



X-ray fluorescence spectrometry for environmental analysis: Basic principles, instrumentation, applications and recent trends

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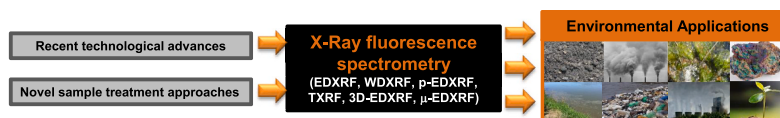
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HIGHLIGHTS

- Analytical applications of X-Ray Fluorescence in the environmental field.
- Summary of significance advances in XRF systems and sample treatment strategies.
- Study cases: geological, vegetal, aerosols, aqueous extracts, waters and wastes.

GRAPHICAL ABSTRACT



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ABSTRACT

In recent years, the conceptual advancement on green analytical chemistry (GAC) has moved in parallel with efforts to incorporate new screening or quantitative low-cost analytical tools to solve analytical problems. In this sense, the role of solid state techniques that allow the non-invasive analysis (or with a minimum sample treatment) of solid samples cannot be neglected.

This review describes the basic principles, instrumentation and advances in the application of X-ray fluorescence instrumentation to the environmental sciences research topics, published between 2006 and 2020.

Obviously, and because of the enormous number of works that can be found in the literature, it is not possible to exhaustively cover all published articles and the diversity of topics related to the environment in which a solid state technique like XRF has been applied successfully.

It is a question of making a compilation of the instrumentation in use, the significant advances in XRF spectrometry and sample treatment strategies to highlight the potential of its implementation for environmental assessment.

1. Introduction

X-ray fluorescence spectrometry (XRF) is a well-established analytical atomic technique for qualitative and quantitative chemical analysis of environmental samples with various matrices and a wide elemental range (which can encompass from B to U, in atomic number order). XRF can offer rapid, non-destructive and multi-elemental analytical results with sensitivity in the range of 10^{-8} g (depending on the element of

interest) and it is perfectly suited for most environmental research studies. The truly multi-elemental character, acceptable speed and economy, ease of automation, portability and the possibility to directly analyse solid samples (without a previous acid digestion) are the most important features among the many that have made it a very mature analytical tool for routine control in diverse scenarios. Apart from well-known classical industrial applications, XRF can be successfully employed in direct field analysis for agronomy research, on-line analysis

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of atmospheric particulate matter, remote acquisition of XRF spectral data as well as for analytical support for the research environmental laboratory (Beckhoff et al., 2006).

Methodological development and technological advances in X-ray fluorescence analysis, observed in recent years, have made it possible to perform elemental analysis of any kind of materials, including those existing in all compartments of our surrounding environment, whatever its natural or anthropogenic origin. The tremendous growth of environmental analysis in the last decades is primarily due to a necessity to assess the quality of our environment, based on the availability of reliable analytical data.

Recent technological development, including the design of X-ray miniaturized sources, the production of low-power micro-focus tubes, the novel X-ray optics devices, non-toxic carbon-based higher transmittance X-ray detectors windows and the improvement in signal detection systems have made it possible to extend XRF to the determination of low-Z elements and to obtain 2D or 3D information on a micrometre level. Likewise, recent designs and commercialization of benchtop and portable instrumentation, that offer extreme simplicity of operation in a low-cost design, have promoted even more the approach of XRF for many analytical problems, which can be even efficiently solved at on-site or on-line situation.

During the last fifteen years, the use of XRF as a widespread

analytical technique has experienced a remarkable increase. The number of scientific articles published in indexed journals, by using “XRF” and “environment” keywords through the Scopus platform, has gone from about thirty per year in 2006 up to two hundred in 2020, as shown in Fig. 1A. Interestingly, the XRF share the prominent figures of 27% of environmental studies regarding other spectroscopic techniques (Fig. 1B). Also, it is worth mentioning the notorious importance of ICP-MS role in current environmental investigations, surely due to its multi-elemental and isotope detection ICP-MS capabilities, and additionally, its low detection limits. Over the last fifteen years, the application of different X-ray fluorescence configurations to environmental analysis has also changed. Comparing the first years to the last ones of this survey, an increase of ca. 70% of indexed XRF environmental contribution within all XRF applications is observed. In fact, a significant increase of XRF environmental related studies within all XRF contributions was verified from 2006 to 2020, which presented Pearson’s r value of 0.80). This trend surely shows XRF instrumental advances in recent years, in which new XRF analytical capabilities has been brought about and myriad of environmental XRF application come to reality.

This article highlights the State-of-the Art of XRF with regards to currently available instrumentation as well as recent applications in environmental and related fields, trying to complement other recent JAASXRF spectroscopy updates (Vanhoof et al., 2021). The main types

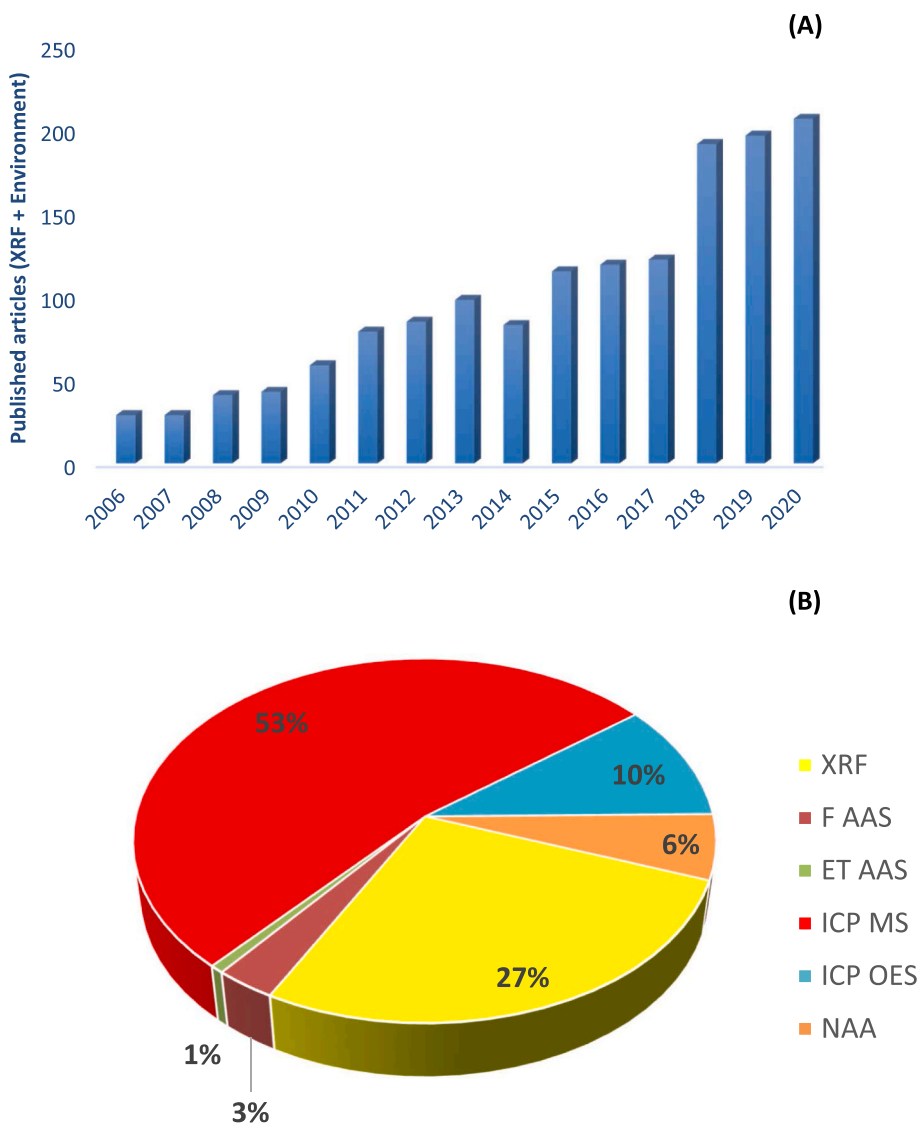


Fig. 1. (A) Number of articles annually published on XRF in the environmental field in the last fifteen years, (B)-Contributions of articles published about environmental analysis in the period 2006–2020 using different analytical techniques. Source: Scopus database. Abbreviations: X-ray fluorescence spectrometry (XRF), Flame atomic absorption spectrometry (FAAS), Electrothermal atomic absorption spectrometry (ETAAS), Inductively coupled plasma mass spectrometry (ICP-MS), Inductively coupled plasma atomic emission spectroscopy (ICP-OES), Neutron activation analysis (NAA).

of environmental samples analysed by XRF that are considered in this review include geological, vegetal, atmospheric particulate matter, aqueous extracts and water samples. Other types of samples such as waste products are also briefly discussed in the last section of the manuscript.

2. XRF instrumentation configurations

At present, there are different types of X-ray fluorescence systems commercially available. The selection of the most suitable spectrometer is based on the demands for a given purpose. Table 1 presents a summary of the features and analytical capabilities of XRF systems used in environmental sample analysis. In this section a brief summary of the XRF instrumentation configurations available is presented. More detailed information about basic principles and components of XRF spectrometers can be found elsewhere (Marguí, 2013).

2.1. EDXRF and WDXRF

Traditionally, the X-ray fluorescence (XRF) instrumentation is divided into two main branches, the wavelength dispersive X-ray fluorescence (WDXRF) and the energy dispersive X-ray fluorescence (EDXRF). Basically, the main difference between them is how they discriminate the energies of the X-ray photons arising from the sample. The former system utilized a crystal, resulting in a high resolution system, and the latter one relies on a semiconductor detector (Marguí et al., 2009b). Among all XRF features shown in Table 1, the lower price, the portable and simultaneous multielemental capabilities of EDXRF put the energy dispersive system several steps ahead over the WDXRF in environmental applications.

Over the last fifteen years, the energy dispersive is by large the most utilized XRF system in environment studies (ca. 96%), in comparison with WDXRF (4%). The reason for this trend is explained due to advances in EDXRF features during last decades. In the 80's, most benchtop EDXRF equipment requires the N₂ cooled Si (Li) detector. However, nowadays the free N₂ Peltier cooled SiPIN and silicon drift detector (SDD) have a widespread use, being practically part of all EDXRF systems (West et al., 2010).

Compared with conventional EDXRF techniques, 3D-EDXRF (EDXRF with polarized X-ray beam) has the advantages of increased sensitivity and specificity for trace element analysis. The use of suitable secondary targets (made of different materials) between the X-ray tube and the sample allows one not only increasing x-ray production due to the choice of quasi-monochromatic radiation with energy close to the photoelectric

absorption edge of a given element of interest, but also to reduce the intensity of the measured continuum radiation, thus significantly increasing the signal-to-noise ratio and improving the limits of detection (Marguí et al., 2009b; Yanada et al., 2007).

