Review

Portable X-ray Fluorescence Analysis of Organic Amendments: A Review

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Featured Application: Portable X-ray fluorescence could be used for precise elemental analysis of organic amendments and compost. The analysis could be achieved without prior sample preparation and very quickly (a few minutes) which would allow fast decision making.

Abstract: Portable XRF spectrometry (pXRF) has recently undergone significant technological improvements and is being applied in a wide range of studies. Despite pXRF advantages, this technique has rarely been used to characterize organic amendments and residues. This article reviews those studies undertaken to date in which pXRF is used to characterize these products. Published studies show that pXRF correctly measures elements such as Fe, Pb, Zn, Mn, Ca, and K but gives conflicting results for elements such as Cr, Ni, and As. Among the reasons that may cause the low performance of the technique with certain elements or under certain measurement conditions would be the inadequacy of the analytical comparison procedures used (i.e., digestion with *aqua regia*), the lack of knowledge of the interfering effects of organic matter, and sample moisture on the XRF signals and the need for a standardized protocol for performing the measurements. However, the speed and low cost of the procedure forecast a greater future use of this technique, especially in cooperation with other fast spectroscopic techniques based on near-infrared (NIRS) or mid-infrared (MIR) spectroscopies. Chemometric procedures based on one or more of these techniques will allow the prediction of elements below the detection limit of pXRF instruments (Cd, Hg), or other properties of organic amendments (organic matter, N, electrical conductivity, cation exchange capacity).

Keywords: biosolids; compost; hand-held XRF; manure; pXRF

1. Introduction

On a global level, legal regulations within the framework of correct waste management are, fortunately, increasingly numerous and detailed in their requirements. Compliance with waste management requirements requires the characterization of the waste being handled, and for doing this the fastest possible analytical procedures are essential. In particular, under the premises of the circular economy, many states have established regulations that favor the recycling of organic matter and nutrients contained in organic waste, such as manure, sewage sludge, and selectively collected municipal waste. While setting the agronomic quality of organic waste and its derived products (compost, growing media, amendments, and organic fertilizers) to maintain a high environmental quality standard, these regulations emphasize the absence of elements and potentially polluting substances, among which are heavy metals and various trace elements.

In recent years, portable XRF spectrometry (pXRF) has undergone significant technological improvements and is applied in a wide range of studies [1,2]. The technique is being applied in fields such as archaeology, mining and geology, environment, and for the elemental analysis of various materials (alloys, rocks, soils, and sediments, among others) The pXRF technique has several important advantages over conventional laboratory analysis procedures if applied to organic amendments:

- It is very fast and allows you to obtain results in minutes;
- Pre-sample preparation can be significantly reduced. Although it may be convenient to carry out the sample drying and grinding steps, the laborious digestion steps are avoided;
- Hardly any laboratory waste is generated (in particular, acid digestion solutions are avoided), making it a green laboratory technique;
- Used in the laboratory, the space required is much less than that required by other conventional techniques;
- Under proper supervision, the personnel performing the measurements do not require advanced training in analytical techniques;
- The price of the equipment is less than that of conventional techniques, which, together with its greater speed, lowers the unit costs of analysis;
- Its use in the field allows, at least qualitatively, on-site verification, in situ decision-making, or the selection of the most appropriate samples for a broader study.

1.1. Fundamentals and Evolution of pXRF

Portable X-ray fluorescence spectrometry allows the identification and quantification of elements from Mg to U in the periodic table. The primary X-rays are incident on the sample and, as a result, the absorption of an incident X-ray photon by an atom takes place as long as its energy is greater than the binding energy of the core-shell electron. The absorption of incident photons results in the emission of the core-shell/subshell electron (also known as a photoelectron), leaving a core-shell/subshell vacancy (i.e., the atom is in an excited state). XRF emissions occur in the aftermath of absorption by two competitive atomic de-excitation processes: (1) characteristic or X-ray fluorescence (XRF) and (2) Auger electron emissions. Both processes imply an electron transition from an upper subshell to a lower one within the atom. They are the basis of spectroscopic methods to identify the atom since both the XRF photons and the Auger electron have unique energies characterizing the electron transition in the given atom. XRF spectroscopy methods, however, are more practical than Auger electron spectroscopic methods due to the high attenuation of electrons in matter. The de-excitation transitions occur at characteristic energies unique to each particular element, so XRF can be used to determine the elements in the sample. In modern portable instruments, the primary X-ray radiation is generated in a vacuum-tight tube containing a cathode (Figure 1). The small coin-size of the field-emission X-ray tubes and their much simpler design than the large Coolidge-type tube used in industrial or diagnostic X-ray imaging applications allowed miniaturization. A high voltage of 20–60 kV accelerates the electrons towards a metal (such as Ag, Rh, Ta, Au, W, and others) target anode. When the electrons collide with the metal target, X-rays corresponding to characteristic K and L line fluorescence of the target atoms and a lower intensity continuum are produced.
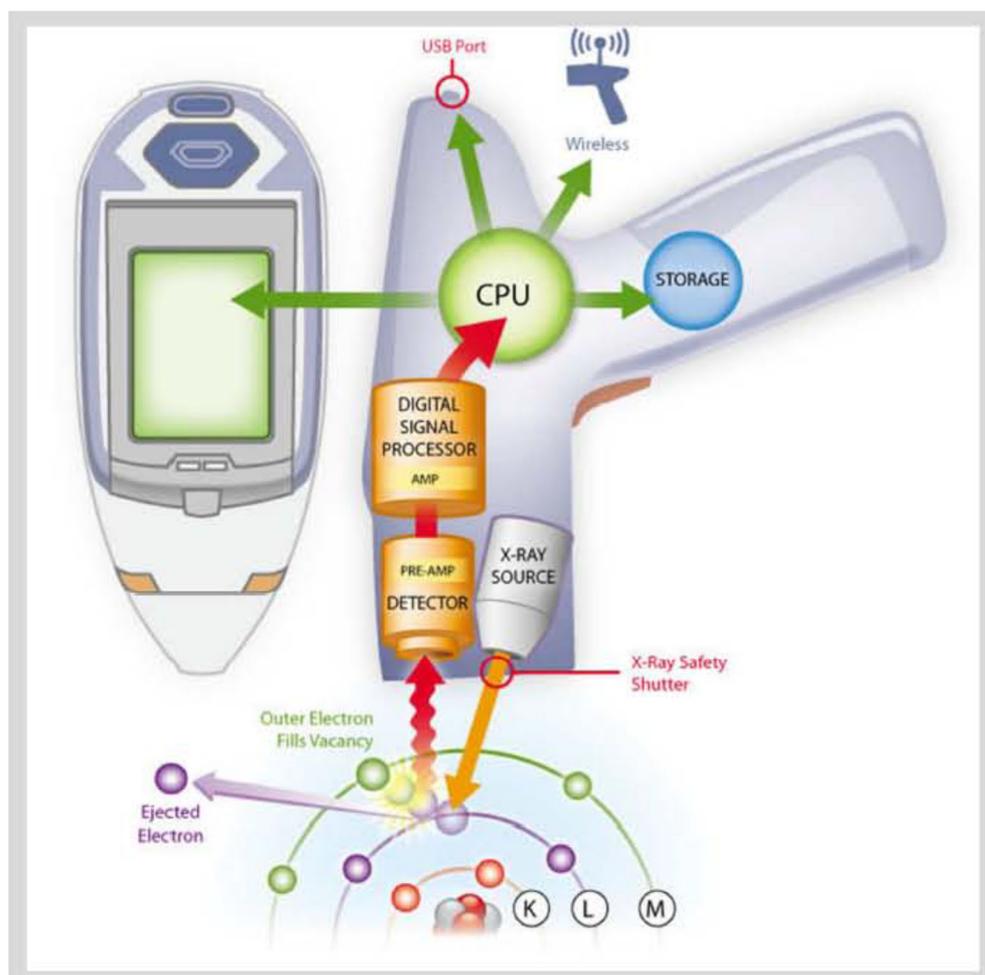
Figure 1. Functional schematic of a portable pXRF instrument (with permission of ThermoFisher, Waltham, MA, USA).

