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Université du Québec
à Chicoutimi

**Validation de l'adéquation de la fluorescence X portative
pour le contrôle de qualité du quartzite
dans un environnement industriel**

Par

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RÉSUMÉ

Cette étude traite d'une problématique de représentativité concernant la caractérisation chimique du quartzite¹ dans un procédé de transformation industrielle. Le but de ce projet est de concevoir un protocole permettant une caractérisation adéquate de cet intrant. Pour répondre à la situation, il faut assembler deux disciplines soit la chimie analytique (fluorescence X) et la théorie de l'échantillonnage. La particularité de ce travail est de quantifier l'erreur d'échantillonnage ainsi que l'erreur analytique. La rapidité d'analyse et la mobilité de la fluorescence X portative (XRFp) ont fait de cet appareil (Niton XL3t GOLDD+) un atout majeur pour ce projet. De plus en plus, celui-ci est utilisé dans le cadre de l'analyse environnementale ou encore, pour l'exploration et l'exploitation minière. Cependant, peu d'études traitent de son utilisation en tant qu'instrument de contrôle de qualité en milieu industriel. La validation et l'adéquation de cet appareil ont été effectuées en qualifiant et quantifiant les limites de détection, l'exactitude, la précision, la dérive instrumentale, la représentativité de la surface analysée et finalement, la méthode de préparation des échantillons. Les résultats ont démontré que la limite de détection du TiO₂, Fe₂O₃ et le CaO est légèrement en-dessous de 70 µg/g. Les analyses de pastilles pressées présentent des résultats comparables à la fluorescence X de laboratoire et sont jugées adéquates. En effet, ces résultats sont près des valeurs des matériaux de référence analysés. Il a été déterminé que cinq mesures étaient suffisantes afin de caractériser un morceau de quartzite de 10 cm³. Les mesures « in situ » sont plus rapides que la méthode conventionnelle d'analyse, mais la concentration de certaines phases, par exemple, l'ilménite et la mauvaise planéité de la surface, provoquent quelques résultats erratiques. L'essai de réplique et celui

¹ Le quartzite est une roche siliceuse composée principalement de SiO₂ lorsque celle-ci est pure on va parler d'un minerai de quartz.

de l'optimisation de la masse échantillonnée ont permis d'identifier et de quantifier les erreurs du protocole d'échantillonnage actuel. Les échantillons sélectionnés aléatoirement dans la pile de quartzite (*grab sampling*) présentent, dans presque tous les cas de figures, des résultats plus variables que ceux des échantillons composites puisque les résultats obtenus, avec les échantillons sélectionnés par intervalle sur toute la diagonale du lot, ne démontrent aucune autocorrélation, et ce, peu importe la distance entre deux échantillons, indiquant une certaine homogénéité dans la pile de quartzite au moment de l'échantillonnage. Les résultats démontrent qu'un XRFp convient pour des analyses quantitatives dans un contexte industriel si, toutefois, l'échantillon demeure sous forme de pastille. Notons que même avec un grand nombre d'essais, l'approche « in situ » demeure difficile pour les éléments légers tels que : l' Al_2O_3 , le MgO et le CaO. La prise d'échantillons composites permet donc de diminuer de moitié l'erreur d'échantillonnage (écart-type relatif) démontrant l'avantage de ce protocole d'échantillonnage. Cependant, le gain de rapidité à utiliser une XRFp versus une XRF de laboratoire est faible à cause des échantillons présentant une surface non plane qu'il faut faire plusieurs mesures par échantillon avec la XRFp.

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LISTE DES ABRÉVIATIONS

TOS : Theory Of Sampling

XRF : X-ray fluorescence (spectrométrie de fluorescence des rayons X)

XRFp : Fluorescence X portable

HHXRF : Handheld X-ray fluorescence

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AVANT-PROPOS

Ce présent mémoire est présenté sous la forme d'articles scientifiques. De cette manière, le corps du texte est divisé en deux chapitres. Le premier chapitre correspond à un article publié (18 juin 2018) dans le périodique arbitré *Minerals Engineering* selon leurs barèmes éditoriaux (Annexe 1). Le second chapitre présente le deuxième articles réalisé dans le cadre de ce mémoire qui également soumis à *Minerals Engineering*. Il est à noter que cet article est toujours en attente d'arbitrage au moment du dépôt de ce mémoire. Les données brutes sont présentées dans un disque optique (CD-ROM) en Annexe 2 (pochette du mémoire relié). Précisons que l'article accepté ainsi que le second article soumis sont rédigés en anglais afin de correspondre au standard universel de la publication scientifique. Cependant, le résumé, l'introduction ainsi que la conclusion de ce projet de recherche ont été écrits en français. Plusieurs facteurs ont fait en sorte que ce sujet me motivait. Outre, le défi de la réalisation d'une maîtrise, l'amélioration de procédés industriels m'a toujours intéressé. Cette maîtrise présentait une problématique de taille, puisque la consommation quotidienne, en intrant de cet industriel, représente environ 350 tonnes métriques. Dans le cadre de ce projet, c'est le quartzite qui a été désigné comme intrant à caractériser (environ 155 tonnes métriques/jour). L'utilisation de la fluorescence X portative allié à la théorie de l'échantillonnage présentait tous les attributs pour répondre aux problématiques du projet. Néanmoins, la pureté du matériel ainsi que la planéité des échantillons analysés ont lésé grandement à la performance des analyses « in situ² ».

²

Selon l'Office québécois de la langue française, le terme « in situ » signifie : au lieu même.

Dans le même ordre d'idée, il serait intéressant de répéter l'expérimentation avec un intrant industriel de moins grande pureté afin de permettre la réalisation d'un protocole performant de la qualité des intrants. Le développement d'un outil permettrait d'aplanir la surface ce qui serait un outil indispensable pour la poursuite de ce projet.

INTRODUCTION

Depuis l'industrialisation, les entreprises tendent à augmenter leur productivité, mais cela nécessite un plus grand apport en matières premières et un meilleur contrôle de la qualité. Conséquemment, la caractérisation de ces matières devient de plus en plus critique en rapidité et en qualité. En effet, il s'avère très complexe d'obtenir des résultats représentatifs si le lot à analyser représente plusieurs centaines de tonnes. Un intrant de mauvaise qualité ou de qualité variable empoisonnera le procédé de transformation, donnant ainsi un produit fini de qualité inférieure ou non conforme ce qui occasionne des pertes financières importantes. L'industrie en général est consciente de cette problématique, mais il est coûteux et complexe de caractériser, de manière représentative, tous les intrants d'un procédé. Voici différents facteurs expliquant que les entreprises éprouvent souvent de la difficulté à caractériser leur matière première :

1. Manque de main-d'œuvre;
2. Analyses chimiques coûteuses;
3. Échantillonnage non représentatif;
4. Difficultés liées à l'accessibilité de la totalité du matériel (pile, silo, etc.);
5. Trop peu d'analyses effectuées;
6. Manque d'expertise ou de compétences.
7. Manque de précision d'analyse.
8. Limite de détection trop haute par rapports aux concentrations dans le matériel.

Les objectifs du projet consistent à tester la performance d'un outil d'analyse chimique portatif, de tester différents protocoles d'échantillonnage, de développer un protocole de caractérisation rapide et performant permettant d'obtenir un résultat représentatif de caractérisation chimique.

Pour ce faire, il faut assembler deux disciplines soit : **l'échantillonnage** et **l'analyse chimique** (la fluorescence X dans ce cas). Bien que la fluorescence X existe depuis plus de 100 ans, les appareils portatifs ont fait leur apparition en 1994. Cette nouvelle technologie permet de quantifier et de qualifier la matière analysée avec peu de préparation de surface et cela, dans un délai très court. L'utilisation de la fluorescence X portative (XRFp), par sa mobilité, permet d'obtenir une quantification chimique directement sur la localisation « in situ » dans un délai raccourci comparativement à celle de type laboratoire. Cette avenue, bien qu'audacieuse, pourrait permettre une alternative plus qu'intéressante pour beaucoup d'entreprises qui ne possèdent pas toutes les infrastructures requises pour la caractérisation chimique conventionnelle. Les travaux ont été réalisés en collaboration avec un producteur de ferrosilicium, soit l'entreprise Elkem Métal Canada inc., qui présente la problématique de caractérisation avec le quartzite utilisé dans leur procédé. Le gisement utilisé par cette compagnie se trouve se situe dans le secteur de la Galette à environ 140 km au nord-est de la ville de Québec. Plusieurs gisements de quartz de haute pureté ont été découverts dans les années 40 et étudiés par plusieurs chercheurs (Rondot, 1979). Dans le cadre de son mémoire de recherche Guy Tremblay (Tremblay, 1984) mentionne plusieurs minéraux accessoires tels que sillimanite, rutile, biotite, fuchsite, muscovite, chlorite, magnétite, pyrite, ilménite, hématite et pyrrhotine. Ces minéraux autres que le quartz représente 1 à 3 % massiques et leurs distributions est non homogène. Bien que le quartz soit parmi les minéraux les plus abondants dans la croûte continentale, les gisements de hautes puretés eux sont très en demande surtout pour les applications de hautes technologies tels que le domaine de la télécommunication, l'optique, l'électronique, les semi-conducteurs et pour des applications

de silicium solaire (Götze et Möckel 2012). Chez cet industriel, pour permettre de réduire le temps d'analyse, le fournisseur de quartzite envoie en analyse un échantillon d'environ 3 kg hebdomadairement. Dans cette entreprise, la consommation de quartzite est d'environ 155 tonnes métriques (t) par jour. La problématique considérée ici est qu'un échantillon de 3 kg représenterait une semaine de production chez le producteur de ferrosilicium soit aux alentours de 1080 tonnes métriques. Selon Boon et al. (2007), plus de 80 % de l'erreur³ d'estimation d'un lot serait causée par l'échantillonnage même et moins de 20 % de l'erreur est due à l'analyse. Outre le quartzite comme matière première, la production de ferrosilicium nécessite un apport de ferraille, charbon et copeaux de bois. Chez Elkem Métal Canada, les rebuts de ferraille sont utilisés. Le choix d'une ferraille plutôt qu'une autre est le résultat de considérations économiques et de la quantité d'impuretés que celle-ci peut contenir telles Al, Ca, P, Cr, Ti, etc. Présentement, l'énergie additionnelle et les quantités supplémentaires d'agents réducteurs requises pour réduire des minerais de fer tels que la magnétite par exemple n'est pas économiquement viable pour le moment. Le charbon est un minéral organique solide de différentes compositions et propriétés. Il existe une grande variété de charbon dans le monde mais chez Elkem Métal Canada, l'anhracite est le type de charbon qui est utilisé pour ses excellentes propriétés (carbone fixe élevé, forte capacité calorifique, faible teneur en soufre etc...). Celui-ci est utilisé afin d'ajouter du carbone libre à l'intérieur du four. L'apport de carbone est nécessaire afin de réduire le quartzite dans la fournaise. Le bois est ajouté au four est sous forme de copeaux et est utilisé pour deux fonctions : améliorer la circulation des gaz en augmentant la perméabilité du mélange et comme apport

³ **Note** : Selon l'Office québécois de la langue française, le terme « erreur » ne devrait pas être utilisé dans ce contexte, le mot incertitude serait plus adéquat. Son utilisation est nécessaire pour être en accord avec la littérature de la théorie de l'échantillonnage.

supplémentaire de carbone libre. En effet, 12 % du carbone libre total de la fournaise proviennent des copeaux de bois. L'aluminium et le titane provenant de ces intrants sont les deux éléments nuisibles à la réalisation de certains produits qui demandent des spécifications très restreintes. Selon la composition moyenne des intrants, 33 % de l'aluminium et 56 % pour le titane proviennent du quartzite. L'aluminium, tant qu'à lui, doit être maintenu le plus bas possible, et ce, lors de la production de ferrosilicium à faible teneur en aluminium. Toutefois, cet élément est moins nuisible que le titane puisqu'il est possible, lors de l'affinage du produit, de diminuer sa teneur par l'ajout de boulettes de fer oxydé. Cependant, l'ajout d'oxydes (de fer) dans le bain de métal liquide n'est pas sans conséquence pour le recouvrement du silicium métallique. Ce projet se divise en deux parties : la section analytique et la section sur l'échantillonnage. Pour la section analytique, diverses expérimentations testent différents paramètres tels que : la dérive, la limite de détection, la justesse, la précision et le calibrage de la XRFp ainsi que le nombre de mesures nécessaires pour caractériser « in situ » un morceau de quartzite. Ces étapes d'analyses ont permis de valider l'adéquation de la XRFp pour le quartzite de haute pureté. Dans la seconde section, différents protocoles d'échantillonnage, par exemple l'échantillonnage en vrac, (*grab sampling*) ont tous été testés. Des essais de répliques ainsi que d'optimisation ont permis d'évaluer le protocole utilisé par l'industriel et ainsi qualifier et quantifier les différentes variables, dont les plus nuisibles. La méthode de calcul par variogramme a permis de déterminer l'hétérogénéité que l'on retrouve dans une pile de quartzite de plus de 5000 tonnes métriques. Plus de 500 analyses « in situ » ont été réalisées afin de valider l'adéquation de la XRFp pour le nouveau protocole.

CHAPITRE I

VALIDATION DE L'ADÉQUATION DE LA FLUORESCENCE X PORTATIVE POUR LE CONTRÔLE QUALITÉ DU QUARTZITE DANS UN CONTEXTE INDUSTRIEL

Titre en anglais du manuscrit soumis :

Suitability of using a handheld XRF for quality control of quartzite in an industrial setting.

Auteurs :

Dany Desroches, L. Paul Bedard, Samuel Lemieux et Kim H. Esbensen

Journal :

Minerals Engineering (accepté)⁴

Cette version est légèrement différente de la version publiée pour tenir compte des modifications suggérées par les évaluateurs du mémoire.

Contributions des auteurs :

SL est l'instigateur ainsi que le représentant industriel dans le cadre de ce projet. Les différents essais ont été élaborés par PB et réalisés par DD. Le suivi des essais et la validation des résultats ont été assurés par PB. L'analyse et l'interprétation des données ont été faites par DD et PB. L'élaboration du manuscrit a été faite par DD et PB. Les corrections finales suites à la soumission de l'article ont été effectuées par PB.

⁴ Des corrections mineures ont été appliquées sur cet article versus celui publié.

Résumé en français :

La fluorescence X portative (XRFp) est un outil d'analyse souvent utilisé pour la caractérisation chimique, l'analyse environnementale ou l'exploration minière. Par conséquent, peu d'études traitent de son utilisation potentielle en tant qu'instrument de contrôle de qualité dans un contexte industriel, tels que le traitement du minerai ou encore, la transformation. Le quartzite est un matériau d'essai idéal puisqu'il s'agit d'une matrice simple permettant d'obtenir une meilleure isolation des différents paramètres, y compris la détection des limites, l'exactitude, la précision, la dérive instrumentale, la représentativité de surface et la préparation des échantillons. Dans cette étude, nous avons déterminé que la limite de détection spécifique était inférieure à 70 µg/g pour TiO₂, Fe₂O₃ et CaO. Les valeurs mesurées pour TiO₂, Fe₂O₃ et CaO étaient similaires aux valeurs des matériaux de références (échantillon sous forme de pastille pressée), tandis que les valeurs pour les éléments légers, et ce, à faible concentration (Al₂O₃ et MgO) étaient moins exactes et moins précises. Dans un contexte industriel, le temps est un enjeu critique, afin de minimiser celui-ci des analyses « in situ » ont été réalisées. En effet, cet appareil permet de caractériser chimiquement un minéral sans aucune préparation d'échantillon. Il a été déterminé que cinq mesures étaient suffisantes afin de caractériser un morceau de quartzite de 10 cm³. Les mesures « in situ » sont plus rapides que la méthode conventionnelle, mais la concentration de certaines phases locales et la mauvaise planéité de la surface provoque des résultats erratiques. Les essais réalisés suggèrent, cependant, que HHXRF pourrait être utilisé comme instrument de contrôle du quartzite dans un contexte industriel.

