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On the Influence and Correction of Water Content on pXRF Analysis of Lateritic Nickel Ore Deposits in the Context of Open Pit Mines of New-Caledonia

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Abstract: In a number of applications, the use of portable X-ray fluorescence (pXRF) instruments offers a time and cost-saving alternative to standard laboratory instruments. This is particularly true in a mining context where decisions must be taken quickly in the field. However, pXRF is a technique known to be efficient, provided that samples are well prepared, i.e., dried and finely ground. On the mine face, little-to-no sample preparation is conceivable as mining vehicles must be able to operate continuously. Therefore, solutions have to be found even for raw materials and one of the most critical problems is the sample water content, in particular in the context of open pit mines in a tropical area. A large number of analysis shows that knowledge of humidity enables the measured concentration to be effectively corrected for the three instruments used (Niton, X-met, Titan). It is possible to overcome the difficulty of measuring water content in the field by fixing it to its maximum value (saturation). The results show that the saturation method is reliable, or at least, promising.

Keywords: pXRF; mine; nickel; iron; water content; dilution law; Beer-Lambert law; saturation

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1. Introduction

The advantage of pXRF, compared to other chemical analysis methods, is that it allows the analysis of elements in concentrations ranging from a few tens of mg kg^{-1} to several percent, on raw samples, whether in the field or in the laboratory, in a very short time, thus allowing a rapid diagnosis, without delay. Thus, this method makes it possible to identify and quantify chemical elements at an acceptable cost and within acceptable deadlines and to delimit areas more or less concentrated in these elements. Because of fluctuations in measurements due to the matrix effects, particle size, heterogeneity of materials and moisture content, it is not intended to replace the usual techniques of chemical analysis with their precision and standards. On the other hand, knowledge of the different parameters that can influence the measurement and their consideration allows an improvement in the quantification of certain chemical elements.

The use of portable X-ray fluorescence (pXRF) devices in mining contexts, whether during the exploration, the borehole mining or the mining phases [1–7], has shown its value even if the on-site results are out of step with the results of chemical analyses carried out in the laboratory and the dispersions can sometimes be significant.

In New Caledonia, mining companies have been using this type of equipment for a few years but are struggling to obtain reliable results. The calibrations are based on empirical laws rather than physical laws. The main advance is to make corrections a posteriori according to the water content of the material. Currently, these devices are mainly used on finely ground materials, saprolitic materials have too much variability. This equipment is

used profitably at the level of prospecting which is satisfied with relative indications that are not very precise and where they make it possible to guide the taking of a representative sample. On cored or destructive soundings and on the operating front, difficulties arise in terms of the accuracy of the measurements and their reproducibility.

Finally, on ore stock where certified analyses are needed, these devices cannot replace conventional analysis methods. It is therefore in the field up to the sounding workshop, then logging, that progress can be envisaged. The need to improve the analytical protocol based on real scientific bases was expressed by the college of industrialists of the CNRT (Centre National de Recherche Technologique). However, this research must not lead to solutions that are too cumbersome to implement in the field, making the technology lose all logistical advantage.

Obtaining an average value in accordance with the reference value requires a correction of the local measurement (water content) as well as an adequate sampling strategy. There are several quantitative XRF analysis methods, being either compensation methods (dilution, internal standard, standard addition or Compton scatter) or correction of the matrix effects methods (fundamental parameters, empirical influence coefficient or theoretical influence coefficient) [3,7–15]. The implementation of compensation methods on mine site is not possible since a complex preparation before is necessary (drying and grinding). The methods used in the mining context are matrix correction methods.

It is therefore necessary to work on improving the accuracy of the measurement and the sampling strategy by focusing on three points: water content, particle size and sampling. The control of these different parameters should eventually make it possible to obtain chemical analyses "close" to the concentrations determined by conventional laboratory methods. Although three points are important, this study focuses more on the water content in the quantification of chemical elements.

Soils can naturally contain high water content, especially in humid tropical environments. Within the sample, water replaces ambient air that fills porosities or fractures [16]. On the surface of the sample, pressure due to contact of pXRF device can induce release of water from macro pores and then can form a thin layer of water [17]. The protective film conventionally used during pXRF measurements can lead to formation of a layer of water on the surface of the sample [18]. Whatever its origin, water influences the intensity of X-rays in two ways. First, water absorbs X-rays more than air, so the absorption of the sample increases with the water content. Secondly, the water scatters the primary X-ray from the source and thus increases the intensity of the background. Both effects will decrease the net area of fluorescence peaks. While the presence of water will greatly affect results for light elements, concentrations measured for heavy elements ($Z > 40$ or $Z > 26$) [17] remain almost constant.

Whatever the element considered, it is generally accepted that moisture contents up to 20% do not significantly influence XRF intensity and the quantification by this method [19–21]. For higher water contents, several correction laws have been proposed to obtain concentration in the dry sample from wet sample measurement. Ge and coauthors [16] assume that reduction of XRF intensity is proportional to the increment of water content and propose a relationship derived from Beer Lambert's law. Ge and coauthors also show that the sum of the intensities resulting from coherent and incoherent scattering of primary X-ray from the source is a linear function of water content. By using this second relationship, measurement of the water content is no longer necessary and only measurement of the intensities is required. Bastos and coauthors [22] retained Ge and coauthors hypothesis but uses the background intensity at low energy instead of scattered intensity [22]. This correction law can give satisfactory results for water contents up to 136.8% [23]. Phedorin and Goldberg [24] and Kido and coauthors [18] have also proposed correction laws based on Beer Lambert's law. The correction proposed by [24] requires an iterative algorithm and to know all macroscopic cross sections. The law proposed by [18] requires knowledge of the mass absorption coefficient of the dry sample. These constraints make their use more complex and these laws are therefore rarely used. More

recently, Ribeiro and coauthors [25] applied several correction laws (linear, second-degree polynomial and power) to measurements made on Brazilian soils. Finally, they proposed to use a power law to fit measured data.

In this paper, two water content compensation laws were applied to Caledonian ore samples. The dilution law which compensates the variation of the mass concentration induced by the addition of water and the classical law introduced in Ge and co-authors [16]. On the other hand, this study shows a strong correlation between the concentrations measured for the dry sample and for the sample whose water content is close to the concentration of the saturated ore. By saturating the sample with water, after a calibration phase as it is classically required for dry samples, it is possible to obtain directly the Fe and Ni contents of the dry sample.

2. Materials and Methods

2.1. Portable XRF (pXRF)

The characteristics of the devices used during this project are very similar (Table 1). They are all equipped with a tube capable of operating at high voltages of 45 to 50 kV, allowing measurement of the heaviest elements. Their multi-element detection range is also close, at about 30–35 elements. On the other hand, the technologies of detection systems, hardware and software ergonomics, as well as the implementation of quantification algorithms (FP, coefficients of influence, etc.) may vary from one manufacturer to another. The standardization of the XL3t mining mode is based on fundamental parameters but also uses the Compton scatter (inelastic collisions) to standardize to 100%. The information on how the normalize of the intensities was done, was not available for the two other instruments. Rousseau [26] showed that the normalization conditions may introduce a bias in the results.

Table 1. Specifications of the instruments used in this work.

Manufacturer	Thermo Fisher® Boston, MA, USA	Oxford Instrument® Abingdon, Oxfordshire, UK	Bruker® Billera, MA, USA
Model	Niton GOLDD + 900	XMET 7500	S1 Titan 800
Anode	Ag	Rh	Rh
Tube voltage (kV)	50	45	50
Tube current (µA)	200	50	200
Spot size (mm)	7	9	5
Resolution (eV)	<185	<150	<145
Detector	SDD GOLDD	SDD	Fast SDD
Element range	Mg to U	Mg to U	Mg to U
Application mode	Mining Cu/Zn	mining_fp	Ni-Co Ore Rock (NiOreRock method)

In the laboratory, the devices were operated in a benchtop stand using an AC adapter to create the ideal measurement conditions for the sample cups. The devices were allowed to warm up for a minimum period of 30–45 min before measurements.

In all situations, in the laboratory or in the field, the measurement time was set to 10 s. This measurement time is deliberately short and it is a compromise, obtaining an acceptable accuracy and minimizing the muscular tension of the operator. In situ, the operator will have to use the pXRF instrument several times a day and sometimes in uncomfortable positions, so it is essential to reduce the measurement time as much as possible.

As in situ conditions can be very hard for a pXRF in an open mine, X-ray tubes and detectors can easily be damaged. In order to protect nozzle instruments, all mining operators cover their instruments with a protective tape, e.g., Kapton® for Niton and 3M scotch® (ref. E5016C) for Xmet (Figure 1). In the case of Titan pXRF, as it has a built-in protective shield, no other protection was added. Adding a film will attenuate and scatter the radiation. It will strongly attenuate the low energy radiation typical of the fluorescence

of light elements while it will have a negligible influence on the fluorescence of the heavier elements [27].

Figure 1. Protective tape, Kapton on the **left**, 3M scotch on the **right**.

2.2. Samples Description

2.2.1. Geological Setting

The obduction of the peridotite layer on sedimentary formations and the basaltic unit of Poya is attributed to the Late Eocene [28–32]. Originally covering a large part of Grande-Terre in New-Caledonia, the formation was gradually stripped by a succession of episodes of chemical and mechanical alteration. Currently, the remains of this formation cover about a third of Grande-Terre and are represented by:

- the ultrabasic massif to the south and its extension on the east coast of New Caledonia (mines of Goro, Tontouta, Camp des Sapins, Thio, Nakéty, Boa Kaine, Kouaoua, Poro, Monéo);
- a sequence of klippes on the edge of the west coast (Kopéto-Boulinda, Koniambo, Ouazangou-Taom, Tiébaghi, Poum, Bélep island, etc.).

