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Applicability of a field portable X-ray fluorescence for analyzing elemental concentration of waste samples

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Abstract

Determining the chemical properties of waste is crucial to ensure the most effective utilization of waste. The standard laboratory measurements can produce accurate results, but analysis is labor- and time-consuming. The variety of elements that field portable X-ray fluorescence spectrometry (FPXRF) can detect from selected waste materials was studied, including how the results compared with those of inductively coupled plasma mass spectrometry (ICP-MS) measurements. The selected materials were fine fraction reject from solid recovered fuel production, fly ash, biowaste, and compost. Based on the results, FPXRF is reported to be best suited for waste samples, such as ash and compost, because of their physical properties, as follows: not too moist, quite small particle size, and not too heterogeneous. The results obtained from FPXRF showed the lowest relative standard deviation for ash material. The analysis of the limits of agreement between FPXRF and ICP-MS showed that FPXRF was mainly suitable for qualitative assessment. Furthermore, regression analysis showed a linear correlation between FPXRF and ICP-MS results for calcium and zinc in the selected materials. Keeping the limitations in mind, FPXRF could be used for qualitative analysis in waste treatment processes, such as first quality control of waste materials.

Keywords: field portable x-ray fluorescence spectrometry, inductively coupled plasma mass spectrometry, elemental analysis, waste

1 Introduction

Waste recovery is becoming increasingly important as natural resources are being depleted. Information on elements, such as potentially toxic trace elements, and on concentrations of waste is required for the determination of suitable utilization methods or safe final disposal locations. For example, to dispose fine fraction reject from solid recovered fuel (SRF) production to a landfill for non-hazardous waste in Finland, it is mandatory to find out if the concentrations of certain substances, such as As, Cd, Hg, Cu and Pb, exceed the limits in regulation (333/221).

Currently, the properties of waste are measured in laboratories with analytical methods, such as inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS). While these laboratory analyses are accurate, there are some problems related to them (Weindorf et al., 2012). Due to the heterogeneous nature of waste, large amounts of samples are needed to obtain representative results. However, the number of samples is limited when ICP-MS and AAS methods are used because they are time-consuming, costly, and require experienced technicians (Kilbride et al., 2006). Another problem involves sample preparation, which may be prone to sample contamination, resulting in inaccurate results (Hou et al., 2004). Based on the few laboratory tests, a decision can be made on the utilization or the disposal of a large quantity of materials.

Measuring element concentrations online with sufficient accuracy could provide significant benefits to enable the utilization of materials. This would allow directing fraction, which is most probably suitable for utilization to a pile that is different from fraction that is unsuitable for utilization. For example, in deciding the treatment for ash, online measurement could guide a conveyor so that ash requiring heavy metal removal (Havukainen et al., 2016) would be separated (and dumped on a different pile) from ash that has concentrations safely below the limits and requires less treatment. Field portable X-ray fluorescence spectrometry (FPXRF) could be one solution to tackle the challenges posed by laboratory analysis. FPXRF is a fast, nondestructive technique that can provide qualitative or quantitative elemental analysis of any kind of sample material (Hou et al., 2004; Kalnicky and Singhvi, 2001). One advantage of FPXRF is that the technique requires no or only little sample preparation, which enables rapid nondestructive analysis.

The review by Gałuszka et al. (2015) showed that there has been development in portable instruments, including FPXRF, which has been used for example in rapid on-site screening of soil samples (Miller et al., 2013) and measuring lead in dust wipe samples (Sterling et al., 2000). Miller et al. (2013) used portable XRF for measuring mercury contamination of soil from industrial complex and found that the sample heterogeneity causes complexity for the measurements while Sterling et al (2000) found that portable XRF can be used for rapid on-site evaluation of dust wipes. Kilbride et al. (2006) used two types of FPXRF to measure soil samples and compared metal concentrations using FPXRF against ICP-optical emission spectrometry (OES) analysis. The X-ray tube instrument successfully measured Fe and Pb concentrations, whereas the dual source XRF instrument was able to measure Fe, Cu, Pb, Zn, Cd, and Mn concentrations (Kilbride et al., 2006). Similarly, Radu and Diamond (2009)

studied heavy metal contamination of soils in mining facilities. Pb, As, Cu, and Zn concentrations were analyzed by using FPXRF and AAS. FPXRF demonstrated an excellent correlation with the AAS method. Gutiérrez-Ginés et al. (2013) studied heavy metal concentrations in soil and plant samples by using FPXRF. The samples were collected from abandoned mine sites and sealed landfills in Spain. The results showed a high quality of the measurements of As, Ca, Cd, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sr, Ti, and Zn concentrations. Additionally, the FPXRF analysis was found to save on costs, materials, and time when compared with accurate laboratory analysis (Gutiérrez-Ginés et al., 2013).