Suitability of using a handheld XRF for quality control of quartzite in an industrial setting

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Abstract

Handheld XRF (HHXRF) is an analytical tool often used for chemical characterization, environmental analysis or mineral exploration. However, few studies deal with its potential use as a quality control instrument within an industrial context, such as mineral processing or transformation. Quartz is an ideal test material; it is a simple matrix allowing for better isolation of different parameters including detection limits, precision and accuracy, instrumental drift, surface representativeness and sample preparation. In this study, we determined that the specific limit of detection was lower than 70 µg/g for TiO₂, Fe₂O₃ and CaO. The HHXRF analyzed pressed pellets of matrix-matched reference materials. Estimates for TiO₂, Fe₂O₃ and CaO were similar to certified values, while estimates for low concentration light elements (Al₂O₃ and MgO) were less accurate. For faster and higher throughput, as often required in an industrial context, HHXRF can be used directly on mineral sample without sample preparation. Five in-situ determinations on a 10-cm-sided block of quartz, produced an accuracy acceptable for industrial needs. However, in-situ determinations are limited by the flatness of the analytical surface, and minute accessory phases can induce some erratic results. Our tests suggest, however, that HHXRF is generally suitable for the controlling the quality of quartz in an industrial context.

Keywords: Handheld XRF, portable, suitability, performance quartzite, quality control, analytical chemistry, HHXRF, pXRF

1. Introduction

X-ray fluorescence analysis has existed for over 100 years, and portable (and handheld) X-ray fluorescence (HHXRF) devices are now commercially available. Three significant improvements were applied to this kind of instruments since the first handheld one piece in 1994 by Niton with the XL-309

- The silicon drift detector (SDD)
- New miniature X-ray tube
- Reduction of the weight

This new technology has the potential of quantifying samples in the field as it requires minimal surface preparation of the sample and a minimal amount of time for analysis (Ene et al., 2010). For the most part, applications of HHXRF cover four major areas: classification of metallurgical samples, analysis of contaminants in the environment, mineral exploration, and applications in the arts (Alberti et al., 2017; Gazley and Fisher, 2014; Hall et al., 2016; Higuera et al., 2012; Lemièrre, 2018; Lemièrre et al., 2014; Potts and West, 2008; Ramsey and Boon, 2012; among others). These portable instruments have given researchers in art conservation and archaeology the opportunity to study a broad range of materials with greater accessibility and flexibility than ever before. In addition, the low relative cost of handheld XRF has led many museums, academic institutions, and cultural centres to invest in the devices for paint pigment characterization, chemistry of sculpture material, paper chemistry, etc. (Shugar and Mass, 2012). In addition, many industries require stringent results to monitor materials used in their industrial processes. In many cases, this characterization must be done

in situ within very short time frame. Examples of such requirements abound in the mining and mineral processing sectors. To increase profitability, industry needs to increase production capacity with a concomitant need of processing a greater amount of raw material. Increased processing capacity often implies larger lots to be characterized, coupled with a need for faster results. Thus, these requirements can render the task of obtaining representative results more difficult and complex if, for example, the analytical target is several hundred metrics tons (Pitard, 2009). Moreover, in the case of quartzite, contaminating elements are at low concentrations. HHXRF can address such issues as it can obtain fast, in situ result usually with minimal sample preparation (Alberti et al., 2017; Gazley and Fisher, 2014; Lemière, 2018; Taylor et al., 2005). The usefulness of HHXRF has been demonstrated for geochemical analyses (Gazley and Fisher, 2014; Hall et al., 2016; Hall et al., 2014; Lemière, 2018; Linge et al., 2017; Ross et al., 2014a, 2014b; among others). However, the ability for HHXRF to provide accurate results in an industrial setting has not been demonstrated. With its high throughput and mobility, HHXRF could improve the sampling of large areas or lots (Ramsey and Boon, 2012; Ramsey et al., 2013). This would be even more important where the input material is coarse, such as in ferrosilicon production, requiring a large portion of samples to be tested to ensure an assessment is representative of the ensemble. However, HHXRF performance in an industrial setting must be established before its use in quantitative work. Its potential is critically dependent upon proven accuracy and precision (Petersen and Esbensen, 2005). Only few publications deal with its performance with respect to specific matrices such as quartzite or that tests its analytical performance within a realistic industrial context. Some studies have looked at blanks (Knight et al., 2013) or carbonates (de Winter et al., 2017; Quye-Sawyer et al., 2015) but these were not specific to industrial needs. The ferrosilicon production industry requires a continuous

control of quartzite quality and presents good test conditions for HHXRF. Coal, scrap iron and birch are also added to quartzite to make the ferrosilicon, but they are not considered in the present study. Quartzite is a relatively simple matrix to analyze. The challenge lies in the low concentrations of contamination elements and their spatial heterogeneity (small discrete minerals such as ilmenite (FeTiO_3) or magnetite (Fe_3O_4)). The most important elements to monitor for ferrosilicon production are Mg, Al, P, K, Ca, Ti and Fe. The HHXRF use in this paper is expected to provide quantitative and representative analyses of these elements. As the matrix is essentially SiO_2 (>98% m/m), Si is not characterized as its high concentration lies beyond the calibration range. In the specific context of ferrosilicon production, quartzite fragments are relatively large (10 cm), increasing the difficulty in ensuring the representativeness of samples. Representativeness is compromised because few of these large fragments would fit in a typical sampling bag.

This makes the need for a case study of HHXRF performance even more pertinent. We evaluated the performance of a HHXRF Niton XL3t GOLDD + analyzer with respect to analytical modes, corrections, precision and accuracy, in-situ analysis (sample preparation), detection limits and instrument drift. We validated HHXRF accuracy through an inter-laboratory testing. HHXRF then analyzed the raw materials of a ferrosilicon producer, the Elkem ferrosilicon plant (Chicoutimi, Québec, Canada), to assess its potential use.

2. Materials and methods

2.1 Analytical instrument

The XL3t GOLDD+ (Niton) was developed by Thermo Fisher Scientific (Tewksbury, Massachusetts, United States). Compared to its predecessors, this model has lower detection limits for most elements and an improved performance for light elements (Mg, Al, Si, P, S) (Thermo Fisher Scientific, 2013). The instrument's sensitivity is advertised as being more

precise with use of a silicon drift detector (SDD) than the older conventional Si-Pin (diode) detector. The XL3t GOLDD+ has the technical characteristics to be an adequate instrument for this study although there are now more advanced instruments available with lower detection limit, better sensitivity, calculation algorithm and software.

2.2 Instrument settings and calibration

2.2.1 Analytical mode and acquisition time

The HHXRF Niton, can operate in several analytical *modes*. Mode selection should depend on the nature of the material being analyzed. The existing modes on this Niton instrument are *General Metal*, *Soils*, *Mining Cu/Zn*, and *TestAllGeo*. Given that mode selection has been discussed previously (Bourke and Ross, 2016; Hall et al., 2016; Lemière, 2018), we retained *TestAllGeo* mode as it provided the best detection limits for light elements while having good precision and accuracy for TiO₂ and Fe₂O₃. We tested acquisition time (60 seconds was chosen as the optimal acquisition time) using a protocol similar to Gazley and Fisher (2014), Fisher et al. (2014), and de Winter (2017).

2.2.3 Limits of detection

The quartzite used in the production of ferrosilicon is of high purity. Consequently, the HHXRF must be able to analyze samples having low concentrations of contaminating elements. The limit of detection (LoD) is a key parameter that needs to be determined to assess the capacity of an analytical instrument. Most studies addressing the LoD of HHXRF assess relatively complex matrices, such as ore, soils, and rocks having complex mineralogy (de Winter et al., 2017; Gazley and Fisher, 2014; Lemière, 2018; among others). Moreover, iron (abundant in most geological samples) negatively affects the detection of trace elements (Lemière, 2018); however in quartzite, Fe is in very low concentrations. A specific detection

limit must therefore be developed for quartzite matrices. The LoD is defined as the smallest concentration or mass of the analyte that can be detected within a specified degree of certainty (IUPAC, 1978). Since the detection limit concept has many different significations, we applied Potts' (1987) terminology for detection limits: lower limit of determination (LLD; 3σ), limit of determination (LoD; 6σ), and limit of quantification (LoQ; 10σ). It is assumed, that the limit of detection (LoD) is equal to $LoQ / 3.3$ (Vial and Jardy, 1999). LoD is often expressed as a function of the standard deviation (σ) above the background (Potts, 1987; Potts and West, 2008; Thomsen et al., 2003; Uhrovčik, 2014; among others). However, many approaches can be used to define the detection limits of HHXRF: 1) establishing a limit of 3σ above background at low concentrations (Conrey et al., 2014; Dahl et al., 2013; Potts and West, 2008), 2) reporting the detection limits listed by the manufacturer (Luck and Simandl, 2014; Simandl et al., 2014), 3) using a variant of the Eurachem approach (Currie, 1995): the concentration for which the relative standard deviation of repeated analyses with diminishing concentrations reach a certain (satisfactory) level (Le Vaillant et al., 2014), and 4) providing detection limits without any explanation (Lemière et al., 2014; Ross et al., 2014a, 2014b). Given the lack of consensus for determining LoD and detection levels for HHXRF (Vial and Jardy, 1999), this issue deserves more investigation. For HHXRF, using 3σ values above background is troublesome as: 1) spectra cannot be readily interpreted on the instrument and need to be uploaded to a computer, 2) the instrument often provides results that agree with the accepted results for the Certified Reference Materials (CRM) but that are well below the detection limits calculated by this approach suggesting, that calculated detection limits do not match the instrument's capacity, and 3) such methods are operator-dependent (Vial and Jardy, 1999). Given that a manufacturer wishes to promote an instrument and its performance, it is expected that the advertised LoD are optimistic (Table 1), although

they likely represent valid guidelines. For this project, we retained the Eurachem approach. This method provides realistic results for the analyzed matrix, it is easily determined from results reported on an HHXRF, the results agree with instrument specifications, and it reflects realistic analytical conditions (matrix, analysis time, analytes, sample preparation, etc.). The Eurachem method calculates the relative standard deviation for each element across multiple measurements on a set of reference materials having decreasing concentrations. In many cases, it is difficult to obtain the high RSD of 30 % equivalent to the detection limit (Thomsen et al., 2003) due to the lack of adequately low concentration samples.

Table 1. Detection limits for elements within a quartzite matrix (no helium purge; Niton values from Thermo Fisher Scientific, 2013)

Elements	TiO₂ (ppm)	Al₂O₃ (ppm)	Fe₂O₃ (ppm)	MgO (ppm)	CaO (ppm)
Estimated detection limit	28	1100	66	3400	66
Niton detection limit	17	900	50	5800	70

The values obtained with the Eurachem approach approximate those of the manufacturer (Table 1). This approach for estimating detection limit values was the most realistic, although specific only to the quartzite matrix.

2.2.4 Instrument correction

X-ray fluorescence, although very effective, does not in itself provide accurate results with respect to the analyzed material. Therefore, a correction is desirable and, in most cases, mandatory (de Winter et al. 2017; Fisher et al., 2014; Gazley and Fisher 2014; Lemière, 2018; Le Vaillant et al., 2014; among others). To generate the correction factors from a series of correction curves, we used a set of CRM having a similar quartzite-rich matrix (Table 2). The low number of well-determined silica-rich CRM limits the number used to generate the correction. Given that the instrument already applies a calibration and a matrix correction,

most studies rely on a simple linear regression (Fisher et al., 2014; Gazley and Fisher, 2014; Lemière, 2018; Le Vaillant et al., 2014). We determined correction factors by analyzing each CRM 10 times, each for 120 s. For calibration purposes, we used a longer counting time as all subsequent results depended on this developed calibration. MgO concentrations in the reference materials were too low for a reliable correction regression (Fig. 1; Table 2). Slopes were near 1 for Fe₂O₃ and ranged between 1.16 and 1.33 for Al₂O₃, TiO₂ and CaO. A divergence of the slope away from 1 relates to differences in response and larger uncertainties in the values for reference material values at low concentrations.

Table 2. Values for certificates of analysis of certified reference materials (CRM) used to create a correction factor. They all have more than 70 % SiO₂.

Issuing Body		TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)
Centre de Recherche Pétrographique Géochimique	AC-E	0.110			0.340
Society of Glass technology / UK	STD sand No.6	0.024	0.060	0.032	
Society of Glass technology / UK	STD sand No.8	0.073	2.070	0.260	0.060
Society of Glass technology / UK	STD sand No.9	0.045	1.350	0.103	0.020
Institut de Pequisas Technologicas	IPT 61	0.026	0.054	0.014	
Institut de Pequisas Technologicas	IPT 62	0.036	0.110	0.072	
LGC Standards	Un-SpS	0.035	0.248	0.053	0.029
International Associations of Geoanalyst	GEO PT-14			0.472	0.392
Nationnal Institute of Standard and Technology	SRM 2709a				2.672
Nationnal Institute of Standard and Technology	SRM 2780				0.273
Canadian Certified Reference Materials Project	TILL-4PP				1.250

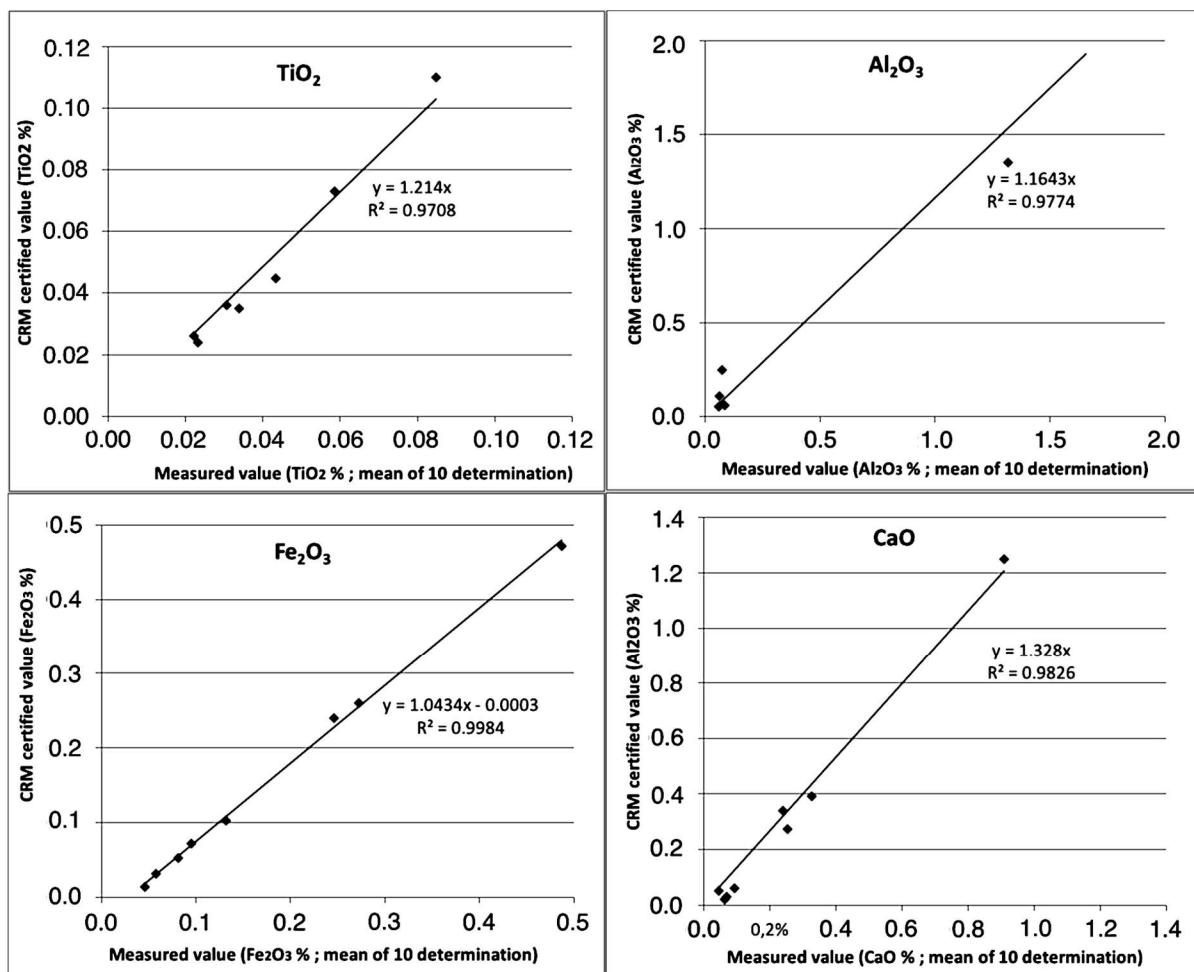


Fig. 1. Calibration curves of measured versus certified values for a) TiO₂, b) Al₂O₃, c) Fe₂O₃, and d) CaO.

