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Optimising Sample Preparation and Calibrations in EDXRF for Quantitative Soil Analysis

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Abstract: Energy-dispersive X-ray fluorescence spectrometry (EDXRF) is a rapid and inexpensive method for soil analysis; however, analytical results are influenced by particle size effects and spectral interferences. The objective of this study was to optimise sample preparation and calibrations to improve the accuracy of EDXRF for soil tests. Methods of sample preparation were compared by calculating the recoveries of 13 elements in four International Soil-Analytical Exchange (ISE) standards prepared as loose powder (LP), pressed pellet (PP), and pressed pellet with wax binder (PPB). A matching library (ML) was created and evaluated against the fundamental parameters (FP) calibration using 20 ISE standards. Additionally, EDXRF results of 41 tillage soils were compared with Inductively coupled plasma optical emission spectrometry (ICP-OES) results. The PPB had most recoveries within the acceptable range of 80–120%; conversely, PP yielded the poorest element recoveries. For the calibration, the ML provided better recoveries of Ni, Pb, Cu, Mg, S, P, and Cr; however, for Zn, and Mn, it had the opposite effect. Furthermore, EDXRF results compared with ICP-OES separated by soil texture class for Al, K, Mn, and Fe. In conclusion, the EDXRF is suitable for quantifying both trace elements and macronutrients in contaminated soils and has the potential to provide screening or prediction of soil texture in agriculture.

Keywords: calibration; elemental analysis; soil; spectrometry; X-Ray fluorescence

1. Introduction

Traditional wet chemistry methods for quantifying trace elements and macronutrients in soil [1–3] are expensive and labour-/time-intensive [4,5]. Reliant on two principal digestion schemes, both approaches have their flaws. Firstly, there is hydrofluoric (HF) acid digestion, which completely liberates silica bound elements in soil to obtain the total concentration, known as 'real totals' [6]. However, due to the toxicity of HF, an alternative method, *aqua regia* digestion [7] is used more commonly for routine analysis [6,8,9]. *Aqua regia*, though, provides only partial digestion and is thus referred to as a 'pseudo' total [5,10,11].

Alternatively, Energy-dispersive X-ray fluorescence (EDXRF) spectrometry provides total element concentrations and is effective for rapid and non-destructive multi-element analysis of numerous environmental samples, including soils [12–15]. Moreover, this technique requires minimal sample preparation and is available in portable forms, making it suitable for on-site analysis [14–18].

EDXRF instruments themselves have become increasingly more sensitive, stable, and affordable. However, errors in the measurement can still arise due to problems during sample preparation, namely surface irregularity, moisture, and sample inhomogeneity [19–21]. This can lead to a reduction in performance and that is why for many applications EDXRF is used principally as a screening/qualitative tool [22].

A further confounding issue is matrix effects, which can result in spectral interferences. These problems arise because the easiest and most widely used mode of analysis for EDXRF is a standardless, iterative concentration calibration called Fundamental Parameters (FP). These measurement errors, though, can be corrected by the development of an empirical/matrix-matched calibration [23]. However, empirical standards must be site-specific, certified using wet chemistry methods, and require a minimum of 10 soil standards for the calibration to be accurate [13,22,24]. For specialist applications, the time and costs associated with these external calibrations are warranted, but for more general agronomic soil testing the set-up is not practical. However, a compromise can be achieved by using an alternative calibration, termed a matching library (ML), that requires fewer standards [25].

An ML-like empirical calibration assumes that a linear relationship exists between the net intensity of peaks for an analyte and the concentration within a sample, i.e., holistically integrating any matrix effects into the measurement [26]. Furthermore, if commercial certified reference materials (CRMs) are used as ML standards, it is relatively easy for the optimised protocols to be replicated by other users/laboratories. Therefore, the objective of this study was to optimise sample preparation and to develop a practical/rapid/reproducible soil calibration for EDXRF as a quantitative soil analysis tool, evaluating this across a range of representative soils varying in element composition and texture class. Enhancing the analytical performance of EDXRF has extensive benefits, such as improving the speed and ease of validating soil screening methods [22], and its potential use in precision farming management.

2. Materials and Methods

2.1. Sample Archives

This study used three sets of soil archives consisting of 24 international soil-analytical exchange (ISE) samples, 4 CRMs, and 41 tillage soils from the study by Metzger et al. [27]. The ISE samples were from the Wageningen Evaluating Programs for Analytical Laboratories (WEPAL) to test laboratory proficiency across the world. The program sends samples to participating labs to compare results across different labs in different countries, and Teagasc takes part in this program and receives samples each year. The WEPAL soil samples in this study were not artificially/technically generated. The ISE samples were received as air-dried, ball-milled, homogenous soils with different concentrations of elements ranging from low to high. A summary of the distribution of each archive is shown in Figure 1.
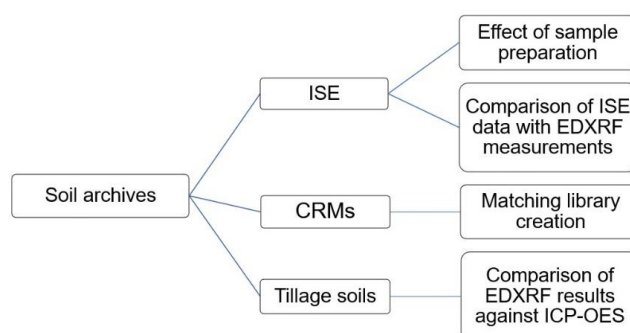

Figure 1. Distribution of sample archive showing how each objective for this study was fulfilled using the three different archives: international soil exchange (ISE), certified reference materials (CRMs), and tillage soils.

The four CRMS were obtained from the National Research Centre for Certified Reference Materials, Beijing, China (*n* = 2), WEPAL, Netherlands (*n* = 1), and the Federal Institute for Materials Research and Testing, Germany (*n* = 1). The 41 tillage soils were obtained from tillage farms across the South and East of the Republic of Ireland.