One of the recent applications of FPXRF is the identification of As, Cu, Cr in wood waste (Block et al., 2007; Hasan et al., 2011). Burlakovs et al. (2015) found that FPXRF could be used for fast, semi-quantitative evaluation of certain metallic elements in samples from landfill mining tests. McWhirt et al. (2012) were able to measure Ca, Cr, Cu, Fe, K, Mn, P, and Zn concentrations from dried compost samples by using FPXRF, whereas As detection was found to be unsuccessful. Similarly, Weindorf et al. (2008) concluded that FPXRF was effective in detecting concentrations of Ni, Cu, Zn, Se, Mo, and Pb but was unable to measure Hg, Cd, or As.

Only a few studies have been conducted using FPXRF to characterize solid wastes, such as ash, compost, and fine fraction reject from SRF production. In fact, this present study is one of the first to examine fine fraction reject from SRF production by using FPXRF. The objective of this study is to find out which elements can be measured with FPXRF and how these results compare with those of laboratory measurements using ICP-MS. The aim is to preliminarily estimate whether FPXRF would be suitable for online waste measurements to aid in faster decision making and better utilization of waste. The research focuses on measuring solid wastes and waste processing products or rejects that have relatively small particle sizes.

2 Materials and methods

2.1 Sample details and preparation

Four different waste materials were selected to evaluate the suitability of FPXRF measurements of different types of waste products, including fine fraction reject, fly ash, biowaste, and compost. The waste materials were mixed homogeneously, and three samples of each material were placed in 0.5-liter zip-lock bags. The fine fraction reject came from the manufacturing of SRF, which consisted of commercial and industrial waste. The fine fraction reject is the underflow from the star screen, which is located after primary shredding and the belt magnet but before the air classifier. The particle size ranges between 0 and 15 mm. To compare the particle size's effect on the measurement results, a part of the fine fraction was ground to a 2-mm size by mechanical milling. The fly ash came from the Finnish power plant using bark and logging residues as fuel. The biowaste and the compost came from the same anaerobic digestion and composting plant. The plant processes separately collect biowaste, sewage sludge, and garden waste. The digestion residue is converted into a compost product, which can be used as a fertilizer. Both moist and dried samples of biowaste and compost were

used in FPXRF measurements to compare the impact of moisture in FPXRF measurements. Moisture measurements were separately performed for each of the three zip-lock bags. ICP-MS measurements were performed for the ground fine fraction reject, ash, and dried compost. A schematic overview of the treatment of the samples before the analysis can be seen from supplementary data Figure S1.

2.2 Field portable X-ray fluorescence (FPXRF) analysis

The Niton XL3t 900s XRF analyzer (Thermo Scientific Inc.) with an X-ray tube operated at 50 keV and a geometrically optimized large drift detector (GOLDD) was used in this study. The analyzer is able to measure a range of elements from magnesium to uranium. The standard configuration mode, known as the mining mode, was used in the measurements. The mining mode was selected to measure the waste samples because it could be assumed that these were the most similar to heterogeneous soil samples. More information about the analyzer can be found from the supplementary material presented in Table S1, and the limits of detection (LOD) are shown in Table S2. The waste samples were analyzed through the zip-lock bags. Each of the three zip-lock bags was scanned eight times, four points from both sides through the bag, meaning that one waste material was scanned a total of 24 times. The analysis time for one scan was 80 seconds, meaning that the total analysis time for one zip-lock bag was a little less than 11 minutes. The measuring time of 80 seconds was selected since a longer measurement time did not reduce significantly the standard deviation of the measurement.