At the end of last century, the use of radioactive X-ray sources (e.g. ⁵⁵Fe, ¹⁰⁹Cd, ²⁴¹Am) dominated in portable XRF analysers (P-EDXRF). These sources were well suited for use in portable devices as they were small (cylinders of approximately 5 mm height and diameter) and did not require external power. However, the short half-life of some isotopes, the strict regulatory requirements associated with transportation of radioactive materials and the limited sensitivity available for trace metal determination represented significant barriers to widespread adoption. Recent technological advances have led to the availability of compact, low-power, metal-ceramic X-ray tubes that can be cooled by air which have largely replaced radioactive X-ray sources in low cost handheld systems. Portable XRF instrumentation is now available as small and light units (ca. 2 kg for a handheld system). Additionally, computational advances afford promptly results for mathematical quantification methods such as Fundamental Parameters (FP). Therefore, with the use of handheld XRF units, it is possible to measure directly in the field which is particularly interesting to provide near real-time data necessary to guide critical field decisions in the context of contamination, removal and remediation actions. One of the limitations of most of these systems is that measurements have to be performed in air which leads to higher limits of detection for light elements in comparison with EDXRF and WDXRF systems, which allow performing measurement under vacuum or He atmosphere. Nevertheless, it is interesting to remark that at present some portable XRF units are also equipped with helium purge or optional portable vacuum pump which leads to an improvement of the analytical performance of such systems (Skupio, 2020).

Micro X-ray fluorescence (μ -EDXRF) is one of the most recent branches of XRF, which has developed very fast since the development of capillary optics and pixelated detectors (Haschke, 2014). The main particularity of μ -EDXRF instrumentation compared to conventional EDXRF systems is the concentration of the X-ray beam down to a smaller size by introducing adequate focusing optics, usually monocapillary or polycapillary lenses, between the X-ray source and the sample. Standard microbeam spectrometers are also usually equipped with a conventional microscope (or just a camera) for a precise selection of the measurement spot and for viewing the area on a PC monitor during the measurement procedure. Moreover, the use of an XYZ programmable motorized stage enables fully automatic measurements and the possibility to perform the fluorescence spectroscopy in different modes: point analysis, line scan or

Table 1
General properties and application of XRF instrumentation in environmental analysis.

	WDXRF	EDXRF	P-EDXRF	3D-EDXRF	μ -EDXRF	TXRF
Simultaneous multielemental capability	No	Yes	Yes	Yes	Yes	Yes
Analytes (L: low Z, M: Mid Z, H: High Z)	L, M, H	L, M, H	,M, H	L, M, H	L, M, H	M, H
Amount of sample	tenth of mg to few g	tenth of mg to few g	n.a. ^a	tenth of mg to few g	n.a. ^a	few mg/ μ L
Type of chemical information	Quali SemiQuanti Quanti	Quali SemiQuanti Quanti	Quali SemiQuanti Quanti	Quali SemiQuanti Quanti	Quali SemiQuanti	Quali SemiQuanti Quanti
Type of sample	Solid ^b	Solid ^b	Solid ^b	Solid ^b	Solid	Liquid Solid
Bulk analysis	Yes	Yes	Yes	Yes	No	Yes
Analyte distribution information	No	No	No	No	Yes	No
Portability (<i>in situ</i> analysis)	No	Yes/No ^c	Yes	No	No	Yes/No ^d
Main field of application (W:water, V:vegetation, A: air pollution, G: geological)	V, G,A	V, A, G	V, G	V, A, G	V,G	W, A, V
Capital costs	High	Medium	Low	High	High	Medium

^a n.a.: not applicable (direct analysis of the solid sample).

^b Liquid samples can be analysed after a preconcentration procedure.

^c There is in the market only a standard laboratory WDXRF spectrometer with the advent of small spot-mapping capability (Thermo Fisher Scientific Inc., 2012).

^d Only for transportable (low power) XRF systems.

using an area scan.

This technology has great potential to obtain 2D images in environmental applications which require micrometre scale investigations (Fittschen et al., 2017; Neves et al., 2019; Rodrigues et al., 2018, 2021; Serranti et al., 2020). Recently, benchtop μ -XRF have become available and its use in environmental studies has been increased. Currently, these systems afford microfocus X-ray tube, collimator or mono/polycapillary lenses, SDD detector and lateral resolution as low as 5 μ m up to 2 mm. The above-mentioned features have simplified the use and promoted a widespread application of EDXRF in environmental studies, and particularly, fostering *in situ* application.

2.2. TXRF

TXRF is a variation of EDXRF in which the primary beam strikes the sample at a glancing angle of less than 0.1° and not at an angle of about 45° . Moreover, due to the grazing incident excitation angle, the detector can be positioned very close to the sample leading to a large solid angle for the detection of the fluorescence signal. These facts contribute to an improvement of the limits of detection compared to conventional EDXRF spectrometers. To perform analysis under total-reflection conditions, samples must be provided as thin films on a reflective carrier. Therefore, TXRF has also microanalytical capability which is especially suited in the case of mass-limited sample analysis.

Since the TXRF analysis relies on thin film condition, matrix effect can be neglected and the quantification strategy is quite simple in comparison with conventional XRF (Klockenkämper and von Bohlen, 2014), more specific details can be found in section 4. Nowadays commercial TXRF setups offer automatic quantification procedures only based on the sample X-ray spectrum, mass of sample and the internal standard, which results in a high throughput and less analyst effort (Bruker, 2022; Gallardo et al., 2016a,b). In the last years, the development and commercialization of bench top TXRF instrumentation, which offer extreme simplicity of operation in a low-cost compact design, have promoted a widespread application of the technique. Low power TXRF brings the total reflection system to *in situ* environmental applications. For instance, Kunimura and Kawai (2010) described a TXRF equipment with a 1 W X-ray tube at 20 kV. This system does not use any monochromator, thus the sample is excited by a polychromatic X-ray beam and detection limit as low as 26 ng is obtained for Co. Following the same trend, Liu et al. (2013) evaluated excitation conditions for a portable TXRF and the limit of detection got at impressive sub ng levels for nine elements utilizing 10 min acquisition time. Then, portable TXRF shows as a promising tool for *in situ* environmental and geological studies and more intense use in these fields is expected in years to come.

Usually, TXRF is not proper technique for detection of low Z analyte in air atmosphere analysis condition. At present, there is no commercial system operated under vacuum but in the last years a lot of efforts have been made at research level to cope with this fact. Tarsoy et al. (2010) evaluated the analytical capabilities of the TXRF spectrometer designed in the Atominstut TU Wien (Vienna, Austria) furnished with medium atomic number Cr-anode X-ray tube, multilayer monochromator and ultra-thin window SDD detector, for low Z analyte, determination (from C to P). Limit of detection of 5 mg/L (10 ng absolute) for F was reported. In a similar way, Prost et al. (2015) determined light elements ($Z \geq 6$) by using high power Cr and Cu anode X-ray tubes and also a lower power one furnished with a thin window. For the X-ray detection, a 300 nm ultrathin window SDD was selected. Limits of detection for analytes with atomic number higher than 11 was in nanogram range. Therefore, it is expected than in the future the design of commercial available TXRF systems for the proper determination of light elements will increase the applicability of TXRF to environmental studies.

3. Most commonly used sample preparation strategies

In XRF, the sample preparation procedure is at least as important as

the analytical technique itself and it strongly influences the final quantitative result. The application of an improper sampling or sample preparation method can introduce large errors in the final results (Marguí et al., 2016). The ideal sample for XRF analysis must have a perfectly flat surface, taking into account that XRF systems are calibrated based on a fixed geometry (sample to source and sample to detector distances). Even for largely flat samples, surface finish can affect the analysis results, particularly for lighter elements. Another important feature in XRF analysis is the effective thickness of the measured samples that it is controlled by the density of the sample and its ability to absorb the characteristic fluorescence X-rays from the elements present. Depending on the sample thickness, matrix effects will be present and a proper quantification method will be necessary to obtain reliable results (see section 4). Therefore, all these facts have to be considered before choosing the best sample treatment procedure for each particular application. So far, a myriad of sample preparation strategies has proved to be suitable for environmental samples analysis by XRF (Marguí et al., 2016). Fig. 2 shows the most common sample strategies in his research field. Basically, these methods can be separated for solid or liquid samples. For the former samples, pressed pellet, loose powder, fused bead and acid digestion are the sample preparation strategies of choice. But, before this step, the solid sample has to be properly homogenised. As general rule, proper particle size must be lower than 60 μ m for a suitable XRF analysis (Beckhoff et al., 2006), but for vegetable sample in some applications larger particle sizes can be acceptable (Omote et al., 1995). Pressed pellet is a traditional and well-established XRF sample preparation strategy, in which the final analytical result is one of the best in terms of repeatability. For the pelletization of some type of samples, such as soil and geological ones, the addition of a binder (wax, cellulose, boric acid, starch) is usually required to avoid pellet breakage. As already stated, another possibility of powder materials preparation is to present them directly to the spectrometer as loose powders, packed in cells or spread out on film materials. Although the repeatability of the results obtained by the loose powder method is not as good as in the case of pressed pellets (surface effects prone to be more severe), the time saving in the sample preparation is significant and it is a method for considering. Samples exhibiting difficulties to go into solution easily or tending to remain heterogeneous after grinding and pelletizing, are often treated by the technique of flux fusion. This sample preparation method is mostly applied for geological and soil sample analysis. This method affords the most homogeneous sample preparation and additionally offers matrix effect diminishing. However, the fusion techniques have the drawback of the time and material costs involved and due to the dilution effects, and thus the trace determination in the sample is critically constrained (Marguí et al., 2016). Therefore, this sample preparation strategy is mostly reduced to the determination of major components in solid samples.

In the specific case of TXRF analysis, solid samples can be also prepared by suspending several milligrams of the powdered material in an adequate disperser agent without the need to digest the sample. This sample preparation method proved to be a reliable analytical option for metal determination in plant tissues (Dalipi et al., 2017; de Almeida et al., 2020) and soil samples (Bilo et al., 2019; Gallardo et al., 2016a) as long as metal concentrations are at the mg kg⁻¹ level and the particle size to prepare the suspension is fine enough (Bilo et al., 2014; Gallardo et al., 2016a). Although the precision of solid suspension measurements by TXRF (RSD 15–20%) is lower than that associated with other methodologies, the benefits of this fast and less time-consuming analytical approach make it useful for some types of environmental studies, above all for mass-limited sample analysis.

