2.98		0.019
Average:	33.78	5.29	5.42	18.41	2.92	0.217	0.019
Median	33.77	5.30	5.40	18.28	2.96	0.219	0.019
Standard Deviation:	0.14	0.05	0.12	0.59	0.09	0.037	0.001
Upper Outlier Limit	34.09	5.39	5.51	19.46	3.13	0.274	0.021
Lower Outlier Limit	33.44	5.21	5.29	17.09	2.79	0.163	0.017
Number of Results:	11	9	9	10	11	10	7
Highest Result:	34.030	5.365	5.636	19.550	3.081	0.281	0.022
Lowest Results:	33.600	5.200	5.260	17.713	2.787	0.153	0.018

## Table A. 27: Low grade method round robin result

Outliers - Calculated Z-Values									
LAB ID	%Mn	%Fe	%SiO <sub>2</sub>	%CaO	%MgO	%Al <sub>2</sub> O <sub>3</sub>	%P		
1	1.86	-1.96	-5.88	-3.08	-1.81	0.58	0.00		
2	-1.16	-0.39	0.26	1.28	0.00	0.23	5.06		
Low grade PP	-0.46	-0.79	0.09	0.81	0.11	-0.23	2.17		
4	-0.46	4.91	0.00		0.10	1.67	4.91		
5	0.00	0.00	-0.37	-0.95	-0.66	-3.45	-9.03		
7	-0.88	0.59	-0.35	-0.57	-6.06	-0.23			
10	-1.16	-1.37	-1.21	0.76	-1.84	-1.75	0.72		
12	0.95	-5.69	-0.60	-0.42	-1.38	-0.50	-0.72		
14	0.61	1.27	2.04	-0.03	1.29	-1.37	-5.42		
16	0.78	0.35	1.37	-0.81	0.56	0.50	-0.07		
18	-19.29	-4.91	5.06	2.14	-0.69	0.58	-0.72		
19	0.95	0.00	5.36	0.03	0.21	6.21	0.00		
$ Z  \leq 2$ Satisfactory									
$2 \leq  Z  \geq 3$ Questionable									
$ Z  \ge 3$ Unsatisfactory									
No results									

## Table A. 28: Low grade method round robin Z- score evaluation

### Quality control results

Month	%Mn	%Fe	%CaO	%MgO	%SIO2	%Al2O3	%P
Jun-15	39.45	4.28	13.14	3.07	4.74	0.25	0.02
Jul-15	39.40	4.27	13.09	3.06	4.74	0.387	0.020
Aug-15	39.45	4.19	13.17	3.15	4.56	0.216	0.02
Sep-15	39.43	4.22	13.22	3.20	4.56	0.223	0.02
Oct-15	39.41	4.17	13.10	3.03	4.65	0.191	0.02
Nov-15	39.40	4.23	13.15	3.08	4.73	0.261	0.02
Average	39.42	4.23	13.14	3.10	4.66	0.26	0.02
Standard Deviation:	0.026	0.041	0.048	0.063	0.087	0.070	0.001

# Table A. 29: Low grade press pellet RR1 quality control samples results over six months

RR1 Consensus value							
	%Mn	%Fe	%CaO	%MgO	%SIO2	%Al2O3	%P
True value	39.381	4.214	13.236	3.052	4.651	0.215	0.023
Standard Deviation:	0.258	0.076	0.766	0.258	0.407	0.048	0.013

Month	%Mn	%Fe	%CaO	%MgO	%SIO2	%Al2O3	%P
Jun-15	45.15	12.61	6.70	0.40	3.81	0.36	0.04
Jul-15	45.18	12.63	6.70	0.39	3.94	0.39	0.04
Aug-15	45.16	13.40	6.78	0.12	3.42	0.38	0.03
Sep-15	44.92	12.65	6.76	0.54	4.35	0.35	0.04
Oct-15	45.15	12.62	6.64	0.39	3.58	0.36	0.04
Nov-15	45.30	12.64	6.74	0.44	3.84	0.75	0.03
Average	45.14	12.76	6.72	0.38	3.82	0.43	0.04
Standard Deviation:	0.123	0.315	0.051	0.140	0.319	0.158	0.004

 Table A. 30: High grade press pellet Wes 6 quality control samples results

 over six months

Wes 6 Consensus value							
	%Mn	%Fe	%CaO	%MgO	%SIO2	%Al2O3	%P
True value	45.141	12.702	6.613	0.810	4.100	0.358	0.035
Standard Deviation:	0.264	0.524	0.259	0.221	0.382	0.048	0.0044

Month	%Mn	%Fe	%CaO	%MgO	%SIO2	%Al2O	%P
						3	
Jun-15	49.36	9.89	5.23	0.52	5.49	0.42	0.05
Jul-15	49.51	9.58	5.14	0.54	5.22	0.39	0.05
Aug-15	49.55	9.33	5.26	0.51	4.79	0.42	0.04
Sep-15	49.75	9.28	5.23	0.56	4.81	0.39	0.04
Oct-15	49.71	10.09	5.32	0.61	4.68	0.35	0.03
Nov-15	49.70	9.97	5.43	0.70	4.77	0.41	0.02
Average	49.59	9.69	5.27	0.57	4.96	0.40	0.04
Standard	0.151	0.343	0.098	0.069	0.320	0.027	0.011
Deviation:							