2.1.1. ISE Samples for the Comparison of XRF Sample Preparation Methods and Calibrations

A total of 24 ISE used for this study were divided into two sets; four samples were kept to examine the effect of different sample preparations, and the remaining 20 samples were used to compare our XRF-determined values with those reported by WEPAL. The ISE selected were described by soil type as: clay (*n* = 8), sandy soil (*n* = 7), sandy clay (*n* = 1) calcareous soil (*n* = 2), Löss (*n* = 1), riverclay (*n* = 1), alluvium (*n* = 1), marshland (*n* = 1), Braunerde-pseudoclay (*n* = 1) and calcareous brown soil (*n* = 1), a summary of the concentration range of elements is shown in Table 1. For this study, only ISE samples with 'real totals' were used. The final results of the 'real totals' for each element reported by the participating labs were calculated and represented as a normal distribution approximation (NDA) mean by WEPAL.

Table 1. ISE samples reported mean total concentrations of the 13 elements selected for this study. The results below show the range of the mean results (normal distribution approximation) and the standard deviation (SD) for a minimum of 20 participating labs per analysis, which includes wet chemistry and spectrometry results. All units in mg kg^{-1} except Al, Ca and Fe which are in g kg^{-1}.

ISE Normal Distribution Approximation (NDA) Results				Calculated Limit of Detection (LOD) for the XRF Used for This Study
Element	NDA Mean		NDA SD		Mean LOD
	Max	Min	Max	Min	mg kg^{-1}
Al **	94.94	16.18	5.11	0.52	88.6
Ca **	221	1.186	9	0.08	56.3
Fe **	60.07	2.62	3.62	0.16	5.64
K	21865	5987.7	1199	153	3.4
S	2831	197.1	524	27.7	4
P	2694	162.9	157	12.7	10.3
Mg	21042	312	1794	63.8	114.8
Mn	1479	75.09	85	9.06	12.1
Cu	152.3	5.06	7.14	1.05	1.7
Cr	254.8	19.29	23.7	2.28	5.6
Ni	111.6	6.59	5.5	0.998	1.9
Pb	296.6	4.32	21.8	0.981	2.4
Zn	1037	17.7	43	2.4	1.2

** units in g kg^{-1}.

The NDA mean and standard deviation indicated by WEPAL for the 'real totals' was considered the true value of the ISE samples for comparison and calculating the recoveries of the elements in this study. 'Real totals' as reported by WEPAL are determined by a range of procedures, namely: total acid digestion with HF and final medium such as HCl, H_2SO_4, HNO_3 and $HClO_4$; total analysis with mixtures of acids (HNO_3+conc HCl or conc.H_2SO_4+conc. HNO_3), followed by ICP-AES, ICP-MS; real total neutron activation analysis followed by neutron activation analysis; and samples prepared as glass beads or pressed pellet followed by XRF determination. In this study, EDXRF was used to determine the element concentration of 20 ISE samples, and values were calculated as % recoveries relative to those reported by WEPAL for the same samples. The % recovery was calculated using the formula (EDXRF results/ISE NDA mean) * 100).

2.1.2. Samples for Matching Library Creation

Four CRMs were acquired to use as a matching library. These samples were used to correct or adjust XRF values determined on the ISE samples (n = 20) derived from the standardless fundamental parameters method (FP). The CRMs used in this study were BAM-U110, ISE 921, GBW07403, and GBW07405, a summary of the elemental concentration of the CRMs is shown in Appendix A, Table A1. The BAM-U110 is a contaminated soil, and thus was selected for the high concentrations of trace elements, while the GBW07403 was selected to represent low concentrations. A total of 13 elements made up the ML calibration, and Si was added as a balance compound for non-measuring components to enable the algorithms on the EDXRF to make correct calculations of element concentrations. For uniformity in the data, the element concentrations listed in the Certificate of Analysis for elements such as Si, Fe, Al, K, Mg, Mn, and P were used instead of the oxide concentration.

2.1.3. Assessing Impact of Soil Texture—Irish Tillage Soils Archive

A set of 41 tillage soil samples consisting of four texture classes—sandy loam (n = 16), clay loam (n = 6), loam (n = 18), sandy clay loam (n = 1)—was sampled from farms across the South and East of the Republic of Ireland as described and reported by Metzger et al. [27]. The samples were taken at a depth of 5–10 cm, after which they were dried at 40 °C and sieved to 2 mm. The particle size distribution was determined using the sieve-pipette method [28].

2.2. Sample Preparation for EDXRF Analysis

Of the four ISE samples, two were clay soil samples (ISE 952 and 961), one was sandy clay (ISE 992), and one was described as sand (ISE 995). The sample preparations for EDXRF analysis in this study included loose powder (LP), pressed powder pellet (PP), and pressed powder pellet with binder (PPB). Each sample preparation had four replicates. Preparing samples as LP involved 8 g of soil, weighed out into an XRF cup (32 mm double open-ended plastic rings with 4 μm thick propylene X-ray film at the base) [29,30]. A low pressure of 200 inch lbs was placed on the sample for 30 s, after which the height was measured and recorded. For PP, 8 g of soil in an XRF aluminium cup was placed in a die set, after which 15 tons of pressure was placed on the die set for 30 s using a Specac manual hydraulic press [31]. Samples prepared as PPB were prepared by weighing out 8 g of soil into a Fluxana mixing container with a polyamide ball, after which a Fluxana cereox binder (wax) was added at a ratio of 0.25 to the soil. The sample was mixed at high speed for 60 s with a Fluxana MU-K Mixer, and 20 tons of pressure was added to create the pellet. A visual display of the different sample preparation is shown in Appendix A, Figure A1.