In some applications dealing with the analysis of solid samples by XRF, the use of more complex sample treatments, similar to those involved in atomic spectroscopic techniques, is required. Commonly, wet ashing, involving digestion with strong acids, is used to destroy the organic matter and dissolve the analytes in a wide variety of environmental solid matrices before the XRF analysis (Fernández-Ruiz et al.,

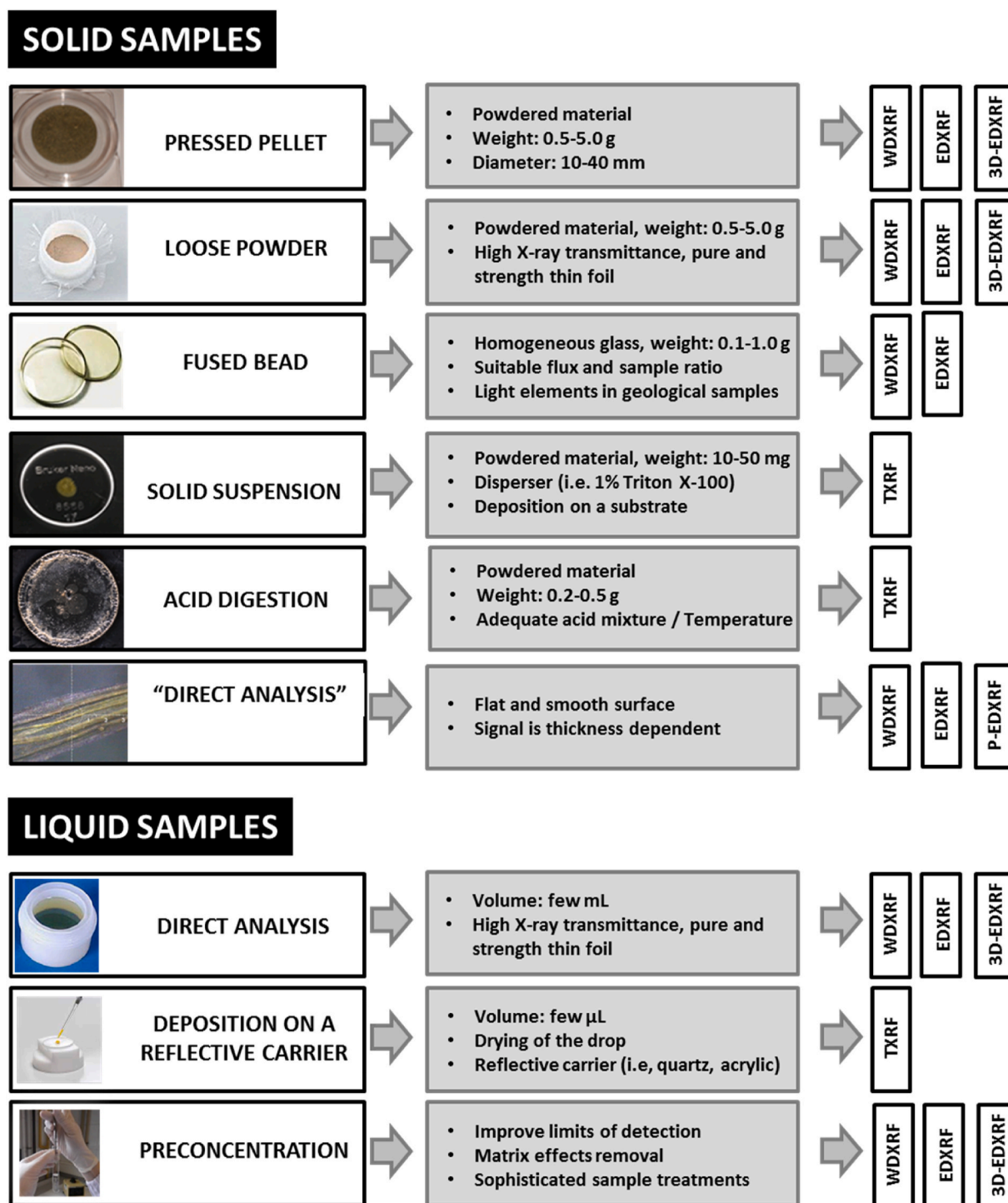


Fig. 2. Most common sample preparation strategies for XRF in environmental studies.

2020).

Finally, environmental samples can be also directly analysed without any or very simple sample treatment by XRF. This is, for instance, the case of element distribution studies within the sample performed by μ -EDXRF. However, in such cases, special attention must be paid to ensure a thin flat surface to obtain reliable results.

For liquid samples, the simpler sample preparation method is the direct analysis of few millilitres placed in a cup with a thin-film (Mylar, polyethylene, Kapton) bottom in a non-evacuated XRF setup. The drawback of this strategy is the high scattering of the excitation X-ray due to lower atomic number matrix that causes an increase of the

spectrum background and worsens the limit of detection (mg/L level). On the contrary, in TXRF analysis, few microliters of liquid sample are deposited and dried on a reflective carrier. The advantage of this method is the low scattering of the excitation X-ray due to the total reflection phenomenon on the carrier and also the diminute mass sample required. LODs typically are in the low $\mu\text{g L}^{-1}$, depending on the sample matrix.

It is interesting to mention that liquid samples can be also analysed after applying a preconcentration procedure in order to eliminate interferences and/or improve detection limits. In section 4.4 a summary of the recent trends in preconcentration strategies to be used in combination with XRF for water and aqueous extracts analysis are discussed in

detail.

4. Qualitative and quantitative X-ray fluorescence analysis

Qualitative analysis is an unbeatable feature of EDXRF due to its multielemental capability and the possibility to perform solid analysis with a minimum sample treatment. In this view, screening analysis is a seamless application for EDXRF, even more due to the widespread use of portable XRF systems (Leroux et al., 2018; McComb et al., 2014; Peng et al., 2020; Turner et al., 2015). However, some of the limitations of XRF in this domain are the limited sensitivity for some environmental-relevant elements and also overlapping issues of some characteristic X-ray lines (eg. As-K α and Pb-L α lines). Particularly, the limit of detection for most elements is still within mg kg $^{-1}$ range and a lower sensitivity is even found for light elements (e.g. atomic number lower than 12). So far, those limitations seem an intrinsic feature of this technique but new analytical instrumental improvements (eg. thinner X-ray detector window, better resolution and higher detector count rate capabilities) as well as novel separation/pre-concentration strategies are currently coping with these restrictions. Therefore, the potential for environmental applications of XRF seems endless.

Nowadays, most of XRF environmental studies are related to quantitative analysis. The strategy of the quantification depends on type of sample, analyte, sample preparation and even the available XRF instrumentation. From the point of view of XRF analysis, samples are grouped depending on their thickness (thin film, intermediate or infinite thick) as shown in Fig. 3. The former type is the easiest XRF quantification condition, in which matrix effects are negligible and thus the XRF elemental intensity is directly correlated with the concentration by the sensitivity (eg. aerosol or aquatic suspended matter deposited on a filter, liquid deposit on a carrier). For thin film quantitative analyses, the calibration may be performed by a set of elemental and multielemental standards. In the specific case of TXRF analysis, quantification is usually performed by the addition of a suitable internal standard (IS) to the sample and the elemental concentration is determined considering the analytical signals of the analyte and IS, their respective instrumental sensitivities and the IS concentration (Marguí, 2013).

As it can be seen in Fig. 3, intermediate and thick samples (eg. pellet, powder and fused beads) require strategies to take into account self-

absorption and enhancement matrix effects. If the variation in matrix effects is mainly due to absorption, scattered X-rays can be used to correct the intensity of the analyte. In practice the inelastic (Compton effect) scattered radiation method is quite simple and consists of plotting the corrected intensity of the analyte versus the concentration of the analyte to obtain a calibration. As inelastic scattering increases with decreasing mean atomic number, is it particularly suitable for matrix correction of elements within light matrices. Nevertheless if a mixture of absorption and enhancement matrix effects is present, more sophisticated matrix correction models such as fundamental parameters (FP) or influence coefficient algorithms are required.

FP method is based on the physics of X-rays and consists of obtaining the theoretical composition of the sample from the measured intensities and spectral fitting procedures. It is especially suited as quantitative procedure for environmental applications as far as most sample matrix composition is known. The advantage of this method is that it does not require a large number of standards and additionally the FP approach is commonly available in most commercial XRF software. Nevertheless, at least a trueness checking of the FP method is recommended by using adequate certified reference material. Another type of matrix correction approach is the calculation of theoretical or empirical influence coefficients. The influence coefficients depend on the analyte element and its characteristic spectral line chosen for the analysis, the matrix elements and their concentration, the energy of the incident radiation and the geometry of the system. Once calculated is possible to estimate the matrix correction term by the measurement of several adequate standards containing know element weight fractions. Although the use of a set of reference materials with similar matrix to the samples is not a problem for some environmental studies (i.e. vegetal samples, sediments, soils), it is more difficult for other types of environmental samples due to the scarcity of commercially available reference materials (i.e. sewage sludge). In such cases, a potential alternative is the preparation of synthetic standards in the laboratory or to use a set of well characterized samples with a reference technique as calibration standards (Bilo et al., 2019).

For further qualitative and quantitative EDXRF information for environmental analysis readers can refer to some specific publications (Marguí et al., 2009b, 2010e, 2014, 2016).

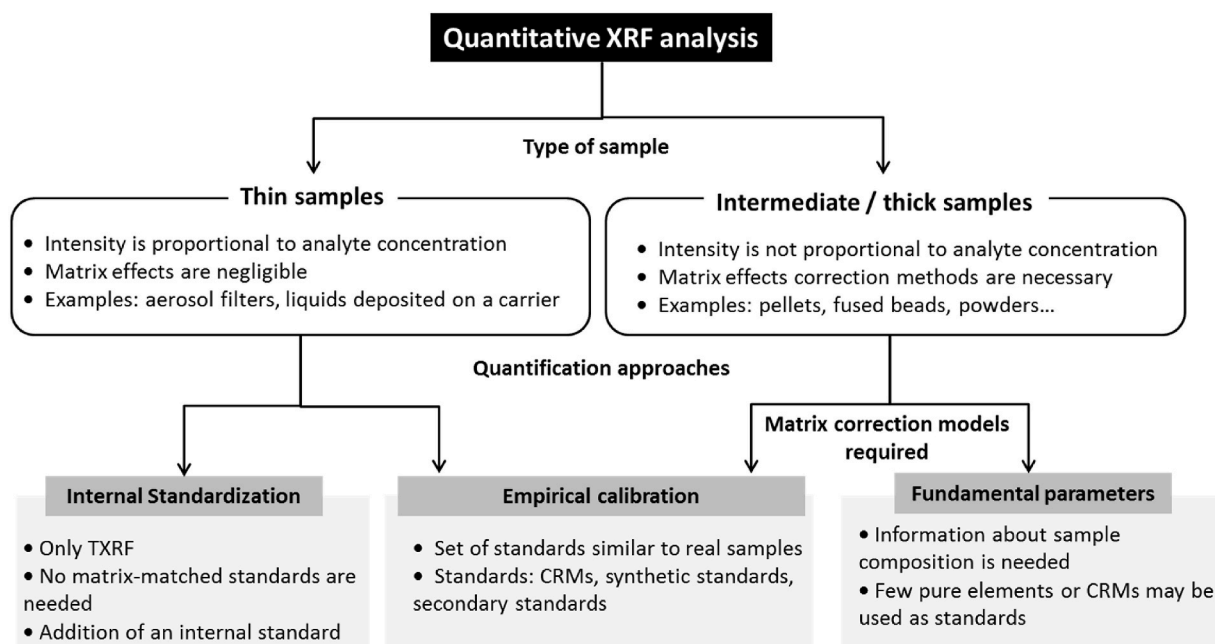


Fig. 3. Quantitative approaches commonly used in XRF analysis.