Peridotites, rocks of the Earth's mantle that rarely appear on the surface of the earth, consist mainly of silicates rich in metallic elements including iron, magnesium, manganese, chromium, nickel and cobalt. The alteration of peridotites in hot and humid tropical environments is a supergene process that causes the hydrolysis of the components of the rock and its dissolution. Some elements are leached (Si, Mg), while others remain in place (Fe, Cr, Ni, Co, Mn). Under the action of a humid tropical climate, the peridotites were gradually altered by hydrolysis of ferromagnesian silicates leading to a typical weathering profile [33] composed, from the bottom to the top: fractured peridotic fresh rock, saprolites, yellow limonite, red limonite, nodular layer and ferricrete.

This basic succession has many variations and gaps. While in source rock, Ni and Co are in low concentrations (0.3% and 0.01% respectively), these same elements are concentrated in saprolite and limonite horizons with contents of the order of one percent.

In saprolites, the distribution of Ni is very variable, as is the physical heterogeneity of the material. Economically sized ore bodies are currently mined at an average grade greater than 2% Ni + Co. Ni is hosted by Ni-bearing serpentines that make up the majority of the saprolite horizon, and by less abundant, but high grade, garnierites (green, fine grained mixtures of serpentine, talc, chlorite, sepiolite and smectite).

In the limonite horizon, the content of metals is less fluctuating but overall lower, less than 2% Ni + Co, because these levels almost entirely devoid of magnesia and silica, mainly consisting of iron oxy-hydroxides partially crystallized in fine grained goethite, have a lower Ni retention capacity. Cobalt is often concentrated at the base of yellow limonite in the form of concretions of asbolane, a complex manganese oxide.

A very complete article on the mineral resources and prospectivity of ultramafic rocks in New Caledonia has recently been published and covers all the knowledge acquired on the subject [32].

The Ni ores currently mined in New Caledonia are of two types:

- Saprolitic or garnieritic silicate ores of high contents (>2%);
- Limonitic ores of lower grades (<2%).

Although the two types can coexist in the same mining area, the mining techniques and industrial processes to which they are subject are different. The Société le Nickel (SLN) operates mainly saprolitic ores in five centres. Koniambo Nickel SAS (KNS) will mine saprolitic and limonitic ore by pyrometallurgical treatment. The Valé Company, in the South, mainly processes limonitic ore by a hydrometallurgical process. The other "small miners" are divided between conventional exploitation and the export of saprolites and limonites.

2.2.2. Reference Samples

During this two years project, we have used a database made of 27 reference samples (14 limonites and 13 saprolites) that have passed a round Robin test. This base is shared by all the major mining companies and the Geological Survey (SGNC), a department of New Caledonia's Direction for Industry, Mining and Energy (DIMENC). Minimum and maximum elemental concentrations are given in Table 2.

Table 2. Minimum (min) and maximum (max) values of reference samples concentrations.

	Fe (%)	Ni (%)	Mg (%)	Si (%)	Cr (%)	Al (%)	Mn (%)	Ca (%)
min value	4.96	0.09	0.13	0.52	0.17	0.10	0.04	0.01
max value	53.96	3.29	22.26	31.55	3.54	12.75	4.10	0.43

Reference concentrations of these samples were established by XRF in a New-Caledonian accredited laboratory (Ni, Lab).

All samples were prepared by the loose powder technique in plastic cups covered with a protective 6.0 µm Mylar® polyester film (FluXana, Bedburg-Hau, Germany). Cups were then filled with powders of at least 1 cm thickness, eventually covered with cotton fibers and finally closed in order to hold the setup firmly (Figure 2).

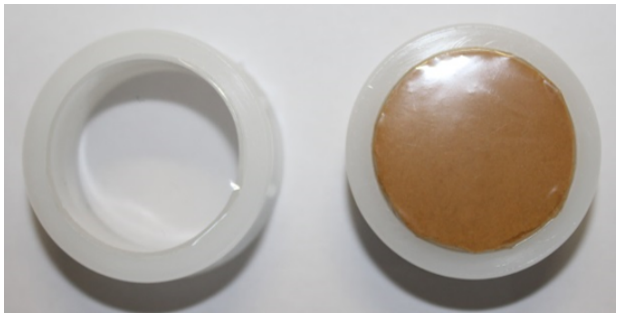


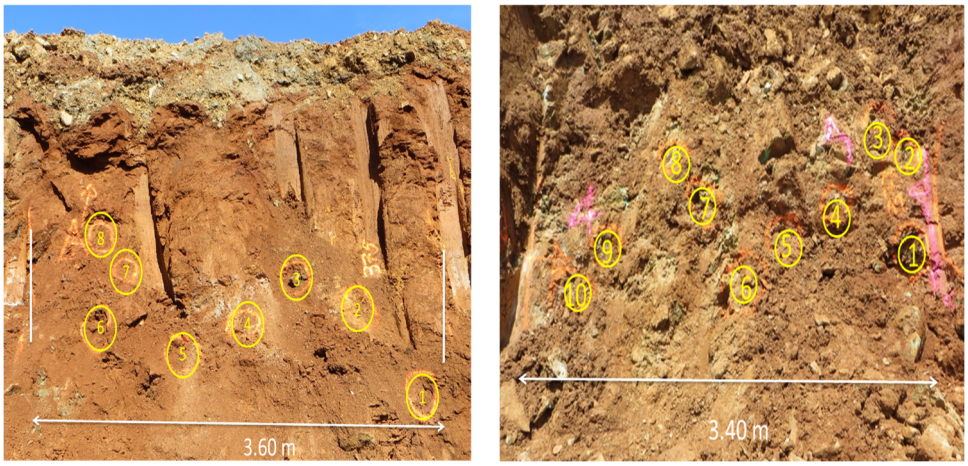
Figure 2. On the **left**: an empty cup and on the **right**: a filled cup with a powder.

Each sample was analyzed with the three pXRF, three times or more during 10 s, and results were then averaged.

2.2.3. Field Sampling

Two sampling campaigns have been conducted in different mines across the territory during this project. The first one took place at the beginning in order to collect samples for the laboratory analysis, the second at the end to test the developed method. All samples, about 5 kg each, were initially sent to a NATA/ISO/IEC17025 accredited laboratory to be weighed, dried at 105 °C until no mass change, weighed again, crushed at 3 mm and split with a rifle sampler. An aliquot of 1 kg was then crushed at 75 µm, split again in a rifle and one part was finally analyzed by XRF on fused disks. This first step allowed us to have access to the concentration of eleven elements/compounds (Ni, Co, Fe_2O_3, MgO, SiO_2, Cr_2O_3, Al_2O_3, MnO, CaO, CuO and ZnO) and to the water content of samples in the

field. During the first campaign, 30 samples (11 limonites and 19 saprolites) were collected. Concentrations range from 0.27 wt% to 3.36 wt% and from 4.7 wt% to 52.9 wt% for Ni and Fe, respectively. Water content ranges from 0.75 wt% to 48.03 wt%. Figure 3 shows two panels, a limonitic one on the left and a saprolitic one on the right; their width is about 3.5 m and their height about 2 m. Circles represent the sampling points, and each one was first measured with the three pXRF before being collected in a bag and sent to the accredited laboratory. pXRF measurements are not presented in this paper, as samples were primarily collected for water analysis in the lab.



(**a**) (**b**)

Figure 3. Examples of Ni ore panels sampled during the project: (**a**) Limonite; (**b**) Saprolite.

During the second campaign, 18 samples (12 limonites and 6 saprolites) were collected. Concentrations range from 1.31 wt% to 4.47 wt% for Ni and from 8.8 wt% to 52.4 wt% for Fe.

2.3. Methods

2.3.1. Laboratory Analysis

In order to evaluate how water content affects pXRF analyses on crushed samples, a series of measurements has been made at different water contents with the 30 samples collected during the first field campaign (Figure 4). The process is as follows:

- Weighing of the empty cup (only one side is covered with a thin Mylar® film, the other is left open to facilitate water evaporation during drying);
- Sample saturation with water;
- Filling the cup with the wetted powder;
- Weighing and analysis with the 3 pXRF (one measurement of 10 s);
- Drying in a ventilated oven at 70 °C during one hour;
- Weighing and analysis with the 3 pXRF.

The two last steps were repeated seven or eight times in a day. After the last measurement, each sample was gently dried at 30 °C during 16 h and 2 more hours at 105 °C, then finally weighed and analyzed. The last step gives us element concentrations and masses of the dry samples.

The saturation is achieved by using a vacuum filtration system. The ore is placed on a filter and then water is added in excess to the Büchner funnel. The mass of added water is approximately 8 g and the mass of the dry sample is approximately 6 g. This initial volume of water corresponds to approximately 3 times the volume of the solid phase and 2 times the mass of water contained in the wettest sample. A vacuum is then created in the Büchner flask using a water aspirator vacuum pump to remove excess water. After approximately one minute, the water reaches the upper surface of the sample. The pumping system is

then stopped and the sample is immediately placed in the cup. This method does not guarantee that we really reach saturation, as samples could be over-saturated, but it has the advantage of being reproducible. We are probably closed to the saturation, however, and we will not be able, in the field, to precisely saturate the sample.