It is possible to find the fundamentals of X-ray spectrometry in the classic book of Jenkins [3], detailed descriptions of technological aspects in the Beckhof et al. handbook [4], recent developments of pXRF in reviews such as those of Vanhoof et al. and West et al. [5,6], and some others specific to fields such as geochemistry [7] and soils and environmental samples [8]. It is also possible to find interesting reviews focused on the historical development of the technique, such as that by Bosco G.L. [9], who reported on the 2012 James L. Waters Symposium. Bosco's review described the development and commercialization of portable, hand-held X-ray fluorescence (XRF) spectrometers, the birth and the maturation of pXRF spectrometers, the performance improvements in miniature X-ray sources made by his company, Moxtek, the development of detectors, and the evolution of analytical capabilities of pXRF analyzers. In the symposium summarized by Bosco [9], Lee Grodzins described the birth and the maturation of hand-held XRF spectrometers. The development of hand-held XRF devices is mostly due to Dr. Lee Grodzins, Professor of Physics at MIT, who founded the Niton Corporation in 1986. Among many awards, Lee Grodzins received the 2021 Birks Award for his contributions [10] to the development of portable XRF devices.

1.2. Reference Procedures for Organic Amendments

The standardized procedures for the determination of the content of heavy metals and other properties in compost and organic amendments usually imply the previous drying and grinding (at least to less than 0.5 mm) of the sample. The sample is then digested in strong acids. For most metals, two digestion procedures are available. Probably, the digestion with *aqua regia* (EN 13650:2001 [11], ISO 54321 [12]) is the most widely used. The European procedures are equivalent to US EPA methods 3050B and 3051 [13] intended for sediments, sludges, soils, and oils. These procedures will not totally dissolve most soil improvers or growing media, and the efficiency of extraction for particular elements differs from element to element and might also differ for the same element in different matrices. The very strong acid digestion will dissolve almost all elements that could become "environmentally available", but elements bound in silicate structures are not normally dissolved by these procedures as they are not usually mobile in the environment. Therefore, the concentration of extractable elements in *aqua regia*, which is sometimes called "*pseudo-total* concentration" cannot be considered as "total" but rather represent a fraction, greater or lesser depending on the chemical structure of the sample constituents. Complete digestion, including silicates, could be achieved by procedure EN 13656:2020 [14] which uses a mixture of hydrochloric (HCl), nitric (HNO3), and tetrafluoroboric (HBF4) or hydrofluoric (HF) acids, or by the alternative US EPA method 3052 [13] which is applicable to the microwave-assisted acid digestion of siliceous matrices (ashes, sediments, and soils), and organic matrices (biological tissues, oils, oil contaminated soils, sludges, and other complex matrices) if a total decomposition analysis is required. Elements extractable by these procedures can be described as "total". The following methods of the United States Composting Council [15] are equivalent to US EPA methods and also contemplate the use of hydrofluoric acid for siliceous matrices: 04.12-A (Microwave-Assisted Nitric Acid Digestion of Compost), 04.12-B (Nitric Acid Digestion of Compost and Soils), 04.12-C (Dry Ash Sample Digestion for Plant Nutrients), and 04.12-E (*Aqua Regia* Procedure).

After sample digestion, element concentrations can be measured by inductively coupled plasma optical emission spectrometry (ICP-OES) or other adequate techniques.

Recently, spectroscopic methods such as near-infrared spectroscopy (NIRS) and Fourier-transform infrared spectroscopy (FTIRS) have been proposed for compost analysis [16]. While pXRF is an elemental detection and quantitation technique, the infrared spectroscopies identify molecules via quantized absorption of infrared light by molecules in their transitions between various vibration/rotational quantum states. The resulting spectra can be linked to several measured compost indicators. NIRS and FTIR can be used as an estimate of the compost indicator if good correlation between the spectral signal and the indicator is obtained. The spectroscopic measurements thus allow for fast screening of chemical properties and compost stability and are time and cost efficient.

There are two standard European protocols for applying XRF to residues. The standard EN 15309:2007 [17] specifies the procedure for a quantitative determination of major and trace element concentrations in homogeneous solid waste, soil, and soil-like material by energy dispersive X-ray fluorescence (EDXRF) spectrometry or wavelength dispersive X-ray fluorescence (WDXRF) spectrometry using a calibration with matrix-matched standards. The procedure is therefore the standardized method for laboratory instruments and requires careful and time-consuming sample preparation. The method is applicable for the elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, Ta, W, Hg, Tl, Pb, Bi, Th, and U at concentrations between approximately 0.0001% (10 mg kg^{-1}) and 100%, depending on the element and the instrument used. The XRF standard EN 16424:2014 [18,19] is dedicated to pXRF field equipment (hand-held or desktop portable) and specifies a detection method for the determination of the elemental composition of waste materials for on-site verification. The absence or presence of specific elements is shown qualitatively with an indication of the concentration level. This method is intended for rapid and exploratory analysis of pasty or solid materials.

Equivalent to standard EN 16424:2014, although intended for field determination of elemental concentrations in soils and sediments, the USEPA Method 6200 [20] describes in detail the application of pXRF, providing information that should be known by anyone who intends starting on this technique.

XRF-based procedures determine total concentrations of the elements. Therefore, comparison of results obtained with XRF with those obtained by incomplete digestions (such as *aqua regia*) should be made with caution. In particular, there could be differences in the elements associated with the crystal lattices of silicates and other hardly soluble minerals, which would result in lower values when the digestions are used.

One of the most common concepts needed for the validation of analytical methods is the limit of detection (LOD). The LOD can be interpreted as the smallest amount or concentration of analyte in the test sample that can be reliably distinguished from zero [21]. A common related concept is that of limit of quantification (LOQ), which is the concentration or amount below which the analytical method cannot operate with an acceptable precision. LOQ and LOD can be calculated by the following equation [21,22]:

$$LOQ = 10 \ \sigma_Q \approx 3 \ LOD, \tag{1}$$

where σ_Q is the standard deviation when the signal is at LOQ.

The standard deviation can be calculated from replicate analyses of a low-concentration sample. Nevertheless, USEPA method 6200 [20] recommends that actual measured performance will be obtained on a certified reference material of the appropriate matrix and within the appropriate calibration range for the application. This is considered the best estimate of the true method sensitivity, as opposed to a statistical determination based on the standard deviation of replicate analyses of a low-concentration sample.

1.3. Legislative Framework

This section summarizes the current regulations in the European Union regarding organic amendments, organic fertilizers, growing media, and sewage sludge. The limit values for potentially toxic elements (PTEs) (Table 1) have been taken from these regulations and will be compared in the results section with the LOQ.