2.3. EDXRF Analysis

The elemental composition of all samples was analysed with a Rigaku NEX CG benchtop EDXRF. The instrument has a nine-place sample changer with a spin function and is fitted with a Pd X-ray tube for the production of X-rays and a silicon drift detector. Additionally, the instrument uses secondary targets in Cartesian Geometry for indirect excitation to improve the sensitivity of trace element analysis by reducing the background intensity. The secondary targets used for this study were Mo, Cu, Rx9, and Si. All samples for the sample preparation study were analysed with the FP [24,32,33]. Operationally the Rigaku EDXRF system allows the creation of 'alpha corrections' or matching libraries to correct FP-derived analytical results. In addition, all PP and PPB samples were run under vacuum, and the LP under helium to improve light element sensitivity [34,35]. A summary of the instrument settings for the analysis of samples prepared as PP and PPB are shown in Appendix A, Table A2. To ascertain the reliability of the quantitative results from the EDXRF, a library calibration using pure elements is run weekly to check for instrumental drift. The drift monitor samples used for this study were Cu, Sn, SiO$_2$, and a Multi-channel analyser (MCA), all supplied by the manufacturer. Additionally, the MCA was run daily before the start of any analysis. In addition, CRMs are added to every set

of soil samples analysed on the EDXRF to check the accuracy of the analytical results. Furthermore, the EDXRF limit of detection (LOD) was calculated as described by Kadachi and Al-Eshaikh [36] and Scott Rees (Rigaku Tech support) [37] using the formula below:

$$LOD \; = \; \frac{3}{s} \sqrt{\frac{I_b}{T}}$$

where s = sensitivity in counts per ppm; I_b = background intensity; and T = counting time in seconds

A summary of the average LODs for the different elements is shown in Table 1.

2.4. ICP-OES Analysis

A reverse *aqua regia* digestion was used for the extraction of elements for the tillage soils. This involved adding 2.5 mL hydrochloric acid, 7.5 mL nitric acid and 2 mL distilled water to 0.5 g of soil followed by microwave digestion [7,38]. Digested samples were filtered with a Whatman 42 filter paper, after which they were analysed with an Agilent 5100 inductively coupled plasma optical emission spectrometer (ICP-OES).

2.5. Data Analysis

All statistics were analysed with SigmaPlot v14. A one-way ANOVA was performed to determine the significance of the difference between the EDXRF sample preparation methods for element recoveries. Prior to the analyses, tests for normality and equal variance were performed on the element recoveries using the Shapiro–Wilk and Brown–Forsythe tests, respectively. For the data that failed the equal variance test, a Kruskal–Wallis analysis was made on ranks. All pairwise multiple comparisons were made with the Holm–Sidak method. A summary of the statistical analysis is shown in Supplementary Table S1. Agreement between the ICP-OES and the EDXRF data was compared using the Bland–Altman [39–41] function in SigmaPlot v14. Additionally, the concordance correlation coefficient which measures agreement between methods [42] was computed using SAS 9.4. Summary data are available in Supplementary Table S2.

3. Results and Discussion

3.1. Effects of Sample Preparation on EDXRF Analytical Results

The effect of sample preparation on EDXRF results was expressed using % recovery of element concentration as a measure of accuracy and the results for four ISE samples with different sample preparation methods are presented in Figure 2. Recovery of 100% was used as the benchmark indicating the accuracy of the method; however, a deviation of ± 20% was deemed acceptable [17,43]. The recoveries of the elements for the sample preparation methods varied between ISE samples and ranged from 87–708%. The lowest recovery was reported for Al in clay 1 (ISE 952) with PPB and the highest recovery was recorded for S in the sand (ISE 995) using the PP in Figure 2.

The recoveries of K, Fe, and Zn for LP, PP, and PPB were within ± 20% for all ISE samples except for Fe and Zn in the sand sample, irrespective of the sample preparation method used. Additionally, Al, Pb, Mn, Ca, and Ni recoveries were within 100% ± 20% for all the sample preparation methods except sand (ISE 995), as shown in Figure 2. Thus, it can be inferred that when EDXRF is used for analysing soils with low silica, such as clay and sandy clay soils, high-pressure methods such as the PP and PPB may not be necessary, as the low-pressure method—the LP—is as suitable as the former. However, a one-way ANOVA showed that there were significant differences ($p < 0.05$) between the LP and PP, LP, and PPB methods for the recoveries of Al, Fe, and K in clay and sandy clay soils. In addition, for Mn, Ni, Zn, Pb, and Ca, the significant difference in recoveries between the methods varied for each soil (Supplementary Table S1).

Furthermore, Cu, Mg, P, and S recoveries were >120% (acceptable limit) for both LP and PP in all soil samples except clay 1 (ISE 952). PPB reduced Mg, P, and S recoveries >120% to approximately

less than half of the other methods (Figure 2). Additionally, from Figure 2, the sandy soil (ISE 995) had recoveries >120% for Cu, Ca, Cr, Mg, S, and P, irrespective of the method; this is the only sample with Ca recovery >120% for all the methods. This may be due to particle size effects, especially for high silica samples; the presence of larger particles reduces the intensity reaching the XRF detector, thereby limiting the instrument's ability to accurately quantify these elements [35]. According to Markowicz [19] and Parsons et al. [44], particle size effects are not removed even after samples have been pelletized as also observed in the current study. Also, Cu concentrations in all the soils were overestimated, irrespective of the sample preparation used. This may have resulted from the X-ray detector's inability to properly separate different energies of two peaks whose spectra are smaller than the detector's resolution, or elements with similar peaks overlapping with each other, such as Tantalum (Ta) Lα and Hafnium (Hf) Lα [21,45].
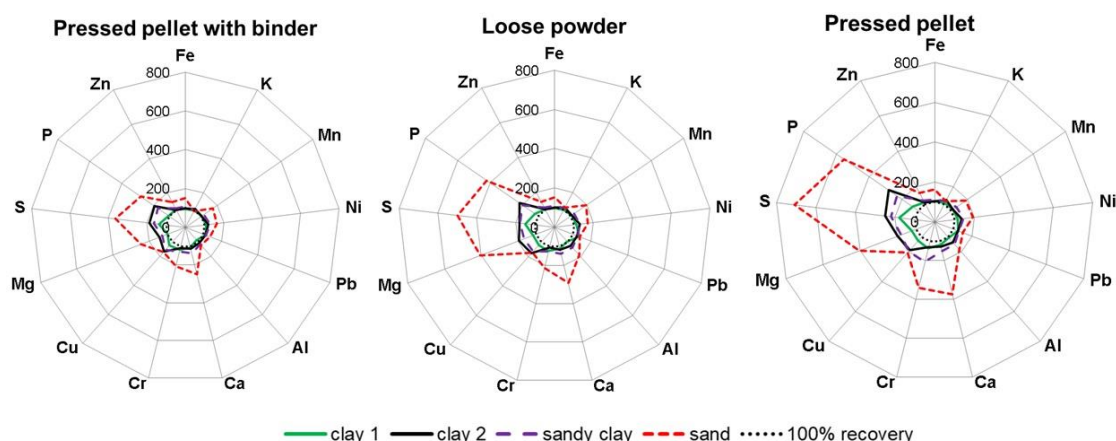

Figure 2. Effects of sample preparation on EDXRF analytical results using elemental recovery as a measure of accuracy with 100% recovery as the benchmark. All samples are from ISE archives (*n* = 4), clay 1 (ISE 952), clay 2 (ISE 961), sandy clay (ISE 992), and sand (ISE 995).