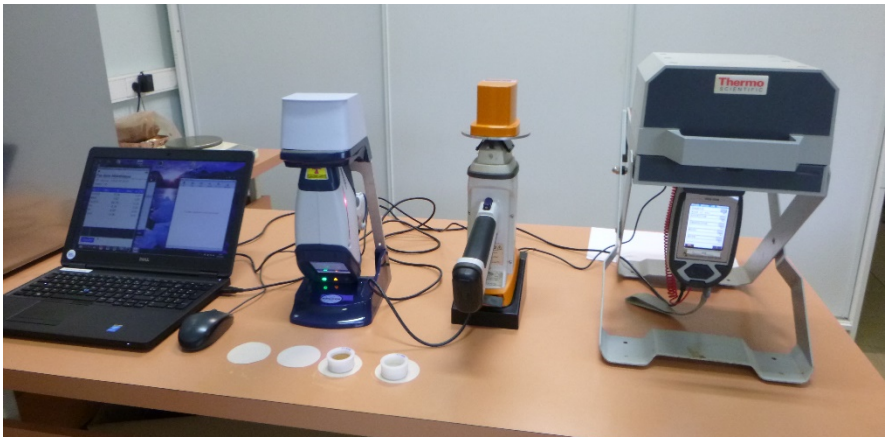


Figure 4. Presentation of the three pXRF devices and their stands during the measurement phase of wetted samples in the lab.

Furthermore, as the measured concentrations may vary depending on the position of the measuring head on the cup, a machined mechanical support with the footprint of the cup was designed and used in order to ensure correct positioning.

2.3.2. Field Measurements (Saturation)

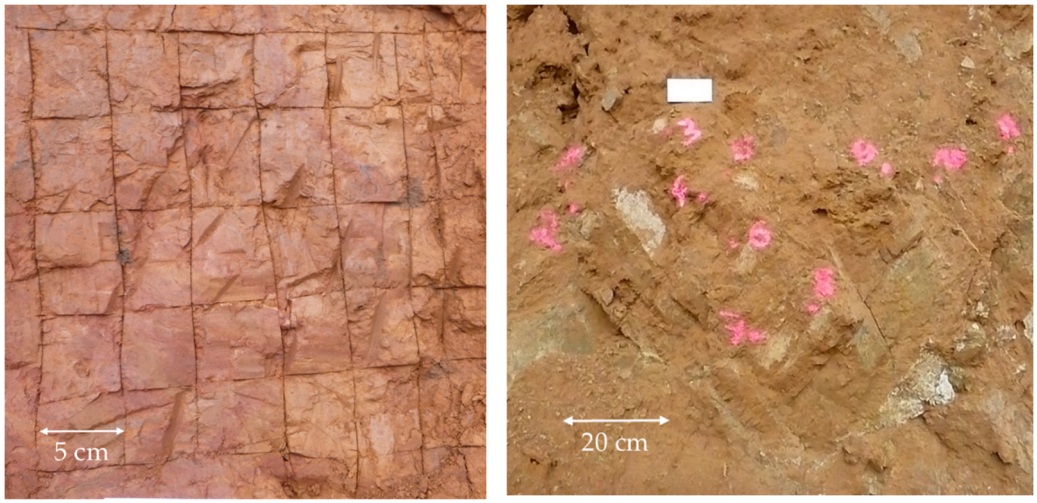
Water content of Ni-ore in humid climate as in New Caledonia can vary from a few percent to fifty percent and even more in the lateritic profiles. Iron-rich limonitic layers are made of soft porous and permeable material that can easily retain water. Saprolitic layers are less weathered than lateritic ones, they can be very rocky or a mix of rock fragments of different size and soft material.

During the second field campaign, and in order to test our saturation method in both limonitic and saprolitic layers, we have used two sampling processes:

- In the presence of a wet, cohesive and homogeneous material, e.g., in a limonitic horizon, we have drawn a 5 × 5 grid directly on the panel as shown in the Figure 5a;
- In other situations, sampling points were randomly distributed over the area of interest as shown in Figure 5b.

Each measurement point (cell of the grid or random point) was saturated with water with a hand spray as shown in Figure 6, measured with the three pXRF and a sample was taken over the grid or around each random point, collected in a bag and sent to the lab. At the end, for a given sample, all local pXRF data were averaged in order to be compared to the reference value issued from the bag. A total of 13 samples measured and collected in this way have been used to calibrate the instruments on saturated samples.

This process has the advantage, from the miner's point of view, of being quick and simple, but sample saturation cannot be strictly ensured. In practice, we added water until the wetted area stopped absorbing but this process is, for sure, operator dependent. However, the calibration phase, which consists in confronting pXRF measurements with reference values obtained on XRF fused disks, will allow us to correct for systematic errors if there are some, and above all, to determine measurement errors, including those induced by the proposed saturation process.



(**a**) (**b**)

Figure 5. Two sampling processes depending on panel humidity and cohesion: (**a**) a 5 × 5 grid in a limonitic panel; (**b**) random sampling in a saprolitic panel.

Figure 6. Water saturation in the field.

2.4. Statistical Analyses

To validate the correction step between measured concentrations and reference concentrations or to compare the correction models according to the water content, the mean error (ME), the root-mean-square error (RMSE) and the coefficient of determination (R^2) have been calculated.

$$\mathrm{ME} = \frac{1}{n}\sum_{i=1}^{n}(e_i - r_i) \tag{1}$$

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(e_i - r_i)^2} \tag{2}$$

where n is the number of observations, e_i is the corrected pXRF value and r_i is the reference value for the calibration step or the value measured at zero water content during the water correction step. A value of ME close to zero indicates that corrected values are centered around the reference values and that there is no systematic error. The RMSE quantifies the accuracy of the correction. If the correction is perfect, RMSE is equal to 0. The coefficient of determination, also called r-squared (R^2), is the square of correlation coefficient R. The coefficient of determination is a measure of the scatter about the regression line and is a

measure of the strength of the linear association. It ranges in value from 0.0 (no linear association) to 1.0 (perfect linear association).

3. Results

3.1. Calibration with Reference Samples

3.1.1. Single Linear Regression

Even on dry and finely ground samples, a fine-tuning of concentrations is always needed to compensate for the systematic biases induced by cups tape and nozzle protective tape, i.e., Kapton® or Scotch®. Systematic biases can be overcome through a calibration process that consists of finding, for a given element, the relationship between pXRF data (raw data *Cr*) and XRF, ICP-AES or AAS laboratory data (reference data *C*). A simple linear regression analysis can be performed for this purpose. Linear regression produces the slope, a, and the y-intercept, b, of the regression line. A slope of 1.0 and a y-intercept of 0.0 indicate that pXRF is accurate. If not, the values of a and b can be entered directly into the analyser. The simple regression is defined by:

$$[C] = a \times [C_r] + b \tag{3}$$

In addition to calibration factors, linear regression analysis produces statistical parameters such as the coefficient of determination, which can be used to evaluate the goodness of the fit. Table 3 shows the parameters of the simple regression for the two elements and for the three devices.

Table 3. Parameters of the simple regression for the two elements and for the three devices (a: Slope, b: y-intercept, R^2: Coefficient of determination, ME: Mean error, RMSE: Root-mean-square error).

	Element	**Fe**	**Ni**
Niton	a	1.235	1.282
	b	−1.020	0.235
	R^2	0.9992	0.9563
	ME	6.3×10^{-15}	2.6×10^{-16}
	RMSE	0.46	0.159
Xmet	a	1.039	0.842
	b	−1.825	0.247
	R^2	0.9989	0.9652
	ME	4.8×10^{-15}	5.0×10^{-16}
	RMSE	0.56	0.142
Titan	a	1.079	1.134
	b	0.246	0.009
	R^2	0.9987	0.9950
	ME	3.6×10^{-15}	-5.8×10^{-17}
	RMSE	0.61	0.054

The Figure 7 shows the results obtained with the three pXRF devices, Fe on the left and Ni on the right for the 27 reference samples. The coefficient of determination R^2 is close to one for Fe regardless of instrument model. Titan pXRF is also very good for Ni, the Niton and Xmet show more dispersion.

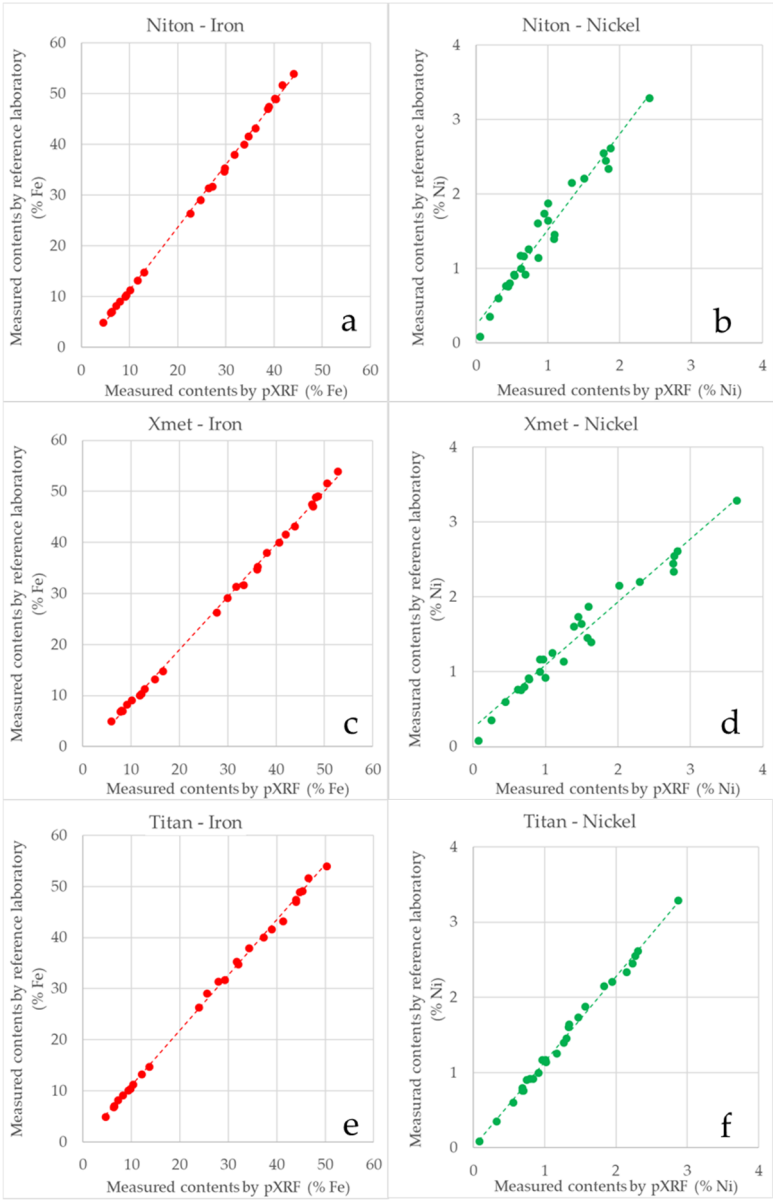


Figure 7. Linear regression for Fe and Ni in the three devices used for measuring: (**a**,**b**) Niton, (**c**,**d**) Xmet and (**e**,**f**) Titan.