5. Application of XRF in the environmental field

It is out of the scope of this review to include all environmental XRF applications published in the last 15 years. On the contrary, in this section, we selected prominent studies focusing on the analysis of most relevant environmental samples with the aim to provide a good basis for current and future XRF users interested in environmental applications.

5.1. Geological samples

Geological samples are one of the most common environmental samples analysed by XRF. It encompasses the determination of major, minor and trace elements and also geological sample characterization. The analysis of these types of solid samples with other spectroscopic techniques usually involves a previous digestion of the sample, which is a difficult and tedious procedure in view of the presence of silicates in most of the geological matrices. The advantage of the XRF technique for geological sample analysis is related to the potential use of a simpler sample preparation in which no acid digestion is required. Usually geological samples are prepared as pellets (Schramm, 2016), as loose powders (dos Santos et al., 2021) or as fusion beads (Moore et al., 2018; Schramm, 2016). In last years, miniaturized sample treatments involving the use of a reduced amount of sample (0.01–0.2 g sample for bead preparation, 0.1 g sample for pellet preparation, 0.2–0.5 g for loose powders) have been proposed in combination with WDXRF analysis (Amosova et al., 2016; Gazulla et al., 2012; Ichikawa et al., 2016; Rydberg, 2014) to be able to characterize samples that owing to their size could otherwise only be analysed by μ -XRF or electron microscopy. Although the WDXRF is a well-known technique for geological sample analysis, the EDXRF has been recently preferred in this field due to the possibility to get simultaneous screening sample information. We selected and commented notorious applications of XRF for soil and sediments and for geological studies in 5.1.1 and 5.1.2 sections, respectively.

5.1.1. Soils and sediments

Elemental determination in soil and sediments are of high importance in environmental studies. It encompasses studies such as weathering processes, elemental cycles and more recently environmentally toxic elements monitoring mostly due to anthropogenic activity contributions. Both EDXRF and WDXRF are traditional analytical techniques for elemental determination in soil and sediments. Recently, TXRF has also been used to get appropriate geochemical data for interpretation of field data (Bilo et al., 2019; Pashkova et al., 2018).

An interesting application of XRF in soils and sediment analyses is the determination of halides (Pashkova et al., 2016) (Gallardo et al., 2016a). Halides are difficult to be measured by classical spectroscopy techniques due to the fact that samples must be convert in liquid by utilizing acid solutions, and elements such as Br and I are lost during the sample preparation step (Yamasaki et al., 2015). In addition, most recently some studies evaluate soil fertility by using EDXRF and multivariate analysis (dos Santos et al., 2020; Tavares et al., 2020, 2019).

Some other interesting applications of XRF in the soil and sediment field include the possibility of in-situ analysis and also the direct analysis of sediment cores (without a previous sample treatment). As it is shown in Fig. 4, although the undoubted benefits of portable XRF and corescanner XRF systems, the major drawbacks to obtain reliable data are related to the soil moisture and organic matter content and the particle size of the sample. Recently, some studies have been published with the aim to study the effect of such variables in the quality of the obtained results (Parsons et al., 2013; Woodward and Gadd, 2019).

After the publication of the EPA Method 6200 in 2007 (USEPA, 2007), many other studies have been performed using portable XRF (p-EDXRF, also referred as HHXRF, Hand-held XRF) instrumentation (Ravansari et al., 2020). At present it is widely accepted that p-EDXRF is not just a point and shoot method as long as calibration of the system is properly carried out. Table 2 highlights relevant soil environmental studies by portable XRF in the last years. They encompass contamination and remediation investigations and also agricultural parameters evaluation, such as fertility. Soil types include industrial, urban and agricultural one. Elements role range from essential ones for plants (i.e. Mg, S,

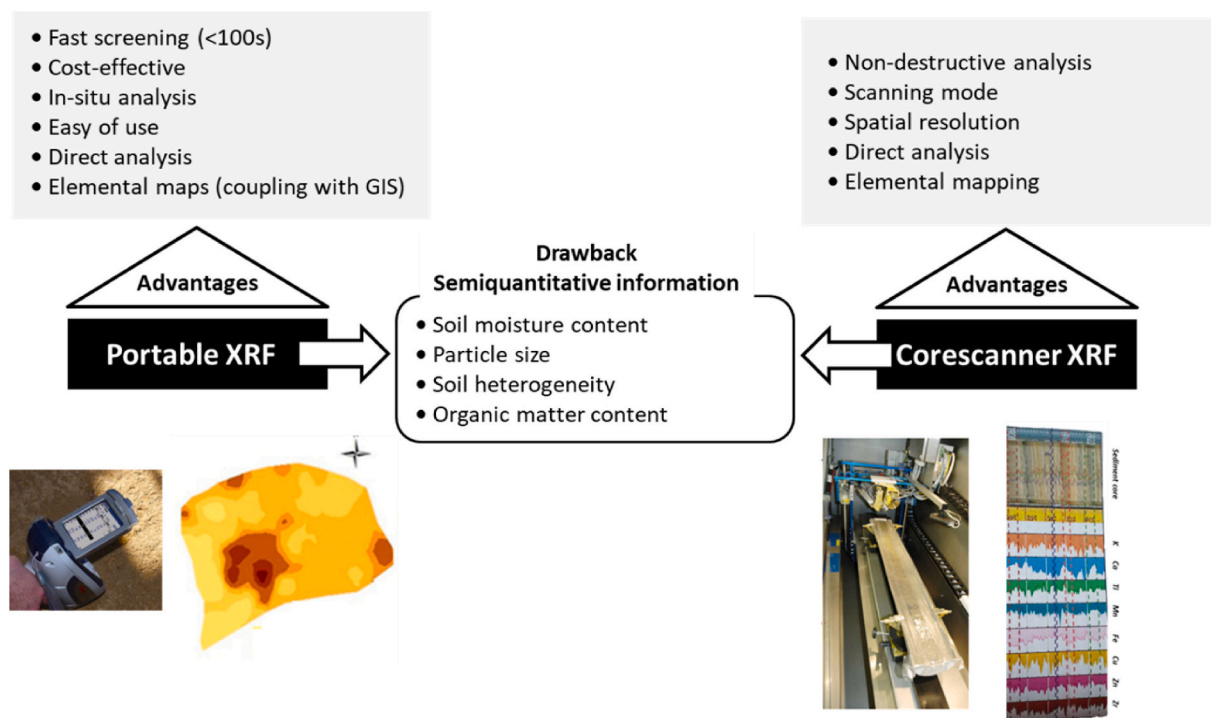


Fig. 4. Advantages and drawbacks of portable and core scanner XRF systems in the environmental field (Figure adapted from literature (Beckhoff et al., 2006; Hu et al., 2014)).

Table 2
Representative examples of application of portable XRF instrumentation to soil analysis.

Application	Soil type	Elements	LOD (mg/kg)	Measurement Time (s)	X-ray source	Remarks	Reference
Evaluation of metal contamination and remediation	Different contamination soil types	Pb, Fe, Zn, Cu, As	10	30	X-ray tube (Ag, 40 kV)	Elemental distribution maps (coupling with GIS)	Chou et al. (2010)
	Soil gardens	Pb	n.a (mg/kg level)	60	Radioisotope ¹⁰⁹ Cd	Quality control test according to the USEPA Method 6200	Clark et al. (2006)
	Alluvial soils (mining area)	Pb	n.a (mg/kg level)	30	X-ray tube (Ag, 40 kV, 50 μA)	2D and 3D Pb distribution	Hürkamp et al. (2009)
	Urban soils	Pb, Cu, Zn, As	10	n.a.	X-ray tube (Ag, 35 kV)	Elemental distribution maps (coupling with GIS)	Carr et al. (2008)
	Industrial	Cu, Pb, As, Cd, Zn, Fe, Ni, Mn	10	300	Radioisotope ¹⁰⁹ Cd/ ²⁴¹ Am	Comparison Radioisotope/X-ray tube sources	Kilbride et al. (2006)
					X-ray tube (Ag, 40 kV, 50 μA)	Quality control according to US EPA protocol -	
	Floodplain soils	As	6.8	100	X-ray tube (Ag, 40 kV, 50 μA)	Evaluation of sample treatments (insitu/ex situ analysis). Comparison ICP.	Parsons et al. (2013)
	Different contamination soil types	Mn, Zn, Pb	3–9	20	X-ray tube (Ta, 50 kV, 4W)	Evaluation of <i>in situ</i> /ex situ analysis. Comparison ICP-MS	Rouillon et al. (2017)
	Agricultural soils	As, Pb, Cu, Zn	n.a. (mg/kg level)	90	X-ray tube (Ag, 40 kV, 50 μA)	Elemental distribution maps (coupling with GIS)	Hu et al. (2014)
	Mining soils	As, Pb, Zn, Cu	1–50	90	X-ray tube (Ag, 40 kV, 50 μA)	Quality control according to US EPA protocol	Peinado et al. (2010)
Evaluation of soil parameters and fertility	Agricultural soils	Ca	n.a.	60	X-ray tube (Ta, 35 kV)	Tests on natural and synthetic soils. Evaluation of sample treatments (<i>in situ</i> /ex situ analysis).	Zhu and Weindorf (2009)
	Agricultural soils	Ca, Ti, V, Cr, Fe, Cu, Sr, Zr	n.a.	90	X-ray tube (Rh, 15–40 keV)	Evaluation of cation exchange capacity (CEC)	Sharma et al. (2015)
	Salt-impacted soils	Cl, S, K, Ca	60 (Cl)	90	X-ray tube (Ta/Au, 10–40 kV)	Evaluation of soil salinity	Swanhart et al. (2014)
	Agricultural soils	Mg, Ca, K	n.a.	90	X-ray tube (Rh, 8–50 kV)	Determination of soil base saturation percentage (BSP)	Rawal et al. (2019)
	Agricultural soils	K, Ca	n.a.	90	X-ray tube (Rh, 15 kV)	Predict exchange nutrient in soil	Tavares et al. (2019)

GIS: Geographic information system.