Another factor that may have affected the recoveries of the light elements could have been the critical analytical depth. This is the depth at which X-ray photons are absorbed or escape from a sample [46]. The critical analytical depth increases as X-ray energy and atomic number increases, thus lighter elements have a shallow critical analytical depth [46,47]. According to Ichikawa and Nakamura [46], shallow analytical depth has a negative influence on the accuracy and reproducibility of XRF analytical results. The critical analytical depth for light elements such as Mg, S, and P can sometimes be smaller than the larger particle size in soil [48]. Furthermore, for soils such as sand, pulverisation may not produce uniform particles, and if the critical analytical depth is less than the largest particle size, the EDXRF will measure a high proportion of elements in the finer fractions [22]. This may account for the high recoveries of some light elements using the LP and PP sample preparation method as shown in Figure 2. However, the addition of the binder to the PPB fills the spaces between the coarse grains, which may have reduced the particle size effects.

The effect of three different sample preparation methods on recoveries of elements in different soil analyses has been highlighted. The PP was less suitable for the sand sample due to the surface irregularity and inhomogeneity of samples, which affected the accuracy of P, S, Mg, Cr, and Ca quantification by the EDXRF. Additionally, the LP had the same problem with the quantification of P, S, Mg, Cr, and Ca elements in the sand; however, unlike the PP, the poor recoveries (>120%) were not more than 5 times above the benchmark (Figure 2). It may be that the LP is more heterogeneous than the PP. From the data shown in Figure 2, we conclude that the PPB is more suitable for multi-elemental analysis of different soils, with the advantage of reducing interference arising from particle size effects. Although this method requires an extra step for the addition and mixing of the wax binder, we have shown that this stage improves the results of EDXRF measurement.

3.2. Influence of Matching Library on EDXRF Results Using ISE Samples

The sample preparation study indicated that Cr, Cu, S, P, and Mg values would need corrections to improve results; thus, ML made up of four CRMs was created to adjust values derived from FP calibration. Additionally, the elements Al, K, Ca, Mn, Zn, Fe, Pb, and Ni were included in the ML calibration to account for spectral interference corrections [21]. Twenty ISE samples with 'real totals' values (NDA mean in Table 1) were compared against EDXRF values determined with ML and without a matching library (FP); all ISE samples were prepared as pressed pellet with wax binder and measured 11 times to determine the relative standard deviation (RSD), which is a measure of precision.

Figure 3 represents elements for which the EDXRF had a quantification problem earlier in this study, such as P, S, Cr, Cu, and Mg, while Figure 4 represents elements that did not need any corrections, namely, Pb, Ni, Zn, and Mn. At low concentrations in soils in Figure 3, element recoveries were above the maximum limit of 120% with the FP method. Rousseau [49] indicated that decreasing concentration decreases the intensity of an element line and is later overshadowed by background intensity, especially for 'blanks' or soils with a negligible concentration of elements. Thus, recoveries >120% observed at low concentrations in Figure 3 likely resulted from interferences from the background intensity influencing the sensitivity of the instrument [26,49]. A preliminary examination of spectra was carried out to investigate this issue, and three CRMs of varying concentrations of the elements were analysed with the FP method. After this, a visual evaluation of the spectrum was made on the Mo, Cu, Rx9, and Si secondary targets on the EDXRF. Peak interferences were not observed on any of the secondary targets for the element lines. However, on the Cu target, a lower peak than normal was observed for the element line Cr-Kα for GBW07403 (Appendix A, Table A1) at a low concentration of 32 mg kg^{-1}. Additionally, the background intensity was 61.66 cps and higher than the intensity of 17.25 cps for Cr-Kα. The spectrum of the Cu target is shown in Appendix A, Figure A2. Furthermore, from Appendix A, Figure A2, the background intensity of 41.04 cps for Pb-Lβ1 in GBW07403 at a low concentration of 26 mg kg^{-1} was higher than the intensity of 25.36 cps.
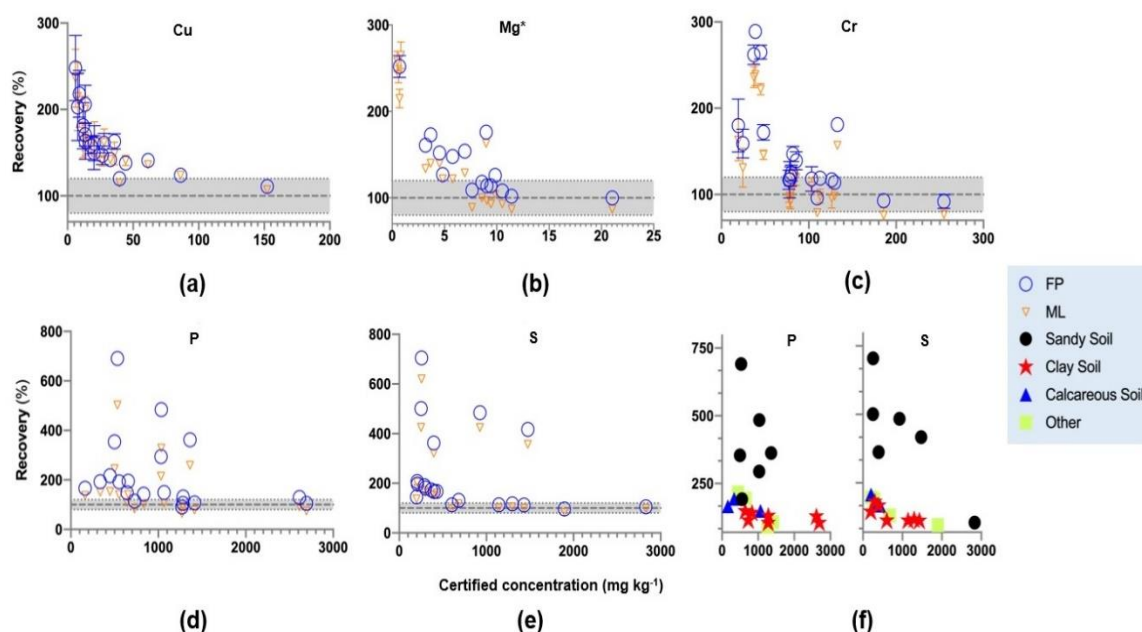