3.1.2. Multiple Linear Regression

In a sample containing both Ni and Fe, it is well known that Ni may be underestimated. Ni, after being excited by the primary X-ray source, emits a Kα radiation that may be absorbed by Fe. This two steps phenomenon is called secondary fluorescence Secondary fluorescence effects are considered in the Fundamental Parameter (FP) calculations but our samples contain a very high concentration of Fe compared to Ni, especially in the limonite layer. Although we do not have precise information on how FP algorithms are implemented by each manufacturer, we can here suspect that for the Niton and the Xmet devices, they cannot deal with such high concentrations. However, we can perform a posteriori calibration of Ni concentration with a multiple linear regression that includes both measured Ni and Fe.

In order to improve results for the determination of Ni concentration in the presence of Fe, we propose to apply the following multiple linear regression:

$$[Ni] = a \times [Ni_r] + b \times [Ni_r] \times [Fe_r] + c \quad (4)$$

where Ni is the corrected Ni concentration and Ni_r and Fe_r are the raw concentration of Ni and Fe, respectively.

When we separate our initial set in two subsets, one for the limonites and the other for the saprolites, results on the Ni are greatly improved for both instruments. However, this would imply management of two calibration sets. With a multilinear regression, no distinction has to be made, as shown in Figure 8.

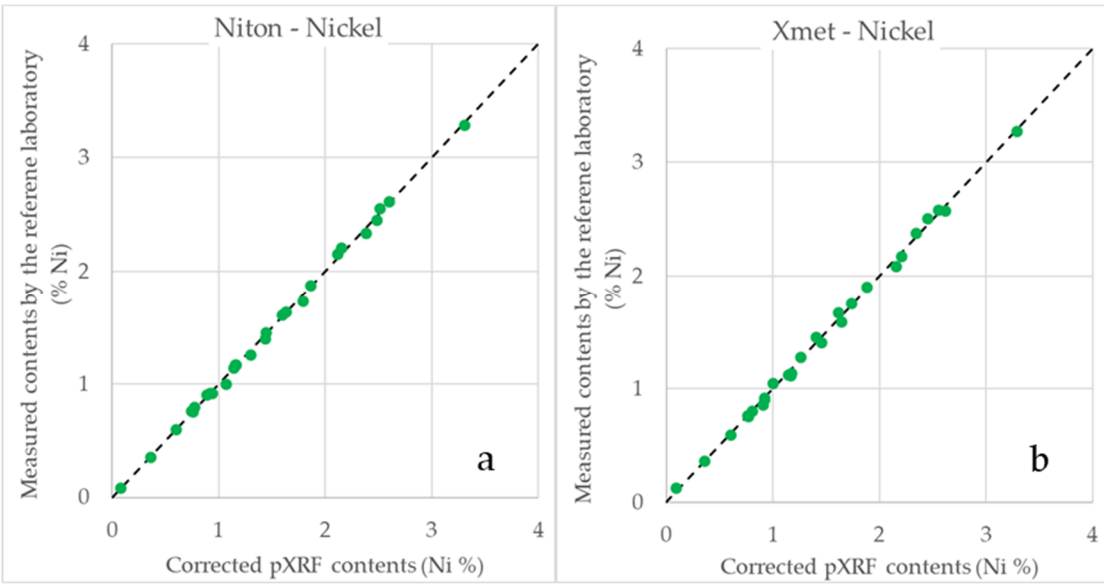


Figure 8. Results from multiple linear regression corrections for Ni, (**a**) for the Niton device and (**b**) for the Xmet device.

Table 4 gives the regression parameters for the Niton and Xmet devices.

Table 4. Parameters of the multiple linear regression for the Ni and for Niton and Xmet (a: Regression coefficient for $[Ni_r]$, b: Regression coefficient for $[Ni_r] \times [Fe_r]$, c: y-intercept, R^2: Coefficient of determination, ME: Mean error, RMSE: Root-mean-square error).

	Element	Ni
Niton	a	1.2166
	b	0.0164
	c	0.0068
	R^2	0.9985
	ME	3.8×10^{-16}
	RMSE	0.029
Xmet	a	0.7913
	b	0.0077
	c	0.0645
	R^2	0.9977
	ME	1.2×10^{-16}
	RMSE	0.037

Using multiple linear regression instead of simple linear regression greatly improves the goodness of fit. The coefficient of determination is closer to 1 and the root-mean-square error is divided by 4. When concentration of an element is highly variable, it may be necessary to correct matrix effects related to this element to improve the quantification.

3.2. Laboratory Study of Water Content Influence

The data were obtained from samples artificially moistened in the laboratory. Figure 9 shows how water content influences Ni and Fe concentration for the three instruments.

Ni dry is the raw concentration of Ni measured on the dry sample; no other correction has been applied. One sample is represented on a vertical line. The most wetted sample (–saturation) is the lower point and the dry one is located on the bisector, represented by a dashed line on the following figures.

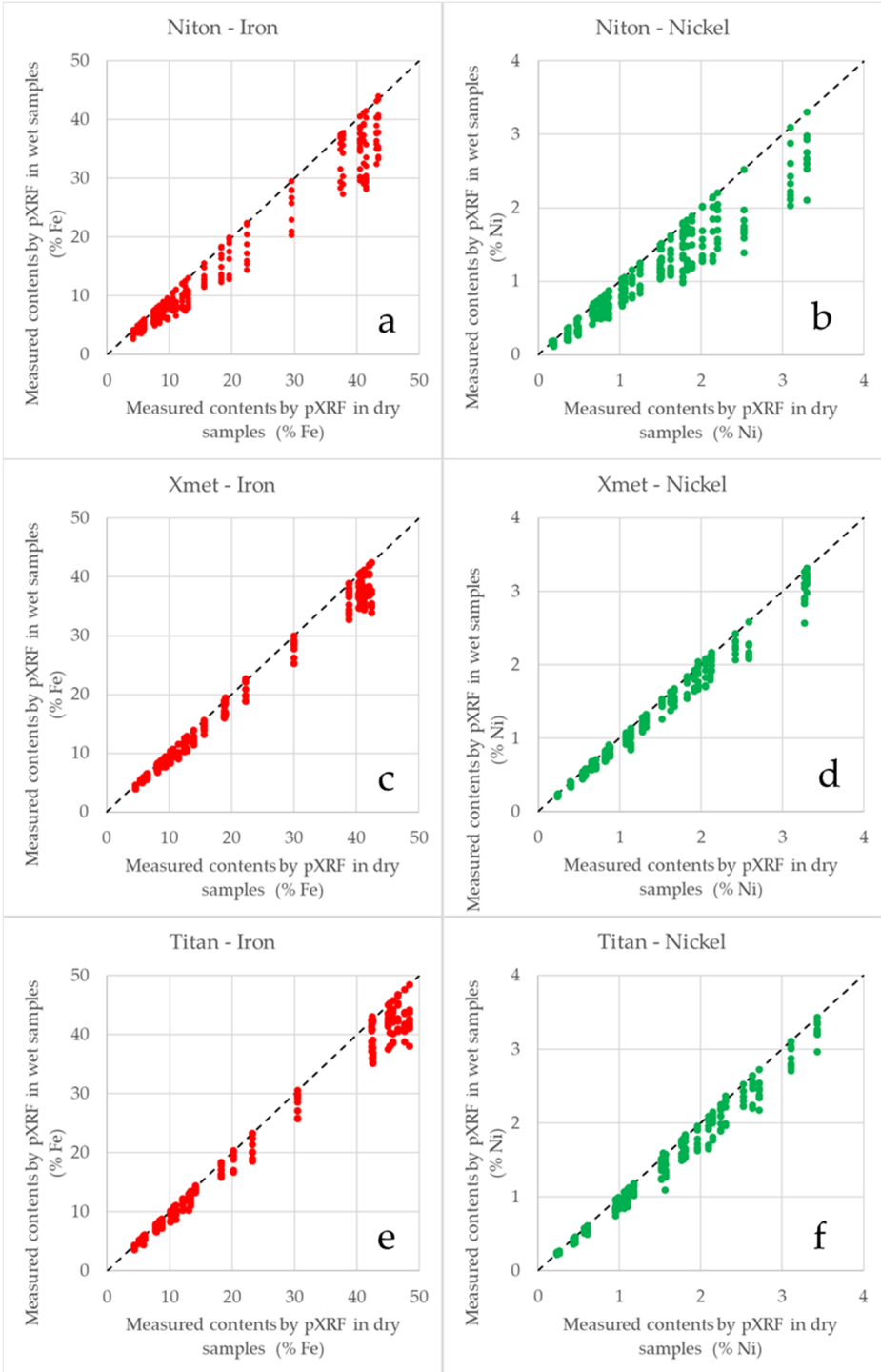


Figure 9. Influence of water content on Fe and Ni concentrations: (**a**,**b**) Niton, (**c**,**d**) Xmet and (**e**,**f**) Titan. The bisector is represented by the dashed line on the figures.