Table 1. Maximum allowable concentrations (mg kg^{-1}) of potentially toxic elements in organic amendments in the European regulations.

	Limit	Product	Ref.
As	40	Organic fertilizer, organo-mineral fertilizer, organic soil improver, growing media, plant biostimulant	[23]
Cd	1.5	Organic fertilizer	[23]
	3	Organo-mineral fertilizer ($P_2O_5 < 5\%$)	[23]
	2	Organic soil improver	[23]
	1.5	Growing media	[23]
	1.5	Plant biostimulant	[23]
	1	Ecolabel for soil improvers, mulch and organic constituents of growing media	[24]
	3	Ecolabel for growing media, including mineral growing media	[24]
	20–40	Sewage sludge	[25]
Cr	100	Ecolabel for soil improvers, mulch and organic constituents of growing media	[24]
	150	Ecolabel for growing media, including mineral growing media	[24]
Cu	300	Organic fertilizer, organic soil improver	[23]
	600	Organo-mineral fertilizer, plant biostimulant	[23]
	200	Growing media	[23]
	100	Ecolabel for soil improvers, mulch and organic constituents of growing media, and growing media, including mineral growing media	[24]
	1000–1750	Sewage sludge	[25]
Hg	1	Organic fertilizer, organo-mineral fertilizer, organic soil improver, growing medium, plant biostimulant	[23]

		Ecolabel for soil improvers, mulch and organic constituents of growing media, and growing media, including mineral growing media	[24]
	16–25	Sewage sludge	[25]
Ni	50	Organic fertilizer, organo-mineral fertilizer, organic soil improver, growing medium, plant biostimulant	[23]
	90	Ecolabel for soil improvers, mulch and organic constituents of growing media, and growing media, including mineral growing media	[24]
	300–400	Sewage sludge	[25]
Pb	120	Organic fertilizer, organo-mineral fertilizer, organic soil improver, growing medium, plant biostimulant	[23]
	100	Ecolabel for soil improvers, mulch and organic constituents of growing media	[24]
	150	Ecolabel for growing media, including mineral growing media	[24]
	750–1200	Sewage sludge	[25]
Zn	800	Organic fertilizer, organic soil improver	[23]
	1500	Organo-mineral fertilizer, plant biostimulant	[23]
	500	Growing media	[23]
	300	Ecolabel for soil improvers, mulch and organic constituents of growing media, and growing media, including mineral growing media	[24]
	2500–4000	Sewage sludge	[25]

It is necessary to indicate here that XRF is not considered in European legislation as an accepted procedure for the analytical characterization of organic amendments and fertilizers. It is also an unknown procedure for use in compost and other organic amendments in scientific and technical publications, with a few exceptions that will be cited in this review. An example is a recent report by Amery et al. [16] which indicated that heavy metal contents in the compost can be determined on a dried and ground sample after the destruction of the sample in strong acids, e.g., *aqua regia*. This report, while mentioning spectroscopic methods as indicated before, only considers near-infrared spectroscopy (NIRS) and Fourier-transform infrared spectroscopy (FTIRS).

1.4. Objectives

Despite its advantages, pXRF has rarely been used for the characterization of organic amendments and organic residues. This review includes the studies undertaken to date in which pXRF is used for these materials. A summary of the main results and conclusions of the commented studies is given, with special mention of the handicaps that make the results not entirely accurate for certain samples or elements analyzed. Interference effects on measurements due to sample moisture (unavoidable under the context of an in situ use), organic matter content, and other measurement conditions are discussed. Due to the small number of studies performed in organic matrices, previous studies undertaken in other matrices, such as soils and sediments, are used. Finally, the future possibilities of the technique for its use in the characterization of organic amendments will be critically evaluated.

2. Materials and Methods

We followed the extension PRISMA-S [26] of the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines [27].

2.1. Information Sources and Methods

The electronic databases Scopus and Web of Science were systematically searched from inception to 19 April 2022 and 22 April 2022, respectively.

2.2. Search Strategies

Database search terms are indicated in Appendix A.

The term "portable" applied to XRF refers both to laboratory equipment that is small in size but can be transported and to true portable equipment (gun type), hand-held instruments designed for use in the field. Frequently, no distinction is made between the

two types, designating as pXRF that which is strictly hand-held XRF. In any case, the search was performed with both terms. Beyond the distinction between hand-held or portable laboratory equipment, this review aims to include those instruments for which typical sample preparation for XRF, such as pressed or bound bead preparation, is not required. On the contrary, equipment in which measurements are made on the samples as they are or dried and ground to a fine powder are considered.

Several related articles not found in the primary search have been included. These have generally been articles or reviews in which the test samples were soils, but with the characteristic of high content of organic matter. These articles have been located from the references cited in the primary articles of the search.

2.3. Eligibility Criteria

The articles reviewed were selected after reading the titles and abstracts. Several unrelated articles dealing with other types of samples unrelated to our goal were discarded. The following inclusion criteria were also followed: the full text of the article was available, it was published in a peer review journal, and it had been written in English.

No quality assessment of the studies was performed a priori.

3. Results and Discussion

The basic search in SCOPUS provided 23 records of which only 13 papers [28–40] deals with organic amendments. The other papers focused on soils or archaeological studies and were discarded. The basic search in Web of Science provided 18 records, of which there was only one additional congress communication [41] to those of the search in SCOPUS. The other papers focused on soils or archaeological studies and were discarded. Table 2 shows a summary including the most relevant details of these studies.

3.1. Determination of Elemental Content with pXRF

In addition to the results of the indicated searches, the oldest study that we know which uses pXRF in manure compost samples is that of Weindorf et al. (2008) [42]. This article does not appear in the database searches performed, possibly because it does not include the search terms among its keywords or its title. The study evaluated the LOD of the pXRF technique on compost concerning EPA-regulated metals and concluded that the LOD of Ni, Cu, Zn, Se, Mo, and Pb were enough to use the technique as a screening tool. On the contrary, pXRF was not effective at detecting Hg, Cd, or As. Leaving aside the different legal regulations and the different instruments involved, the impossibility of determining the metals Cd and Hg in these matrices coincides with what is stated in Section 3.3.

Chronologically, the following study on the subject is that of McWhirt et al. [28] in 2012. The authors calculated LOD in compost samples for the elements As, Ca, Cd, Cr, Cu, Fe, K, Mn, P, and Zn and stated substantial improvements for all elements compared to the previous study by Weindorf [42] attributable to improvements in technology. Their conclusion was that pXRF was able to acceptably quantify Ca, Cr, Cu, Fe, K, Mn, P, and Zn in dry samples but the divergences were important for As and Co.

Healy et al. [39] characterized metals in Irish sludges that had undergone treatment by thermal drying, lime stabilization, or anaerobic digestion. Correlation coefficients between pXRF and ICP-MS (*aqua regia* digestion) results indicated the suitability and satisfactory use of the pXRF technique for the quantification of Fe, Cu, Se, Zn, and Pb (r > 0.90). However, it should be noted that the regulated levels in sludge are higher than for other amendments (Table 1).