Cl, K, Mn and Fe) and also potentially toxic elements (i.e. Cr, Pb, Ni and As). Limits of detection using portable instrumentation are within 1–60 mg kg⁻¹ depending on the element, which is adequate for a myriad of soil inorganic constituent's studies. The measuring time for soil analysis by XRF (20–500 s) is similar or even shorter than that associated with EDXRF laboratory instrumentation. It is also interesting to highlight from Table 2 that sample excitation is mostly carried out by an X-ray tube and the use of the radioisotope X-ray source are increasingly scarcer, and nowadays practically not utilized any longer. In addition, the recent portable XRF and GIS (Geographic Information Systems) coupling allows elemental maps which are especially suited in studies dealing with the determination of hotspots in contaminated areas (Kim and Choi, 2019).

As shown in Fig. 4, the corescaner system brings the opportunity of the sample scanning, spatial resolution and even elemental mapping of unprocessed sediments which is of special interest in paleo-environmental changes and climate variability studies (Rothwell and Cloudace, 2015). In this sense, for instance, Löwemark et al. (2008) evaluated Mn content in central Arctic Ocean sediment by core scanner XRF, which suggested the Mn cycles are due to the alteration of environmental conditions, highlighting column ventilation and riverine input, then relating to interglacial and glacial variations. Westerhold and Röhl (2009) showed the cyclostratigraphy of the tropical western Atlantic of the early Eocene by XRF core scanning. This study contributed to a better understanding of the Cenozoic cooling trend. In addition, since XRF core scanning may face sample heterogeneity, the method must be carefully evaluated. Dunlea et al. (2020) compared XRF core scanning results of marine sediments from 7 laboratories. Count rates (cps) were different among laboratories, but elemental ratio showed more consistent result. In addition, log-ratio showed a more

similar result than linear calibration data. Attention must be paid in smaller-scale analysis, in which the lack of reproducibility is quite frequent.

5.1.2. Other geological materials

It is also common the use of XRF as a support and complementary analytical technique in geochemical research, due to its fast, multi-elemental and no-destructive analysis features. For instance, XRF is used for characterizing the composition and purity of rocks and minerals, in combination with methods that provide insight into the crystallographic structure such as X-ray diffraction analysis (XRD) or other spectroscopic methods. Siyanbola et al. (2005) applied a EDXRF method for Nigerian zircons composition determination. In this study, besides zirconium, 21 other elements (minor and trace levels) were also quantified. Likewise, Charlier et al. (2007) determined major and trace elements by XRF and LA-ICP-MS in ilmenite from the Tellnes deposit, SW Norway, thus affording a better understanding of this ilmenite formation deposit. Moore et al. (2018) studied the Steens basalt, southeast Oregon, USA, by using XRF and ICP-MS. The stratigraphic data from these analyses unfold changes in lava flow and rock mineral composition, and consequently reveals the magma alterations balance along the time.

In some geochemical studies, it is also of interest to get information about element composition at microscale level. For instance, studying impurities in rock systems is important to gain an understanding on how the minerals themselves had been synthesized and how inhomogeneous coloured patterns are formed. At present, this is possible by analysing the target sample using μ-EDXRF. Using such analytical approach, samples can be analysed without a previous sample treatment (Zhang and Sakurai, 2009) or after preparing a thin section of the target solid sample (Genna et al., 2011). Recently, Maltsev and co-workers also

reported the use of TXRF for elemental analysis of apatite microcrystals in geological applications (Maltsev et al., 2020, 2021). In both cases, nitric acid digestion of a small amount of the mineral powder or single apatite microcrystal was used as sample treatment approach.

In the mining sector, recognition of wall rock and valuable grade ore portions within a mining site is of crucial importance. In this sense, p-EDXRF systems are of special interest for mining engineers to outline blocks of similar ore content and also to study the metal content in remaining mining wastes after the mine closure (Marguí et al., 2007).

Finally, it is also important to mention the increasing interest in the determination of rare earth elements (REEs) in geological materials in view of the wide range of industrial applications of these elements including manufacturing of phones, computers and wind turbines. In this sense XRF has been proved to be a potential analytical technique for such purpose (Batchu and Regadío, 2019). However, the quality of the obtained results depends on the choice of the sample preparation method, the measurement conditions, the calibration strategy and also the proper selection of the analytical lines, in view of the severe overlapping issues of REEs characteristic X-ray lines with those from other major elements present in the geological materials (Schramm, 2016). Very recently, Akhmetzhanov et al. (2021) evaluated multi and univariate calibration for REEs determination in ores by TXRF and WDXRF.

5.2. Vegetal samples

Plants require inorganic elements for functioning and complete their life cycle. The evaluation of those elements fosters a better understanding of the elemental role and shows the nutritional status of a plant. Besides the physiological and agronomical importance, environmental studies on potentially toxic elements in vegetables from either natural or anthropogenic sources have been also increased in last years.

Among many analytical techniques for screening and monitoring inorganic constituents in plants, XRF must be highlighted due to the simplicity, multielemental capability and minimum sample treatment required for analysis (Marguí et al., 2009b). In Table 3 a summary of published methods using XRF for the analysis of different types of vegetation samples is displayed. Details about the determined elements as well as the sample preparation procedure and XRF system used in these studies are also included in this table.

The combination of selective excitation and reduction of the background of X-ray spectra when using polarised-beam EDXRF (3D-EDXRF) instrumentation leads to a significant improvement in the sensitivity achieved for trace elements in vegetal samples compared to WDXRF and EDXRF, and determination of some important pollutant elements (Cd, Hg, As, Pb) is feasible at the low mg/kg range. For this reason, as it is shown in Table 3, a significant part of the reported studies dealing with the analysis of vegetal samples has been performed using 3D-EDXRF systems.

The application of portable EDXRF instrumentation for multielemental analysis of plant materials has been also documented. For instance, p-EDXRF was employed to scan a large set of vegetation matrices (i.e., thatch, deciduous leaves, grasses, tree bark, and herbaceous plants) to study the potential metal contamination of a smelter-impacted area (McGladdery et al., 2018). It is also important to remark the role of TXRF for the determination of minor and trace elements in the analysis of vegetal mass-limited samples such as biofilms and mosses. Interestingly, since TXRF requires a very small amount of the sample for analysis (micrograms), the digestion procedure can be directly carried out on the surface of the sample carrier where the sample is deposited (Hoefler et al., 2006), shown in Table 3. In addition to trace metals, TXRF has also been used to determine carbon content for a better understanding of the biofilm growth. However, for such purpose, a specially designed TXRF spectrometer with a Cr X-ray source, a vacuum chamber and a detector with an ultra-thin window was required (Óvári et al., 2009). It is interesting to note that, in the last years, other publications have highlighted the potential of TXRF as a reliable

technique for multielemental analysis of other type of samples such as mosses (Natali et al., 2016), soybean root and shoot (de Almeida et al., 2020), vegetal foodstuff (Dalipi et al., 2017) and microgreens (Allegretta et al., 2019).

In some studies, it is of paramount importance to get information about the element location or distribution within vegetal tissues. For that, imaging techniques with an adequate lateral resolution are required, such as μ -EDXRF. Usually, most of the studies dealing with μ -EDXRF in plant sciences are combining high-brilliance synchrotron radiation and high-performance X-ray microfocusing optics (SR- μ -XRF). Using this approach very rapid bulk analysis on small areas (spot smaller than 1 mm) with very low detection limits are assessed, allowing the investigation of different aspects of plant sciences (i.e., plant physiology, morphology, ecology, biochemistry, etc.), even at cellular level, as it has been reported in a review published by Vijayan et al. (2015). Analytical methods for elemental mapping in vegetation tissues by using laboratory μ -EDXRF systems, with a lower sensitivity and resolution, have also been described for instance for the mapping of macro and micro nutrients in bio-fortified wheat grains (Ramos et al., 2016) and Ce monitoring in soybean roots exposed to CeO₂ 25 nm (Rodrigues et al., 2021) as well as in carrot sections grown in soils irrigated with municipal treated wastewater (Gallardo et al., 2016b).

As it is shown in Table 3, one of the most commonly used sample treatment approaches when dealing with the analysis of vegetal samples by EDXRF, WDXRF and 3D-EDXRF is the preparation of a pressed pellet (0.1–4 g, \varnothing : 13–40 mm) from the powdered material. Due to the binding capacities of cellulose, the addition of a binder it is usually not necessary to create stable pellets. As aforementioned, in applications where the amount of samples available is smaller, TXRF is preferred. In this case, sample preparation consists of a preparation of a suspension from the grounded material or the application of a digestion procedure. Finally, it is interesting to remark that for quantification purposes, FP-based and empirical calibration are the methods of choice but also in some cases, Compton normalization is used to compensate absorption effects arising from the vegetal matrix.

5.3. Atmospheric particulate matter

Atmospheric particulate matter (PM) is one of most critical pollutants in air. Its source may be either natural or anthropogenic. PM is composed of solids or droplets and traditionally it is divided into two categories based on the particle size: coarse particles or PM₁₀ ($\varnothing < 10 \mu\text{m}$) and fine particles or PM_{2.5} ($\varnothing < 2.5 \mu\text{m}$). However, even more fine particles ($\varnothing < 0.5 \mu\text{m}$) are a matter of increasing concern. In the last years, the main aims of environmental studies related with PM are focussed on the evaluation of air pollution or workplace air quality.

Usually, PM sampling consist of the collection of particles of different size ranges on different substrates by means of an impactor device. Then, the loaded-substrate is used to estimate the content of PM and also its chemical composition. One of the advantages of XRF over other analytical techniques such as ICP-OES or ICP-MS is the possibility to analyse the loaded-substrate directly or with a minimum sample treatment. In Fig. 5, a summary of the most commonly analytical XRF approaches for the elemental characterization of PM is displayed. As it can be seen, one of the strategies is the use of filters made of different low Z materials (i.e., polytetrafluoroethylene (PTFE), polyvinylchloride (PVC), Polypropylene (PPE), Polycarbonate (PC)) as sampling substrates. Then, the loaded filter can be directly analysed by WDXRF, EDXRF, 3D-EDXRF or p-EDXRF. Due to its portability, the last ones are especially suited to be used in indoor studies to evaluate the workplace air quality. It is also interesting to mention that recently real-time measurements of elements in PM₁₀ and PM_{2.5} have been reported using a EDXRF spectrometer designed for online analysis (Rai et al., 2020). In Table 4, representative examples of applications of XRF in air pollution studies are presented. In spite of the simple sample treatment required to carry out the XRF analysis of the loaded filter, quantification

Table 3
Types of vegetation samples analysed by XRF techniques in environmental studies.