Figure 9 shows two different behaviors between the Niton on one side and both Xmet and Titan on the other side. Water has more influence in the Niton device, the spread is more pronounced compared to the other two. This does not mean one instrument is better

than another, only that they do not have the same response when samples are wet. At this step, we do not have enough information on how internal algorithms work but Figure 9 clearly shows that different approaches are used.

3.2.1. Correction Using the Dilution Law

The dilution law can be express as follow [34]:

$$C_c = C_w \frac{m_w}{m_d} \tag{5}$$

where m_w and m_d are wet and dry masses of the sample, respectively, C_c is the corrected element concentration and C_w is the measured element concentration under wet condition. This law is a general one, meaning that it can be applied regardless of the element under consideration (Ni, Fe, Co, etc.).

The sample set from the first field campaign is made of 19 saprolites and 11 limonites. Figures 10 and 11 show the concentrations ratio versus the masses ratio for Ni (up) and Fe (down) in both profiles (left and right) for the Niton (Figure 10) and Xmet pXRF (Figure 11).

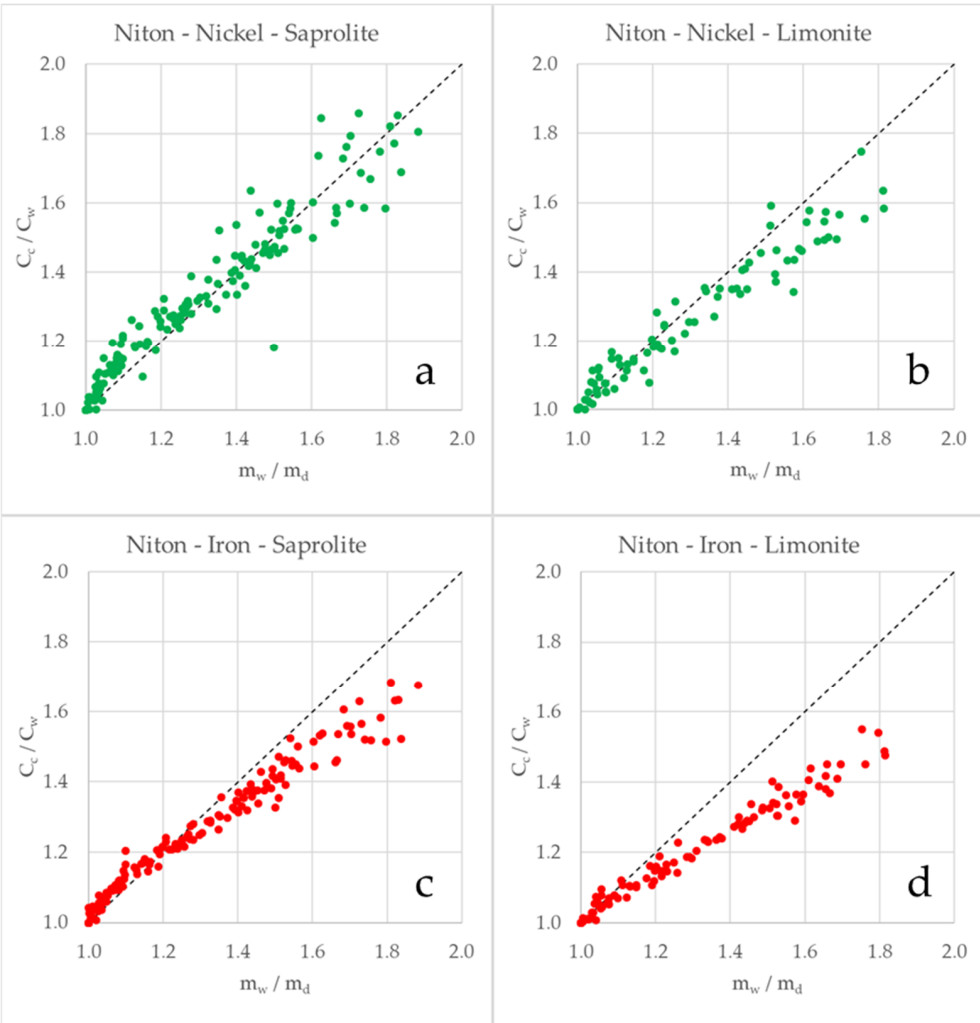


Figure 10. Data from the Niton after correction with the dilution law: (**a**) Ni in the saprolite layer; (**b**) Ni in the limonite layer; (**c**) Fein the saprolite layer; (**d**) Fe in the limonite layer.

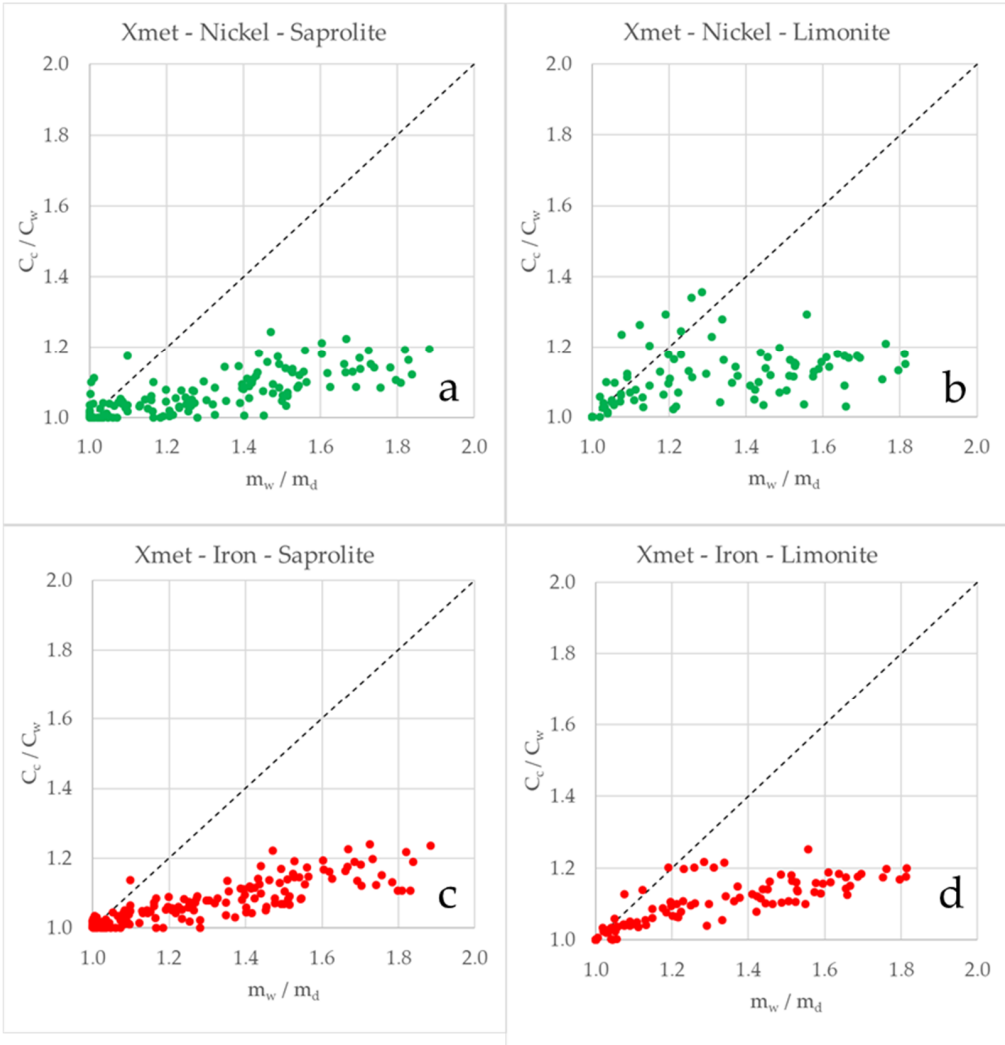


Figure 11. Data from the Xmet after correction with the dilution law: (**a**) Ni in the saprolite layer; (**b**) Ni in the limonite layer; (**c**) Fein the saprolite layer; (**d**) Fe in the limonite layer.

If the situation was totally ideal (dilution law fully adapted and no sample preparation and measurement errors), all the points should be located on the dashed line (bisector). Figure 10 shows that Fe is farther from the bisector than Ni. The dilutions law could be a candidate only for the Ni in the saprolite layer because in this situation, data are centered on the bisector. In the limonite layer, data for the Ni are slightly under this line. For Fe, data are also more distant to the bisector in the limonite layer than in the saprolite one. This difference of behavior is probably due to physical characteristics (porosity, density and particle size) of each layer. Because element concentrations are derived from an algorithm that run in the Niton, we believe this algorithm is somehow influenced by one or more physical parameters of the sample.

Figure 11 shows that data are far away from the bisector, the dilution law is not a good candidate for the Xmet. The same conclusion applied to for the Titan. However, some practical considerations can be derived from Figure 11. We have seen that the Niton device clearly behaves differently between the saprolite and the limonite layers. The Xmet behaves the same way in both layers, so we can conclude their quantification algorithms are implemented in a different way.