2.2.5 Instrument precision and accuracy

Precision is defined as the agreement within a defined range of measured values for repeated measurements on the same sample under constant conditions (Thompson, 2012). Accuracy, or correctness, is defined as the difference between the measured value and the “true value”, or in our study, the value of the certificate of analysis of a CRM (Potts, 1987). The precision is quantified by the coefficient of variation (RSD), where $RSD = \left(\frac{\sigma}{x_{moy}}\right) \times 100$ (Thompson, 2012; Potts, 1987). A RSD value between 0 and 16% indicates that the estimates are reliable and vary minimally. RSD values between 16 and 33.3% are elevated, and the produced

average value may include large uncertainties. Above a value of 33.3 %, the RSD is considered too great and the average is not reliable. We tested precision using Standard Sand No.8, a CRM from the Society of Glass Technology (Table 3). The precision for 4 elements (Ti, Al, Fe, Mg) is excellent with RDS < 3%. The precision for Ca is acceptable with RDS at 10 %. In contract, the accuracy for all elements appear poor prior to calibration correction. This improves for Ti, Al and Ca after calibration correction, but remains poor for Mg and Fe. In the case of TiO₂, the accuracy values were misleading as both certified and obtained values were almost identical, but accuracy was reduced as the value is divided by a small concentration. Absolute differences were quite small except for Fe₂O₃ and MgO (Table 3).

Table 3. Precision and accuracy for CRM SGT8 as determined with HHXRF. Results were obtained from 40 measurements using an analysis time of 60 s in the *TestAllGeo* mode.

Oxides	TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	CaO (%)
Certified value	0.07	2.07	0.26	0.06	0.12
Without correction					
Mean of 40 measurements	0.06	1.69	0.13	0.53	0.08
Accuracy (%)	-21	-18	-49	785	-33
RSD (%)	2.73	3.82	2.70	0.29	10.09
Minimum	0.05	1.57	0.12	0.00	0.07
Maximum	0.06	1.83	0.14	0.01	0.10
With correction					
Mean of 40 measurements	0.07	1.97	0.14	0.53	0.11
Accuracy (%)	-4.58	-4.94	-46	785	-11

Note: accuracy = (obtained value - certified value) / certified value

3. Results

3.1 Inter-laboratory assessment of HHXRF performance for quartzite

We compared our assessment of HHXRF performance with that of commercial laboratories. A piece of quartzite was crushed, pulverized, and divided into 12 respective test mass portions, and sent for XRF analysis at three laboratories (Elkem, GeoLabs Inc., and ALS Minerals). ALS Minerals (Val d'Or, Québec, Canada) and Geo Labs (Sudbury, Ontario, Canada) are commercial laboratories that offer analytical services for geological materials. In addition, we prepared three test mass portions for the HHXRF (*TestAllGeo* mode with an analysis time of 60 seconds). The splitting of the crushed and homogenized batch of quartzite followed theory of sampling (TOS) principles (Petersen et al., 2004). Each laboratory applied their own analytical protocol (Table 4). Although the relative differences between the results were quite large, the absolute differences relative to the average of the three laboratories were negligible given the very low concentrations involved. The HHXRF provided poor results for Al_2O_3 in this range of value. Calibration for this element did not improve the accuracy; it actually worsened the estimate (Table 4). Differences between the concentration estimates of two reputed commercial laboratories (ALS Minerals and Geo Labs) indicates that at such low concentrations, high performance industrial XRF instruments also produce more erratic results (Table 4). Given the low concentration of the elements of interest, the small absolute difference in concentrations for the different results, and the inter-laboratory variability, the HHXRF provides results that match industrial needs, excluding the Al_2O_3 results.

Table 4. Results of inter-laboratory comparative analyses of a typical quartzite sample used for ferrosilicon production.

Oxides	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO
ALS Minerals (<i>n</i> = 3)	0.037%	0.19%	0.51%	0.037%	0.020%
Elkem (<i>n</i> = 3)	0.051%	0.10%	0.037%	0.004%	LoD
Geo Labs Inc. (<i>n</i> = 3)	0.050%	0.17%	0.56%	0.017%	0.033%
Mean (all labs) (<i>n</i> = 9)	0.046%	0.15%	0.37%	0.019%	0.027%
HHXRF	0.037%	0.49%	0.28%	LoD	0.018%
Accuracy	-20%	222%	-25%	N/A	-34%
HHXRF (calibrated value)	0.045%	0.57%	0.29%	N/A	0.02%
Accuracy	-3%	274%	-21%	N/A	-13%

*LoD: Below limit of detection ; *n : the number of measurements

3.2 In-situ versus ex-situ (prepared pellet) measured values

The quartzite used for the ferrosilicon alloy at Elkem is exploited near Saint-Urbain (Québec, Canada) by Sitec Inc. The quartzite had negligible weathering. Moreover, the coarse crushing (10-cm-side) done at the mine site provided many relatively flat surfaces. Therefore, HHXRF in-situ measurements with this material should yield good quality estimates as XRF analysis must be performed on flat surfaces (Potts et al., 1997). Analyzing only the sample surface could also make representativeness an issue. For a silica matrix having a 2 cm² surface sampled by HHXRF, a penetration depth of 0.2 mm can be assumed (Potts et al., 2008). Analytes located below this depth and outside of this area cannot be detected. In contrast, laboratory XRF offers optimal representativeness because a relatively large mass of sample is first pulverized and then homogenized. This is followed by a proper mass reduction (Petersen and Esbensen, 2005; Petersen et al., 2004) to produce a test sample that is more representative than a natural rock surface. To compare field (HHXRF) and laboratory (XRF) screening, we analyzed ten representative blocks of quartzite (10-cm-side) 20 times (at 60 s of counting) with HHXRF and then compared the results obtained for the quartzite prepared by standard XRF preparation procedures (crushing, pulverization, homogenization with

proper mass reduction, and palletization) (Fig. 2). We excluded results that differed markedly from each other for the same quartzite block as these were interpreted to be the effect of inadequate surface flatness as no minerals other than quartzite were observed on rock surface without magnification. CaO and MgO were not compared as multiple samples having below detection limit values (found using either the HHXRF or the XRF) resulted in too few results to provide a meaningful comparison. For concentration estimates obtained without correction (correction factors were included for measurements of pellets but are not appropriate for unprepared surfaces), values for TiO_2 , Fe_2O_3 and Al_2O_3 differed between the in situ (HHXRF) and ex situ (Desktop XRF) analyses (Fig. 2). The lower values for in situ Fe_2O_3 and TiO_2 measurements result due to contamination from the crushing and pulverizing equipment (made of hardened steel) for samples analyzed by laboratory XRF at Elkem Métal Canada (Fig. 2). It is important to know the producer of ferrosilicon use the same device to prepare the sample of the production and for the analysis of quartzite. However, small heterogeneities (small areas having a much higher concentrations of these elements) could also explain some of the difference. To test this idea, we produced detailed chemical maps using a microXRF, as described in Bédard et al. (2016). Maps were acquired with an Eagle III (EDAX, Mahwah, New Jersey, USA) dispersive energy micro-XRF instrument having a voltage of 40 kV and a current of 40 μA to maintain a dead time of 25–30%. A Rh tube focused with a poly-capillary lens at nominally 50 μm produced the X-rays. In total, 10 000 measurements (each lasting 10 seconds) on a grid covering approximately 25 mm^2 were used to create the maps. Each point of analysis was juxtaposed to the next without overlap between beam footprints. Net intensity counts (background corrected) were used to ensure minimal modifications of the signal. A geographic information system (GIS) software was used to

map results. For each map, average, relative standard deviation, maximum and minimum values, kurtosis and skewness were computed to detect any spurious analytical issues. Chemical maps were acquired for six samples; an example is presented in Fig. 3. The presence of small minerals (such as ilmenite, FeTiO_3) could increase by many times a single HHXRF measurement. Given that ilmenite contains approximately 50% TiO_2 , a single ilmenite grain occupying 0.1% of the total sample volume would increase results by 0.05% TiO_2 , about equal to the determined TiO_2 concentration. Other minerals such rutile (TiO_2), hematite (Fe_2O_3), and magnetite (Fe_3O_4) are fairly common in such rocks. Depending on the spatial distribution of these small minerals and the HHXRF beam location, individual determinations can differ enough to create the discrepancy between a large volume of pulverized and homogenized samples versus a few local determinations using an HHXRF. Moreover, the large differences in Al_2O_3 are interpreted to be related to the lower sensitivity of Al_2O_3 with the HHXRF than with a laboratory XRF. The Al_2O_3 represent a major issue for both method in-situ and ex-situ (Table 4). with this low concentration contain in the quartzite used by the ferrosilicon producer.

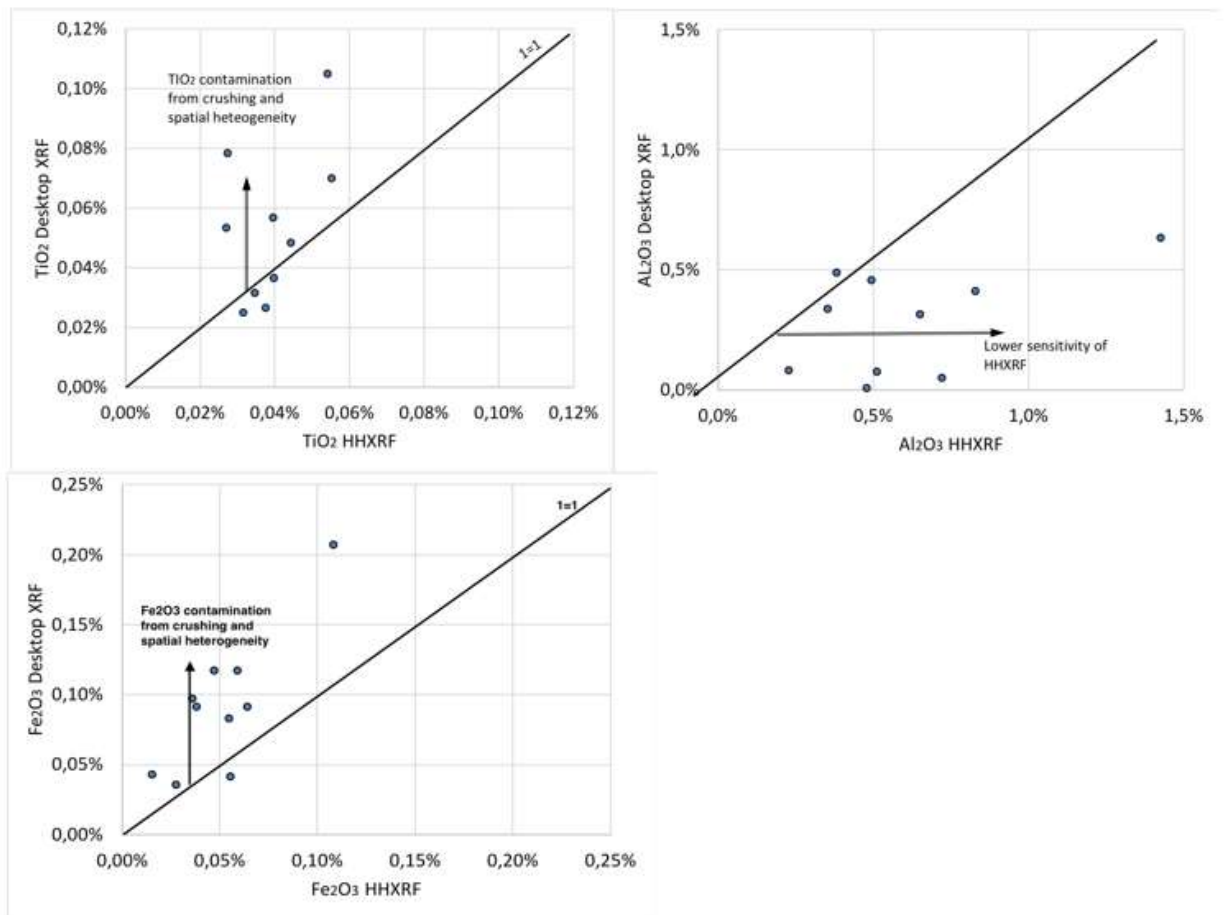


Fig. 2. Comparison of in-situ (HHXRF) versus ex-situ (Laboratory XRF; ex-situ) measurements of Fe_2O_3 , TiO_2 , and Al_2O_3 for large quartzite samples (10-cm-side).