Type of sample	Elements	Sample preparation	XRF system	Remarks	Reference
Biofilms	C	Direct analysis TXRF substrate	TXRF (Cr, 30 kV, 1900W)	TXRF substrates <40 µg, IS: Ag (L line)	Hoefler et al. (2006)
	C	Lyophilisation MW digestion (HNO ₃)	TXRF (Cr, 30 kV, 12 mA)	Polished granite/Plexiglas substrates 50–100 mg, IS: Ti (sample), 2.5 µL deposition	Óvári et al. (2009)
Mosses	K, Ca, Ti, Cr, Mn, Fe, Ni, Co, CU, Zn, Pb	Drying, grinding (powder) Pressed pellet (100 mg, Ø:13 mm)	EDXRF (⁵⁵ Fe, ²⁴¹ Am)	Method of multiple standard additions Normalization by Compton peak	Ozdemir et al. (2010)
	Al, As, Br, Ca, Ce, Cl, Cr, Cu, Fe, K, Mn, Ni, V, P, Pb, Rb, S, Sr, Ti, Zn	Slurry preparation (4–8 mg/1 mL deionized water, electromagnetic vibration)	TXRF (Mo, 60 kV, 60 mA)	4–8 mg, IS: Ga, 100 µL deposition Comparison slurry/digestion	Natali et al. (2016)
Lichens	K, S, Ca, Ti, Mn, Fe, Ni, Cu Zn, Cl, Br, Sr, Pb, Rb	Drying MW digestion (HNO ₃)	Portable TXRF (Mo, 50 kV, 0.75 mA)	150 mg, IS: Ga, 10 µL deposition	Borgese et al. (2009)
	Ca, K, Fe, Ba, Ti, Sr	Drying, grinding (powder) Pressed pellet (100 mg, Ø:13 mm)	EDXRF (⁵⁵ Fe, ²⁴¹ Am)	Method of multiple standard additions Normalization by Compton peak	Aslan et al. (2010)
Algae	Cu	Cells digestion (HNO ₃ +H ₂ O ₂)	TXRF (Mo)	IS: Ga, 10 µL deposition	Sabatini et al. (2009)
	As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Zn	Dissection of sections from the mid-thallus	P-EDXRF (Ag, 50 kV, 0.2 mA)	Quantification by fundamental parameters based alpha coefficient correction model	Bull et al. (2017)
Fungi	Nd, Pb, Th, U	Drying, grinding (powder) Pressed pellet (5 g, Ø:40 mm).	WDXRF (Rh, 4 kW)	Addition of binder to make the pellet	Campos et al. (2009)
	K, Mg, Fe, Zn	Drying, grinding (powder) Loose powder (2 g, plastic cup)	EDXRF (Rh, 50 kV, 0.1 mA)		Radulescu et al. (2010)
Seeds	n.a. (Chemometric study of the EDXRF spectra) P, K, S, Ca, Fe, Mg, Cl, Na	Direct analysis 32 mm cells (Mylar film)	EDXRF (Rh, 4–50 kV, 50W)	Chemometric study for samples classification	Alexandre and Bueno (2006)
Leaves	Na, Mg, Al, P, S, K, Ca, Mn, Fe, Co, Zn, As, Sr, Pb	Drying, grinding (powder) Pressed pellet (1 g + 0.5 g boric acid)	WDXRF (Rh, 20–60 kV)		Barua et al. (2008)
	Cd, Pb, As, Cu, Fe, Zn	Drying, grinding (powder) Pressed pellet (Ø:32 mm)	WDXRF (Rh, 1 kW)	Quantification by empirical calibration (CRMs and synthetic cellulose standards)	Marguí et al. (2005)
	Pb, Zn, Cu, Fe, Mn, Cr	SMART Store: the leaf punch between two organic foils (thickness of 75 mm each) one side adhesive. Then, it cuts the sandwiched sample in a disc, 30 mm diameter	3D-EDXRF (Gd, 25–100 kV, 600W)	Targets: Al ₂ O ₃ (Cd), KBr (Fe, Cu, Zn, As), Zr (Pb)	Marguí et al. (2006)
	K,Ca, Cr, Ti, V, Mn, Ni, Cu, Zn, Ga, Rb, Sr, Fe	Vegetation was compressed into a small bundle (~2 cm thick) and secured on both ends with rubber bands	TXRF (Mo, 50 kV, 0.75 mA)	Quantification by empirical calibration (Cd) and standardless fundamental parameters (Fe, Cu, Zn, As, Pb)	Bilo et al. (2017)
	Pb, Zn	Direct analysis	EDXRF (Mo, 30 kV, 10 mA)	Comparison SMART Store/digestion	Adebiyi and Asubiojo (2008)
	K, Ca, Cr, Ti, V, Mn, Ni, Cu, Zn, As, Sr, Y, Pb	Drying, grinding (powder) Pressed pellet (Ø: 13 mm).	P-EDXRF (Rh, 10–40 kV)	Study of different sample treatments	McGladdery et al. (2018)
Medicinal plants	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Mo, Te, I, Ba, La Ce	Drying, grinding (powder) Pressed pellet (4 g, Ø: 32 mm).	µ-EDXRF (200 µm)	Element distribution maps	Marguí et al. (2009a)
	K, Mg, Ca, P, S, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cl, Br, I, Al, Rb, Sr, Cd, Sn, Pb	Drying, grinding (powder) Pressed pellet	TXRF (Mo)	500 mg, IS: Se, 2 µL deposition	Turnau et al. (2010)
	Ti, Mn, Fe, Cr, Ni, Cu, Zn, Sr, Ba	Drying, grinding (powder) Pressed pellet (1 g)	3D-EDXRF (Rh, 400W)	Addition of binder to make the pellet	Üstündağ (2009)
	K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ba, Pb	Drying MW digestion (EPA 3052)	3D-EDXRF (Pd, 400W)	Normalization by Compton peak Calibration using a set of CRMs	Desideri et al. (2010)
Vegetal foodstuff	K, Ca, Mn, Fe, Ni, CU, Zn, Br, Rb, Sr	Lyophilisation, grinding (powder) Pressed pellet (30–50 mg/cm ²)	WDXRF (Rh, 50 kV, 40 mA)	Calibration using a set of CRMs	Chuparina and Aisueva (2011)
	As	Drying Digestion (HNO ₃ + H ₂ O ₂)	Portable TXRF (Mo, 50 kV, 0.75 mA)	250 mg, IS: Ga, 10 µL deposition	Dalipi et al. (2018)
	K,Ca, Mn, Fe, Cu, Zn, Br, Rb, Sr, Pb, As, Sn	Slurry preparation (20 mg/1 mL deionized water, 5 min sonication)	EDXRF (¹⁰⁹ Cd, 3–20 keV)	Quantification by fundamental parameter method Cauliflower	Gupta et al. (2010)
			TXRF (Mo, 40 kV, 20 mA)	200 mg, IS: Co, 5 µL deposition Onion samples	Marcó Parra (2011)
			Portable TXRF (W, 50 kV, 1 mA)	20 mg, IS: Ga, 10 µL deposition Comparison slurry/digestion, IS/external calibration	Dalipi et al. (2017)

(continued on next page)

Table 3 (continued)

Type of sample	Elements	Sample preparation	XRF system	Remarks	Reference
	P, S, K, Ca, Cl, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr	Slurry preparation (100 mg/5 mL 1% Triton X-100 solution, 15 min sonication)	Portable TXRF (Mo, 50 kV, 600 μ A)	100 mg, IS: Ga, 10 μ L deposition Comparison with ICP-OES results	Allegretta et al. (2019)
	Na, Mg, Al, Si, P, Cl, K, Ca, Mn, Fe, Cu, Zn, Br, Sr, Pb	EDXRF: Drying, grinding (powder) Pressed pellet (2 g, ϕ :40 mm). μ -EDXRF: Tangential/longitudinal cuts (0.2 mm) and lyophilisation	EDXRF (Pd, max.50W) μ -EDXRF (25 μ m, polycapillary)	EDXRF: Quantification by empirical calibration using a set of CRMs μ -EDXRF: element distribution maps Carrots	Gallardo et al. (2016b)
	Se, S, Na, Ca, K, Co, Cu, Mn	Direct analysis	μ -EDXRF (30 μ m, polycapillary)	Element distribution maps Cowpea plants	Silva et al. (2018)
	P, K, Ca, Zn, Fe, Mn	Tangential/longitudinal cuts	μ -EDXRF (25 μ m, polycapillary)	μ -EDXRF: element distribution maps Wheat grains	Ramos et al. (2016)

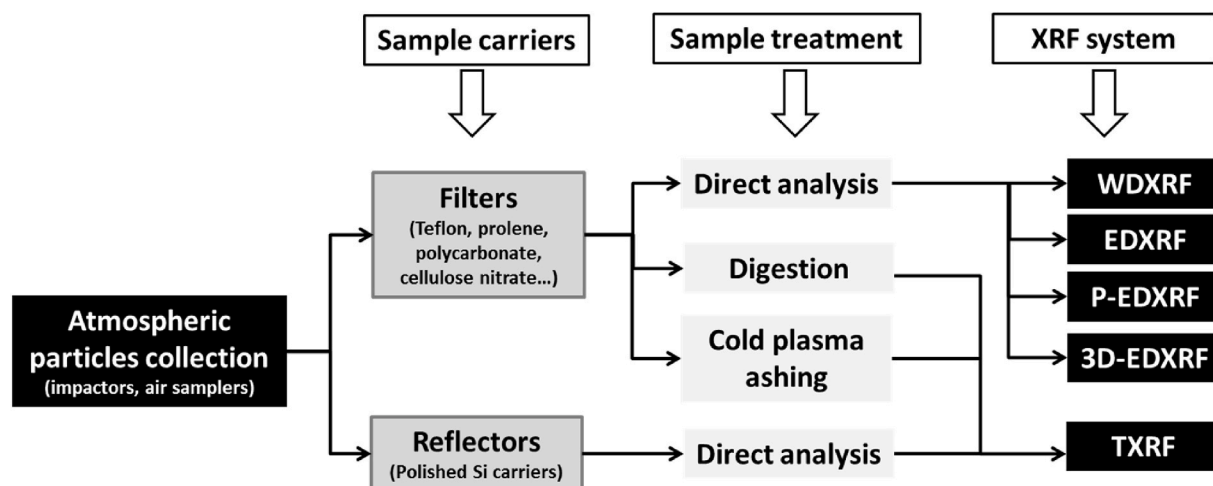


Fig. 5. Most commonly used XRF strategies in air pollution studies.

approaches including matrix correction models are sometimes necessary to obtain reliable results. This step is sometimes critical in view of the limited number of suitable PM reference materials commercially available. For this reason, multielemental standard reference materials prepared as aerosol PM deposited on PC filters can be also utilized (Yatkin et al., 2018). Other important features to obtain reliable analytical results in the direct analysis of aerosol filters include the volume/spatial homogeneity of the sample and the stability of the analytical signal (Rousseau et al., 1996). As it can be seen in Table 4, limits of detection using direct XRF analysis of the loaded filters are in the range of 0.01–150 ng/m^3 depending on the element of interest and type of XRF spectrometer used. Lower limits of detection (pg/m^3 range) can be assessed using more sensitive instrumentation such as TXRF.