3.2.2. Correction Using a Method Derived from Beer-Lambert Law

In presence of pore water in the sample and if the composition of the matrix remains unchanged, the reduction in X-rays intensity associated with the analyte (dI_x) is directly proportional to the increment of the water content in the sample (dw) [16,22]:

$$dI_x = -\mu_m I_x dw \tag{6}$$

where the correlation coefficient μ_m is constant and I_x is the X-ray intensity typical of the analyte at the water content w. If I_x is equal to I_0 when $w = 0$, the integration of the previous equation gives:

$$I_x = I_0 \cdot e^{-\mu_m w} \tag{7}$$

Instruments do not give the intensities, so mass concentrations are used in the correction law as in a few studies [27,35,36].

$$\frac{C_0}{C_w} = e^{\sigma w} \tag{8}$$

where C_w and C_0 are the elemental concentrations in wet (water content w express in %) and dry conditions, respectively, and σ is an attenuation coefficient (due to soil content, [23]).

Table 5 gives, for the three devices, the attenuation coefficients obtained after fitting data with the Beer-Lambert law (Equation (8)) and parameters characterizing the quality of this correction.

Table 5. Parameters of correction by Beer-Lambert law proposed by Ge and coauthors [16] for the two elements and for the three devices (σ: Attenuation coefficient, ME: Mean error, RMSE: Root-mean-square error).

	Element	**Fe**	**Ni**
Niton	σ	0.0063	0.0075
	ME	0.056	−0.023
	RMSE	1.05	0.083
Xmet	σ	0.0027	0.0024
	ME	−0.22	−0.015
	RMSE	1.07	0.079
Titan	σ	0.0027	0.0026
	ME	−0.29	−0.004
	RMSE	1.19	0.067

Figure 12 shows corrected concentrations by the Beer-Lambert law as function of dry sample concentrations. Comparison with Figure 9 shows that concentrations after correction are closer to dry sample concentrations. However, this correction is not perfect and a significant difference may still exist between the corrected concentration and the reference concentration.

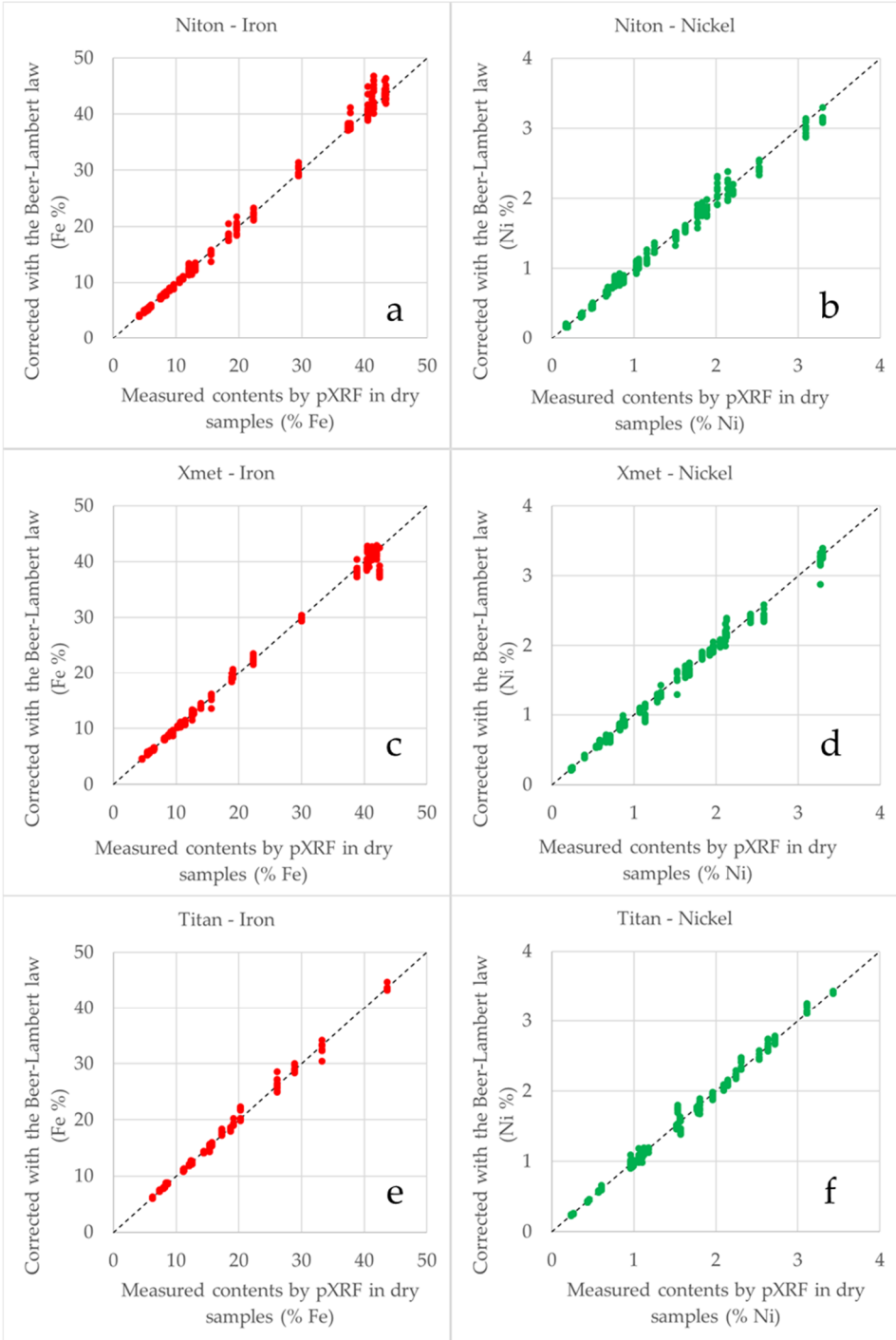


Figure 12. Ni and Fe concentrations after correction with the Beer-Lambert law: (**a**,**b**) Niton, (**c**,**d**) Xmet and (**e**,**f**) Titan.

3.2.3. pXRF Measurements at Water Saturation in the Laboratory

In Figure 9, it can be seen that measurements made at highest values of water content (lower point) vary almost linearly with concentrations in dry samples. Table 6 shows parameters of the linear fit. Values of the coefficients of determination confirm the veracity of this observation ($R^2 > 0.98$).

Using a linear function is therefore possible to estimate concentrations in the dry sample from measurements made in water-saturated samples as shown in Figure 13.

Root-mean-square error values remain relatively large but mean errors are close to 0, so quantification can certainly be improved by increasing the number of measurements.

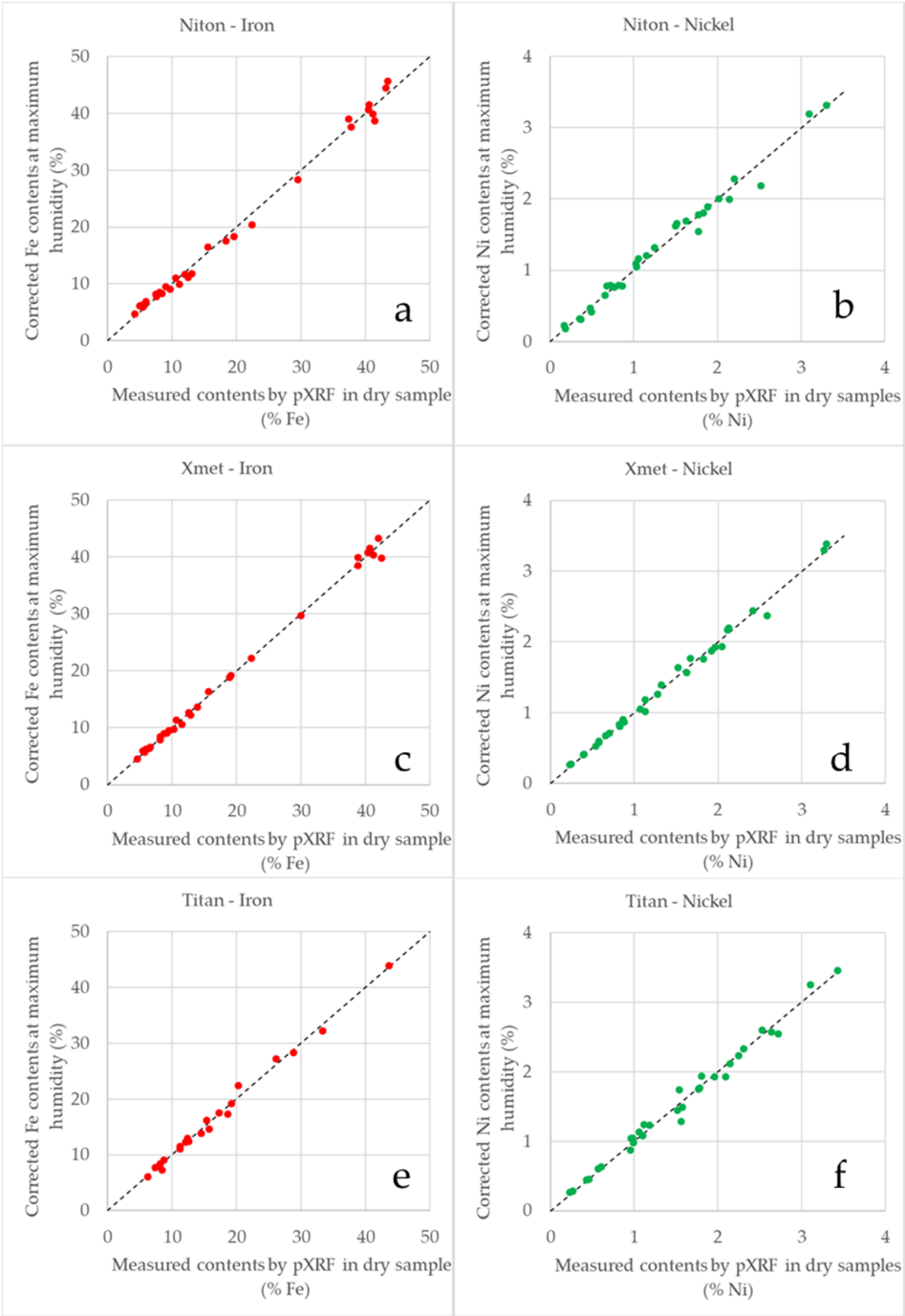


Figure 13. The relationship between corrected Ni and Fe concentrations measured at maximum humidity and concentrations on dry samples: (**a**,**b**) Niton, (**c**,**d**) Xmet and (**e**,**f**) Titan.

