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Proceeding Paper

# Fast and Cost-Effective Quantitative Assessment of the Chemical and Mineral Composition of Heavy Mineral Sands Ores: Application of the New SOLSA Combined XRF-XRD Analytical Solution to the Grande Cote Operation Ti-Zr Mine †

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**Abstract:** Mine optimisation and anticipation of ore behaviour in the mineral processing and separation circuits are major economic drivers for all mining operations. Recent methodological developments with the inception of geometallurgy across multiple commodities have highlighted the importance of mineralogy in addition to elemental grades. In the last few decades, many quantitative tools have been developed, mostly SEM-based such as QEMSCAN<sup>®</sup>, and used to provide the quantitative mineralogical compositions of samples. Their main drawback is the time and cost associated with sample preparation, acquisition time, and data QA/QC. The combined XRF-XRD of the SOLSA (Sonic On-Line drilling and Sampling Analysis) analytical solution brings a new methodology able to produce quantitative mineralogical and geochemical data at a speed compatible with a production environment. Its range of applications covers the entire life of a mining operation, from the initial exploration stage to mineral processing control, as well as waste management and environmental monitoring.

**Keywords:** coupled XRD-XRF analysis; quantitative analysis; heavy mineral sands; exploration

## 1. Introduction

SOLSA (Sonic On-Line drilling and Sampling Analysis) is an ambitious project funded by the European Union that started in 2016. It delivered a prototype of a combined integrated sampling and analysis platform designed for use in the fields of mineral exploration, grade, and processes monitoring during operation [1] “<https://solsa-dem-up.eu/en>” (accessed on 3 November 2023). It aims to fast track and enhance ore body knowledge in order to facilitate the large-scale acquisition of the ore mineralogy and chemistry data needed to link ores to their processing characteristics. The goal is to provide an efficient tool for geometallurgy by quickly delivering, in the field, mineralogical and chemical analyses of drill cores or powdered samples, leading to the facilitation of fast exploration, mining, and processing decisions. In addition, better ore-knowledge allows for the anticipation of the mineralogy for both ore and gangue. It contributes to the anticipation and de-risking of new

mining projects from the exploration stage through the integration of what could be the future life-of-mine mineral processing or corporate social responsibility (CSR) challenges.

Over the last 30 years, many instruments and approaches have been developed to provide the quantitative modal mineralogy of ore samples, e.g., [2,3]. Most of the techniques employ SEM-EDS-based technologies to identify and classify the particles based on their elemental composition. They are particularly useful for understanding deportment and liberation and allow for process modelling based on the properties of the particles such as size or density. However, it is always necessary to validate the calculated mineral proportions from the data processing software. In fact, calculations and mineral proportion interpretations are based on the chemistry and density of the minerals. Therefore, the calculated composition requires a cross validation by comparing to an independent bulk geochemical analysis using X-ray fluorescence or ICP-MS. Another approach is to back calculate the modal mineralogical composition from the bulk geochemical analyses using element-to-mineral (EML) conversion methodologies. While EML can be easily applied to large geochemical datasets, limitations arise from the difficulty to assign certain elements to the mineral phases that are present in the samples.

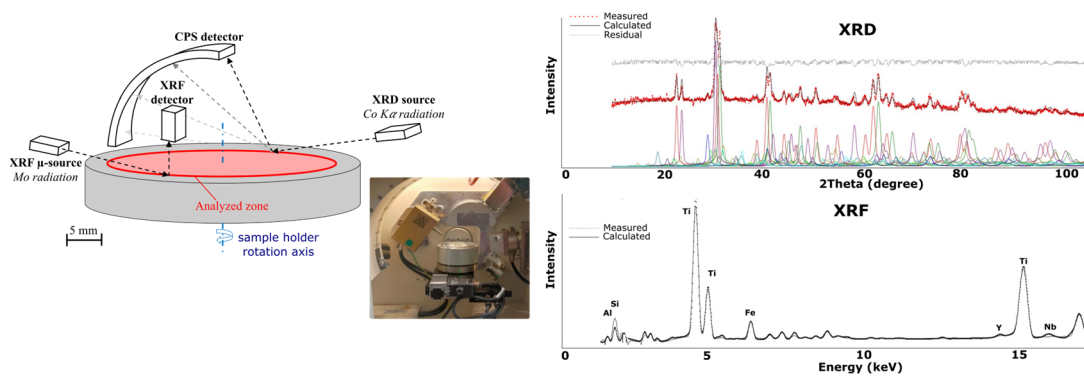
The example in this article is taken from Eramet's Grande Côte Operation (GCO) heavy mineral sands mine, in which primary detrital minerals, such as ilmenite, are subject to alteration, therefore producing a range of Fe and Ti-bearing minerals and are often accompanied by changes in oxidation state. Such mineral transformations in turn translate into different physical properties (e.g., magnetism) that could impact the methodologies used for their separation. With techniques based on the calculation and theoretical structural formulae of minerals, difficulties arise when the mineral phases of interest are impossible to differentiate based on their chemical composition alone. Polymorphs such as  $\text{TiO}_2$  (anatase-brookite-rutile) have different physical properties [4], hence different responses in the densimetric, magnetic, and electrostatic separation circuits of the ore processing plant. Researchers have already demonstrated the interest of using quantitative XRD for optimization and quality control during heavy mineral sands processing [5].