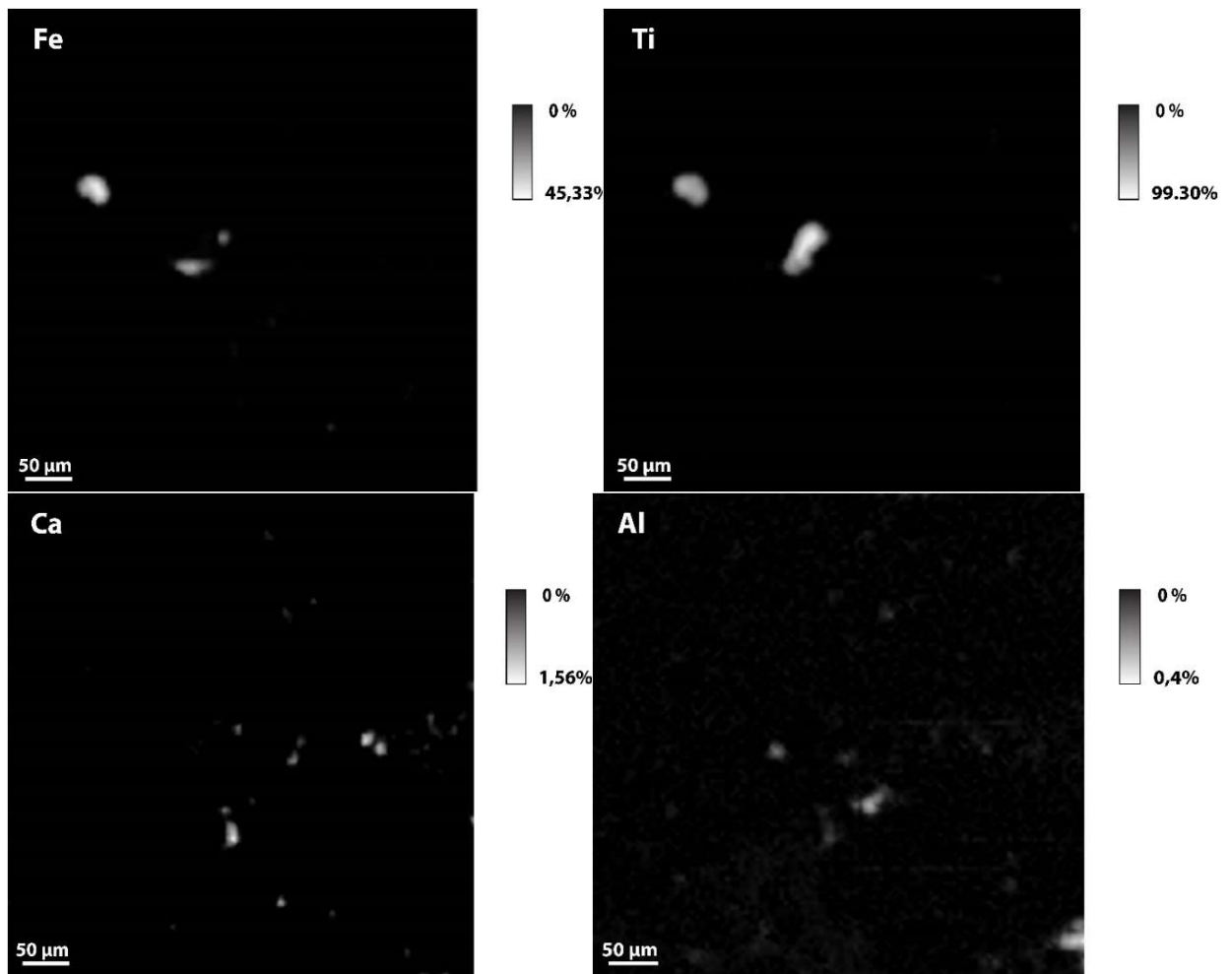


Fig. 3. Detailed microXRF chemical maps for Al, Ca, Fe and Ti on a quartz sample having small chemical heterogeneities. The scale on the right-hand side of map shows the net counts range (not actual concentrations). The Mg map is not presented as Mg values were below the detection limit.

Taking 50 measurements for each quartzite sample, each measurement having an acquisition time of 60 s, is time-consuming. As such we undertook a test to assess the performance of in situ measurement against fully prepared samples as a function of the number of analyses to determine the optimal number of measurements. The test will serve to maximize efficiency in an industrial context. For this experiment, ten representative blocks of quartzite were selected and on each block we made 20 measurements (n) with the HHXRF (Fig. 4). Accuracy improved markedly after eight measurements, reaching 11–13% for accuracy. However, to minimize analysis time and increase the analysis frequency, a slightly lower accuracy could be considered acceptable. The accuracy obtained for five measurements of TiO_2 and Fe_2O_3 is very similar to that obtained to eight (Fig. 4). For Al_2O_3 at least 10 measurements would be necessary. As such, within an industrial setting, five measurements are optimal.

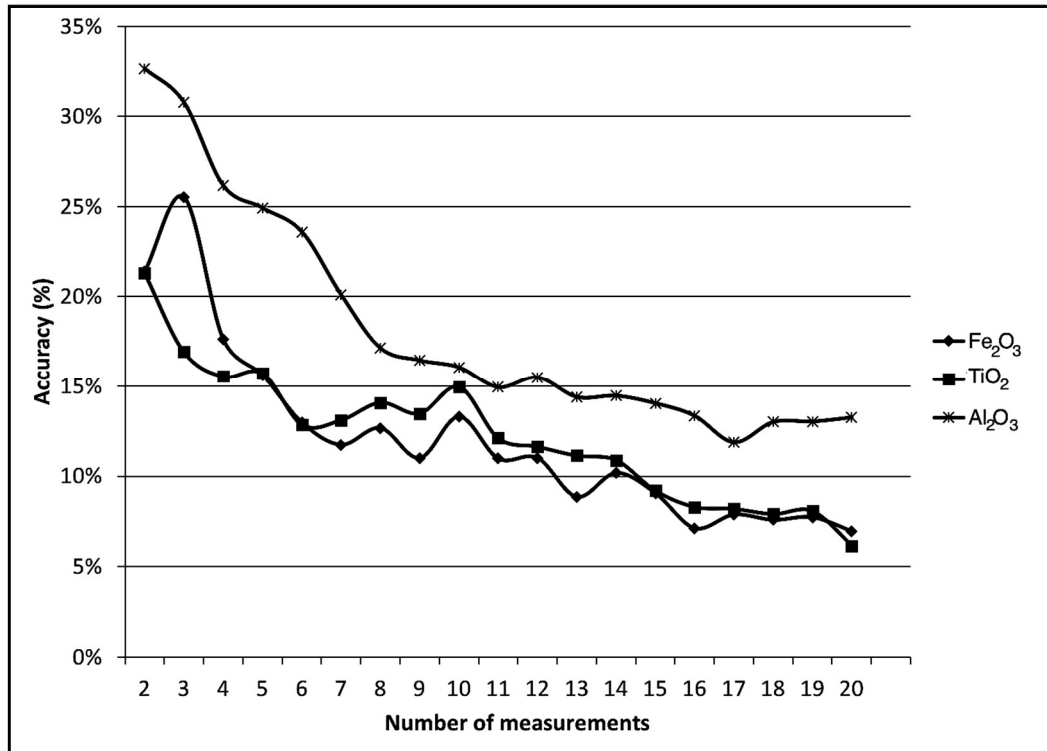


Fig. 4. Number of measurements versus accuracy for the in-situ determination of Al₂O₃, CaO, Fe₂O₃ and TiO₂ from a 10-cm-sided quartzite block. MgO values were under the limit of detection. Plotted values represent the mean accuracy of all quartzite blocks at $n+1$.

3.3 Analysis of dust

Given our goal of accurately estimating the composition quartzite of a lot, it is important to deal with the potential of trace concentrations of some fine-grained minerals such as zircon (ZrSiO₄) or ilmenite (FeTiO₃) that might be under-represented by in-situ or ex-situ analyses and which may accumulate as dust at the bottom of the quartzite pile. It is likely that crushed quartzite will fracture along surfaces having a mechanical heterogeneity, such as fine-grained minerals. As quartzite is a hard mineral, transportation-induced motion in trucks and other processing-related activities generate much dust. Given that quartzite fractures where there are fine-grained minerals in the matrix, the dust related to fracturing should be analyzed to assess if sampling only the larger quartzite specimens provides an adequate portrait of the overall quartzite lot. As such, we sampled a series of quartzite pieces having a large amount

of surface dust. The samples were placed in an oven and dried at 130 °C for 3 h to collect the humidity-bound dust. The collected dust was then homogenized, pulverized, split, pelletized (Herzog), and analyzed by laboratory X-ray fluorescence (Rigaku, Austin, Texas, USA) at Elkem Metal Canada Inc., using a routine protocol for quartzite. The dust contained higher concentrations of TiO₂, Fe₂O₃, and Al₂O₃ (Table 5). The estimated average routine quartzite is based on thousands of analyses conducted over the year at the Elkem plant. As expected, small minerals rich in Fe₂O₃, Al₂O₃, and TiO₂, (such as hematite (Fe₂O₃), magnetite (Fe₃O₄), ilmenite (FeTiO₃), rutile (TiO₂), feldspar (KAlSi₃O₈, NaAlSi₃O₈, CaAl₂Si₃O₈), and/or kyanite (Al₂SiO₅)) had separated from larger pieces of quartzite. However, the ratio of dust mass versus a quartzite piece averages only 0.05%; this would increase Al₂O₃ concentrations by about 0.001 wt% ($0.9995 \times 0.29 + 0.0005 \times 1.52 = 0.291\%$ Al₂O₃ versus 0.290% Al₂O₃ without dust). Thus, the compositional difference between the dust and quartzite pieces can be neglected due to their low proportions.

Table 5. Concentration of elements within quartzite blocks and quartzite dust.

Oxides	TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	CaO (%)
Mean quartzite block concentration (>1000 measurements)	0.05	0.29	0.09	0.03	0.01
Quartzite dust concentration	0.10	1.52	0.43	0.04	0.09

3.4 Instrumental drift

Drift is a systematic error (bias) signifying variable measurements over time, and the extent of this drift is unique for each instrument. The effect of drift can be reduced by a single calibration or by frequently correcting for drift over time. To characterize drift, we repeatedly tested a sample, 3 times per hour for 12 hours on a CRM NIST-1413 (Fig. 5).

Magnesium concentrations were not considered as values were too close to the detection limit. Most variability fell within 5% of the initial value although an important drift in the measurement occurred after eight hours. This drift was likely due to battery drain.

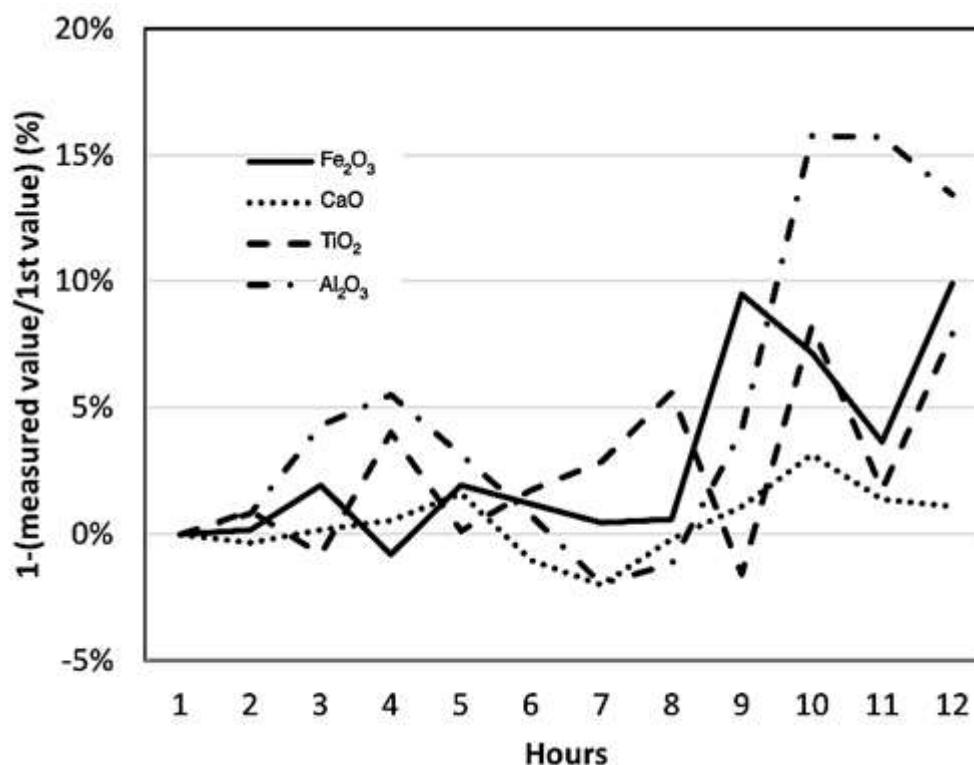


Fig. 5. Instrumental drift over time for a Niton XL3t GOLDD+ handheld XRF measuring Al₂O₃, TiO₂, Fe₂O₃ and CaO in a quartzite sample.

3.5 Suitability for industrial purposes

For ferrosilicon, the major contaminant is titanium. Calculated from the mass ratio of quartzite, 56% of all titanium from materials (quartzite, coal, scrap iron, birch) comes from quartzite. The processing limit for Ti is 0.2% with a maximum for quartzite of 0.15%. We can use these limits to calculate a maximum uncertainty of less than 25%. To be effective from an industrial point of view, it is necessary to obtain a representative result of a lot within a very short period of time. We determined that five measurements with HHXRF permitted the in-situ analysis of a block of quartzite (10-cm-side) with an accuracy of 13% for Fe₂O₃,

TiO₂ and CaO (accuracy for Al₂O₃ was 24%). The performance of the HHXRF Niton XL3t GOLDD+ provided similar results to laboratory-based results, albeit with a lower accuracy. However, HHXRF is much faster and requires no sample preparation.

4. Conclusion

In summary, handheld XRF (HHXRF) provides a rapid chemical analysis of quartzite. In-situ analysis with minimal sample preparation is a major asset for this device. Application of a correction value, derived from results obtained for certified reference materials, significantly improves the accuracy of HHXRF measurements. The correction must be developed using materials having a similar matrix and surface preparation as the specimen being analyzed. Numerous LoD protocols exist, however many are neither practical nor able to provide realistic results. We propose the use of a protocol where replicate determinations are taken from a set of samples having a range of concentrations toward the lower end. As concentrations are reduced, instrument precision decreases and a practical threshold can be set to define a detection limit. The quality (flatness) of the analyzed surface is also critical for in-situ determinations, and the presence of minute heterogeneities (accessory minerals) can be problematic. Chemical characterization of high purity quartzite is complex; however, our results show that an HHXRF (in this study a Niton XL3t GOLDD+) is suitable for quantitative analyses of quartzite within an industrial context.

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Conflict of Interest

The authors declare no conflict of interest.

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CHAPITRE II

ÉCHANTILLONNAGE REPRÉSENTATIF ET TRAITEMENT EN LABORATOIRE POUR LA SURVEILLANCE DE LA QUALITÉ DES MATIÈRES PREMIÈRES DE QUARTZITE DANS UNE USINE DE FERROSILICIUM

Titre en anglais du manuscrit soumis :

Representative sampling and laboratory processing for quartzite raw material quality monitoring at a ferrosilicon plant.

Auteurs :

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Journal :

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Contributions des auteurs :

SL est l'instigateur ainsi que le représentant industriel dans le cadre de ce projet. Des rencontres entre les auteurs ont été effectuées afin de discuter de l'élaboration de la méthodologie et l'interprétation des résultats obtenus (DD, PB, KE et SL). La conception théorique des différents essais et son adaptation à un contexte industriel a été effectué par KE. La réalisation de la méthodologie et l'acquisition de donnée ont été réalisé par DD. La rédaction de l'article a été effectuée par DD, PB et KE. Les corrections finales suites à la soumission de l'article ont été effectuées par PB.

⁵ Des corrections mineures ont été appliquées sur cet article versus celui en attente des évaluations d'arbitrage.