Figure 3. Scatterplot of (**a**) Cu, (**b**) Mg (**c**) Cr, (**d**) P, (**e**) S (**f**) P and S concentration against recovery in different soil types of ISE samples (*n* = 20) comparing fundamental parameters (FP)-derived results and matching library (ML)-adjusted analytical results on the energy-dispersive X-ray fluorescence spectrometer. The solid line denotes the target value of 100% recovery, and the grey shaded region denotes the acceptable limit of ± 20%. All units in mg kg^{-1} except Mg * which is in g kg^{-1}.
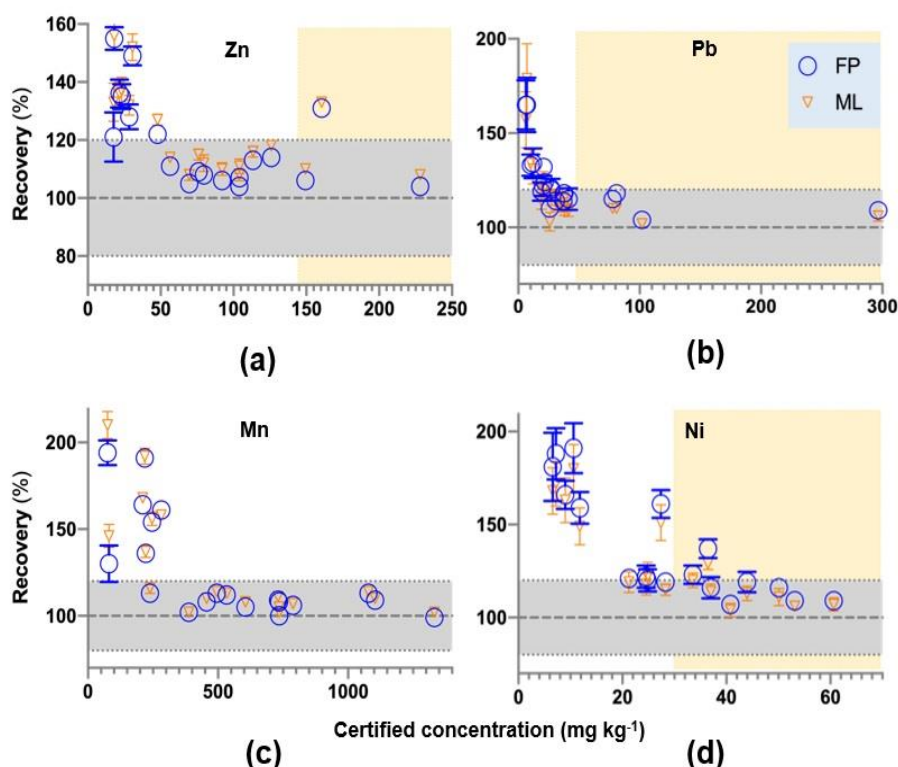
Figure 4. Scatterplot of (**a**) Zn, (**b**) Pb, (**c**) Mn and (**d**) Ni concentration against recovery in different soil types of ISE samples (*n* = 20) comparing fundamental parameters (FP)-derived results and matching library (ML)-adjusted analytical results on the energy-dispersive X-ray fluorescence spectrometer. The solid line denotes the target value of 100% recovery and the grey shaded region denotes the acceptable limit of ± 20%. Yellow shading represents an acceptable range of element concentrations in 86/278/EEC.

However, the ML brought the recoveries closer to the target value within the 20% boundary, especially for P, Cr, and S, as illustrated in Figure 3c–e. It can be inferred that the ML reduces the effect of background intensity on the signal reaching the detector. In addition, the recoveries of P and S >150% were in the sandy soils (Figure 3f). This was also observed for Cu, Cr, and Mg (Figure 3); however, one sample with high S concentration recorded recovery within the limit of 80–120%. Sandy soils or high quartz soils analysed with EDXRF may be strongly influenced by particle size and matrix effects compared to other soil types, as observed in Figure 3f. Saini et al. [50] indicated that elements with low atomic numbers, such as P and Mg, suffer from errors arising from the complex scattering of low-energy X-rays because of inhomogeneous distribution of mineral grains and different particle size. The authors suggest that the addition of a binder in the preparation of pressed pellets reduces these effects provided the particle size is <75 μm. Although a wax binder was added to the sandy soils during sample preparation for this current study, particle size effects were not completely removed.

In addition, high-quartz soils are difficult to pelletize; thus, to reduce the effect of particle size and matrix effects, it may be necessary that samples be prepared as fused beads [51,52]. Additionally, Li et al. [53] suggests that soils with high quartz could be prepared as pressed pellet, covered with 3.6 μm polyester film and high pressure of 2000 kN added without the need for a binder. However, these additional steps may be time-consuming and reduce the advantage of the EDXRF as a rapid and inexpensive method; we recommend that for the analysis of sandy soils, an ML made up exclusively of sandy soils be used to improve analytical results.

For soils in Figure 3, it was also observed that Cu concentration <80 mg kg^{-1} produced recoveries >120%. The overestimation of Cu in these soils indicates that the EDXRF is not a sensitive analytical method for soils with low concentration. According to Sacristan et al. [43], the EDXRF is suitable for

Cu analysis in soils, because they observed a high correlation between portable EDXRF peak height and Cu concentration in soil. However, all the soil samples used for the previous study were dosed with concentrations >500 mg kg^{-1}. Rouillon and Taylor [17] suggest that a high concentration of Cu influences correlation, thus causing low concentration to cluster together to create a high correlation ($R^2 > 0.90$).