As shown in Fig. 5 and Table 4, in TXRF analysis, the loaded filters are digested before deposition on the sample carriers (i.e., quartz reflector) (Zereini et al., 2005) or can be cut, fixed on the reflector and cold plasma ashed (CPA). Wagner and Mages (2010) showed that CPA is superior to conventional pressure digestion methods with regard to the ease of sample preparation and contamination. More recently, Borgese et al. (2020) proposed an alternative procedure to prepare filter samples for their measurement in TXRF spectrometers. This method, named SMART STORE®, consists of plasticizing the loaded filter between two thin polymeric foils, cutting in a disc of 30 mm diameter which is placed on a disc carrier for further TXRF analysis. This procedure allows the reduction of the preparation time and the sample is not destroyed, making possible the re-analysis. Finally, in more specific studies, another possibility to avoid intermediate wet-chemical preparation steps is to directly collect the aerosol particles on the sample carrier used

to perform TXRF analysis. In this sense, Prost et al. (2017) demonstrated that the direct collection of aerosol particles on greased quartz reflectors using a PM10 impactor, reduce the risk of contamination and samples can be measured directly and undiluted. In a recent publication, acrylic glass discs and silicon wafers were shown to be suitable carriers, with sufficiently smooth and clean surfaces, for TXRF analysis of PM as well (Seeger et al., 2021). Finally, in addition to PM characterization, TXRF has also been used to determine the concentration of airborne Hg (Böttger et al., 2020). In this case, Hg was trap onto quartz reflectors coated with Ag nanoparticles and further analysed by TXRF. Using this analytical approach, a limit of detection of 0.018 $\mu\text{g}/\text{m}^3$ was obtained, which was suitable in view of the European regulated threshold.

5.4. Water and aqueous extracts

In the last years, great concern has been raised about chemical pollution of waterbodies. In fact, at European level, the health of water resources has been identified as a mission area in the next research and innovation framework programme Horizon Europe. Inorganic pollutants monitoring in waters is usually performed by sensitive multielemental techniques such as ICP-MS, which allow the direct analysis of liquid samples. However, XRF has also been used for the determination of inorganic pollutants in different types of water samples including drinking (Borgese et al., 2014), rain (Dhara and Misra, 2011), river (Melquiades et al., 2011), ground (Espinoza-Quinones et al., 2015), thermal (Marguí et al., 2010a), waste (Marguí et al., 2010d) and sea (Peng et al., 2012; Yadav and Jha, 2013) waters. In some environmental studies it is also of special interest the determination of inorganic

Table 4
Representative examples of application of XRF systems in air pollution studies (PM elemental characterization).

Aim	Elements	LOD	Sample carrier	Sample preparation	XRF system	Reference
Evolution of anthropogenic aerosols composition	Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Hg, Pb	0.003–60 (ng/m ³)	Plastic support (Perspex®)	Direct analysis	TXRF (Mo, 50kV, 50W)	Lammel et al. (2007)
Composition and sources of aerosol particles	S, Cl, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Pb	0.01 (ng/m ³)	Polycarbonate filters	Cold plasma ashing	TXRF (Mo, 50 kV, 55 mA)	Wagner and Mages (2010)
Elemental characterization of PM ₁₀ aerosol particles	K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Pb	0.03–0.1 (ng/m ³)	Quartz reflectors	Direct analysis ^a	TXRF	Prost et al. (2017)
Study of airborne silver nanoparticles from fabrics	Ag	4 (ng/m ³)	Si-wafer reflectors	Direct analysis	TXRF (Mo, 50 kV, 50W)	Menzel and Fittschen (2014)
Synthetic PM samples prepared in the laboratory	Pb	0.011 (µg/cm ²)	PTFE membranes	SMART STORE®	TXRF (Mo, Rh)	Borgese et al. (2020)
Characterization of PM _{2.5} and PM ₁₀ in indoor and outdoor environments	Fe, Zn, Mn, Cu, Pb, U, Ti, Ni, As, Cr, Sr	<1.1 (ng/m ³)	Teflon filters	Direct analysis	3D-EDXRF (W, Mo, Sm targets)	Niu et al. (2010)
PM ₁₀ composition after an intense Sahara dust transport	Si, Al, Fe, K, Ca, Mg, Ti, S, Ni, Cu, Zn, Mn	1-100 (ng/cm ²)	Nucleopore membranes (pore size: 0.45 µm)	Direct analysis	3D-EDXRF (Pd, 60 kV, 50W)	Remoundaki et al. (2011)
PM ₁₀ , PM _{2.5} and PM ₁ daily samples collected in sites with different morphological and urbanization characteristics	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Zr, Mo Ba, Pb	1-10 (ng/m ³)	Teflon filters (pore size: 2 µm)	Direct analysis	EDXRF (Ag, 50 kV, 1 mA)	Mazzei et al. (2008)
PM _{2.5} composition to evaluate potential contamination sources	Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Pb	0.04–11 (ng/m ³)	Teflon filters (pore size: 3 µm)	Direct analysis	EDXRF (Mo, 40 kV, 40W)	Aboh et al. (2007)
Characterization of particles in a dental office (PM ₁₀)	Na, Mg, Al, Si, P, S, Cl, K, Ca, Zn, Se, Br, Sr, Zr, As, Ba	0.01–2 (ng/m ³)	Teflon membrane filters	Direct analysis	EDXRF (n.a.)	Sotiriou et al. (2008)
Quantitative XRF results for single aerosol particles	Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb	0.41–11.7 (ng/cm ²)	Mylar film	Direct analysis	µ-EDXRF (Mo, 60kV-200mA, 300 × 300 µm ²)	Sun et al. (2011)
Characterization and health effects ultrafine ash aerosols from coal combustion	Si, Al, Ca, Fe, Mg, Na, K, Cl, S	n.a.	Polycarbonate filters	Direct analysis	WDXRF	Linak et al. (2007)
Airborne lead levels in workplaces	Pb	6.79 (µg/sample)	Cellulose ester membrane filters	Direct analysis	P-EDXRF (¹⁰⁹ Cd source)	Kim et al. (2007)
Assessment of worker inhalation exposures to metals	Cr, Cu, Fe, Mn, Ni, Pb, Zn	n.a.	Cellulose, glass fibre, PTFE, PVC, PPE filters	Direct analysis	P-EDXRF (¹⁰⁹ Cd source)	Lawryk et al. (2009)

PTFE: polytetrafluoroethylene, PVC: polyvinylchloride, PPE: Polypropylene.

^a After removing the Vaseline (to reduce particle bounce-off) by cold plasma ashing.

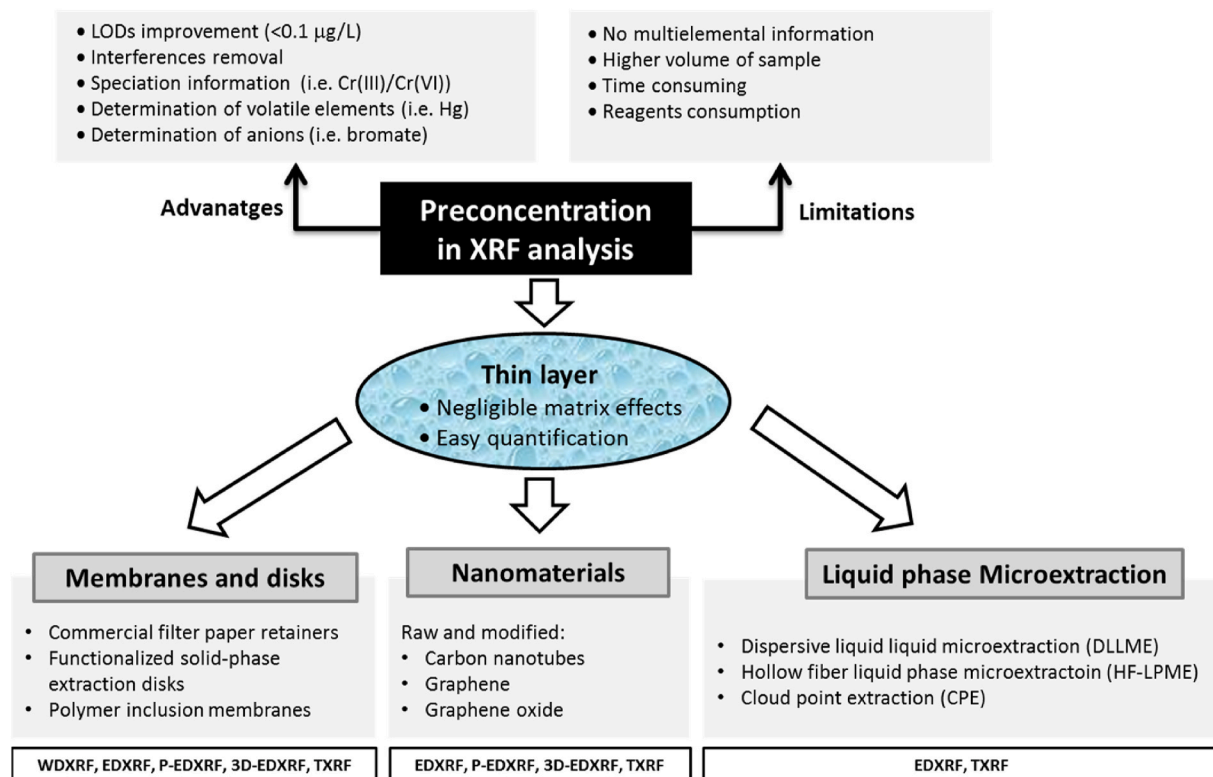


Fig. 6. Overview of advantages, limitations and basic principles of recent preconcentration procedures used in combination with XRF analysis.

pollutants in soil extracts and extraction solutions used, for instance, to simulate rain water-soil interactions and the so-called total metal free content in soils, among others. XRF spectrometry has proved to be also effective for such purpose (Gallardo et al., 2016a; Marguí et al., 2010a).

Usually, liquid analysis by XRF is performed using TXRF instrumentation which is especially suited for that purpose (Pashkova and Revenko, 2015). Other EDXRF and WDXRF systems have also been used but, as mentioned in section 3, the main constraints are their high limit of detection (usually in the mg/L level), which are not adequate for most environmental studies. To circumvent this limitation, in most cases, a previous preconcentration procedure is applied. Many preconcentration methods have been proposed in the literature (Marguí et al., 2010e) so far but considering that XRF operates best on solid samples and gives optimal sensitivity and accuracy for thin, homogeneous targets, those procedures leading to solid thin targets are the preferred ones to be used in combination with XRF (Marguí et al., 2014). As it is shown in Fig. 6, an overview of the advantages, limitations and basic principles of recent preconcentration procedures used in combination with different XRF systems is shown. It is important to remark that when using a preconcentration procedure you can extend the analytical capabilities of XRF systems to the determination of inorganic species (Marguí et al., 2014), volatile elements (i.e., Hg (Marguí et al., 2010c)) and anions (i.e., perchlorate (Hatzistavros and Kallithrakas-Kontos, 2011)), which is not possible by direct analysis of the liquid sample. However, the main limitations of preconcentration procedures are the higher volume of sample needed and the consumption of reagents and time.