The aim of the present work is to consolidate the validation of the data acquisition and signal processing procedures associated with SOLSA's benchtop analyser, thus, to evaluate the uncertainties and compare the quantitative results with established quantitative mineralogy based on Qemscan<sup>®</sup> (Quantitative Evaluation of Minerals by Scanning electron microscopy) data. The advantages and limitations of the technique are discussed and replaced in the context of mass data acquisition procedures capable of feeding ore body knowledge with the geological and mineralogical data on which the geometallurgical models are based.

## 2. Materials and Methods

### 2.1. A Novel Coupled XRD and XRF Technique and Methodology

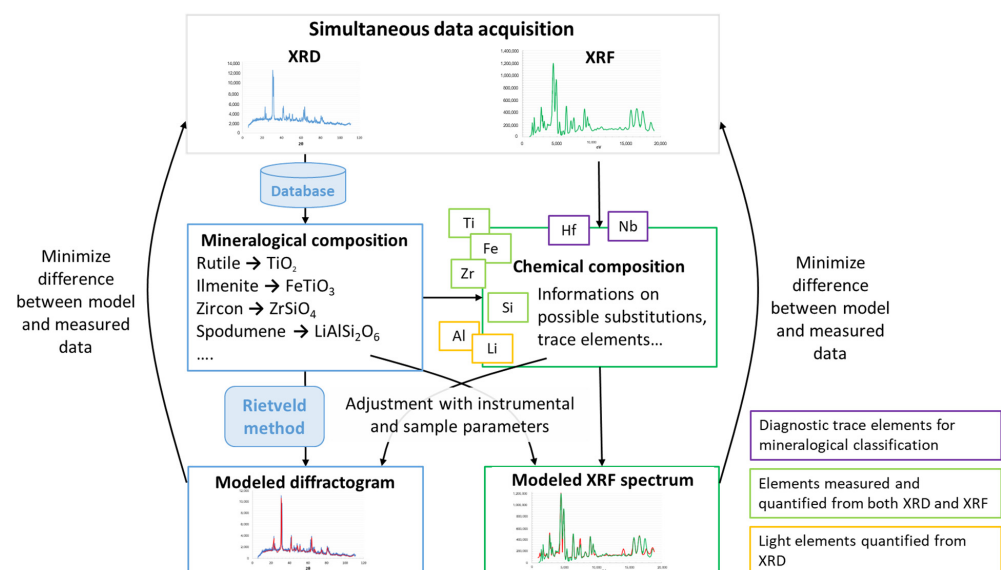
SOLSA's coupled analysis is a true combined approach to merging both XRD and XRF data acquisition and analysis. Custom analytical X-ray instrumentation (Figure 1) has been developed to perform the simultaneous data acquisition, by using a single X-ray source and dedicated detectors to collect the diffracted and fluorescent X-ray photons from the same sample volume. Additionally, a combined XRD/XRF data analysis methodology has been implemented by extending Rietveld-based code to incorporate the full pattern fitting of XRF spectra starting from the phases instead of a simple elemental composition matrix [6].



**Figure 1.** Schematic representation of the combined XRD-XRF acquisition platform as well as the signal generated simultaneously on both detectors. On the left, the sample holder and position of the detectors, and on the right, example of an acquisition. Modified from [7].

## 2.2. Data Acquisition and Processing

XRF-XRD combined measurements were performed by the SOLSA combined instruments (Figures 1 and 2) allowing for the simultaneous measurement of XRF and XRD signals. X-ray fluorescence spectra were acquired using a Mo micro-source radiation and an Amptek X-123 (AMPTEK INC, Bedford, MA, USA) SDD (Silicon Drift Detector) detector placed over the sample to ensure the measurement of lighter elements down to  $Z = 12$  (Mg). Data were collected for a quantitative XRF model from 0.1 to 15 keV. X-ray powder diffraction data were acquired in asymmetric mode using Co  $K\alpha$  average radiation ( $K\alpha_1 = 1.78900 \text{ \AA}$  and  $K\alpha_2 = 1.79289 \text{ \AA}$ ) and equipped with an INEL curved position sensitive detector which spans the entire  $5 \leq 2\theta \leq 120^\circ$  range simultaneously. For this diffractometer, the instrumental function was also defined using yttrium oxide ( $Y_2O_3$ ) standard powder following the analytical procedure described in [7]. This instrument's configuration is accompanied by the use of a modular sample holder (Figure 1) capable of accommodating samples of different shapes, thus allowing the combined XRF-XRD analysis to be carried out on both prepared samples (e.g., a fine powder) and on samples with little or no preparation (e.g., coarse granulometric fractions, a cutting, a rock), as long as the surface to be analysed is flat.