2.3 Laboratory analysis using inductively coupled plasma mass spectrometry (ICP-MS)

The comparative elemental analysis was performed by using ICP-MS (Agilent Technologies 7900) (SFS-EN ISO 16968). The LOD and the limit of quantification of ICP-MS are shown in the supplementary material (Table S3). Elemental analysis by ICP-MS requires liquid samples; thus, solid samples have to be converted into liquid form by microwave digestion. Before the digestion, the samples were pretreated by drying them in an oven for 12 hours at 105 °C and subsequently ground in a mortar to obtain smaller particle sizes. Four 0.1-g samples were prepared from each of the three zip-lock bags, meaning that one waste material was analyzed 12 times. For the digestion, the 0.1-g samples were weighed in a test tube, and 4 ml of concentrated nitric acid (HNO_3 at 67%) and 1 ml of concentrated hydrochloric acid (HCl at 37%) were added. The digestion was accomplished by using an UltraWAVE Single Reaction Chamber Microwave Digestion (Milestone Inc.). After the digestion, the samples were diluted and analyzed by using the ICP-MS analyzer. The concentration of potassium was not measured with ICP-MS. In addition, the ICP-MS method was unable to determine Cl concentration; therefore, Cl was measured by ion exchange-chromatography (IC). Chloride was analyzed according to the standard SFS-EN ISO 10304-2 with the Thermo Fisher ICS - 1100 equipment. The used column consisted of IonPac AG22 (4 x 50mm + AS22 (4 x 250mm) and eluent 4.5 mM Na_2CO_3 + 1.4 mM $NaHCO_3$. Water extraction was done for the samples before the IC analysis.

2.4 Data analysis

The element concentration and the precision of analysis were reported by FPXRF on an individual element basis for each scan. The mean value, standard deviation (SD), relative standard deviation (RSD), and minimum and maximum values for each waste sample were determined. The mean value and the SD were calculated for each sample on the basis of 24 measurements. Used to evaluate a method's precision, RSD is the ratio of the SD and the mean concentration of an element (EPA, 2007). For FPXRF measurement data to be considered precise, the RSD should not exceed 20% (EPA, 2007).

The Bland-Altman plot analysis with limits of agreement (LA) (Martin Bland and Altman, 1986) was used to assess the agreement between the FPXRF and the ICP-MS measurements. The average values of the measured element concentrations of the three zip-lock bags per material were used in the analysis. The range of the LA was compared with the range of the values obtained from the ICP-MS measurement to estimate the agreement. The LA values are calculated based on the mean difference between the measurements and the SD of the differences, using Equation (1) (Ranganathan et al., 2017):

$$LA = \text{mean difference} \pm 1.96 \times \text{SD of differences} \tag{1}$$

A linear regression analysis was used to obtain prediction models and model performance statistics. The analysis was used to investigate the relationship between the element concentrations measured by using ICP-MS and FPXRF. The data were log transformed to satisfy the assumptions of the linear regression and to standardize variance (EPA, 2007). The coefficient of determination (R^2) was used to describe the accuracy of fit. The closer R^2 is to 1, the better the model is able to explain the linear relationship between the measurement methods. The coefficient of determination and the RSD are used to characterize the data generated by FPXRF. Table 1 shows the criteria for characterizing the data quality.

Table 1. Criteria for characterizing data quality (EPA, 2007; Kilbride et al., 2006).

Data quality level	Statistical requirement	
	R^2	RSD
Definitive	0.9–1	≤ 10%
Quantitative	0.7–0.9	< 20%
Qualitative	< 0.7	> 20%

R^2 = coefficient of determination, RSD = relative standard deviation

3 Results and discussion

3.1 The results of FPXRF

Tables 2 and 3 summarize the element concentration ranges of the SRF waste samples measured by FPXRF. According to the EPA, the FPXRF measurement data can be characterized as quantitative when the RSD is less than 20%, with the exception of Cr, whose RSD should be less than 30% (EPA, 2007). The coarse fine fraction reject performed poorly since the RSD was less than 20% only for Cd and Cl. The grinding of the fine fraction reject

reduced the RSD of Pb, Zn, Cu, Fe, Ca, K, Cd, and V but increased the RSD of Cr and Cl. These findings indicate that the grinding of samples can produce more accurate results from the RSD perspective. Additionally, after the grinding, As and Mn could be detected from the sample, which were not detected in the coarse fine fraction reject. In terms of RSD, the concentrations of Zn, Fe, Ca, K, Cd, and V in the ground fine fraction reject were quantitative, according to EPA standards. Ash, which is already much more homogeneous than fine fraction reject, performed much better; almost all the results were quantitative, and the concentrations of Pb, As, Ca, K, and Cl could even be considered definitive (RSD ≤ 10%).

Table 2. Element concentrations (mg/kg) determined by FPXRF in SRF fine fraction and ash samples.