Résumé en français :

L'échantillonnage est une étape critique, mais trop souvent négligé dans le milieu industriel. De manière générale, on considère l'échantillonnage comme une étape simple ou l'on prend un échantillon aléatoire dans une pile afin de caractériser celle-ci. Les laboratoires sont souvent obsédés par des incertitudes analytiques, mais ceux-ci ignorent que l'erreur d'échantillonnage lié à l'échantillon analysé pourrait être plus de 20 à 100 fois plus grande. L'amélioration de la représentativité de l'échantillonnage aura un impact considérable sur l'estimation du lot qui est le véritable objectif du suivi de la qualité. Afin de valider l'efficacité de la HHXRF, des essais comparatifs ont été réalisés directement à l'usine de production de ferrosilicium avec un appareil de type laboratoire XRF. Dans la littérature de la théorie de l'échantillonnage, on retrouve plusieurs types d'erreur pouvant influencer les résultats tels que **l'erreur fondamentale d'échantillonnage**, l'erreur de ségrégation, l'erreur de délimitation, l'erreur d'extraction ainsi que l'erreur de préparation de l'échantillon qui ont tous été prises en compte lors de l'élaboration des essais de cet article. En effet, plusieurs expérimentations ont été développées et réalisées afin de déterminer la masse optimale d'un échantillon, les variations à travers un lot (analyse variographique), les distinctions entre les résultats des échantillons sélectionnés aléatoirement versus des échantillons composites. Les protocoles d'échantillonnage et la préparation des échantillons sont décrits en détail dans cet article. Les résultats de HHXRF sont comparés à ceux obtenus à partir d'un XRF de type laboratoire en utilisant les mêmes échantillons. Il est vraisemblable que plus le poids échantillonné est élevé plus le résultat obtenu sera près de la valeur réel du lot. Afin de respecter les normes en santé et sécurité au travail, la masse optimale d'un échantillon a été déterminé à 10 kg. L'exactitude pour un échantillon de 10 kg est de 18 % contre 35 % à 1 kg.

Parmi toutes les étapes requises pour l'obtention d'un résultat analytique, l'échantillonnage primaire est la variable la plus prépondérante sur l'erreur globale. L'analyse variographique montre un effet de pépite pure suggérant très peu d'hétérogénéité spatiale dans le lot. Les résultats de l'appareil HHXRF et ceux du XRF de type laboratoire sont comparables. Pour les deux appareils d'analyses, l'échantillon composite présente des erreurs deux fois plus petites que l'échantillon sélectionné aléatoirement. Un échantillon composite effectué avec l'appareil portatif fournit une meilleure stratégie d'échantillonnage qu'un échantillon sélectionné aléatoirement et analysé par un appareil XRF de type laboratoire.

Abstract:

Sampling is critical in the industrial context. In many cases, it is considered a simple matter and a grab sample is the only sampling protocol considered. Laboratories are often obsessed with analytical uncertainties (or errors) but ignore the sampling error which could be more than 20 to 100 times larger. Improving the sampling representativeness could have tremendous impact on the estimation of the whole lot⁶ which is the real goal of quality monitoring. The capacity for HHXRF to achieve a satisfactory representability in place of larger desktop XRF (laboratory XRF) in a full-scale industrial setting at a ferrosilicon plant has been undertaken. The different sampling errors (Fundamental Sampling Error, Grouping and Segregation Error, Increment Delimitation, Increment Extraction, Increment Preparation Error) were considered. A set of experiments have been undertaken that needs to be determined to assess the optimal sample mass, a transect analysis for the variations across the lot, a set of composite samples to compare with a grab sample. Three sample methods will be compare in this paper as the grab sampling, composite sample and transect method. The grab sampling consists in the action of taking a random sample in a lot. The composite sample is the result of a series of sample grab sampling which will mix together and reduced to obtain a single sample in the end. The transect method consists of realizing several grab sampling at a defined interval of time or distance. Sampling protocols and sample preparation are described in detail. HHXRF results are compared with those obtained from a desktop XRF) on the same samples. The optimal sample mass is 10 kg considering the large size (10 cm side) of quartzite blocks used in ferrosilicon plant, the better accuracy (18 % as opposed to 35 % at 1 kg) and the sample bag limit that a technician can realistically transport from sampling point to

⁶ In context of the Theory Of Sampling, we use the term “lot” but in other context this term is common called “batch”.

preparation facilities. The main contribution to the global estimation error is from the primary sampling. The transect analysis show a pure nugget effect suggesting a very little spatial heterogeneity in the lot (The nugget effect represent the lag between the first and the second sample). HHXRF and desktop XRF results compare favorably. The error (variability) of the concentrations of contaminating elements was halved when composite sampling was used as opposed to grab sampling. The handheld XRF used in conjunction with composite sampling provide a better sampling strategy than a conventional grab sample analyzed with a desktop XRF.

Keywords: Sampling; Quartzite; X-ray fluorescence; ferrosilicon; Quality control; HHXRF; Handheld, Theory Of Sampling (TOS)

1. Introduction

The Theory of Sampling (TOS) is addressing the single most important phenomenon when characterizing material systems, heterogeneity. Indeed, if materials were homogeneous, there would be no reason for sampling ever to be a problem – any sample would be a perfect reflection of the entire lot and all its features. Alas all material lots in science, technology and industry are significantly heterogeneous – it is only a matter of scale (only the heterogeneity *within* an analytical aliquot can legitimately be looked away from). Currently, sampling is an obligation that is all too often trivialized in industry, with severe consequences. Few industry professionals are capable of performing sampling in a representative fashion if this entails the least bit of work effort over status quo regarding the present sampling protocols – with the result that there is every chance for a continuation to extract just one, or a few haphazardly collected specimens (grab sampling). It must be emphasized that the objective of sampling is to provide information pertaining to the entire lot with a known and acceptable level of reliability (representative sampling). Grab sampling is today the most often performed type of sampling in very many industrial situations. The grab sampling is carried out as a single sampling operation and consist to select aleatory a sample in the whole lot. Unfortunately grab sampling could never be able to deliver a representative sample, Comprehensive referral is made to a new international sampling standard, (DS 3077, 2013), and to a select key literature (Gy, 1998; Pitard, 2009; Esbensen and Julius, 2009; Esbensen and Wagner, 2014; Esbensen et al. 2018), in which abundant documentation for this statement can be found. There was also recently parallel efforts made to elucidate the grab sampling versus composite sampling approach that is advocated and executed in the present study, also within distinctly different application areas, (Bucheli et al., 2014; Esbensen and Appel, 2017). Most laboratories could provide a validated estimate

of the total analytical measurement error, but only very few include the preceding sampling errors. This irrespective of the fact that the sampling error is often ten, twenty to one hundred times larger than analytical error (see references above), as is also mentioned by (Taylor *et al.*, 2007): Typically, more than 80% of total measurement error is caused by the sampling. Unfortunately, very little of this insight and knowledge is appreciated in current industry. The global estimation error (GEE) is defined as the sum of all sampling errors (Total Sampling Error: TSE) plus the total analytical error (Total Analytical Error: TAE) (Esbensen and Petersen, 2005; Esbensen and Wagner, 2014). It is obvious that any decrease in GEE means improved analytical performance. To improve the validity of the measurement characterization, one must consequently revise faulty, or neglected sampling protocols with the aim to find the most significant errors and reduce, or preferentially eliminate these. Examples abound in the mining and mineral processing sectors. In order to increase profitability, industry often wishes to increase production capacity with a concomitant need to process more raw materials. Increased processing capacity frequently implies larger lots to manage, monitor and characterize, often also with a desire for a faster response. All these legitimate desires will unavoidably mean that it can become difficult and complex to obtain representative results from the analytical operations (typically of the order of grams), when the sampling target is of the order of several hundred metric tons. It is especially for such large mass-reduction cases that the Theory of Sampling (TOS) must be invoked guiding the sampling practice (DS3077, 2013; Esbensen and Julius, 2013; Esbensen and Petersen, 2005). The use of a handheld X-ray fluorescence (HHXRF) instrument may address some of these issues with the ability to obtain fast in situ chemical characterization, and crucially often with minimal sample preparation (Taylor, et al., 2005) Combined with improved sampling and high throughputs, the increased mobility of HHXRF can potentially characterize large, and

larger lots are better (Ramsey and Boon, 2012; Ramsey, et al., 2013) , although this has not been demonstrated yet in many industrial contexts that such instruments can provide fit-for-purpose representative results (Bédard and Barnes, 2011; Thompson and Ellison 2006; Thompson and Feam, 1996). In an earlier parallel study, the specific analytical performance of a dedicated HHXRF facility has been evaluated and quantified for the case of quartzite raw material, demonstrating an encouraging potential for this approach (Desroches et al., 2018). In this paper, we look at the possibilities for HHXRF to achieve a satisfactory representativity in place of larger desktop XRF, by evaluating its applicability in a full-scale industrial setting at a large ferrosilicon plant.

1.1 Equipment

The handheld X-ray fluorescence instrument used is a Niton XL3t GOLDD +, developed by Thermo Fisher Scientific (Tewksbury, Massachusetts, United States). The sensitivity and measurement time has been much improved with the introduction of Silicon Drift detectors (SDD) against older Si-Pin detector. Through this improvement, the X-ray chamber geometry has been optimized and now uses a current potential of 50 KV and 200 μ A (Thermo Scientific, 2013). This type of device now achieves almost comparable performance to that of standard laboratories instruments (Desroches et al.; 2018; Lemière, 2018; Gazley and Fisher, 2014; among others). However, because HHXRF has the potential to be used essentially without sample preparation for fast turn-around (direct measurements on mineral surfaces, perhaps with just a quick cleaning wipe), where conditions are quite different than for prepared samples such XRF pressed pellets, we want to evaluate this instrument in the demanding and tough industrial setting of raw material quartzite quality assurance. In the present context the ultimate target is successful quantification of very low contaminant

concentrations in run-of-the-mine quartzite intended for ferrosilicon production. The current laboratory XRF facility will be used for analytical comparison (reference analytical approach involving a significant sampling/processing/analysis effort), using a WDX Primini, developed by Rigaku (Tokyo, Japan). The present model uses sequential type X-ray fluorescence spectrometer approach. The X-Ray chamber is working in an atmosphere controlled by P10 gas (argon/methane) with a pressure during analysis up to one Pascal. The X-ray tube is Palladium with a voltage of 40 kV and 1,25 mA. The Primini is capable of analyzing elements from fluorine (9) through uranium (92) (Interactive Corporation, 2014).

1.2 Elkem Métal Canada Inc. Plant

Elkem Métal Canada Inc. is a producer of ferrosilicon alloy, with two main production pathways, characterized by a base of 50 or 75% silicon respectively, with several customer-specified additive options (foundry and steel plant). For this type of production, the plant reduces quartzite (SiO_2) by a process which performs a combined blast furnace melting and Söderberg electrolysis. For this process to be successful, the ferrosilicon industry has to control quartzite quality very carefully. Quartzite may at first view seem a simple matrix to analyze, but the difficulty of course lies with its low concentrations of impurities (in the form of discrete minute grains of ilmenite (FeTiO_3) or magnetite (Fe_3O_4)). These impurities exhibit close to an extreme degree of spatial heterogeneity making proper sampling a very significant challenge. Since the matrix is essentially SiO_2 (>98% m/m), the plant doesn't analyze each quartzite shipment individually, but instead rely on traditional grab sampling over contractually specified volumes/time periods. Although quartzite are fairly common rocks in the continental crust, few researchers have investigated its characterization by HHXRF (Desroches et al. 2018).

1.3 Theory Of Sampling (TOS) short review

Sometimes grab sampling may, purely by chance, could be have the true chemical lot composition, but it is never possible to identify when this happens, and in any event the situations where it fails fatally simply dominate. At the outset of the present study it was considered likely that the current sampling approach is problematic and not providing an outcome consistent with reality. It was therefore considered a critical success factor to invoke the Theory of Sampling (TOS) (Gy 1998) as providing the framework in which the specific HHXRF evaluation should be carried out.

1.3.1 Fundamental Sampling principle (FSP)

All units of the lot (minerals, increments (see below)) must be fully and practically accessible by the sampling procedure in use. There cannot be any “restricted zones” in any lot from where sampling is not possible. Thus, TOS stipulates that the entire lot volume must be available for sampling; this is called the Fundamental Sampling Principle (FSP). Occasionally, in practice, the entity responsible for the use of the final analytical results, may decide that samples from the surface of stationary lot will suffice for a “fit-for-purpose” characterization. Such a decision will always be at the express behest of the user – and most emphatically not of TOS! In mining and minerals processing sectors there may be an opinion, or a widely accepted practical assumption, that surficial samples over the entire surface of a stationary lot will be able to characterize the entire, full volume lot. While this is a tacit assumption often found within these application fields, there is no guarantee, from TOS nor from any other reliable source, that this holds true for all lots in question, or to all successive lots in time. Whether such is the case is of course completely dependent upon the effective heterogeneity of the lot(s) in question. Perhaps prior knowledge is at hand that possibly could

support continuation of such operative assumptions? In any case – indeed in every case – this could constitute a breach of due diligence the Fundamental Sampling Principle. For smaller lots, e.g. sub-samples compliance with FSP becomes more and more easy – it is very much easier to get full access to a 55kg sub-lot, or a 10-kg sub-sub-lot etc. than the whole lot who could be represent over than 40+ ton.

1.3.2 Lot

TOS uses the term “lot” to designate the sampling target; i.e. a stockpile, a barrel, a truck or a railroad load or a geological outcrop. The meaning of the term lot is dependent upon the situation. All lots are made up by a specific material, occupies a specific geometrical volume and has a specific lot mass, density etc. The crucial common characteristic of all lots is heterogeneity, which makes sampling of however disparate and different types of lots, a matter of a focused and unified approach, the Theory of Sampling (TOS).

1.3.3 Composite sampling – increments

TOS stipulates the mandate always to use composite sampling using a heterogeneity-determined number of increments (Q). An increment designates an individual extracted unit (often defined by the volume of the sampling tool), i.e. a partial lot unit that, when combined with other such units, makes up a composite sample. The only free parameter in composite sampling is the necessary number of increments needed, Q, needed to result in fit-for-purpose sampling.

1.3.4 Sampling errors

TOS specifies five errors occurring during sampling stationary lots; there are two more, specific errors when sampling moving (dynamic) lots, (Esbensen and Julius, 2013;

Minkkinen and Esbensen, 2009; Pitard, 2009). The first five errors are listed below, not in order of importance, but in their logical order in the sampling process.

- 1) The Fundamental Sampling Error (FSE)
- 2) The Grouping and Segregation Error (GSE)
- 3) The Increment Delimitation Error (IDE)
- 4) The Increment Extraction Error (IEE)
- 5) The Increment Preparation Error (IPE)

The last three sampling errors (IDE, IEE, IPE) are collectively termed the “Incorrect Sampling Errors” (ISE), which are sampling bias-generating errors. These are fatal sampling errors because, if not eliminated from the sampling process, they give rise to a fatal sampling bias. Full details in the TOS literature cited above. All these errors contribute to the Total Sampling Error total (TSE). To this could be added the Increment Weighing Error (IWE) but this is not directly involved in the HHXRF sensor sampling and in conventional sampling increment weight variability less than +/-20% is usually considered acceptable. The Fundamental Sampling Error (FSE) is irreducible without physical modifications of the material. The only way to reduce this error is to reduce the particle size (crushing, comminution). This error is inversely proportional to the realized mass of the sample, but increasing this by itself will not help much representative – any grab sample is still but a miniscule part of the entire lot - another reason for using composite sampling. The Grouping and Segregation Error (GSE) will be higher as a direct consequence of high heterogeneity; most often this is in the form of local “hot spots” (with either high, or lower, average concentration(s), grouping, and/or stratification, segregation. This error is also partially caused by temporal heterogeneity whenever transportation plays a role (i.e. transport induced vibration can displace smaller fragments towards the bottom of the pile). This error can be

reduced, or sometimes almost canceled, by effective composite sampling and/or for smaller lots, by mixing. The Increment Delimitation Error (IDE) is occurring when one is not able to reproduce exactly the same geometric delineation of the increments being sampled. The extraction error (IEE) is the result of extracting increments with a sampling tool which is *selective*, meaning that it does not allow equal opportunity for all particles to be extracted by the tool exactly and only from the delineated volume. This type of error can be reduced by carefully monitoring and maintaining the performance of the sampling tools. IPE covers all errors occurring in handling, mixing, comminution or similar in the laboratory, which are due to:

- 1) Loss or addition of matter (dust, moisture, poor cleaning etc.)
- 2) Chemical or physical alteration
- 3) Negligence or non-adherence to GLP by the laboratory operator

Referral is made to the international standard (DS 3077, 2013), in which the complete TOS framework is laid out for sampling of lots of all dimensionalities and with all levels of heterogeneity. The way TOS has been applied in the present work is described below in the practical context of the present project.