**Figure 2.** Schematic representation of the combined XRD-XRF processing method based first on mineral and chemical element identification (Full Pattern Search Match, FPSM), and then on combined mineralogical and chemical quantification (Rietveld quantification).

The combined XRF-XRD processing was performed using the LUXREM software v0 developed during the SOLSA project. The combined analysis method presented in Figure 2 is based on two powerful new approaches using state-of-the-art methodology. The first, Full Pattern Search Match (FPSM), searches for phases and chemical elements [8] using the Crystallography Open Database (COD) for mineral identification [9]. The second is used for the final quantification of the mineralogical crystal structure and chemical elements. It combines the Rietveld method for XRD fitting with a fundamental approach for XRF simulation in a unique algorithm refining both data simultaneously with a unique sample description [6].

This permits the most accurate description of the physics and eliminates the approximations used in the separated approaches. It can also estimate light elements, such as Li, O, C, etc., which are not quantifiable by standard XRF in air or under gas.

### 2.3. SEM-EDS-Based Automated Mineralogy

SEM-EDS-based automated mineralogy analyses were performed on polished sections using the QEMSCAN<sup>®</sup> system at Eramet Ideas. Acquisitions were made on an FEI Quanta 650F SEM platform with two Bruker Xflash 30 mm<sup>2</sup> silicon drift energy dispersive spectrometer X-ray detectors. The iMeasure v. 5.2 software was used for data acquisition and iDiscover v. 5.2 software was used for spectral interpretation and data processing. The PMA (Particle Mineral Analysis) measurement mode was used to collect X-ray data every 2.5 µm across the surfaces of the polished sections, with a total of 2000 counts per spectrum.

### 2.4. Samples

Table 1 provides information on the sample preparation and analytical techniques used to characterize and quantify the geochemistry and mineralogy of the samples.

**Table 1.** Sample list including standard reference material provided by the GCO mine: AMIS0616 (rutile); AMIS0697 (ilmenite, Kenya) and AMIS0454 (ilmenite, Tronox Mineral Sands (Namakwa Sands Mines); as well as pure commercial products representing different types of mineral concentrates with contrasted mineralogical compositions.

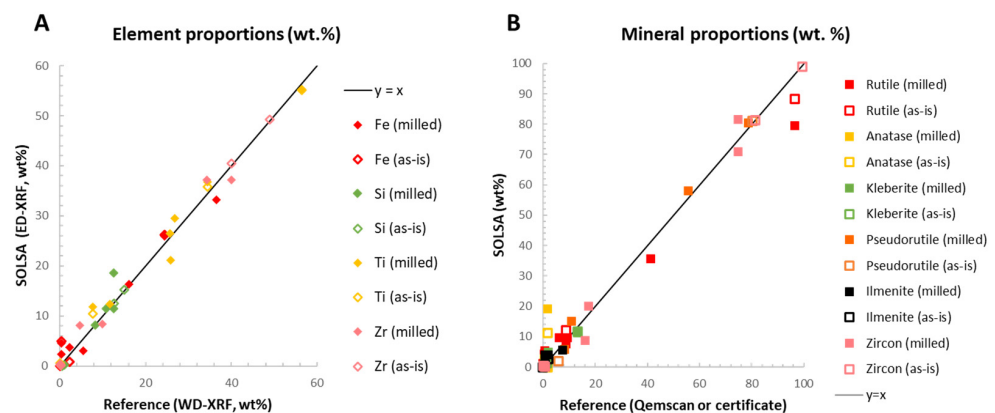
Sample	(Milled)	(As-Is)	Mineralogy	Geochemistry	SOLSA Coupled XRD-XRF Analysis
Rutile concentrate	yes	yes	Qemscan <sup>®</sup>	WD-XRF	yes
Ilmenite concentrate	yes	yes	Qemscan <sup>®</sup>	WD-XRF	yes
Zircon concentrate	no	yes	Qemscan <sup>®</sup>	WD-XRF	yes
AMIS0697	yes	no	Certificate	Certificate	yes
AMIS0454	yes	no	no	Certificate	yes
AMIS0616	yes	no	Certificate	Certificate	yes
Conc 1	yes	yes	Qemscan <sup>®</sup>	WD-XRF	yes
Conc 2	yes	no	Qemscan <sup>®</sup>	WD-XRF	yes