For laboratory samples, the particle size is less than 75 µm and sample wetting is well controlled. It is questionable whether this linear relationship is still valid for a direct measurement on the mining front. This method will be usable anyway if the sample is finely ground.

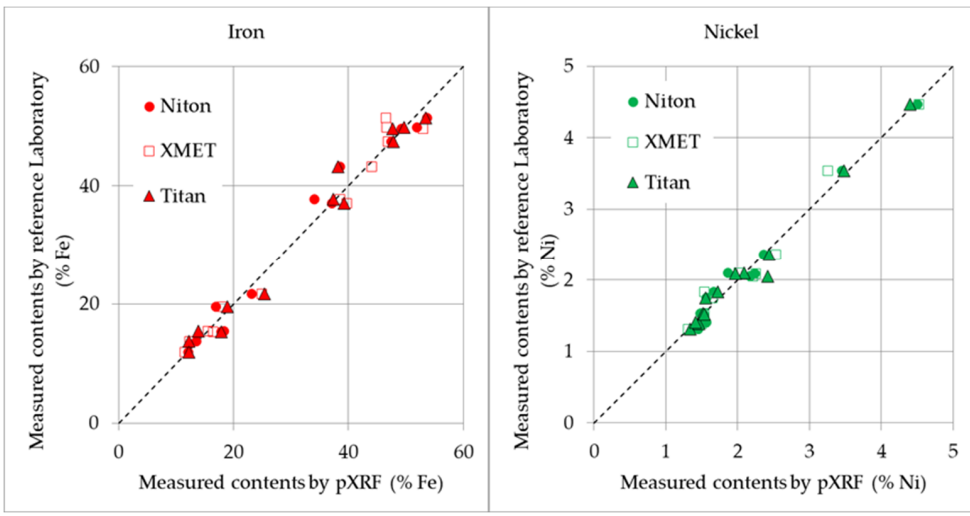
Table 6. Parameters of the linear regression between concentrations at higher water content and concentrations in dry sample for the two elements and for the three devices (a: Slope, b: y-intercept, R^2: Coefficient of determination, ME: Mean error, RMSE: Root-mean-square error).

	Element	Fe	Ni
Niton	a	1.335	1.576
	b	1.142	−0.001
	R^2	0.9936	0.9845
	ME	1.9×10^{-15}	-1.3×10^{-16}
	RMSE	1.13	0.101
Xmet	a	1.177	1.128
	b	−0.072	0.022
	R^2	0.9977	0.9935
	ME	-6.2×10^{-15}	9.0×10^{-17}
	RMSE	0.69	0.067
Titan	a	1.190	1.160
	b	−0.098	0.019
	R^2	0.9966	0.9869
	ME	-5.3×10^{-15}	-1.9×10^{-16}
	RMSE	1.36	0.095

3.3. pXRF Measurements at Water Saturation in the Field

In Section 3.1.1, we have shown that concentrations measured on dry samples are a linear function of the reference concentrations. On the other hand, concentrations measured for saturated samples are a linear function of the concentrations measured for the dry samples (Section 3.2.3). The overall correction law between measurements on saturated samples and reference ones is therefore also linear. As such, we can expect that concentrations measured by pXRF on water-saturated soil are related to reference concentrations by a linear relationship.

Rigorously, the calibration of Ni concentration depends on the Fe concentration for Xmet and Niton (Section 3.1.2). The correction should therefore include terms depending on Fe concentration. The dilution induced by water saturation decreases Fe concentration and its variability, and limits the importance of these terms. These terms do not significantly modify the quality of the correction and therefore we keep a linear correction for its simplicity. The linear regression and results of the correction shown in Figure 14 were established on the same set of samples which contains 13 samples (7 limonites and 6 saprolites).



(**a**) (**b**)

Figure 14. Results of the saturation method after calibration (linear regression): (**a**) Fe oxyde; (**b**) Ni.

The Table 7 quantifies the mean error and the root-mean-square error obtained by a linear correction law.

Table 7. Parameters of the linear regression between in situ measurements of water-saturated samples and contents measured by reference laboratory for the two elements and for the three devices (a: Slope, b: y-intercept, R^2: Coefficient of determination, ME: Mean error, RMSE: Root-mean-square error).

	Element	Fe	Ni
Niton	a	1.978	1.283
	b	−4.739	0.880
	R^2	0.9767	0.9781
	ME	-2.7×10^{-15}	4.1×10^{-16}
	RMSE	2.31	0.131
Xmet	a	1.527	0.776
	b	−7.742	0.753
	R^2	0.9762	0.9711
	ME	1.6×10^{-15}	1.9×10^{-16}
	RMSE	2.33	0.151
Titan	a	1.617	1.215
	b	−2.851	0.434
	R^2	0.9787	0.9789
	ME	1.5×10^{-15}	1.5×10^{-16}
	RMSE	2.21	0.129

The Relative Standard Deviation has also been calculated. It is less than 8% for the Ni and less than 10% for the Fe whatever the pXRF device.

4. Discussion

Concentrations measured by pXRF depend on surface heterogeneities, on the size of particles and thickness of the sample. The values given by the different devices cannot therefore be directly compared with the reference values and a correction step is necessary.

A classic linear regression is used for this step. After correction, results are satisfactory for Fe. RMSE is approximately 0.5% when the range of Fe concentrations varies from 5% to 55%. Corrected measurements are also centered around reference values (ME around 5.10^{-15}). Regarding Ni, for Titan, the precision remains satisfactory. RMSE is around 0.05% when Ni concentrations are included between 1 wt% and 3.3 wt%. Values remain centered around references values (ME of the order of -6.10^{-17}). For Niton and Xmet, RMSE is three times higher than for Titan so corrected measurements are much more dispersed around references values for Niton and Xmet.

It is possible to minimize dispersion of corrected values if two linear regressions are used, one for the limonites and another one for the saprolites. The major drawback of this method is the necessity to determine the nature of the ore to be analyzed. This determination can sometimes be difficult and for certain so-called transition minerals this determination remains subject to interpretation.

For infinitely thick samples, XRF intensity emitted from element i (I_i) at the wavelength λ_i characteristic of element i can be obtained from the Sherman Equation [37]:

$$I_i(\lambda_i) = g_i C_i \int_{\lambda_0}^{\lambda_{edge\ i}} \frac{I_0(\lambda)\mu_i(\lambda)}{\mu_{s'}(\lambda) + \mu_{s''}\ (\lambda_i)} \left[1 + \sum_j C_j \delta_{ij}(\lambda)\right] d\lambda \quad (9)$$

where I_o is the intensity of excitation source at incident wavelength λ, C_i is weight fraction of analyte i, g_i a proportionality constant depending on the instrument used, δ_{ij} is the enhancement contribution of each matrix element j, λ_0 is minimum wavelength of the incident radiation, $\lambda_{edge\ i}$ is wavelength of the edge of considered line of analyte i, $\mu_i(\lambda)$ mass absorption coefficient of element i at wavelength λ, $\mu_{s'}(\lambda)$ and $\mu_{s''}(\lambda_i)$ mass absorp-

tion coefficient of the specimen for incident radiation and for emitted radiation. The two main elements of interest here, Ni and Fe, are subject to enhancement effect because of the proximity of the Ni Kα peak (7.48 keV) to the K absorption edge of Fe (7.11 keV). In such a case, the characteristic X-ray peak of Ni is absorbed by Fe and the characteristic peak of Fe is enhanced by the presence of Ni. Specimen mass absorption coefficient also depends on concentration of all elements. Concentrations values evaluated by devices differ from real concentrations so enhancement effect correction and specimen mass absorption coefficient cannot be accurately corrected. In our samples, Fe is the major element quantified by pXRF and its concentration is up to 55%. As XRF intensity of Ni is influenced by enhancement effect due to Fe, a new term proportional to Ni concentration multiplied by Fe concentration is added to Ni corrective law for the Niton and Xmet devices.

This correction law remains simple and could easily be used by operators on mine. This new correction law divides by 4 the RMSE value obtained with a classical linear correction law and has the major advantage to be usable for saprolitic or limonitic ores.

A challenge for in situ measurements, especially in tropical humid conditions, is to obtain the concentration of elements in dry soil, although the measurement is made on soil that may contain high water content. As usually observed, concentrations of Ni and Fe decrease when water content increases (Figure 9). The measured variations depend on the device used. The concentration range is larger for Niton than for Xmet and Titan.