1.3.5 Replication experiment

In order to quantify the effects of the total sampling, processing and analytical errors combined, there exists an approach called the Replication Experiment (RE) (Juran and Godfrey, 1998; DS 3077, 2013; Esbensen and Julius, 2009; Esbensen and Wagner, 2016). The variability of repeated sampling can be quantified by extracting and analyzing a number of replicate samples; this term needs to be carefully defined, see Esbensen and Wagner (2014). A replication experiment can be applied to any existing sampling procedure, as well

as to any new sampling operation. It is critical to understand that the RE must start, must replicate, from the primary sampling stage, or else the primary sampling error will not be included in the resulting estimate of the total measurement uncertainty, (Juran and Godfrey, 1998; DS 3077, 2013; Esbensen and Julius, 2009; Esbensen and Wagner, 2016). The RE approach can either be applied in the above primary sampling setting, and it can additionally be applied at each *individual* sampling, processing or analytical stage in a hierarchical fashion. This latter approach will allow to quantify the effective errors resulting at each of these stages. This is the way selected here below. The main objective is to quantify the effective error for each sampling step of the compound procedure. For each step evaluation, one needs a minimum of ten replicate sampling operations (Esbensen and Julius, 2009). With the five stages identified here, this translates into fifty analytical samples, as delineated in detail in Figure 1. Starting with replicating the primary sampling 10 times (termed PSE), one randomly selected sample from each of the steps is subsequently treated identically 10 times, cascading down the general pathway shown in Figure 1. outlining the complete setup of this realization of the replication experiment.

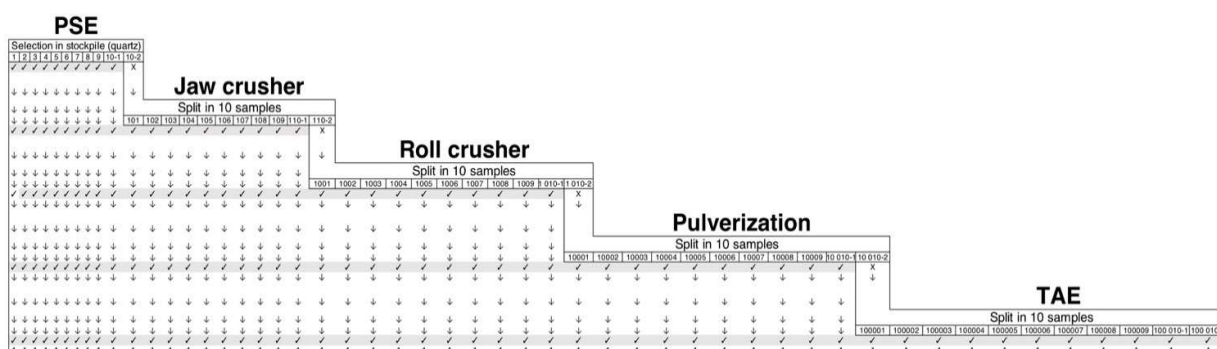


Figure 1. Hierarchical replication experiment; PSE is the Primary Sampling stage and TAE is the Total Analytical Error. At each stage a randomly selected sample is treated 10 times in the following pathway segment (it is shown here as the tenth sample, but this positioning is for illustration clarity only).

1.3.6 Mass reduction

At first view, it may seem easy to reduce sample mass (known as sample splitting). Nevertheless, many mistakes can occur, and significant sampling errors may very well be incurred during some of these, or all steps of mass reduction. In this paper, much effort was spent reducing primary sample masses in a fully representative manner (Petersen, *et al.*, 2004). The first step in mass reduction is crushing. Reducing particle size allows reduction of the total lot heterogeneity by allowing much improved mixing efficiency. This operation will both reduce GSE and FSE, leaving the comminuted particles a significantly more equal chance of being sampled. If the mixing is done with maximum effect, GSE can be almost eliminated, especially for operations that can be controlled at the laboratory scale.

1.3.7 Grab sampling

There can be no doubt that grab sampling to secure a “sample” is demonstrably the least acceptable approach, since it can never be representative, except as an extremely rare accident (Minkkinen and Esbensen, 2009; Esbensen and Julius, 2009). Grab sampling is carried out as a single sampling operation, almost always because, it is argued, this approach is the least expensive, and the least effort-demanding and fastest... Which is all very nice, but the fact remains that this is still the worst approach ever with respect to the only criterion that matters, representativeness. Only in the rare instance in which is the material to be sampled, and analyzed, happens already to be of “uniform composition” may grab sampling turn out to be acceptable (but its use must *always* be evaluated by a replication experiment, no exception). For the kind of materials treated here, and a host of broadly similar material classes, grab sampling is completely irrelevant and totally unacceptable.

1.3.8 Composite sampling

This approach consists in collecting many increments (Q) to form one aggregate sample, the high the number of increments used, the high the likelihood that the resulting composite sample will be fit-for-purpose representative. It is logical that the spatial collection of Q increments will be so as optimally to comply with the Fundamental Sampling Principle. This approach has a profound effect on the Total Sampling Error (TSE), which will decrease simply by increasing the number of increments. Indeed, FSE is inversely proportional to the mass sampled as discussed above, but this is ever only of interest in the case of composite samples. It is imperative to understand that the Q increments must be deployed so as to represent the full geometry (the full volume) of the lot. This is indeed the only fashion in which composite sampling reduces GSE (Grouping and Segregation Error), and this is very often the only approach available for primary sampling.

1.3.8 Mixing

Acknowledging that all particles must have an equal chance of being selected (FSP), lot mixing (at any scale relevant) will reduce the heterogeneity, but never to the state of homogeneity; there will always be a natural, minimum state of heterogeneity for any aggregate material that cannot be transgressed; homogeneity is an ideal state that unfortunately does not exist for all naturally occurring materials in science, technology and industry (Pitard, 2009; Gy, 1998). One can even apply ‘too much’ mixing, with the unwanted potential to partially increase segregation again; too much mixing results in a steady-state mixing, de-mixing situation (Esbensen and Julius, 2013).

1.3.9 Transect sampling and variographic analysis

The transect sampling was used to produce a variogram who allows a superior characterization of the sampling process and the heterogeneity of the lot material and is always to be preferred (DS 3077, 2013; Pitard, 2009; Esbensen et al, 2007). The variogram describe the empirical variance of a given 1-D data series simultaneously at all scales with powerful insight in a graphic delineation, the variogram, as a function of inter-sample distance, called the lag (h). This data series may stem from a process data collection or, as in the present case, from a transect along which relevant samples have been collected for analysis. The variogram calculation has recently been explained in full operative detail by Minitt and Esbensen (2017), as well as in two didactic application studies from the minerals industry (Engström and Esbensen, 2017a, b). The variogram outlines the degree of temporal or spatial autocorrelation present (the variogram range). The most useful variogram feature in the present project context is called the nugget effect, which quantifies the total empirical sampling, preparation and analytical error vs. the process, or transect variability (the sill of the variogram). The derived feature, the nugget effect/sill ratio, in effect decomposes the raw data variability into the total measurement system noise vs. the true (the decomposed) transect variability. On this basis the possibility for a (more-or-less) reduced through transect variability may often come as a surprise.

2. Experiments

2.1 Determination of optimal sample mass

In many industry sectors, there are guidelines, standards and procedures to follow for all critical tasks, but such document does not always specify the optimal, or the required sample mass. Or, worse, a fixed sample mass is stipulated by fiat for all purposes and

objectives, clearly not prepared for lots with variable heterogeneity. Currently, at Elkem Metal Canada Inc., the primary mass of a typical sample is around 10 kg; being the weight limit set so the technician could easily transport the collected material from sampling point to the laboratory. It is noteworthy, that this weight was determined without any preliminary study. An experiment was developed to validate whether this mass was adequate:

- 1) We collected 55 kg of grab samples of quartzite (individual units of quartzite measures about 10 cm side) from the stockpile (Fig. 3);
- 2) These sample were laid out on a table;
- 3) We selected randomly quartzite rocks to form ten sub-samples of increasing mass: the first sub-sample was 1 kg, the second 2 kg, the third 3 kg and so on to add up to 55 kg (1+2+3+4+5+6+7+8+9+10 = 55).
- 4) Each of these sub-samples (1, 2, 3 ... 10 kg) were prepared (crushed, pulverized and mass reduced to the analytical mass (50 g)) and analyzed as a regular sample (same as the fig. 4 but without the mixing stage).

Calculation of accuracy (example for ilmenite):

1. Weighted average:

$$\boxed{\text{WeightedAverage} = \sum_i \left[\frac{\% \beta_i \times i}{55} \right]}$$

i: represent the masses of 1 to 10 kg

β : % of an element (such as Fe₂O₃)

55: represent the total mass of the lot (55 kg)

2. Accuracy for each mass:

$$\boxed{\text{Accuracy}\beta_i = \left[\frac{|\% \beta_i - \text{weightedaverage}|}{\text{weightedaverage}} \right]}$$

Note: This calculation is carried out for each element. To have an overall representative

estimate of accuracy, we suggest including a large number of repetitions. In this project, it was repeated 8 times. The final step is to calculate the *mean* of accuracy for each mass.

3. Mean accuracy

$$meanAccuracy_i = \left[\frac{\sum Accuracy\beta_i + \sum Accuracy\alpha_i + \sum Accuracy\mu_i}{24} \right]$$

i: represent the mass of 1 to 10 kg

β : %Fe₂O₃

α : %Al₂O₃

μ : %TiO₂

24: represent the result of the multiplication of number of elements and the number of repetitions realized (3X8).

2.2 Replication experiment

A replication experiment was carried out, consisting in repeating sampling from the primary sampling stage in the “from-field-to-analysis” pathway in order to determine which stage is contributing the most to the GEE (Esbensen and Wagner, 2016). That needs to be determined to assess a hierarchical replication experiment has been undertaken. Figure 1 illustrates the protocol used. To prepare an analytical quartzite sample, the followings steps are identified:

Primary Sampling Error (arising from the field sampling);

- 1) Primary Crushing Error (Jaw crusher);
- 2) Secondary Crushing Error (Roll crusher);
- 3) Pulverization and Homogenization Error (Herzog Pulverizers, HP-MA);
- 4) Total Analytical Error (TAE).

2.3 Sampling methods

All samples, whether grab, composite and transect samples were collected on the same day, the number of collected samples and with which methods is shown on Figure 2. The estimated mass of this stockpile is 5 000 t. For all these experiments the same method analysis was use to have the most replicate result possible (the operator, time analysis and the program use with the HHXRF).

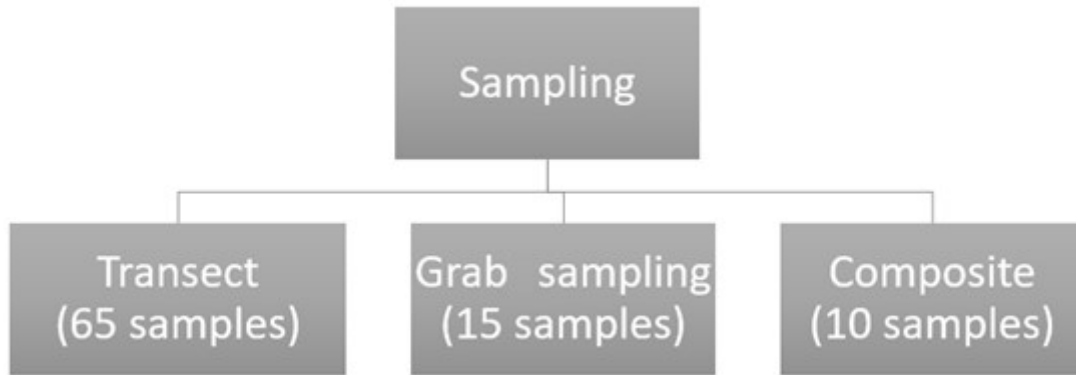


Figure 2. Methods and number of samples collected



Figure 3. Sample collection on the quartzite stockpile. Note that Elkem typically take surface samples. The alignments of sample bags show the transect profile lines.

2.3.1 Grab Sampling

A total of fifteen individual grab samples were also collected. A primary sample mass was aimed for that to represent 10 kg quartzite, collected at *random locations* around the surface of the stockpile. To allow for subsequent comparison between sampling alternatives, a strict identical procedure regarding all subsequent crushing and splitting must be followed in detail as shown in Figure 4.

2.3.2 Composite samples

In this experiment, 10 composite samples each of 150 kg were prepared. The protocol used to realize these composite samples is described in the following steps:

1. Each composite sample was made of 15 individual grab increments of 10 kg, taken *randomly* over the whole surface area of the stockpile (Fig. 3), for a total of 150 kg;
2. Each 10 kg increment was crushed (grain size reduction) and the mass reduced (split) down to about 1.25 kg. The mass reduction procedure was done with a riffle splitter in a TOS-correct way (Petersen et al., 2004). This operation must be done for each increment.
3. The 15 x 1.25 kg samples were then aggregated and mixed ('homogenized') in a plastic barrel (half-filled with 15 x 1.25 kg = 19 kg) rolling on an inclined plane (approx. 30 degrees incline) to ensure efficient mixing (Figure 4.).
4. The barrel content (19 kg) was emptied slowly in the roller crusher and reduce to about 100 mesh and mass reduced 7 times to 0.15 kg.
5. The 0.15 kg is then further pulverized to 400 mesh for XRF analysis;
6. All these steps are repeated for each of the 10 composite samples.