Sample	Pb	As	Zn	Cu	Fe	Mn	Cr	Ca	K	Cd	Cl	V
Coarse fine fraction reject												
Mean	36	n.d.	566	659	7214	n.d.	200	27824	2771	21	2821	102
Min	15		243	132	3757		91	16419	1672	14	1828	53
Max	156		1378	3793	12184		565	53545	4226	26	3944	221
SD	30		282	873	2170		124	8688	622	4	539	46
RSD	84 %		50 %	132 %	30 %		62 %	31 %	22 %	17 %	19 %	45 %
Ground fine fraction reject												
Mean	62	17	756	521	9176	226	202	38825	2858	19	3693	142
Min	36	11	598	347	6890	175	105	34055	2438	14	2685	109
Max	163	27	966	1311	11502	282	768	45486	3369	24	11280	205
SD	29	5	116	216	1377	38	131	2774	261	2	1713	24
RSD	48 %	32 %	15 %	42 %	15 %	17 %	65 %	7 %	9 %	13 %	46 %	17 %
Ash												
Mean	357	39	2138	711	62882	4552	333	94625	19172	n.d.	3541	306
Min	294	33	1703	533	54529	3651	277	72001	17663		2744	144
Max	410	46	2686	1124	77134	6037	443	109933	20986		4142	375
SD	31	5	259	160	5451	558	43	8613	750		355	64
RSD	9 %	14 %	12 %	23 %	9 %	12 %	13 %	9 %	4 %		10 %	21 %

n.d. = not detected, Min = minimum, Max = maximum, SD = standard deviation, RSD = relative standard deviation

Table 3 summarizes the element concentrations of moist and dry compost and biowaste samples on a dry matter basis. The moisture content was on average 60% for biowaste and 36% for compost. The element concentrations of the moist and the dry samples on a dry matter basis were closer to each other for compost samples than for biowaste samples. The moist compost samples had 3–10% lower values for Zn, Fe, and K and 3–10% higher values for Ca and Cl. The moist biowaste samples had 13–37% lower values for Zn, Fe, and K and 21–33% higher values for Ca and Cl. These results seemed to indicate that the higher moisture content of biowaste resulted in a more significant difference between moist and dry samples. Moisture also seemed to affect the detection of some elements in moist compost and biowaste since after the drying, concentrations of Mn in compost and concentrations of Cu, Cr, Mo, and V in biowaste were detected, which were not detected in the moist samples. For compost, the element concentrations on a dry matter basis were quantitative for Zn, Cu, Fe, K, Cl, and V for both moist and dry samples and for Ca and Mn in the dry samples. The concentrations were qualitative for Cr and Ca for the moist samples. The RSD values were

higher for biowaste, but Ca, K, Cd, and Cl concentrations in the moist samples and K, Cl, Mo, and V concentrations in the dry samples could still be considered quantitative. On the other hand, Zn concentration in the moist sample and Zn, Cu, Fe, Cr, Ca, and Cd concentrations in the dry sample could only be considered qualitative. More detailed information about the element concentrations of grinded fine fraction, ash and compost can be found in the supplementary data (Tables S4, S5, and S6).

Table 3. Element concentrations (mg/kg) on a dry matter basis determined by FPXRF in dry and moist compost and biowaste samples.

Sample	Pb	As	Zn	Cu	Fe	Mn	Cr	Ca	K	Cd	Cl	V
Compost, moist												
Mean	n.d.	n.d.	313	131	72891	n.d.	171	21088	13415	n.d.	5965	136
Min			229	105	52767		118	15950	10106		5393	96
Max			355	171	95066		282	82195	14623		7244	160
SD			31	18	8043		36	13963	896		382	16
RSD			313	131	72891	n.d.	171	21088	13415	n.d.	5965	136
Compost, dry												
Mean	n.d.	n.d.	322	153	73517	231	169	19049	14640	n.d.	5801	140
Min			236	117	52773	140	97	16149	13238		4524	89
Max			371	197	83051	327	280	22173	15838		7544	187
SD			33	24	7176	43	39	1680	851		732	23
RSD			322	153	73517	231	169	19049	14640	n.d.	5801	140
Biowaste, moist												
Mean	n.d.	n.d.	74	n.d.	12419	n.d.	n.d.	14861	7587	31	5067	n.d.
Min			38		7704			10064	6257	22	3883	
Max			123		15905			18708	10263	43	7771	
SD			22		2473			2339	876	5	1036	
RSD			30%		20%			16%	12%	15%	20%	
Biowaste, dry												
Mean	n.d.	n.d.	116	53	14148	n.d.	88	11100	8872	17	4172	47
Min			75	35	10235		64	8918	6160	12	3145	38
Max			164	98	22365		100	17891	11242	25	5052	61
SD			24	16	3009		20	2331	969	4	451	8
RSD			21%	31%	21%		23%	21%	11%	21%	11%	17%

n.d. = not detected, Min = minimum, Max = maximum, SD = standard deviation, RSD = relative standard deviation