Shand and Wendler [43] used pXRF for soil analysis but, being Scottish peat soils with very high OM contents, it is really equivalent to the matrices we consider in this review. Shand and Wendler determined the LOD in the organic soils and found values below 5 mg kg^{-1} for Cr, Ni, Zn, As, and Sr, values between 5–10 mg kg^{-1} for Cu, and values

between 10–15 mg kg^{-1} for Mn and Pb. These LOD indicated better sensitivity for Cr, Ni, and Zn and worse for Mn and Pb (and also Fe and Ca) compared to the previous McWhirt study [28]. The authors compared the concentrations of K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, and Pb determined by pXRF with *pseudototal* concentrations determined by *aqua regia* extraction and ICP-OES. Their results indicated that the in-built calibrations of the instrument were not adequate for these organic soils and should be modified. The authors indicated that mineral or peat soils were not completely dissolved by the *aqua regia* reflux procedure they used, leaving behind undissolved refractory minerals such as quartz and feldspars, so comparison of *aqua regia* extraction with pXRF analysis is not straightforward. Nevertheless, the authors attribute the difference between the pXRF vs. *aqua regia* extractable analysis to matrix effects in the pXRF and not to low recovery by *aqua regia*/ICP analysis.

Although it does not appear in the database searches undertaken, it is necessary to cite the article by Tighe and Forster [44]. The authors applied pXRF to litter analysis and found good results only for the major elements calcium and potassium.

In 2018, two studies by Weindorf et al. [30] and Li et al. [24] adapted methods developed for soils and used elemental data as a proxy for the prediction of derived properties, such as compost electrical conductivity (EC) and cation exchange capacity (CEC), respectively. To calculate the elemental contents, the recovery percentages based upon NIST certified reference material 2711a were used to establish correction factors for each element.

Havukainen et al. [32] compared the concentrations obtained by pXRF with those by ICP-MS (following nitric-hydrochloric acids microwave digestion) in several types of waste: fine fraction reject from solid recovered fuel production, fly ash, biowaste, and compost. The results obtained by the two methods were unacceptably divergent. Regression analysis showed a linear correlation only with Ca and Zn values and, thus, linear correction to transform pXRF results to be comparable to ICP-MS results could be possible for these elements. Nevertheless, pXRF is reported to be best suited for samples such as ash and compost because of their following physical properties: not too moist, quite small particle size, and not too heterogeneous. The authors concluded that various factors such as sample moisture content, physical and chemical matrix effects (e.g., inter-element effects, particle size, and homogeneity), instrument resolution, and inconsistent sample positioning affected the reliability of the measurement.

Thomas et al. [34] used pXRF to measure the total elemental content of soils, crops, and organic fertilizer samples (anaerobic digestate, compost, farmyard manure, and straw). The authors measure several nutrients in the amendments but it is not indicated if another comparison method was used. In the case of soils, it is indicated that a CRM sample was used and that the soil calibration does not predict potassium with accuracy, and underpredicts 2–3-fold.

López-Núñez et al. [33] used the technique for organic samples from an interlaboratory program that determined certified *aqua regia* contents. They found good linear correlations between measured and certified values of 16 elements when corrections were applied to pXRF elemental readings by measurements of other main elements, with silicon content being one of the most influential fitting terms in eight of the modelling equations. These results indicate that the low recovery of the *aqua regia* extraction, due to its inability to dissolve silicates, could be responsible for the poor fit of pXRF results when not compared to total matrix digestion.

In the study by Sapkota et al. [35], the correlations among pXRF and ICP-OES (nitric acid digestion) were strong ($R^2 > 0.90$) for all elements (P, K, Ca, Mg, Fe) except Mg ($R^2 = 0.59$) in dried samples (<10% moisture).

Analogous to the previous study, Horf et al. [40] compared pXRF and ICP-OES and found R^2 above 0.8 for the elements P, K, Mg, Ca, S, Mn, Fe, Cu, and Zn when analyzed in dry manure samples. The authors found a clear tendency of improving regression models due to drying, but the R^2 was satisfactory (only) for K in fresh and liquid samples. Despite

the goodness of the regression coefficients, the slopes of several elements (Ca, Cu, Zn, Fe, K) were greater than unity (greater concentration by pXRF than by ICP-OES). Although the authors indicate that the digestion they applied did not yield total concentrations, they considered this to be a small effect that cannot explain the high slopes and considered the bias to be due to element-specific matrix-dependent effects.

Table 3 summarizes the LOQ of various elements in the references mentioned above and compares them with the lowest value established in the legislation for the most demanding type of amendment (extracted from Table 1). The mean LOQ values obtained by the author of this review in organic amendments (unpublished data) and the values indicated by a manufacturer acquired with a reference soil (not specified) [45] are also included in Table 3. As seen in Table 3, the LOQs for Cd and Hg are well above the corresponding lower legal limit, which invalidates the use of pXRF for these measurements. For Cr and Ni, the LOQs were similar to the maximum value of the bibliographic range, which would allow the technique to be applied to a wide variety of types of amendments. For Cu, Pb, and Zn, the LOQs were below the legal limit which indicates that these elements could be detected up to the regulatory level and accurately determined if an adequate calibration is available for amendments. It should be noted that for Cu, Cr, and Ni, our results in samples of organic amendments led to higher LOQs than the data reported in the literature, which could indicate a more intense interfering effect of organic matter depending on the measurement conditions (in our case, the Soil method, with a Niton XL3t 950s GOLDD +, Thermo Scientific, Billerica, MA, USA).

The LOQs of pXRF or their respective LODs are poorer than those of large laboratory-based XRF instruments or of ICP-related techniques.

Several of the previous studies [28,32,43] also evaluated the influence of other factors that will be outlined in the following sections.

The above studies highlight the limited use of pXRF for the analysis of organic amendments. Despite the fact that the evolution of the technique has led to better detection limits that would have allowed the measurement of almost all the elements of interest in these matrices, the results of the various studies are contradictory. In general, they show important divergences between the results obtained by pXRF and the reference analytical procedure used in each study. There may be different reasons to account for these divergences. One explanation could be the different calibration strategies they have used (Table 2). In a majority of studies, the pre-calibrated method called "Soil" has been used in the instruments, but in some studies other pre-calibrated procedures have been used. More information about pre-calibrated analytical modes in different pXRF instruments and their relevance and applicability to geochemical investigations can be found in a recent review by Laperche and Lemière [2]. On some occasions, calibration corrections based on measurements made in reference samples have been used. Measurement results should have been validated by the analysis of a suitable reference material but this procedure has not always been followed. On many occasions, the CRMs used are soils or sediments in the absence of similar organic materials certified for XRF. It is possible that the different pre-calibrations, by making use of different spectral peaks for the same element and different correction formulas, may give rise to different deviations due to the sample matrix, causing a good fit of some elements in some matrices and not in others. We must assume that the Soil method is adapted to materials such as soils and sediments. The Soil method is based on Compton normalization and provides the best results for a wide range of environmental applications. The Soil method is applicable to measure contents below 1% in samples composed mainly of light elements [2]. Soils and sediments are matrices that usually have contents of the organic fraction an order of magnitude lower than the organic amendments, and we do not know a priori the proper adaptation of the in-built method. In a following section, we will review the studies regarding the influence of the organic content.

In most of the studies discussed, the comparison of methods (pXRF vs. wet chemistry method) was elucidated by calculating the correlation (r) or the regression (r or R^2 and

slope) between both procedures. Especially for the case of comparing a simple or approximate method (as is the case of the pXRF measurement of the elements in concentrations closer to the LOQ) with a more precise one, these statistical parameters are inadequate to determine the similarity of methods, as Altman and Bland revealed in their classic work [46]. It would be necessary to use other methods for the statistical comparison of the procedures.