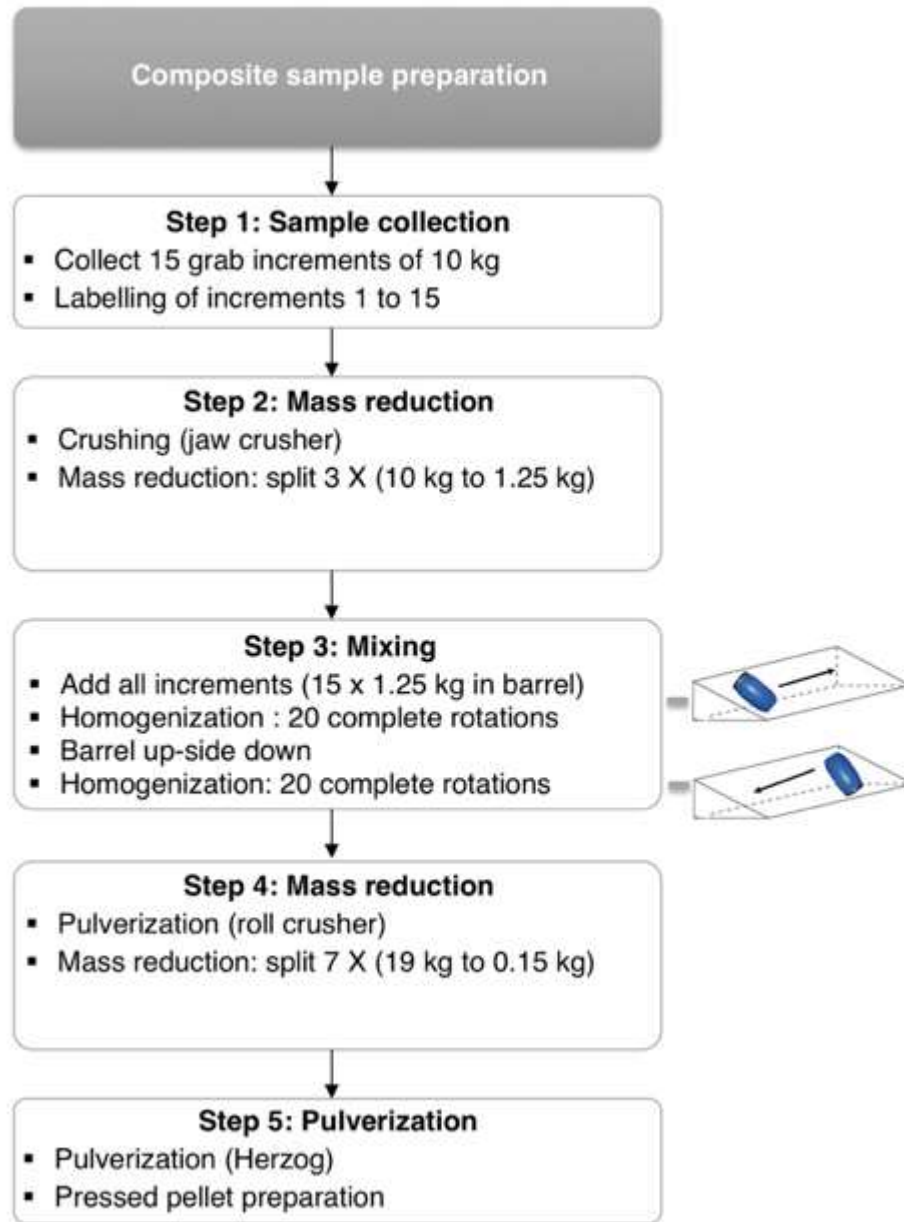


Figure 4. Protocol to prepare the composite sample

2.3.2 Transect (diagonal of a lot)

In this project, transect method was used to characterize a typical stockpile of quartzite (Fig. 3; around 5 000 t). The lag was 30 cm, in total sixty-five samples were taken along a randomly selected directional trace over the surface of the stockpile.

2.4 HHXRF *in-situ*

The main incentive to do *in-situ* measurement is to reduce the preparation time and increase the quantity of analysis. To validate the quality of the *in-situ* protocol, each quartzite block of a 10 kg sample bag was analyzed by HHXRF (Niton XL3t GOLDD+; TestAllGeo mode, 60 seconds measurement time, no corrections). This *in situ* analysis can be carried out with minimal sample preparation, which is the major asset for this type of device. The preceding study of Desroches et al. (2018) strongly suggested that correction of results with reference materials improve significantly the accuracy, in agreement with many similar studies (e.g. Cohen et al., 2017; Quye-Sawyer et al., 2015; Ross et al., 2014; and de Winter et al., 2017). The chemical characterization of high purity quartzite, despite its simple matrix, is highly complex with respect to the spatial heterogeneity displayed by the impurities; the earlier results showed that a handheld XRF (a Niton XL3t GOLDD+) is analytically capable of quantitative analysis in the industrial context down to on a low concentration matrix, but this study was on prepared powder samples. In this fashion, a total of 500 analyses were carried out *in situ* with the HHXRF. For want of a complete analysis of the full stockpile, we used the mean accuracy of all analytical results.

3. Results

3.1 Estimation of the lot

In this paper, the lot was a stockpile of quartzite of approximately 5000 t (Fig. 3). The best estimate of a lot is the true average analytical value if based on the whole lot. In the present case, as in many similar industrial projects, an acceptable best estimate with the lowest cost is always the goal, which means that a compromise sampling needs to be tolerated. The sufficient number of samples and the derived minimum mass will depend on the industrial

process requirements but especially on the degree of heterogeneity encountered. In this project, a total of 230 bags of quartzite, were taken on the stockpile; the mean of all these results has been used as the ‘best’ estimation of the lot concentration for all trace contaminating elements to be analyzed for below. Table 1 show the RSD obtained for a desktop wave-length XRF (Primini, Rigaku) compared with a HHXRF.

Table 1: Comparison of XRF results for different analytical determinations of quartzite trace element chemistry as determined by desktop (reference) versus HHXRF for pressed pellets

Desktop XRF					
Oxydes	TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	CaO (%)
Mean (n=230)	0.055	0.302	0.059	0.024	0.002
RSD (%)	23.4	60.0	57.5	99.7	162.4
HHXRF					
Mean (n=230)	0.044	0.369	0.042	0.684	0.005
RSD (%)	25.2	36.1	39.6	23.7	40.4

Note: For CaO many results are below LoD see Desroches et al. (2018)

Table 1 shows that the desktop results and the HHXRF have similar ranges and broadly provide comparable results. The RSD levels are large because these elements are present in really low concentrations and are light mostly elements (Mg, Ca and Al). The relative standard variation (RSD) for MgO and CaO are extremely large for desktop XRF because of the high sensitivity and the very low absolute concentration of these two elements. Moreover, the more sensitive desktop instrument detects more variations at low concentrations than the handheld instrument at similar low concentration giving a larger RSD for the desktop instrument. A more complete comparison of both instruments on quartzite matrix is presented in Desroches et al. (2018).

3.2 Determination of optimal sample mass

That needs to be determined to assess the optimal sample mass, the procedure described in section 4.1 has been used; results are presented in Figure 5. Chemical analyses were carried out with the desktop Primini XRF. The accuracy (calculated as previously defined) is improved from approximately 35% to 20% when mass increases from 1 kg to 10 kg. Considering the sample weight that can be transported by a technician, sample preparation time and quartzite block size, it has been determined that 10 kg is the effectively the optimal mass.

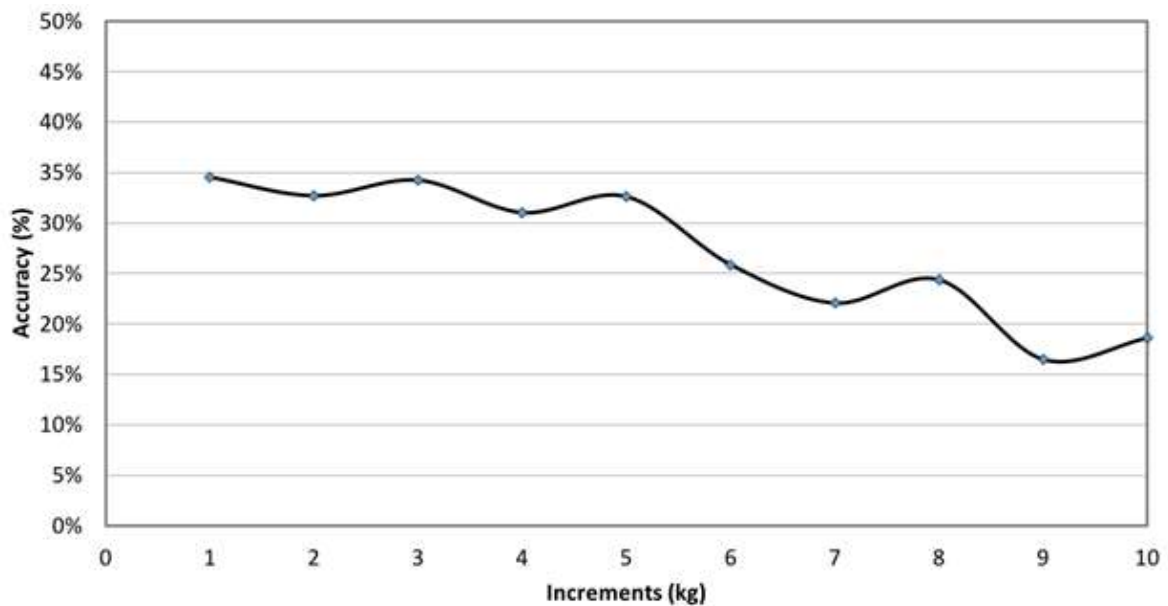


Figure 5. Accuracy versus sample mass

3.3 Replication experiment

This experiment is one of the most important that needs to be determined to assess if the HHXRF procedure is valid for its purpose. This experiment identifies which step contributes the most to the global uncertainty and provides indication to improve the sampling preparation process. The results for iron (Fig. 6) for the complete process show typical relative sample variability values (RSV) suggesting the sample preparation is under control.

The largest RSV comes from the primary sampling. The parts of the jaw and roll crushers that comes into contact with the quartzite are made of steel which contribute to iron contamination and variability.

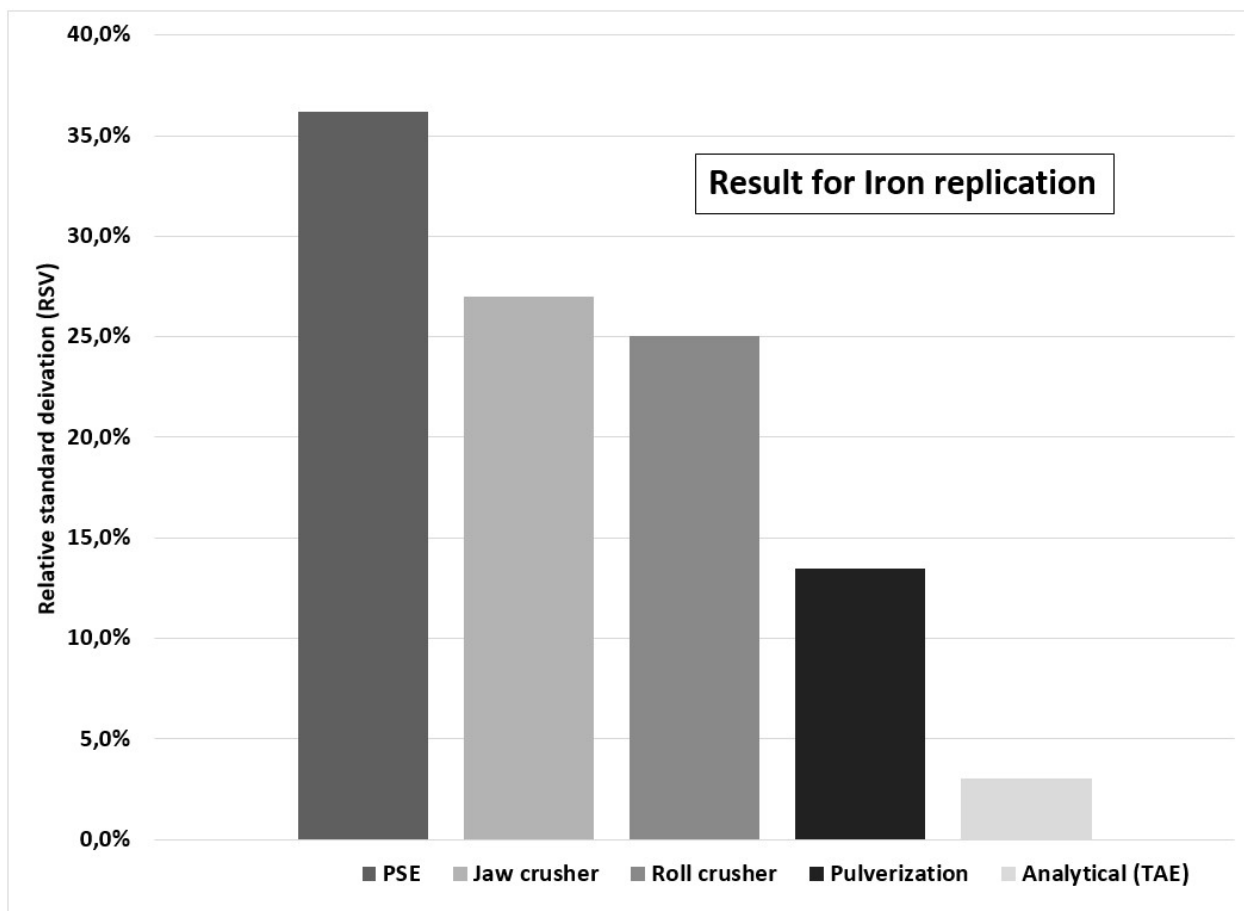


Fig. 6: Hierarchical replication experiment to identify error contributions from each step from sampling to analysis. The vertical scale (RSV; %) is the relative standard deviation (standard deviation/average of replicated results x 100) as proposed by Esbensen and Wagner (2016).

3.4 Variogram

Variograms are known to be sensitive to extreme values (Esbensen et al., 2007). For CaO, almost half the HHXRF values are below detection limits which render the HHXRF meaningless, so CaO was not treated. The remaining element variograms (Fig. 7) show a completely random spatial variation for the major contaminant as Fe₂O₃, Al₂O₃, MgO and

TiO₂ for HHXRF and Primini XRF (Desktop), when gauged with a lag (inter-sample distance) of 30 cm. This can be concluded because all variograms are of the so-called “flat variogram” type (pure nugget effect), showing that there is no spatial auto-correlation even at this lowest lag scale. Rutile shows similar results for HHXRF and Primini with a sill (variance) of 0.08. Al₂O₃, Fe₂O₃ and MgO show similar flat variograms where the HHXRF sills are smaller: 0.15 versus 0.4 for Al₂O₃ and Fe₂O₃, 0.1 versus 0.7 for MgO. The lower sensitivity of HHXRF explains its lower sill added to the lack of crushing providing less contamination. A flat variograms may alternatively reflect a situation in which the lag chosen for the variograms characterization happens to be too large for the small-scale heterogeneity encountered (Minitt and Esbensen, 2017; Engström and Esbensen, 2017a, b). However, the lag chosen in this project is 30 cm and it is interpreted to be the absolute smallest scale of interest for the project (10 cm mineral fragments on average).