3.2 The results of ICP-MS and ion exchange-chromatography

The elemental concentrations of SRF ground fine fraction, compost, and ash were analyzed with ICP-MS and IC (for Cl). The linear regression between FPXRF and ICP-MS measurements could only be performed for Ca, Cr, Fe, Cu, Zn, and V and between FPXRF and IC for Cl because the FPXRF was unable to measure other elements across the entire range of these waste materials (ground fine fraction reject, ash, and compost). Table 4 summarizes the concentrations of these elements and of Pb and As, where comparisons between FPXRF and ICP-MS could be made for ash and ground fine fraction reject, as well as the concentrations of Cd, where a comparison could be made for ground fine fraction reject.

More detailed information about the element concentrations measured by ICP-MS can be found in the supplementary data (Tables S7, S8, and S9). The RSD values of element concentrations in ash were lower than in ground fine fraction reject and compost, highlighting the more homogeneous nature of ash compared with the other two materials. The RSD values of element concentrations in the ash samples were below 10% for almost all elements (Table 4) and below 20% for the rest of the elements. The compost samples performed relatively well, and besides As and Ca, the concentrations of all the other elements were below 20%. Fine fraction reject could be considered the most heterogeneous of all tested materials since its RSD was below 20% only for As, Ca, Cl, and V.

Table 4. Element concentrations (mg/kg) determined by ICP-MS and IC (Cl).

Sample	Pb	As	Zn	Cu	Fe	Mn	Cr	Ca	Cd	Cl	V
Ground fine fraction reject											
Mean	115	12	948	2520	14008	582	418	49337	3	1684	20
Min	54	9	513	305	7305	414	162	42265	1	1660	15
Max	495	16	2935	12017	48075	747	2252	59740	22	1702	26
SD	121	2	729	3560	11280	107	586	5031	6	21	3
RSD	105 %	17 %	77 %	141 %	81 %	18 %	140 %	10 %	222 %	1 %	16 %
Ash											
Mean	274	29	1490	413	42753	3446	221	85375	3	1709	38
Min	232	27	1361	361	40721	3222	206	81206	3	1677	36
Max	350	30	1652	515	45617	3703	252	90245	3	1743	41
SD	32	1	87	53	1501	131	15	3231	0	33	2
RSD	12 %	2 %	6 %	13 %	4 %	4 %	7 %	4 %	3 %	2 %	4 %
Compost											
Mean	17	6	408	178	82722	527	46	33662	0	6062	44
Min	10	3	260	111	54089	350	28	18212	0	5759	28
Max	24	9	457	208	95380	598	52	60592	1	6574	49
SD	3	1	54	26	11225	66	6	11436	0	446	6
RSD	19 %	24 %	13 %	15 %	14 %	12 %	14 %	34 %	16 %	7 %	13 %

Min = minimum, Max = maximum, SD = standard deviation, RSD = relative standard deviation

3.3 Box plot analysis

The results of the ICP-MS and the FPXRF measurements for ground fine fraction reject are summarized in the box plots presented in Figure 1. The boxes represent the first and the third quartiles, and the line in each box signifies the median. The vertical lines above and below the boxes extend to the highest and the lowest data points, respectively, within 1.5 times the interquartile range (IQR), while the values outside this range are presented as outliers. The results of the ICP-MS measurements for ground fine fraction reject revealed the homogeneous nature of the fine fraction reject because besides Mn and V, all the other elements had outliers, some of which considerably differed from the average, such as Cd, whose outlier was eight times larger than the average. This outcome was also evident in the RSD values of the ICP-MS measurements (Table 3), which were highest for ground fine fraction reject. The FPXRF measurements were closest to those of ICP-MS for Ca and Zn, with the averages

being 20% lower than for ICP-MS. The largest difference was for V and Cd, where FPXRF indicated 600% higher average concentrations.
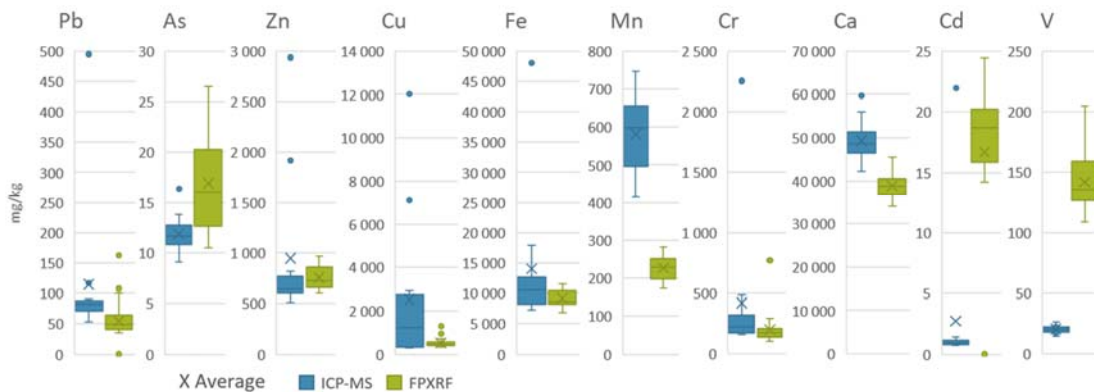