In Figure 4 it was observed that at low concentrations close to the LOD (Table 1), the element recoveries were >120%, with FP similar to Figure 3. Furthermore, from Figures 3 and 4, it can be observed that the EDXRF is concentration-dependent, and at certain concentration thresholds, the recoveries improve (Appendix A, Table A3). In addition, at the concentration threshold for most of the elements, the ML produced average recoveries within the range of 100% ± 20, except for Fe, K, Mn, and Zn (Appendix A, Table A3). For these elements, FP was the most suitable method of analysis compared to the ML. Additionally, when the sand samples were removed from the data, the average recoveries for P and S using the ML dropped from 130% ± 87.04 and 164% ± 130 to 85% ± 14.17 and 100% ± 10, respectively. Moreover, the average recoveries for Cu dropped from 125 ± 14 to 122 ± 14.5 with the removal of the sand samples.

It is well known that Zn, Cu, Mn, and Ni are essential for plant growth at low concentrations and toxic at high concentrations, while Pb and Cr have no known importance to plant health and are detrimental to human health [54,55]. Thus, the European Union (EU) has set a regulation for environmental monitoring of trace elements contamination in agricultural soils amended with sewage sludge. The directive 86/278/EEC [56] indicates the limit values of trace elements allowable in amended soils, which are Cu 50–140 mg kg^{-1}, Ni 30–75 mg kg^{-1}, Pb 50–300 mg kg^{-1}, Zn 150–300 mg kg^{-1}. In addition, Tóth et al. [57] indicated that lower guideline concentrations of 200 mg kg^{-1}, 150 mg kg^{-1}, 200 mg kg^{-1}, 100 mg kg^{-1}, 250 mg kg^{-1} for Cr, Cu, Pb, Ni, Zn, respectively, in soil, may pose ecological risks. The annual cost of management for contaminated areas in Europe alone is approximately €6 billion, and agricultural production is one of the main drivers of soil contamination [58]. Identifying contaminated soils quickly is the key to the rapid implementation of remediation measures. Thus, cost-effective and rapid analysis of contaminated soils USEPA Method 6200 [22] indicates the portable EDXRF as a screening method. However, the method states that for confirmatory results, the more expensive, laborious, and time-consuming techniques such as wet chemistry methods should be used. In this study, the use of the benchtop EDXRF is proposed as a confirmatory technique for contaminated sites identified with the portable EDXRF. The data above demonstrates that the EDXRF can accurately quantify the limit values of trace elements listed in 86/278/EEC [56] and the lower guideline limits proposed by Tóth et al. [57]. Although the FP method on the EDXRF is accurate for measuring contaminated soils, from this study it has been shown that the addition of an ML improves analytical results for trace elements and macronutrients. Furthermore, the instrument is concentration-dependent; thus, for soils deficient in trace elements and macronutrients, it has some limitations. In conclusion, the EDXRF is most suitable for rapid analysis of contaminated soils and can be used as a confirmatory technique for 'hot spot' identification.

3.3. Particle Size Effects on Fe, K, Mn, and Al Determined Using EDXRF Analysis in Tillage Soils

It was observed that soil texture had a strong effect on some elements, specifically Fe, K, Mn, and Al. Figure 5 highlights the influence of four soil texture classes on Fe, K, Mn, and Al values when EDXRF values are plotted against values derived from *aqua regia* digestion followed by ICP-OES. The concordance correlation coefficient (CCC) was computed to determine the level of agreement between the ICP-OES to the EDXRF. CCC is a product of accuracy and precision coefficients, whereby values range from −1 to 1. A value of 1 represents perfect agreement between two methods, while −1 represents disagreement, and 0 represents no agreement between the methods [42].

From Figure 5, it was observed that soils classified as clay loam drifted from the line of agreement at high concentrations of Fe (Figure 5a) and Mn (Figure 5c) compared to loam and sandy loam soils. Clay loam samples separated from the other texture classes due to the high concentration of Fe and

Mn (Figure 5); however, the divergence from the line of agreement suggests EDXRF underestimated the concentrations. The sample preparation results presented earlier indicated that samples prepared as PPB underestimated Fe at high concentrations. Thus, the EDXRF underestimated Fe (Figure 5a) concentration in the clay loam samples. Agreement statistics computed showed a good agreement between the two methods with CCC = 0.898, R^2 = 0.93 and CCC = 0.887, R^2 = 0.92 for Fe and Mn, respectively.
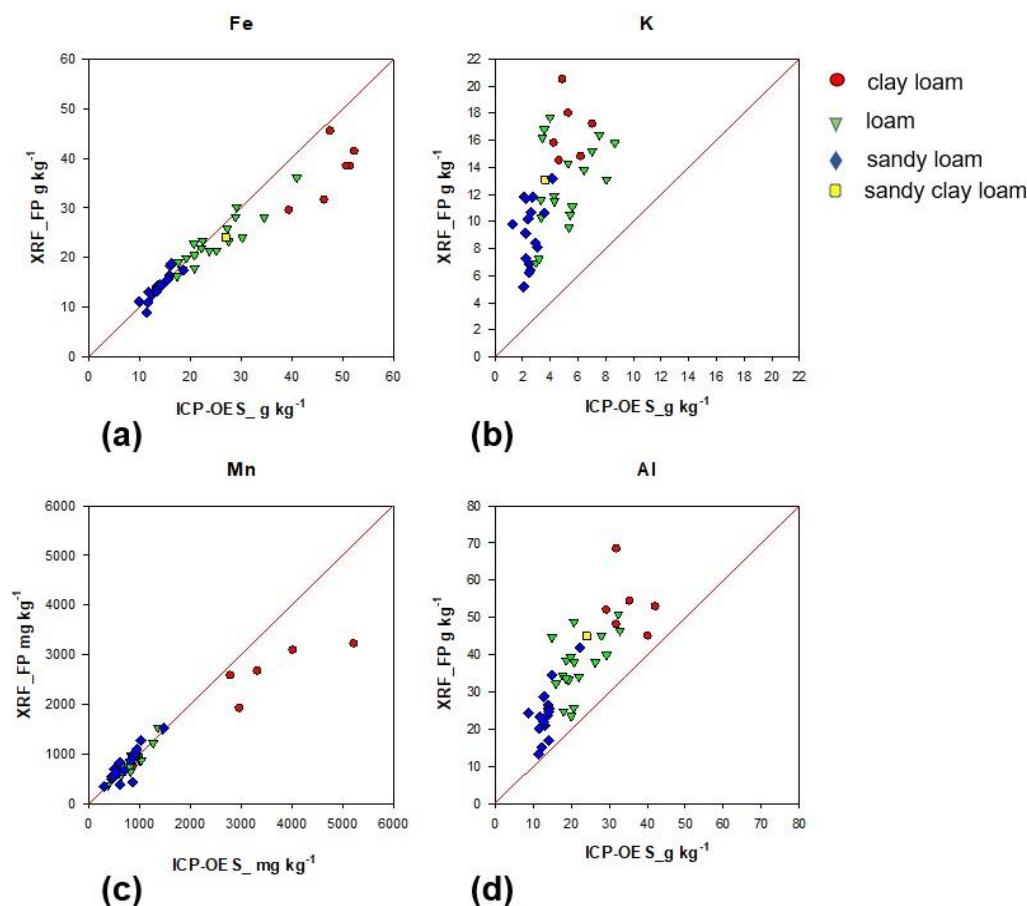