However, the probable reason for the lack of adjustment between the measurements with pXRF and the chosen reference procedure lies in the different recovery that can be obtained with the different extractant mixtures used (*aqua regia*, nitric acid, with or without hydrofluoric acid (HF)) and even the different extraction conditions (microwave, open digestions). García-Delgado et al. [47] tried different digestion procedures on amendments and found that microwave HF acid mixtures obtained the highest trace element recoveries for all tested metals except Al. They verified that Cr, Fe, Ni, and Pb were mainly associated with the residual fraction of the BCR sequential extraction procedure, suggesting that these metals were primarily contained in silicates and other resistant minerals. García-Delgado et al. [47] found the recoveries for Cr, Ni, Mn, Fe, and Pb were between 11 and 23% greater than for non-HF extractions. The recoveries for Cu, Zn, and Cd were about 10% higher when HF was used. The Si recovery was negligible if HF was not used, while that of Al hardly reached 50%. Similar results were obtained for Cu, Fe, and Al recoveries in a similar work by Sandroni and Smith [48] using a sewage sludge CRM. The acid mixtures with HF more efficiently attacks aluminosilicates and the metals extracted with HF were absorbed into aluminosilicate compounds, so *aqua regia* and nitric acid were not able to extract them completely. We also consider that the degree of recovery of the digestions by any wet method could be related to the minerals present in the organic amendments (the local geology) and that it could therefore be very dependent on the nature of each sample, thus complicating obtaining high correlation coefficients between pXRF and the measurements after digestion. This leads to the fact that, as a general rule, pXRF results tend to be higher than those obtained with acid extractions without HF.

Table 2. Details of the studies that make use of pXRF in organic amendments and soils rich in organic matter.

Sample Type (Number of Samples)	Sample Preparation	Instrument	Mode [1]/Measurements Conditions	Elements Studied/Determined [2]	Ref.
Manure compost (70)	field moisture	Alpha Series Handheld (Innov-X Systems, Woburn, MA, USA	5 min scan	**Cu, As, Zn** ($R^2 > 0.80$); Mn, Fe, Ca ($0.67 > R^2 > 0.51$); K ($R^2 = 0.14$)	[42]
Compost from several feed-stocks (36)	moist and dried	Delta Premium DP-4000 (Olympus Innov-X, Woburn, MA, USA)	Soil, 90 s ×3, repositioning	As, **Ca**, Cd, **Cr, Cu, Fe, K, Mn**, Ni, **P**, Pb, **Zn**	[28]
Biosolids (128)	freeze, dried, and ground	Delta 4000 (Olympus Innov-X, Woburn, MA, USA)	Soil, CRM calibration	Cd, **Cr, Cu, Fe**, Hg, Mo, **Ni, Pb**, Sb, **Se**, Sn, **Zn**	[39]
Topsoil (183) 0.87–98.3% SOM [3]	Dried	S-1 Turbo (Bruker Nano, Berlin, Germany)	Soil 120 s ×2	As, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Sr, Ti	[43]
Litter (48)	dried and ground	Tracer III-V (Bruker Nano, Berlin, Germany)	Flooding or not the system with high-purity helium	**Ca, K**, Fe, Mg, Mn, Na, P, S, Al	[44]
Compost (74)	dried	DP-6000 (Olympus, Waltham, MA, USA)	Soil, 90 s ×3, repositioning	Ca, Cl, Cr, Cu, Fe, K, Mn, Pb, Rb, S, Sr, Ti, V, Zn, Zr	[30]
Compost (74)	dried	DP-6000 (Olympus, Waltham, MA, USA)	Soil, 90 s ×3, repositioning	K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, Sr, Pb	[31]
Waste products	moist and dried in zip-lock bags	Niton XL3t 900s (Thermo Scientific, Billerica, MA, USA)	Mining, 80 s ×3 ×8 scan points	As, **Ca**, Cd, Cl, Cr, Cu, Fe, K, Mn, Pb, V, **Zn**	[32]
Organic amendments		TRACER (Bruker Nano, Berlin, Germany)	Plant and soil calibrations with EasyCal software, 90 s	Ca, Fe, K, Mg, Mn, P, S, Zn	[34]
Compost (32)	dried and ground	Niton XL3t 950s GOLDD + (Thermo Scientific, Billerica, MA, USA)	Soil 90 s ×3, Mining-Cu 120 s, ×3	**Al**, As, **Ba, Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, P, Pb, Rb, S, Si, Sr, Ti**, V, **Zn, Zr, and organic matter content**	[33]
Manure (35)	ground, dried, and moist	Tracer III-SD, SN T3S2102 (Bruker Nano, Berlin, Germany)	With internal vacuum, 180 s ×2	**P, K, Ca**, Mg, **Fe**, and **moisture content (dry samples)**	[35]
Liquid pig, cattle manures, and biogas digestates (62)	liquid, dried, filtered	Niton XL3t Ultra 955 Hybrid (Thermo Fisher Scientific, Waltham, MA, USA)	TestAll Geo, 90 s	P, K, Ca, Mg, S, Mn, **Fe, Cu, Zn** (dry filtered samples)	[40]

Standard reference soil with added organic matter to 30% (60)	ground < 74 μm	Niton XL3t GOLDD+ 950 (Thermo Scientific, Billerica, MA, USA)	Soil, 180 s ×3	As, Cr, Cu, Fe, Mn, Pb, Rb, Sr, Th, Ti, V, Zn, and Zr	[49]
Soils and clay fraction (6)	dried, calcined	Berlin, Germany	--	Si, Al, Fe, Ti, P, and Mn	[50]
Soils up to 45% SOM[3] (110)	dried, calcined	Niton XL3t (Thermo Scientific, Billerica, MA, USA)	Soil	Ni, Cu, Pb, Zn, and Cr	[38]

[1] Mode refers to the pre-calibrated procedure in the instruments; [2] Elements with good correlation/well quantified are in bold. [3] SOM: Soil organic matter.

Table 3. Limits of quantification (LOQ mg kg^{-1}) of elements in organic amendments.

	Min [1]	REF [2]	OA [3]	Ins [4]
As	--	3–21	23	21
Cd	1	18–24	39	36
Cr	100	8–66	135	90
Cu	100	15–39	98	45
Hg	1	--	34	27
Ni	50	10–60	116	90
Pb	100	6–45	27	24
Zn	300	5–30	82	36
Mn	--	9–33	280	195
Fe	--	15–1500	1180	--
K	--	90–1100	1260	--
P	--	150–2100	1390 [5]	900 [5]

[1] Minimum value in EU regulations from Table 1. [2] Range of values reported in the bibliographical references [28,40,43,49]. [3] Average values obtained by the author in organic amendments. [4] Optimal detection limits provided by the manufacturer using Soil analysis mode and a certified reference material or [5] Mining mode.

3.2. Organic Matter Effect

Surprisingly, there are no studies evaluating the effect that organic matter content may have on pXRF readings in organic amendment matrices. To know about this subject, we must consider articles that refer to pXRF use in soils with a high content of organic matter. This effect in soils has been recently reviewed by Silva et al. [51] when evaluating the application of pXRF in tropical soils. There is common agreement that soil organic matter may cause a scattering and attenuation of signals when a soil sample is irradiated by X-rays and that the influence and interference magnitude of soil organic matter are still poorly understood. Consequently, the result for a target element could be modified.