## 3. Results

The intrinsic strength of the coupled XRD/XRF methodology is the mutual re-enforcement during data processing, where the chemistry helps refine mineral proportions and vice versa. A comparative approach using well established techniques for both elemental and mineral quantification allows for the comparison of the performance and quality of the data and signal processing obtained with the SOLSA system and the LUXREM data reduction software. It must be noted that there is no per se mineral quantification standard. The standard method for the QA/QC of the mineral proportion with Qemscan<sup>®</sup> is performed with respect to the fused-bead XRF geochemical analysis and the recalculated assay generated from the mineralogical data base.

### 3.1. Chemical Quantification: SOLSA vs. Fused-Bead WD-XRF

Figure 3A, presents the distribution of the same samples analysed using conventional fused-bead XRF as well as SOLSA XRF. This provides a preliminary assessment of the data generated from the SOLSA equipment for both milled and as-is samples at the natural size distribution of the mineral grains forming the concentrate, with the only exception being the AMIS reference materials, which were received already milled. The 1:1 black line represents the ideal reconciliation between the two methods. These preliminary results indicate that both light and heavier elements tend to be quantified within the same order of magnitude with respect to the reference method by WD-XRF. Most datapoints fall below a 10% relative error and only a few have relative errors of around 40 to 50%. Investigation is still ongoing to better understand the outliers. In fact, the same elements were successfully measured with high accuracy relative to the reference values obtained by WD-XRF on aliquots of the same sample.



**Figure 3.** (A) Powder EDXRF from SOLSA vs. fused-bead WD-XRF for milled and as-is all samples on some of the key elements of interest present in the heavy mineral concentrate and reference materials. (B) Mineral proportions calculated by the LUXREM software and compared to the mineral proportion quantification obtain by Qemscan<sup>®</sup>.

### 3.2. Mineral Quantification, SOLSA Coupled XRD-XRF vs. Qemscan<sup>®</sup>

Mineral proportions calculated with the SOLSA equipment are presenting a good agreement with mineral proportion calculation from Qemscan<sup>®</sup> with a distribution of the datapoints near the 1:1 line representing the ideal reconciliation (Figure 3B). Discrepancies between the two methods were anticipated due to the use of two different databases, one using the chemical composition of the pixels, while the other using the crystallographic and fundamental properties of physics to perform advanced Rietveld processing. The differences between TiO<sub>2</sub> polymorphs quantification could provide an understanding of how minerals would be reported in the different mineral separation circuits of the mine processing plant. In addition, mineralogical investigation at the crystal scale with SOLSA might provide a better methodology to understand ilmenite alteration and the subsequent consequences it might have on its separability using high intensity magnetic fields. Both methods provide a similar mineralogical assemblage of the samples providing good confidence that the technique could soon be integrated with other mineralogical and geochemical datasets in use at the mine.

## 4. Concluding Remarks

These are the first preliminary results obtained with coupled XRD-XRF on a real-life practical case of mineral processing optimization at the GCO mine in Senegal. The combined instrument demonstrates its potential to acquire mineralogical and chemical data simultaneously from the same sample. Results could be further improved by database adjustments to better fit the signals or sample preparation procedures, while the counting time of the acquisitions could also be increased to improve statistics.

The acquisition of signals from various types of powder materials, either mill or as-is with different particle size distributions, allowed for the testing of these effects on both the acquisition and processing of the signals coming from the combined instruments. It also contributed to the creation of a site-specific mineralogical database for heavy mineral sands.

Further work will include the full development of a QA/QC procedure for both the mineralogy and the chemistry. These first XRD results also evidenced the already known difficulties of powder measurements [10]. However, the ongoing expansion of the test sample set could contribute to the better consideration of the factors influencing the accuracy of the measurements and the implementation of hardware and software mitigating actions. In parallel the ability to test the mineralogy of the different commercial products in the mine will potentially provide means to improve the recovery of the minerals of interest and better anticipate the yield of the commercial products thanks to better control of the mineralogy. One of the other strengths of the method compared to traditional SEM-based mineral quantification instruments is looking at the mineral transformation at the scale of the crystals forming the minerals. This enables the quantification of mineral phase transformation at a sub-micron scale, a common feature in the alteration of minerals in natural environments, as well as in many extractive metallurgy processes. The application of the combined mineralogical and geochemical data could have multiple uses throughout the life-of-mine cycle, from mineral exploration to the environmental monitoring of industrial wastes.

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