Figure 5. Effect of soil texture on EDXRF- and ICP-OES-determined values of (**a**) Fe, (**b**) K, (**c**) Mn, and (**d**) Al concentrations separation tillage soils with the line of agreement.

For Al and K (Figure 5), a small number of the sandy loams were close to the line of agreement; the opposite is true for both clay loam and loam. This suggests that *aqua regia* underestimated Al and K in all the soils; thus, there was poor agreement between the EDXRF and ICP-OES for Al CCC = 0.40, R^2 = 0.67, and K CCC = 0.102, R^2 = 0.36. This observation is in agreement with Chen et al. [11], who found poor recoveries for Al and K in soils using *aqua regia* without the addition of HF. Additionally, Rao et al. [59], concluded that *aqua regia* was not suitable for K extraction in soils. Finally, comparative studies of the ICP methods against XRF [12–14,17,49,60] do not usually take into consideration the effect of soil texture on agreement between these methods. Although initially this may seem like an unwanted analytical challenge, it also offers an opportunity to potentially use EDXRF for rapid screening or prediction of soil texture.

4. Conclusions

Sample preparation methods had varying effects on multi-element EDXRF soil analysis, and the PPB produced most element recoveries within the benchmark of 80–120% for good accuracy. Thus, this method was used in the preparation of samples to examine the effect of ML on FP calibrations

in EDXRF. The ML improved recoveries for Ni, Pb, Mg, S, P, Cr close to the maximum limit of 120%. However, for Zn, and Mn, the FP had recoveries closer to the 120% limit. The ML can simultaneously improve and be detrimental to soil measurements depending on the elements' targets. An option is to have a hybrid of FP and ML for full element analysis. Additionally, the ML developed here is relatively easy to replicate, and analysts can source the same CRMs as used in this study. Additionally, it was observed that sandy soil had >120% recovery for all the elements, which may have resulted from greater homogeneity and rougher surface of samples. Furthermore, EDXRF results of Mn, Fe, K, and Al were compared to *aqua regia*-digested samples followed by ICP-OES in tillage soils and values separated by texture class.

This study shows that the EDXRF can be optimised for soil analysis by selecting the appropriate sample preparation and ML, with prior knowledge of texture class being a distinct advantage. However, a wide range of different textures was not included, and it will be necessary for future works to consider this. In addition, the benchtop EDXRF could be a possible confirmatory technique for verifying 'hot spot' contamination identified by the screening field portable XRF systems, especially for trace elements, as opposed to wet chemistry methods. This would be an advantage especially for tillage soils, whereby the reuse of sewage sludge and other organic waste is encouraged in agriculture across Europe. However, for sandy soils and soils deficient in trace elements the instrument has some limitations.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4395/10/9/1309/s1. Table S1: One-way ANOVA results showing significant differences for recoveries for trace elements and macronutrients element for the three sample preparation methods. Table S2: Concordance correlation coefficient (CCC) and Bland-Altman results for elements concentration in tillage soils (*n* = 41) using fundamental parameters (FP) and matching library (ML) for EDXRF spectrometry in comparison to ICP-OES analysis. The datasets generated for this study are available at doi.org/10.17034/feca94bd-e9c7-4716-9103-33cafa09a3be.

Appendix A

Table A1. Summary of certified values used in the matching library for XRF analysis. All units in mg kg^{-1}.

	Certified Reference Materials			
Element	**GBW07403**	**GBW07405**	**ISE 921**	**BAM-U110**
Al	64,800	114,247	56,800 ± 1440	* 50,382 ± 1081
Ca	9071	679	43,000 ± 1180	* 40,638 ± 2105
Cu	11.4	144	93.8 ± 5.84	263 ± 12
Cr	32	118	130 ± 10.6	230 ± 13
Fe	13,989	88,269	31,900 ± 1130	* 28,229 ± 663
K	25,226	12,447	19,100 ± 640	* 20,381 ± 4560
Mg	3498	3679	11,100 ± 370	* 8380 ± 735
Mn	304	1360	1190 ± 43	621 ± 20
Ni	12	40	42.4 ± 3.21	101 ± 5
P	320	390	1400 ± 69	* 3648 ± 49
Pb	26	552	167 ± 7.5	197 ± 14
S	120	410	702 ± 79.8	* 10,593
Si	349,290	245,746	271,000 ± 4600	* 258,125
Zn	31	494	522 ± 19.9	1000 ± 50

* reference value only not certified.

Table A2. Measurement conditions for analysis of the elemental composition of soil samples prepared as pressed pellet with binder using benchtop energy dispersive X-ray fluorescence spectrometer. All samples were run under vacuum atmosphere.