Niton uses intensity of the Compton line to quantify the dark matrix. The X-ray absorption by the sample is thus better quantified. This method makes results less sensitive to matrix variations and in consequence increases accuracy of results. The addition of water increases the sample mass and therefore decreases the mass fraction of each of the elements to be quantified. However, concentrations in the dry sample can be obtained from the water content and concentrations measured in the wet sample using dilution law. As expected, dilution law corrects Niton results more effectively than those obtained with the other two devices. For Ni, RMSE is more than seven times smaller for Niton than for Xmet or Titan. Even for Niton, this correction does not fully correct water effects.

Use of Ge and coauthors [16] hypothesis corrects measured concentrations, which become closer to ones observed in dry sample. The three devices give direct access to concentrations but not to intensities, so concentrations were used rather than intensities as in Ge and coauthors initial study. Because of matrix effects, concentration of the analyte is not necessarily proportional to XRF intensity characteristic of the element. This may therefore lead to an error in the correction. For the same reason, water content was estimated from sample weight and not from intensity of primary X-rays scattering. On average RMSE is 1.1% for Fe and 0.08% for Ni.

The attenuation coefficient was considered to be constant for all samples, but it appears that the correction could be improved if an attenuation coefficient specific to each sample is used (see Figure 15). This is consistent with the observations of Stockmann and coauthors [38], who could not find a single attenuation coefficient for three soil samples studied. This suggests that the attenuation coefficient depends on the nature of the soil and therefore in our case on the nature of the ore. For the three instruments, correlation coefficients between the attenuation coefficient and concentrations of the different elements or the density of the sample were calculated. There is no significant correlation. Therefore, a law modifying the attenuation coefficient according to properties of the sample cannot be established.

Laboratory measurements of representative samples of New-Caledonian ores show a linear relationship between the concentrations in dry sample and concentrations measured on samples saturated with water. For all instruments and for Ni and Fe, the coefficient of determination is greater than 0.98, which attests the quality of this adjustment. Sahraoui and Hachicha [35] measured concentrations for 60 soil samples from the North East of Tunisia. They obtained, as for our samples, a good correlation between the Fe concentration in saturated sample and Fe concentration in dry sample (R = 0.949). The coefficient of determination for Ni was 0.819 in [35], so a better correlation is observed for our samples.

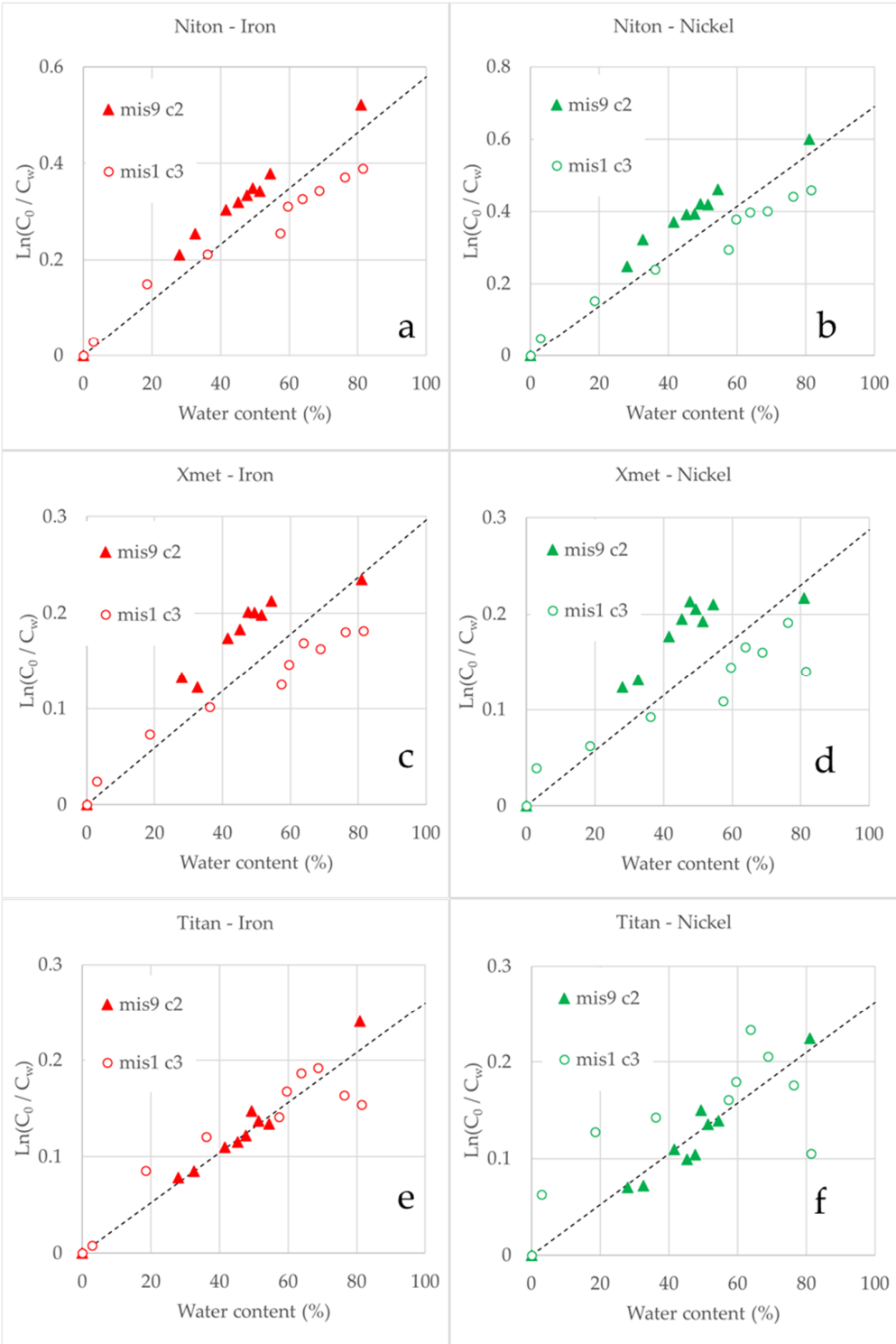


Figure 15. Ni and Fe concentrations in wet conditions divided by concentrations in dry conditions according to water content (expressed in wt%) for 2 samples. The dashed line corresponds to the fitted regression where attenuation coefficients are given in Table 5: (**a**,**b**) Niton, (**c**,**d**) Xmet and (**e**,**f**) Titan.

By using this linear correction, RMSE is approximately equal of those obtained by using the correction proposed by [16]. These two values of RMSE are not strictly comparable because the correction by [16] method was carried out for all humidities whereas for linear correction only the maximum humidity is considered. This indicates that a satisfac-

tory estimation of the concentration of dry sample can be obtained by linear regression. The RMSE value is almost identical for Titan and Niton and is slightly lower for Xmet (1.5 times lower).

In situ, the correction law obtained in laboratory is no longer valid. In particular, in situ type of protective film, particle size and compaction differ from laboratory samples, which has a significant impact on pXRF measurements and on water content of saturated sample. New linear regressions were established, but directly with reference values. Probably due to dilution, Fe concentration has only a negligible influence on Ni correction. A simple linear regression is therefore sufficient for Ni and Fe. The determination coefficients are all higher than 0.97, which shows that a linear correction law is quite appropriate and also shows the validity of this method. RMSE value is approximately 2.3% for Fe and 0.15% for Ni regardless of the considered apparatus. These results are very satisfactory for Ni Root-mean-square error values are almost identical to those calculated from the linear regression linking pXRF measurements on dry samples and reference concentrations. For Fe, these values are two times greater than those obtained by saturation method applied in laboratory. They are also four times larger than those calculated when converting pXRF measurements on dry samples into reference values. In situ, these two corrections are performed in a single step but this does not justify RMSE increase. This difference is certainly explained by the greater dispersity in particle size and in compaction of soils in the natural environment. For some elements, sample grinding may be necessary to improve the quality of the quantification.

5. Conclusions

Although imperfect, correction found by [16] improves the accuracy of the determination of the Ni and Fe contents of the dry sample. Since pXRF equipment only gives concentrations, it is necessary to determine the water content by another method which limits its use.

One way to overcome the difficulty in determining the water content is to fix its value or at least limit its variation between samples, for example by saturating the sample with water. In situ, the Ni and Fe concentrations measured on water saturated samples are a linear function of reference concentrations measured by conventional methods. The coefficient of determination is high ($R^2 > 0.97$) which shows the relevance of this method. For some elements, an initial preparation of the sample before adding water may further improve these results. The pXRF measurements are carried out on wet samples, and XRF intensities will therefore be lower, which will reduce the accuracy of the measurement and increase minimum detectable concentration. Application to a larger number of samples is now necessary to estimate more precisely precision and accuracy of this method.

The underlying phenomenon and mechanisms that imply water content, sample nature and XRF are not yet well understood. Some corrections have been proposed in the literature but in Ni ore mining context, none are able to finely correct XRF measurement on wet samples. Our saturation method is an empirical method that may be calibrated for each environment and probably for each operator. Nerveless, in a mining context, this method has two advantages: (1) no other measuring device is necessary and (2) calibration coefficients can be entered directly in the pXRF device in the same way it is done for dry samples. Hence, the corrected value can be read directly on the device screen, allowing the operator to make decisions in the field.

This work shows that some fundamental questions are still pending. Indeed, our experiments with the Ge method reveal that the physical model is not adapted to our context or that it is not complete, and at least one parameter is missing to take into account the sample nature. Moreover, it is generally admit that moisture is not a major source of errors when moisture content is less than 20% but this aspect has not been properly addressed when a higher content is considered, in particular near or well above saturation. Some additional works should be undertaken to address those two questions.

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