Probably the most detailed study in this regard is that of Ravansari and Lemke [49]. In their study, three organic matter substitutes (cellulose, graphite powder, and confectioner's sugar) were added to a soil standard reference material and the concentrations of 13 elements (As, Cr, Cu, Fe, Mn, Pb, Rb, Sr, Th, Ti, V, Zn, and, Zr) were measured as a function of variable organic matter fractions. Their results demonstrate the attenuation of the pXRF signal with the increase in the organic matter fraction of the sample, although the deviations depend on each element. For example, pXRF-Pb concentrations were not affected, pXRF-As concentrations were underestimated, and Mn showed a more complex behavior, both overestimating and underestimating depending on its concentration. The correction factors for the effect of organic matter were generally less than ±8% for organic matter contents up to 30%.

Costa et al. [50] verified the effect of organic matter removal on oxides determination by pXRF in soil samples (<2 mm) and their clay fraction. The soil organic matter presence led to underestimation of the pXRF results for the lightest oxides (Si and Al) compared to the heaviest oxides (Fe, Ti, and Mn) which were less affected. Soil organic matter in these samples was below 4.4% (44 g kg^{-1}), which is a content one order of magnitude lower than that found in organic amendments. The lightest elements have lower XRF photon energy values and, as a consequence, the effect of organic matter coating the soil particles can be more pronounced. The reduction of the SiO_2 content reached 20–22.5% with respect to the content of the mineral soil (3–5% as SiO_2). The reduction of contents of the light oxides (SiO_2 and Al_2O_3) can be considered relevant. On the contrary, Fe_2O_3, TiO_2, and MnO content reductions obtained by pXRF can be considered irrelevant with variation before and after organic matter combustion lesser than 1%. The authors indicate that the possible effect of organic matter may be related to the scattering of primary and secondary X-rays,

underestimating the results, in the same way that has been observed for soil with a high moisture content.

Shand C.A. and Wendler R. [43] evaluated pXRF analysis of peat and organic soils. They found in an ombrotrophic peat, satisfactory results for Cu (certified content 5.28 ± 1.04 mg kg^{-1}) and Pb (certified content 174 ± 8 mg kg^{-1}) but the concentrations of Ca, Ti, Cr, Ni, and Zn were overestimated by 2–3 times, and Fe by 5 times. In the same study, they analyzed the concentrations of K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, and Pb of 183 Scottish topsoils that had a wide range of organic carbon (OC) concentrations (1.23 to 48.8%). They concluded that modifications to manufacturer calibrations are needed and that empirical calibration of XRF instruments requires unavailable certified reference peats and peat soils, certified for total element concentration across a wide range of elements.

In a recent study, Sut-Lohmann et al. [38] compared the feasibility of common laboratory methods (microwave plasma-AES and pXRF) to evaluate element concentrations in soil highly influenced by sewage waste. The lowest correlation between both methods was obtained for Ni ($R^2 = 0.70$, stronger points scattering), although the correlations were satisfactory for the other elements (Pb, Cu, Zn and Cr). The authors also approached another strategy for the analysis of organic samples with pXRF: the elimination by ignition of the organic matter to then carry out the readings in the calcined samples. This same sample calcination strategy was already used by Vodyanitskii et al. [52] to measure the metals Ba, Sr, V, Cr, Ni, Cu, Zn, Zr, Pb, Y, La, and Ce, although in this case, a nonportable laboratory instrument was used. Sut-Lohmann et al. [38] found that OM removal in the soil sample influences its density and effective volume, which interferes with pXRF elemental analysis. However, if the data were corrected for organic matter, the influence of the matrix on the pXRF measurements was reduced. Their conclusion was that results validate a usage of pXRF as an alternative method for the conventional wet-chemical-based AES analysis for soil samples highly influenced by sewage wastes. However, the authors indicate that the prior calcination invalidates the use of the technique in the field.

These research studies show that we still do not know in detail the effect of organic matter on the elemental determination by pXRF. The results indicate that the response is highly dependent on the element considered and that possibly the interference of organic matter is more relevant in light elements such as Si or Al. Similarly, previous studies indicate that there may be an effect of organic matter on the measurement of Ni, and sometimes Cr, which is consistent with the high LOQs found by us in organic matrices (Table 3). Even for the same element, results have been found in both directions (overestimation and underestimation) in different studies (for example, [43] vs. [50]). It may happen that the direction or magnitude of the interference depends on the calibration method or the instrument model used, which could explain the disparity in results. In a recent study using six instruments of the same analyzer model, Towett et al. [37] observed that the photon counts from each instrument varied by a considerable amount between them and the authors thus concluded the need for individual instrument calibrations.

3.3. Effect of Moisture Content

Although pXRF is used in many different field applications involving the measurement of wet and even liquid samples, it is an accepted fact that water causes a decrease in the pXRF signal [7,8]. In various geological and environmental applications, the effect of moisture content has been shown to be linear, creating a dilution effect on pXRF signals. Under these circumstances, the fit of the pXRF measurements is improved simply by applying a correction factor [8].

Working with compost from several feedstocks, Weindorf et al. [28] found that pXRF moist scans produced overall lower means than both ICP-OES and pXRF dry data. The R^2 values also worsened in all moist models when compared with the corresponding dry dataset. However, the determination of Cu, Pb, and Zn concentrations of compost samples in situ was possible as sample moisture showed little influence on predictability.

Havukainen et al. [32] studied the results in moist and dried samples of biowaste and compost. The element concentrations of the moist and the dry samples, expressed both on a dry matter basis, were closer to each other for compost samples (−10 to 10%) than for biowaste samples (−37 to 33%) due to the greater moisture content of biowaste samples (almost double on average). However, the direction of the difference depends on the element: Zn, Cu, and K presented lower values in the humid samples while Ca and Cl presented higher values with humidity.

Sapkota et al. [35] dedicated a study to the objectives of quantifying the effect of sample moisture content, predicting moisture content, and correcting for moisture effect on elemental concentration determinations in livestock manure. They found that the average intensity of P, K, Ca, Mg, and Fe decreased with increasing sample moisture content. This result in the case of Ca is contrary to that of the previous study by Havukainen et al. [32]. An interesting result of this study is that the authors were able to determine the moisture content ($R^2 = 0.98$) using pXRF spectrum data and random forest regression. For this, they used peaks from the spectrum included in regions that were free of the elemental signals and that had great predictive power for the moisture content. In this way, elemental concentrations could be predicted in all wet samples, with R^2 ranging from 0.90 for element Mg (in order to determine this element, the measurements were made under vacuum conditions) to 0.98 for element Fe.

A review of the effects of moisture on pXRF soil analysis was recently undertaken by Silva et al. [51]. Although the use of pXRF in soils and sediments has been more widespread than in organic amendments, the authors pointed out discrepancies between different studies and indicated that the general influence of humidity is only known between elements that are less or more affected (such as light elements Z < 26 or elements with detectable X-ray fluorescence energy less than 5 keV). Although the aforementioned studies made on soils can provide us with certain information, we must consider the specific characteristics of organic amendments that differentiate them from those.

The presence of water in the measured sample can affect the result in several ways:

1. Dilution of the sample by the additional weight of water since the results are normally expressed on a dry matter basis;
2. By absorbing part of the primary incident X-rays;
3. By scattering the secondary X-rays.