Element	Voltage (kv)	Secondary Target	Peak Detected (KeV)	Measurement Time (s)
Cu	50	Mo	Kα, 8.047	100
Cr	50	Cu	Kα, 5.414	100
Mn	50	Mo	Kα, 5.898	100
Ni	50	Mo	Kα, 7.477	100
Zn	50	Mo	Kα, 8.638	100
Pb	50	Mo	Lβ1, 12.611	100
Al	25	Rx9	Kα, 1.487	100
S	25	Rx9	Kα, 2.308	100
P	25	Rx9	Kα, 2.015	100
Mg	25	Si	Kα,1.254	300
Ca	50	Cu	Kα, 3.691	100
K	50	Cu	Kα, 3.313	100
Fe	50	Mo	Kα, 6.403	100

Table A3. Average recovery of elements based on the concentration threshold of the ISE samples analysed with the fundamental parameters (FP) and matching library (ML) methods on the EDXRF.

| Elements	Concentration Threshold (mg kg^{-1})	Average Recovery Including Sand (%)	Average Recovery (%) Minus Sand	Calibration Method
Al	40760	-	106 ± 10.2 (n = 12)	ML
Ca	3750	120 ± 29 (n = 17)	106 ± 12 (n = 14)	ML
Cr	77.3	101 ± 21 (n = 14)	97 ± 14.9 (n = 12)	ML
Cu	39.66	125 ± 14 (n = 5)	122 ± 14.5 (n = 4)	ML
Fe	6040	106 ± 10.4 (n = 17)	102 ± 4.5 (n = 14)	FP
K	5988	108 ± 10.1 (n = 20)	-	FP
Mg	4844	107 ± 22.8 (n = 12)	102 ± 15.3 (n = 11)	ML
Mn	238	114 ± 18.3 (n = 15)	107 ± 4.9 (n = 13)	FP
Ni	21.27	117 ± 11.9 (n = 14)	113 ± 5.8 (n = 12)	ML
P	727	130 ± 87.04 (n = 12)	85 ± 14.17 (n = 9)	ML
Pb	19.16	113 ± 6.2 (n = 16)	-	ML
S	603.5	164 ± 130 (n = 9)	100 ± 10 (n = 7)	ML
Zn	56.45	109 ± 7.3 (n = 13)	107 ± 3.6 (n = 12)	FP
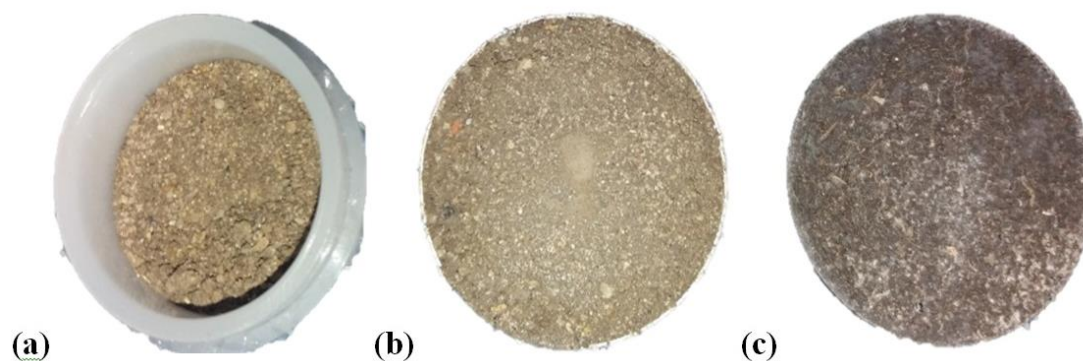
Figure A1. Common methods for soil sample preparation using low and high pressure for analysis on X-ray fluorescence spectroscopy (**a**) loose powder (LP)-200 inch lbs pressure added for 30 s, (**b**) pressed powder pellet (PP)-15 tons pressure added for 30 s, (**c**) pressed powder pellet with wax binder (PPB)-20 tons pressure added for 30 s.
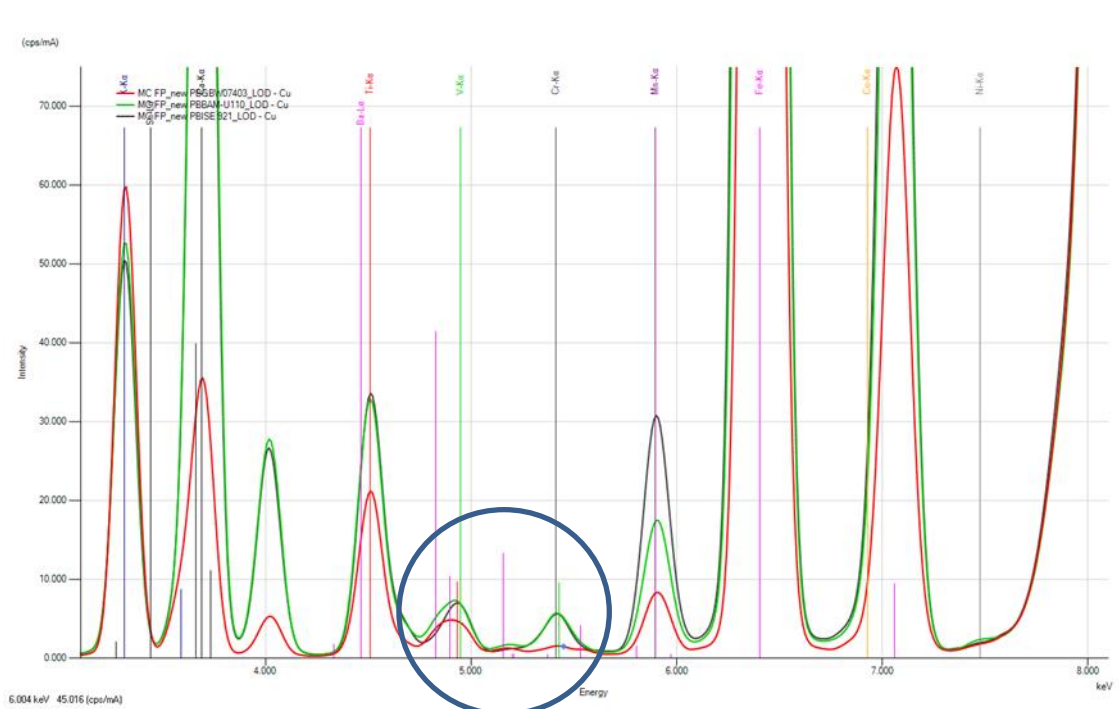

Figure A2. Spectrum of Cu target on EDXRF showing the elements on the target using three CRMs with different concentrations, whereby the red line (GBW07403) signifies elements at low concentrations, the black line (ISE 921) signifying elements at medium concentrations and the green line (BAM-U110) indicating a contaminated soil.

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