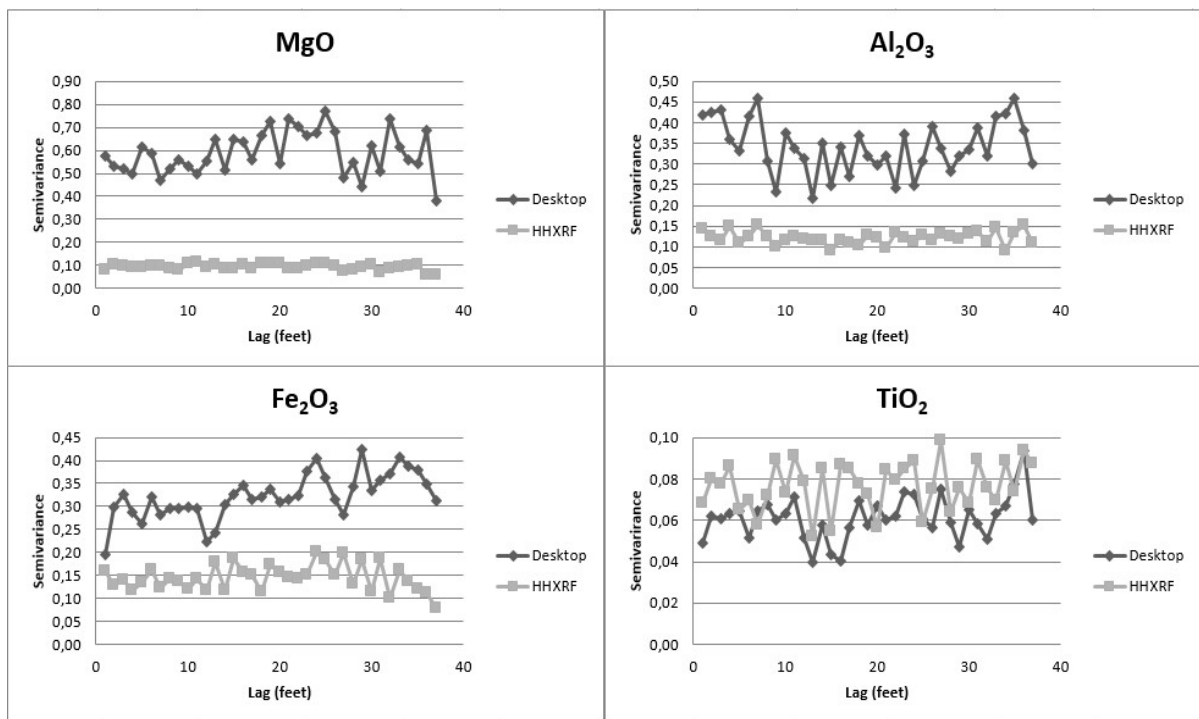


Fig. 7: Variogram of sampling transects comparing Desktop and HHXRF results within a large quartzite lot.

3.5 Heterogeneity (10 kg sampling bags)

The purpose of this experiment was to validate the capability and performance of *in-situ* HHXRF measurements in the industrial context as *compared* with desktop XRF on pressed pellets. The result of in situ measurement represents the mean of each piece of quartzite with five determinations per piece. As discussed in (Desroches et al, 2018), the HHXRF shows good performance analyzing quartzite at this scale although the quality of the results depends on analyzed surface. Highly erratic results (2-3 times the average) created by an irregular surface have been screened out (outliers). Results are also influenced by the presence of minute minerals under the XRF beam (Desroches et al., 2018). A single grain of ilmenite (FeTiO_3), for example, could increase results by 0.05% TiO_2 which is near the concentrations measured. Results of the 10 bags collected and analyzed with in situ HHXRF and Desktop XRF on pressed pellets, are presented in Figure 8. The results for a reference material (CRM STD sand No 8; Society of Glass Technology) is added to demonstrate the reproducibility of the analytical methods alone. It shows that the desktop XRF gives better results for Al_2O_3 and Fe_2O_3 and both instruments (desktop and HHXRF) give similar results for TiO_2 . In all cases, HHXRF and desktop XRF give results that fit the purpose (lower RSD on reference materials than in samples measured). For hematite and rutile, using a composite sample reduces the sampling error approximately by half. For Al_2O_3 , concentrations are too so close to the detection limits and the sensitivity of the HHXRF is insufficient which produce lower variations between measurements. A lower sensitivity will diminishing the differences between measured concentrations so the intensity of a peak with a low concentration for example will be absorb with electronic noise. Moreover, Al_2O_3 is a light element which is also highly influenced by surface quality for in situ measurements. For hematite and rutile, using a composite sample reduces the sampling error approximately by half which is a major

improvement. Fe₂O₃ Desktop XRF results are slightly more variable than HHXRF due to variable contamination during sample preparation as iron crushing, pulverizing and handling instruments are used. At such low concentration, a tiny piece of iron from a sample preparation instrument included in the measured portion increased the concentration significantly. In the case of the rutile, both instruments provide comparable results. It is important to note that although the most significant observation is that composite sample show less variation than grab samples, Figure 8 suggests that the variations between desktop and HHXRF are more important for grab sampling than composite sampling for Al₂O₃ and Fe₂O₃. In both cases, it is an analytical issue (lower sensitivity for Al₂O₃ and different sample preparation method for Fe₂O₃). Overall, the use of composite samples reduces the variations between samples about half and the use of HHXRF is adequate for quality control of quartzite in ferrosilicon production context.

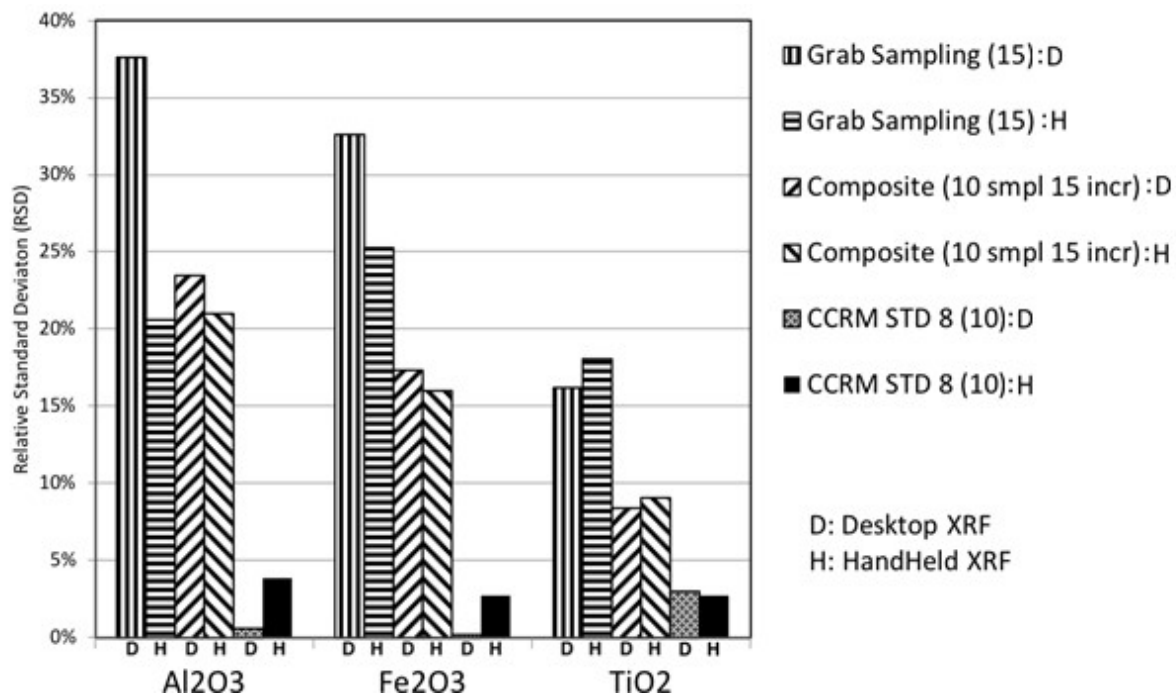


Fig. 8: Comparison of grab and composite sampling and reference material with in situ HHXRF (H) and Desktop XRF (D) on pressed pellets. Results for HHXRF on reference material are on a pressed pellet.

4. Conclusion

A handheld XRF (HHXRF) used in conjunction with composite sampling provides more accurate sampling results than use of a conventional grab sample analyzed with a desktop XRF. Use of a HHXRF offers the advantage of minimal sample preparation and a fast, analytical turnaround. Average lot concentration can be estimated within an hour with a marked improvement in sampling error control. However, HHXRF is limited by its lower sensitivity and is also easily influenced by minute minerals found under the XRF beam and by surface quality (this impact is more pronounced for light elements). Thus, a high number of HHXRF determinations are necessary and will, to a certain extent, compensate for these shortcomings. An acceptable HHXRF-based approach is foreseeable, but frequent assessments of experimental heterogeneity remain necessary. Fortunately, these assessments are relatively easy using the HHXRF approach. Finally, once the necessary economic-logistical compromises have been chosen, a thorough ‘from-the-top’ replication experiment is essential before the HHXRF approach can be used for routine purposes.

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Conflict of Interest

The authors declare no conflict of interest.

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CONCLUSION GÉNÉRALE

Le corps de ce mémoire est présenté sous forme d'articles scientifiques. Le premier chapitre présente l'article qui a été soumis et accepté au périodique : *Minerals Engineering*. Le second chapitre a été également soumis au journal *Minerals Engineering* et est en arbitrage au moment de la soumission de ce mémoire. Dans le cadre de ce projet, seul le quartzite a été caractérisé chimiquement comme intrant d'un procédé industriel. Le but du projet était de développer un protocole de caractérisation rapide et performant permettant d'obtenir un résultat représentatif de caractérisation chimique et de quantifier cette représentativité. La vitesse d'analyse était un prérequis dans ce projet. En effet, le quartzite journalier consommé par l'industriel représente environ 155 tonnes métriques. La capacité de la XRFp (dans ce projet, Niton XL3t GOLDD +) de fournir une analyse chimique rapide du quartzite présentait un atout majeur. Les objectifs primaires consistaient à valider la capacité d'analyse de l'appareil. Les essais de dérives ont démontré qu'après une période de 8 heures les mesures deviennent légèrement plus variables (Desroches, et al, 2018). Les résultats interlaboratoires permettent d'établir que la performance du XRFp est très similaire à des appareils XRF de type laboratoire. Le calibrage de l'appareil permet d'améliorer significativement les résultats initiaux. La méthode pour calculer la limite de détection bien qu'estimative a donnée des résultats très près de ceux du fabricant permettant de valider l'utilisation de ce type d'appareil pour l'analyse du quartzite de haute pureté. Cette méthode présente une excellente alternative à l'absence de protocole de quantification de la limite de détection, à la recopie des limites fournies par le fabriquant ou encore à des protocoles non adaptés au problème que l'on retrouve dans la littérature (Conrey, et al., 2014; Dahl et al., 2013; Potts and West, 2008, Luck and Simandl, 2014; Simandl et al., 2014 et Currie, 1995). Les résultats obtenus pour les essais « in situ » ont démontré l'importance d'avoir une surface

plane ainsi que l'impact des hétérogénéités locales en surface. Un seul grain d'ilménite, par exemple, occupant 0,1 % de l'échantillon peut faire augmenter la valeur en TiO_2 de 0,05 %. Ce projet démontre qu'il est possible d'effectuer des analyses chimiques « in situ » avec ce type d'appareil. Néanmoins, un temps important doit être accordé afin de filtrer les données aberrantes et cela, surtout pour les éléments légers (Al_2O_3 , MgO et CaO). Pour les mesures « in situ », un minimum de 5 analyses par fragment échantillonné doivent être effectuées afin d'obtenir un résultat représentatif. Un plus grand nombre d'analyses doivent être réalisées si l'échantillon présente une surface irrégulière. L'essai de réplique et celui de l'optimisation de la masse échantillonnée ont permis d'identifier et de quantifier les erreurs du protocole utilisées par l'industriel. Les résultats liés à l'échantillonnage ont permis de valider que la pile de quartzite, une fois rendu à l'usine, est relativement homogène. L'étude recommande tout de même la prise d'échantillon composite afin de caractériser le quartzite pour diminuer l'erreur globale de 50 % des teneurs en éléments contaminants. Bien que la caractérisation chimique de quartzite de haute pureté soit complexe, nos résultats montrent qu'un XRFp (dans cette étude un Niton XL3t GOLDD +) convient aux analyses quantitatives du quartzite dans un contexte industriel pour des échantillons sous forme de pastilles pressées. Par conséquent, cette étude démontre qu'il n'est pas possible sans des efforts importants en temps et main d'œuvre d'obtenir des résultats in situ. En conclusion, il y a peu de gain d'utiliser ce type d'appareil dans un tel contexte. Cette résultante serait probablement différente pour un matériel avec une moins grande hétérogénéité de surface.

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ANNEXE 1

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Suitability of using a handheld XRF for quality control of quartz in an industrial setting



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pXRF

ABSTRACT

Handheld XRF (HHXRF) is an analytical tool often used for chemical characterization, environmental analysis or mineral exploration. However, few studies deal with its potential use as a quality control instrument within an industrial context, such as mineral processing or transformation. Quartz is an ideal test material; it is a simple matrix allowing for better isolation of different parameters including detection limits, precision and accuracy, instrumental drift, surface representativeness and sample preparation. In this study, we determined that the specific limit of detection was lower than 70 µg/g for TiO₂, Fe₂O₃ and CaO. The HHXRF analyzed pressed pellets of matrix-matched reference materials. Estimates for TiO₂, Fe₂O₃ and CaO were similar to certified values, while estimates for low concentration light elements (Al₂O₃ and MgO) were less accurate. For faster and higher throughput, as often required in an industrial context, HHXRF can be used directly on mineral sample without sample preparation. Five in-situ determinations on a 10-cm-sided block of quartz, produced an accuracy acceptable for industrial needs. However, in-situ determinations are limited by the flatness of the analytical surface, and minute accessory phases can induce some erratic results. Our tests suggest, however, that HHXRF is generally suitable for the control quality of quartz in an industrial context.

1. Introduction

X-ray fluorescence analysis has existed for over 100 years, and portable (and handheld) X-ray fluorescence (HHXRF) devices are now commercially available. This new technology has the potential of quantifying samples in the field as it requires minimal surface preparation of the sample and a minimal amount of time for analysis (Ene et al., 2010). For the most part, applications of HHXRF cover four major areas: classification of metallurgical samples, analysis of contaminants in the environment, mineral exploration, and applications in the arts (Alberti et al., 2017; Gazley and Fisher, 2014; Hall et al., 2016; Higuera et al., 2012; Lemièrre, 2018; Lemièrre et al., 2014; Potts and West, 2008; Ramsey and Boon, 2012; among others). In addition, many industries require stringent chemical characterization to monitor materials used in their industrial processes. In many cases, this characterization must be done in situ within very short time frame (real time). Examples of such requirements abound in the mining and mineral processing sectors. To increase profitability, industry needs to increase production capacity with a concomitant need of processing a greater amount of raw material. Increased processing capacity often

implies larger lots to be characterized, coupled with a need for faster results. Thus, these requirements can render the task of obtaining representative results more difficult and complex if, for example, the analytical target is several hundred metrics tons (Pitard, 2009). Moreover, in the case of quartz, critical elements (contaminants) are at low concentrations.

HHXRF can address such issues as it can obtain fast, in situ chemical characterization usually with minimal sample preparation (Alberti et al., 2017; Gazley and Fisher, 2014; Lemièrre, 2018; Taylor et al., 2005). The usefulness of HHXRF has been demonstrated for geochemical analyses (Gazley and Fisher, 2014; Hall et al., 2016; Hall et al., 2014; Lemièrre, 2018; Linge et al., 2017; Ross et al., 2014a, 2014b; among others). However, the ability for HHXRF to provide accurate results in an industrial setting has not been demonstrated. With its higher throughput and mobility, HHXRF could improve the sampling of large areas or lots (Ramsey and Boon, 2012; Ramsey et al., 2013). This would be even more important where the input material is coarse, such as in ferrosilicon production, requiring a large portion of samples to be tested to ensure an assessment is representative of the ensemble. However, HHXRF performance in an industrial setting must be

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ANNEXE 2

On retrouve sur un CD-ROM un tableur Excel comprenant toutes les données brutes des différents essais qui ont été réalisés dans le cadre de ce mémoire. Ce CD-ROM sera disponible à la Bibliothèque Paul-Émile-Boulet de l'UQAC.

Le CD-ROM comprend ainsi :

- Les données brutes de tous les essais.
- Le traitement des données tous les essais.
- Les certificats Étalon
- Des photos de différents essais
- Des documents Word interprétant les résultats obtenus
- Les résultats bruts des laboratoires externes
- Plusieurs documents techniques