 Table A. 31: Kalahari Fusion MO196 quality control samples results over six months

MO 196 CRM value								
	%Mn	%Fe	%CaO	%MgO	%SIO2	%Al2O3	%P	
True value	49.58	9.63	5.175	0.582	4.93	0.37	0.03	
Standard	0.276	0.305	0.124	0.192	0.380	0.089	0.0065	
Deviation:								

## High grade PP method energy profile



MnKa Energy Profile

Figure A. 8: MnKa energy profile

Table A. 32: Summary of the Mn energy profile

File Information						
Energy Profile Parameters		Energy Profile data				
Element/Line	Mn_mf	PHD	Threshold	30		
Gonio	No		Window	95		
Crystal	LiF200	Param [Step]	Start	20		
Detector	ExKrBe		End	150		
Collimator	no		Inc.	2		
kV	50					
mA	50	Count.Time [s]	Inc.	2		
PBF/	None	_	Global	20		
PBD						

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Mask	ø29 mm	Count Rate	[kcps]	446.31
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### FeKa Energy Profile



Instrument: ARL 9900



Figure A. 9: FeK $\alpha$  energy profile

Table A	. 33:	Summary	of the	Fe	energy	profile
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File Information							
Energy Profile Parameters		Energy Profile data					
Element/Line	Fe_mf	PHD	Threshold	20			
Gonio			Window	125			
Crystal	LiF200	Param [Step]	Start	20			
Detector	Sc						
Collimator			End	150			
kV	50		Inc.	2			
mA	50	Count.Time [s]	Inc.	2			
PBF/	None		Global	20			
PBD							

Mask	ø29 mm	Count Rate	[kcps]	377.68
Туре	Norm			

### CaKa Energy Profile





Figure A. 10: CaKa energy profile

Table A.	34: S	ummarv	of the	Ca	energy	profile
1 4010 1 1.	0.00	Gilling J	or the	u	energy	prome

File Information					
Energy Profile Parameters		Energy Profile data			
Element/Line	Ca_m	PHD	Threshold	40	
Gonio	No		Window	75	
Crystal	LiF200	Param [Step]	Start	20	
Detector	ExArBe				
Collimator	No		End	150	
kV	50		Inc.	2	
mA	50	Count.Time [s]	Inc.	2	
PBF/	None		Global	20	
PBD					
Mask	ø29 mm				







Figure A. 11: MgKα energy profile

Table A.	35:	Summary	of the	Mg	energy	profile
				0		P

File Information					
Energy Profile Parameters		Energy Profile data			
Element/Line	Mg_m	PHD	Threshold	30	
Gonio	No	-	Window	80	
Crystal	AX06	Param [Step]	Start	20	
Detector	FPC	-			
Collimator	No		End	150	
kV	50		Inc.	2	
mA	50	Count.Time [s]	Inc.	2	
PBF/	None		Global	20	
PBD					
Mask	ø29 mm				
Rotation	Yes	Count Rate	[kcps]	8.97	







Figure A. 12: SiKa energy profile

Table A. 36: Summary of the Si energy profile

File Information						
Energy Profile Parameters		Energy Profile data				
Element/Line	Si_m	PHD	Threshold	35		
Gonio	No		Window	85		
Crystal	InSb	Param [Step]	Start	20		
Detector	ExNeBe					
Collimator	No		End	150		
kV	50		Inc.	2		
mA	50	Count.Time [s]	Inc.	2		
PBF/PBD	None		Global	20		
Mask	ø29 mm					
Rotation	Yes	Count Rate	[kcps]	65.59		

### AlKa Energy Profile







Figure A. 13: AlKa Energy Profile

1 u 0 10 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0
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File Information						
Energy Profile Parameters		Energy Profile data				
Element/Line	Al_m	PHD	Threshold	30		
Gonio	No		Window	90		
Crystal	PET	Param [Step]	Start	20		
Detector	ExNeBe					
Collimator	No		End	150		
kV	50		Inc.	2		
mA	50	Count.Time [s]	Inc.	2		
PBF/PBD	None		Global	20		
Mask	ø29 mm					
Rotation	Yes	Count Rate	[kcps]	3.84		

#### PKα Energy Profile





Figure A. 14: PKa energy profile

Table A. 38: Summary of the P energy profile

File Information						
Energy Profile Parameters		Energy Profile data				
Element/Line	P_m	PHD	Threshold	40		
Gonio	No		Window	65		
Crystal	Ge111	Param [Step]	Start	20		
Detector	ExNeBe					
Collimator	No		End	150		
kV	50		Inc.	2		
mA	50	Count.Time [s]	Inc.	2		
PBF/PBD	None		Global	20		