Figure 1. Box plots of ICP-MS and FPXRF measurements for ground fine fraction reject (the dots represent outliers).

The results for the fine fraction reject can be compared to those of the study by Burlakovs et al. (2015), who used FPXRF to measure the reject from landfill mining. Their study found that Ca and Fe concentrations could be reliably measured by FPXRF. Moreover, Pb, Zn, Cu, Mn, and Cr could be screened by FPXRF, but the use of laboratory methods might be necessary to verify the results (Burlakovs et al., 2015). Their study's findings are supported by those of this present study concerning the screening of Pb, Zn, Cu, Mn, and Cr values despite the higher variations among the element concentrations. One reason for this difference could be the pretreatment of the samples in the study of Burlakovs et al. (2015).

Figure 2 presents the box plot analysis of the ash measurements using ICP-MS and FPXRF. The measurements by ICP-MS showed lower variations compared with ground fine fraction reject, and there were also not as many outliers. On the other hand, the FPXRF measurements had more outliers than in the case of the ground fine fraction reject. The FPXRF measurements resulted in higher concentrations of all elements, and the average concentration was closest to that of the ICP-MS measurement for Ca, which was 11% higher in FPXRF. Similar to the ground fine fraction reject, the largest difference was for V, where FPXRF showed 700% higher results. One reason for the differences between the results could be unburned carbon since Xing et al. (2016) found that unburned carbon in biomass ash could lead to inaccurate results for XRF, and heating at 815 °C could improve the consistency and the reliability of ash analysis.
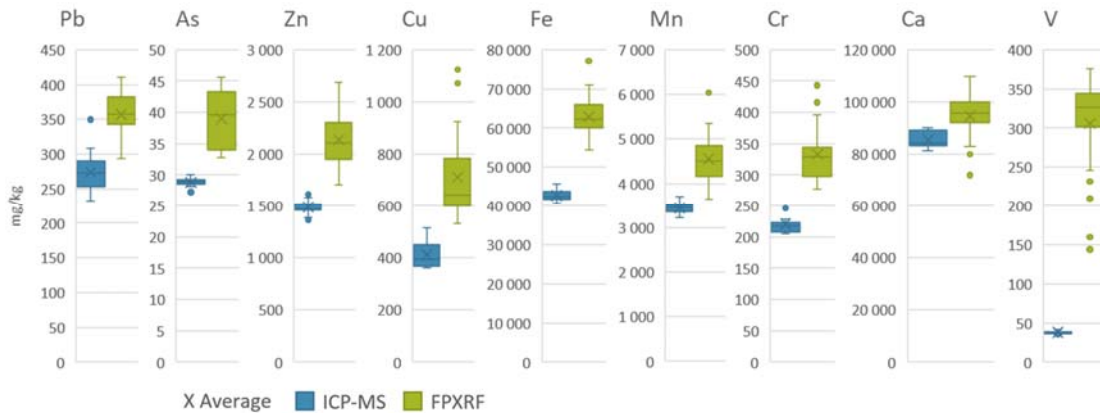
Figure 2. Box plots of ICP-MS and FPXRF measurements of ash (the dots represent outliers).