Regarding dilution, it is a linear effect and we must bear in mind that in organic matrices the water content in situ can be much higher than in mineral matrices such as soil. Water absorption is precisely one of the beneficial effects of organic matter for plant growth. Therefore, the linear factors for the conversion of results from a fresh basis to dry basis could be much higher in the case of organic matrices. Organic amendments are also made up of discrete particles. Each particle can be mostly organic (e.g., plant debris) or mostly mineral (soil particles or small rock fragments). The concentration of chemical elements in these different types of particles can be very different [28,53]; plant nutrients are concentrated in organic materials, while Si, Al and trace elements are usually enriched in the fine fractions; and the water contained in a wet sample can also preferentially be associated with particles of an organic type. The result is that geometrically the distribution of water and chemical elements in the particles of an organic amendment sample is not homogeneous. Therefore, the effects of incident radiation absorption and secondary scattering could vary depending on the specific characteristics of each organic amendment. This could be one of the reasons for the disparity in results that has been mentioned, both for organic amendments and also for soils. The effects of organic matter content and moisture content are likely to overlap when fresh samples are analyzed. In addition, its separation for statistical purposes or for modeling and correcting results could be complicated if a heterogeneous set of samples is studied. The moisture content of an organic sample can also have another effect that has not normally been considered in previous studies. The increase in humidity in organic amendments usually leads to a decrease in

apparent density; this is a compaction of the sample [54]. This is a well-known physical property of organic growing media referred to as shrinkage [55]. In the case of highly compactable materials, this could lead to a high interaction between the effects of organic matter and moisture content, possibly accentuated in conditions close to saturation of the sample with water.

In most of the studies discussed, comparisons of the pXRF technique with other laboratory procedures such as digestion followed by measurement by ICP-OES have been made. In these cases, pXRF has generally been used in the laboratory, after drying, grinding, and sieving the samples, which reduces problems of heterogeneity and facilitates the comparability of procedures under the same conditions. However, the influence of sample moisture is especially relevant if we want to use the technique in situ, under field conditions, preventing the previous steps of sample preparation.

3.4. Other Measurement Conditions

Despite the portable nature of pXRF instruments, most previous studies have been dedicated to standardizing the conditions for the comparisons and calibrations they performed, and thus used the instrument under laboratory conditions. The most common is to place the dry and finely ground sample in XRF sample cups (Figure 2a,b), which are covered with a sufficiently thin protective plastic film (Figure 2c). The most used films are 4 μm prolene [34,35,37,39] and 4 μm polypropylene [33,36,40,43], although some researchers made the measurements directly in plastic (unspecified) bags [28,31,32] (Figure 2d). The thin film between the sample and the X-ray detector can attenuate or scatter fluorescence signals. Thin films attenuate to some extent the low-energy fluorescence signatures from light elements (e.g., Al) but exert negligible attenuation effects on heavier elements. The use of thicker protective barriers such as plastic bags can cause significant effects on measurements for lighter elements. A 50 μm polypropylene barrier attenuates 94% of the aluminum Kα signal [56]. The effects of protective films should be determined for each intended application. Measurements can be made by positioning the capsule or plastic bag directly on the nose of the instrument, or in the opening of a radiation protection stand that allows the instrument to be attached (Figure 2e).

The aforementioned studies on amendments also show wide variations in terms of sample thickness. The sample thicknesses used range from a maximum of 10 cm to 32 mm, 23 mm or greater than 2 cm. In many cases, they do not refer to thickness but to sample weight, from 0.5 g to 10 g, which will reach a different thickness depending on the volume of the sample cup. In their review of factors affecting the environmental assessment of soils with pXRF, Ravansari et al. [56] indicated that the literature is inconsistent regarding required sample thickness and a consensus has not been reached. The pXRF analysis must be performed on infinitely thick samples or. in other words, with a thickness (and diameter) greater than the specific critical thickness of the analyte. If the samples are not infinitely thick, the detected intensities may decrease because the area from which the signal contribution should occur may be replaced by air. The incident beam can penetrate more into organic matrices, so the critical thicknesses in these cases can be greater. As there is no consensus regarding the critical thicknesses (there are published values from 5 to 25 mm) nor a standard procedure to determine them, it must be ensured that the thickness of the infinitely thick sample is reached in each type of matrix [56].
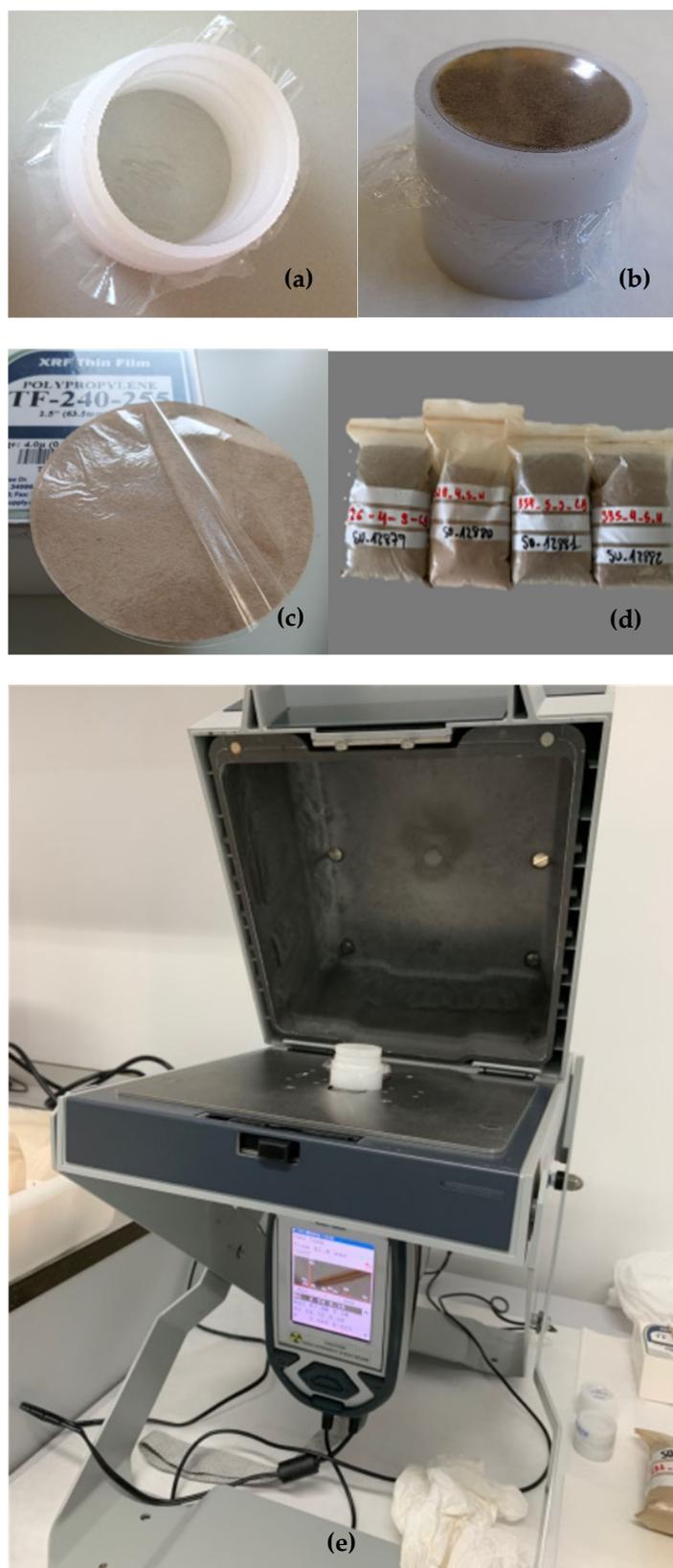
Figure 2. Performing measurements under laboratory conditions: (**a**) pXRF sample cup 25 mm high and 25 mm in diameter with protective film; (**b**) Sample cup filled with finely ground sample; (**c**) Thin protective film; (**d**) Samples in Ziploc bags; (**e**) Instrument attached to protection stand with sample positioned for measurement.