Figure 3 illustrates the box plot comparison of the results between FPXRF and ICP-MS measurements for compost. Figure 3 clearly shows that ICP-MS results in higher values than FPXRF for the majority of the elements and that the middle 50% of the data overlaps only slightly with Cu. The differences between ICP-MS and FPXRF averages are below 10% only for Fe and Cu but above 200% for V and Mn.
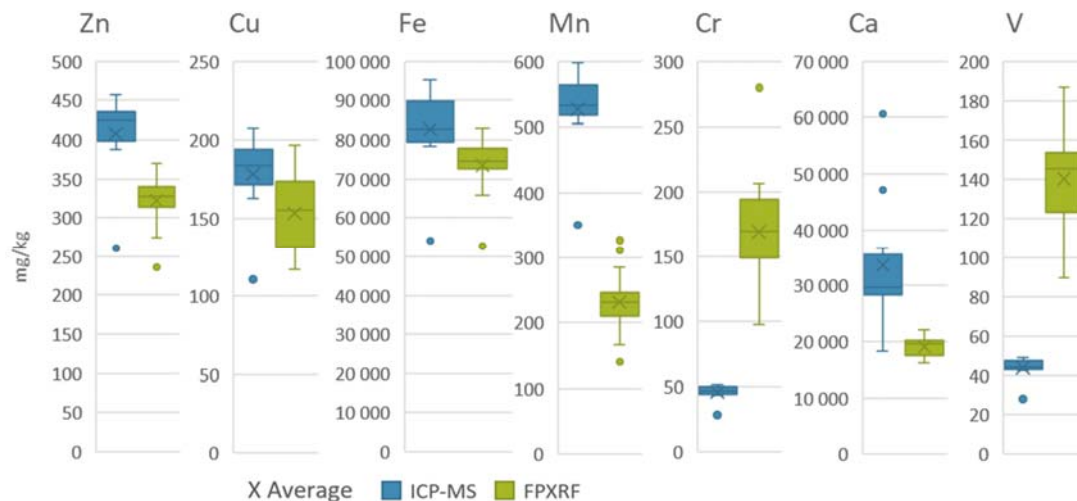

Figure 3. Box plots of ICP-MS and FPXRF measurements of compost (the dots represent outliers).

The compost measurements can be compared with those of the study conducted by McWhirt et al. (2012). They evaluated compost element concentrations by using portable X-ray fluorescence spectrometry (PXRF) and compared the results with inductively coupled plasma atomic emission spectroscopy (ICP-AES). Their results showed high RSD values, 70% and higher, for all elements when measured with PXRF, whereas this present study showed much lower RSD values, ranging from 6% to 23%. The much larger RSD values obtained by McWhirt et al. (2012) could be due to their much wider base of raw materials used for compost, such as biowaste, animal manure, wood chips, and industrial sludge. In this present study, the compost consisted of biowaste, sludge, and garden waste from municipal sources. Weindorf et al. (2008) also compared XRF results with those of ICP-AES and found that XRF was useful for screening excess levels of Ni, Cu, Zn, and Pb, for example, but more accurate

results and a larger list of elements would require the use of ICP, especially at lower concentrations.

3.4 Limits of agreement and regression analysis

The results of the agreement analysis by using the Bland-Altman plot analysis are shown in Table 5, and the Bland-Altman plots are illustrated in the supplementary material (Figures S2 and S3). The mean of the differences shows that on average, FPXRF obtains lower results than those of ICP-MS for Ca, Cr, Fe, and Cu but higher results for Cu, Zn, and V. FPXRF also obtains higher results than those of IC for Cl. The lower and the upper LA values indicate a high range of the difference between FPXRF and ICP-MS results. The range between the lower and the higher limits is 0.98 to 15 times the range between the average minimum and maximum values measured with ICP-MS, being lowest for Ca. For example, for Ca, FPXRF can obtain 33690 mg/kg lower or 19511 mg/kg higher results, leading to a difference of 53201 mg/kg, while the difference between the average minimum and maximum values measured with IPC-MS is 54106 mg/kg. These findings indicate that there is not acceptable level of agreement between the measurement methods for the examined element measurements since the differences are too large.

Table 5. Results of Bland-Altman analysis of agreement between FPXRF and ICP-MS/IC (mg/kg).

	Ca	Cr	Fe	Cu	Zn	V	Cl
Mean of difference	-7 090	-18	-7 313	-601	83	127	507
SD of difference	13 572	212	25 697	1 561	460	106	2 097
Limits of agreement							
Lower	-33 690	-434	-57 678	-3 660	-820	-81	-3 603
Upper	19 511	397	43 051	2 458	985	335	4 616

Table 6 summarizes the results of the regression analysis between FPXRF and ICP-MS measurements for Ca, Cr, Fe, Cu, Zn, and V and between FPXRF and IC for Cl in SRF ground fine fraction, compost, and ash samples. According to the R^2 value, only Ca could be determined as definitive, Zn could be deemed quantitative, Fe is close to being quantitative, and the rest of the elements (Cr, Fe, Cu, V, and Cl) could be categorized as only qualitative. When considering both the R^2 and the RSD of the FPXRF results (Table 2), the results are similar; only Ca could be classified as definitive and Zn as quantitative. McWhirt et al. (2012) found higher R^2 values for the regression between the PXRF and the ICP-AES measurements of elemental concentrations in compost (0.78 to 0.92 for Ca, Cr, Cu, Fe, and Zn), but the agreement between the results was not studied.