Until we have more precise indications of the dimensions of the sample, the maximum possible should be used and it should be verified that an increase or decrease in the thickness used does not produce different results for the analytes of interest.

3.5. Derived Properties

One of the advantages of the pXRF technique is that it can provide extensive information about the chemical composition of a sample. All elements present in concentrations above the LOD from Na (atomic number 11) to U (atomic number 92) can be determined in one quick scan, although special conditions, such as a vacuum, may be necessary for the lighter elements. Having this extensive information on the elemental composition of the sample allows the use of chemometric procedures to predict other physical–chemical properties of the samples.

As mentioned previously, in 2018, the studies by Weindorf et al. [30] and Li et al. [24] used elemental data as a proxy for the prediction of derived properties such as compost electrical conductivity (EC) and cation exchange capacity (CEC), respectively. For the modelling of the derived properties, a principal component regression (PCR) model was used in the Weindorf et al. study for EC and pH, while random forest (RF) regression was used in the Li et al. study for CEC. Measured vs. pXRF predicted compost EC correlated well (coefficient of determination, $R^2 = 0.80$; root mean squared error, RMSE = 1.04 dS m^{-1}) and CEC showed excellent correlation ($R^2 = 0.90$, RMSE = 5.41 meq 100 g^{-1}, for the calibration set of samples). Compost pH was reasonably explained via pXRF ($R^2 = 0.63$, RMSE = 0.35), although the fit was not as good as for the other parameters.

López et al. [33] showed that it was also possible to determine the organic matter content of organic amendment samples from linear regression equations that use the undetermined content data (the difference to 100% of all the elements actually measured) with corrections from elements such as silicon, calcium, or iron. The same authors [36] found multiple linear regression equations that can predict *aqua regia*-soluble concentrations of the elements As, Cd, Cr, Hg, Ni, and Se using pXRF readings of other measurable elements as predictor variables. These target elements were below the LODs of the pXRF instrument used. Several amendment type-dependent singles or multiple linear functions were found based on one, two, or three predictors. The predictor readings corresponded to the concentration of elements of geogenic (Fe, Si, Ti, Cl, Zr Al, Ca, S, Mn, and Ba), anthropogenic (Zn and Pb), and agricultural (P and K) origin. The regression coefficients of these functions were r = 0.90–0.99.

In a recent paper, Towet et al. [37] proposed two types of machine learning methods, forest regression and extreme gradient boosting, for the prediction of ash content, total carbon, nitrogen, and several elements from both pXRF and Diffuse Reflectance Fourier-transform mid-infrared spectroscopy (DRIFT-MIR) data using 98 samples of various organic amendments. The authors found very good regressions from pXRF data for ash, total C, total N, P, K, Ca, S, and Fe ($R^2 > 0.90$) and acceptable regressions for the elements Mg, Na, and Mn ($0.7 > R^2 > 0.9$). In general, the pXRF data gave better predictions for heavier elements and the DRIFT-MIR data gave better predictions for ash, carbon, and lighter elements.

The results of the previous research studies are relevant insofar as:

1. They show the very small number of investigations performed on the chemometric applications of pXRF.
2. They show the potential of pXRF to predict various physical–chemical properties of organic amendments, particularly organic matter and nitrogen contents that are not directly measurable by this technique. Research on the prediction of derived properties has been much more extensive in the application of pXRF to soil analysis [51].
3. They show the possibilities of combining pXRF with other different proximal sensors, particularly MIR and visible-NIRS spectroscopies that allow expanding the determination of physical–chemical characteristics of organic amendments beyond merely

the elemental content of heavy metals and some nutrients. The merging of proximal techniques such as vis-NIR and XRF is very advantageous in soils [57], and given the high proportion of components of an organic nature in organic amendments and fertilizers, their combination should be successful.

4. Conclusions

The mentioned studies show that pXRF can be a suitable technique for the elemental analysis of organic amendments. The speed and ease of performing the analysis, its competitive price, and the absence of polluting residues from the processing of the samples are evident. However, the studies undertaken so far in which this technique has been applied to organic amendments, such as compost, sewage sludge, manure, growing media, or organic fertilizers, have been very few. These studies have shown:

1. The technique generally correctly measures elements such as Fe, Pb, Zn, Mn, Ca, and K; offers contradictory results for elements such as Cr, Ni, and As; and is not suitable due to its high LOD for Cd and Hg.
2. The reasons for the poor performance of the technique with certain elements or under certain measurement conditions are varied:

    *   A mismatch between the total amounts measured with pXRF and those soluble in *aqua regia* used as the reference concentrations in many studies.

    *   The different internal calibration procedures used in different models of instruments.

    *   The unknown effect of measurement conditions such as scan time, sample size, and sample thickness.
3. A not well-known effect of the influence of the high content of organic matter that characterizes this type of sample on the fluorescence signals.
4. The effect of the influence of moisture content on the fluorescence signals, and if there could be some kind of interaction with organic matter, is not known. At the moment, this represents a great challenge for measurements in the field.
5. Despite the poor performance, the prediction using chemometric procedures of other physicochemical properties of organic amendments (such as organic matter, electrical conductivity, cation exchange capacity, moisture content) has given encouraging results. Among these properties would be the contents of elements such as N, Cd, or Hg not directly measurable by pXRF instruments or below their detection limits.

Probably, the achievements obtained by the technique favor its future use to be more common in the characterization of organic amendments. It would be necessary to develop a standardized protocol for this type of matrix. As the first requirement for this, it is necessary to have certified reference materials (CRM) of organic amendments that serve as calibration/verification checks, since soils or sediments are mostly used. Descriptions of methodology in pXRF studies need to be more complete, both in terms of the actual implementation of pXRF methods and contrasting analytical methodology. It is common for studies to omit the sample digestion procedures used, mentioning only the analytical instrument for the final determination (AAS, ICP-OES, etc.).

The complementarity of the pXRF technique with other fast and portable spectroscopic techniques such as those based on MIR or vis-NIR, which are already being explored in other fields, can offer important advantages in the case of organic amendments. NIR or MIR spectroscopic techniques offer information on the organic matrix while fluorescence does it on the inorganic constituents, so their association could pave the way to a green laboratory, free of toxic laboratory waste and able to carry out in situ measurements aimed at decision making.

Institutional Review Board Statement: Not applicable.

Appendix A

Databases search:

The command line ((portable OR "hand held" OR handheld) AND (xrf OR pxrf OR "X-ray fluorescence" OR "x ray fluorescence") AND (compost OR "organic waste" OR "organic residue" OR manure OR sludge)) was used for SCOPUS search in the title, abstract, and keywords. The command line ((ALL = (portable OR pxrf OR "hand held" OR handheld) AND ALL = (xrf OR xrf OR "X-ray fluorescence" OR "x ray fluorescence") AND ALL = (compost OR "organic waste" OR "organic residue" OR manure OR sludge OR biosolid))) was used for the search in Web of Science Core Collection. The searches in Scopus and WoS were undertaken from inception to 19 April 2022 and 22 April 2022, respectively.

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