Table 6. Results of regression analysis between FPXRF and ICP-MS/IC measurements for SRF fine fraction, ash, and compost samples.

	Regression analysis		
Element	R^2	Slope	y-intercept
Ca	0.95	2.09	-5.28
Cr	0.41	0.34	1.51
Fe	0.69	0.90	0.39
Cu	0.37	0.55	1.01
Zn	0.88	1.62	-1.89
V	0.00	-0.12	2.30
Cl	0.19	0.05	3.40

The test of the agreement reveals that the results obtained by the two methods are unacceptably divergent. Additionally, regression analysis shows a linear correlation only with Ca and Zn values. This finding would indicate that a linear correction could be possible for Ca and Zn values to be used to transform FPXRF results to be comparable to ICP-MS results, but this seems impossible for the rest of the elements used in the regression analysis. The regression curves of Ca, Zn, and Fe are presented in the supplementary material (Figure S4).

3.5 Limitations and benefits of FPXRF

Both the physical and the chemical properties of the samples affect measurement accuracy. Based on the RSD values, the FPXRF method can be best applied to waste samples such as ash and compost because they are relatively homogeneous, dry, and have relatively uniform and small particle sizes. This method is not as suitable for biowaste because it is very heterogeneous and has a variable particle size. For the same reasons, the method is also inappropriate for coarse SRF fine fraction reject. FPXRF can be used for qualitative measurements of different types of samples. However, quantitative measurements are more challenging because the number of factors can affect the measurement results (Hou et al., 2004). The sample's moisture content, chemical and physical matrix effects (e.g., inter-element effects, particle size, and homogeneity), instrument resolution, and inconsistent positioning of samples are some examples of these factors (Gutiérrez-Ginés et al., 2013; Hou et al., 2004; Kalnicky and Singhvi, 2001). The reliability and the accuracy of the FPXRF measurement depend on the time used for a single measurement, calibration and reference standards, and pretreatment (e.g., drying, sieving, and homogenization) (Hou et al., 2004; Kalnicky and Singhvi, 2001). In addition, according to the results by Ravansari and Lemke (2018), the organic content of the sample has also elementally dependent response on the FPXRF results.

The FPXRF analysis could provide an alternative analysis method from the green analytical chemistry point of view (Armenta et al., 2008). The need for toxic reagents would be reduced if for example ICP-MS measurements could be reduced or replaced by FPXRF. The device used for the pretreatment of samples for ICP-MS needs strong acids while ICP-MS requires argon in the measurements. These both could be reduced if FPXRF could replace some ICP-MS measurements. Gałuszka et al. (2013) proposed 12 principles of green analytical chemistry and FPXRF could fulfill at least following ones: avoiding analytical waste, minimizing the use of energy and eliminating toxic reagents.

4 Conclusions

The standard laboratory methods provide accurate results for waste measurements, but these methods can be expensive and time-consuming. However, to determine more accurately those portions of waste materials that are or could be suitable for utilization, faster real-time measurement methods are needed. Portable spectrometric measurement devices could meet the demand by allowing a large number of measurements to produce data about the variations and the averages of the properties. However, it should be borne in mind that the sample moisture content, particle size, homogeneity and organic content of sample affect to the

FPXRF measurement results. According to the results obtained in the present study, FPXRF obtains the lowest RSD values for ash samples and the highest values for the coarse fine fraction reject. The variations in element concentrations are lowest for ash, both with FPXRF and ICP-MS. The closest results between the two methods are for Ca.

The analysis of the LA between FPXRF and ICP-MS shows that the upper and the lower limits for most of the elements are divergent and that FPXRF is mainly suitable for qualitative assessment. The regression analysis indicates a linear correlation between FPXRF and ICP-MS results for Ca and Zn values, which could be used in making linear corrections for FPXRF results. Keeping the limitations in mind, FPXRF could be used for qualitative analysis in waste treatment processes, such as first quality control of waste material in waste treatment plants and landfills. In this kind of first quality control, lower cost, speed, and portability could be more important than losses in accuracy. For example, the materials suitable for further utilization (with detected concentrations well below the limits) could be directed to a different pile, separate from the materials requiring further analysis (with concentrations close to the limits). Although the FPXRF measurements could not fully replace the traditional laboratory analysis, they could reduce the number of the latter.

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