As it can be seen in Fig. 6, commercial filter papers and functionalized solid-phase extraction disks have been used as suitable retainers for example for the determination of divalent cations (i.e., Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Fe^{2+}) in waste and mining water samples (Marguí et al., 2012). This approach can be also used for a fast and cost-effective screening and rapid monitoring of water composition in the field, if combined with portable XRF systems (Pessanha et al., 2020; Tighe et al., 2020). Another possibility to collect the target pollutants from water samples is the use of polymer inclusion membranes (PIMs). PIMs are a type of functionalized membranes in which a suitable carrier is immobilized within the chains of a plasticized thermoplastic polymer. PIMs are easy to prepare, possess good mechanical properties and are versatile in terms of the target chemical species they can extract and transport (Almeida et al., 2017). In a recent publication, a PIM made of cellulose triacetate (CTA) and an ionic liquid was shown to effectively extract Hg (II) from different natural waters prior its quantification by EDXRF at ultratrace levels (Elias et al., 2018). In this study, it was also demonstrated that the PIM-sorbent was a suitable medium to preserve the analyte for a 6-month period at room temperature. This finding opens the possibility to explore the use of PIMs also as a suitable medium to cope with stability problems of some analytes during sample storage. The use of PIMs has been also used in combination with TXRF spectrometry to remove matrix effects in the analysis of complex waters samples such as sea water (Hatzistavros and Kallithrakas-Kontos, 2014). In the case of TXRF analysis, the membranes are directly created on the centre of the sample carrier and thus the quantities of the reagents needed are significantly reduced in comparison when they are applied in combination with conventional XRF systems. Another interesting approach for the labile elemental determination in aquatic samples is the coupling of the diffusive gradient in thin films (DGT) technique to the EDXRF (Almeida et al., 2012; Chen et al., 2013).

In the last years, some authors have also explored the design of novel focussed-tuneable absorbent materials to expand the applications of XRF in the field of water analysis. In this category it is important to highlight the potential of solid nano-adsorbents. Their large surface area, fast sorption kinetics and their low resistance to diffusion are features especially relevant in adsorption of both organic and inorganic species in complex samples. Carbon-based nanomaterials (i.e., Carbon nanotubes (CNTs), graphene (G), graphene oxide (GO)) are especially convenient to be used as solid sorbents in combination with XRF due to

the fact that carbon atoms do not emit characteristic X-ray radiation in the spectrum region of interest. Moreover, due to the very small particle size of this type of nanomaterials, particle size effects can be neglected and the loaded materials with the analytes of interest can be directly analysed by XRF without a previous elution step (Marguí et al., 2014). One of the former studies published on this topic demonstrated the usefulness of CNTs as solid sorbents for multielemental preconcentration (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Se, Pb and Cd) in water samples. The developed method was applied in combination with different XRF systems (including large-scale WDXRF, EDXRF and 3D-EDXRF) (Marguí et al., 2013b). More recently, a nanocomposite prepared from graphene nanosheets and cerium nanoparticles (G/CeO₂) was applied in combination with EDXRF for ultratrace element determination and to the speciation of selenium in environmental waters (Baranik et al., 2018). The usefulness of preconcentration using nanomaterials and TXRF analysis, after a suspension preparation of the loaded nanomaterial, have also been proved in several studies including the determination of ultratraces of Cd in Pb in different types of water samples (Kocot et al., 2013) or the determination of divalent ions and inorganic arsenic species in estuarine and ground waters (Sitko et al., 2015).

Finally, liquid phase microextraction procedures (LPME) have been also employed as suitable preconcentration strategies to be used in combination with XRF. In LPME systems only several μL of solvent are required to concentrate analytes from the liquid sample and thus it is in line with the principles of green analytical chemistry. After the LPME procedure, the preconcentrated sample (small drop) is deposited and dried on a suitable thin-film substrate for conventional XRF analysis or it can be deposited directly on a quartz reflector if using TXRF.

Some examples of application include the determination of Se at trace levels in soil extracts (Marguí et al., 2010b), the determination of inorganic Sb speciation in mineral water samples and the determination of trace levels of Cd (Marguí et al., 2013a) or Fe, Co, Zn, Pb, Se and Pb (Sitko et al., 2011) in different types of environmental waters. In the last years a variant of LPME called cloud point extraction (CPE) has been applied in combination with several detection analytical techniques for the determination and/or fractionation of metallic nanoparticles (Chao et al., 2011). In this method, NPs are encapsulated in the micelles after the addition of a surfactant (usually TritonTM X-114) and concentrated to a small volume with the assistance of centrifugation. Some recent publications have proved also the usefulness of the combination of CPE and TXRF for the quantification of AgNPs and AuNPs in water samples and soil extracts (Bahadir et al., 2018; Torrent et al., 2018).

In view of the design and use of novel extraction materials and the development of novel extraction procedures it is expected the development of new interesting applications of XRF in the field of water analysis.

5.5. Solid wastes

Technologies have evolved at a fast pace in the last decades. Besides new products launched in the market, an increasing amount and variety of by-product wastes has also been generated. In this context, *in situ* and expeditious analysis system for characterization and regulatory compliance tests of a myriad of technological waste is required. The non-destructive and solid direct analysis XRF technique shows undoubtedly a promising tool in this environment field. Below, a summary of the most common applications in the field of solid wastes analysis is presented.

Since the implementation of the new EU Directives on restriction on hazardous substances (RoHS) and waste electrical and electronic equipment (WEEE) in July 2006, the development of analytical methods to control the level of these hazardous substances is making significant progress. In this sense, p-EDXRF systems have been successfully applied without any sample preparation as screening tools for compliance testing of different types of wastes (construction, shredder materials, waste wood, and slag from a municipal incinerator waste) (Vanhoof et al., 2013). However, characterization of metals in most electronic

wastes is very difficult owing to their great heterogeneity and the mixture of different electronic products. In these cases, a previous treatment of the sample before XRF analysis is required. It seems that a size reduction of the particles down to 1.5 mm could be already sufficient for decision making with respect to RoHS compliance. However, to ensure analytical results with relative standard deviations of less than 20%, as recommended by the EN62321, further particle size reduction might be required. Of course, it depends on the mass fraction of the element under investigation (Wienold et al., 2011). Another drawback in the framework of RoHS and WEEE is the lack of suitable standards required to set up a quantitative method. The whole solution for the analysis of the huge variety of material matrices involved in the RoHS Directive is not achieved at present. In this sense, Mans et al. (2007) produced granulated and solid body acrylonitrile-butadiene-styrene-based plastic standards containing Br, Cd, Cr, Hg, and Pb. Specifically, EDXRF was successfully utilized as analytical tool for investigation of the potentially toxic elements release from batteries and electronic components deposited in soils (Rodrigues dos Santos et al., 2017).

The brominated flame retardant hexabromocyclododecane (HBCDD) was added some years ago to the list of persistent organic pollutants (POPs) of the Stockholm Convention. In this view, Schlummer et al. (2015) developed a method for identification and quantification of HBCDD in polystyrene foam wastes by Br evaluation utilizing a p-EDXRF system. The obtained results agreed with those obtained using gas chromatography coupled to flame ionization detector. In the field of catalysts, Van Meel et al. (2007) developed a fast procedure, based on the formation of a pressed pellet using wax as a binder material, for the determination of precious metals (Pd, Pt, and Rh) in spent automotive catalyst using 3D-instrumentation. One of the major benefits of the method was to avoid the digestion of the sample which is really difficult due to the complexity of the catalyst matrix.

The increasing occurrence of (micro)plastic litter in the ocean has become an emerging issue of international concern in the last years. From an analytical point of view, it is of special interest to have analytical techniques for a proper identification of the polymer type that (micro)plastics are made of but also to get information regarding the element content in this type of particulate materials. Therefore, is necessary to develop fully validated methods for metal analysis in different polymers to contribute to a better understanding of the role of microplastics as vector and carrier for trace metals in the environment.

In the field of element determination in plastic samples, XRF shows a promising tool for *in situ* characterisation and/or screening but also for quantitative analysis with simple or no sample preparation. An additional advantage of XRF is the possible determination of non-metallic elements (i.e., Br, Cl), which are difficult to be measured by other spectroscopic analytical methods and play an important role in plastics characterization (Aldrian et al., 2015). Tuner and co-workers, bring out the potential of p-EDXRF systems for multielement analysis of different types of petroleum-based plastics (i.e., polystyrene foam, acrylonitrile butadiene styrene (ABS), PVC) collected in the marine environment (Turner et al., 2020). While not as sensitive as ICP-based techniques, portable XRF systems seems to be adequate for the determination of most elements present in plastics with limits of detection in the range of 10–100 mg kg⁻¹.

6. Summary and future perspectives

Over the last past decades, X-ray fluorescence spectrometry (XRF) has evolved into a reduced cost and powerful analytical technique for multielemental analysis of wide variety of samples, mostly in solid state. Technological developments, including the design of X-ray miniaturized sources, the production of low-power micro-focus tubes, the novel X-ray optics devices and the improvement in signal detection systems have made possible the commercialization of benchtop and portable instrumentation (without the use of radioactive sources and consumables) that offer extreme simplicity of operation in a low-cost design.

Unfortunately, this kind of XRF systems present still some weaknesses mostly related to the limited sensitivity for the determination of trace and ultratrace elements and matrix effects caused by elements present in the solid sample. In this sense, matrix correction models and adequate calibration approaches have to be developed to obtain meaningful results. In most cases, this is not an easy task and for this reason the use of XRF in some applications has been limited and questioned by many analytical chemists. In this context, additional research on the development of adequate quantification strategies and the use of chemometrics tools that can help to get more reliable XRF analytical results would be welcome. This point can be of special interest to improve also performance of portable or low cost XRF devices.

In the field of liquid analysis, XRF has been hardly used in comparison with other multielemental atomic spectroscopic techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS). In this sense it is important to highlight the design and use of novel “smart materials” that has become a major trend in the development of novel extraction procedures in the analytical chemistry of the 21st century. Despite of the wide application of such materials for preconcentration purposes before chromatographic or atomic spectroscopic analysis, their potential in combination with XRF spectrometry has been less explored. This is undoubtedly a field of worth investigation which can open new interesting applications of XRF in the field of water analysis. Moreover, if the preconcentration procedure is simple and rapid enough (i.e. filtration procedure using an adequate extraction material) it can be even used for *in-situ* measurements in the field, in view of the availability of portable XRF instrumentation.

Therefore, nowadays, a new horizon has opened up for us. The use of simple, effective and cutting edge sample treatment methods and development of more effective quantification approaches using suitable standards and chemometric tools will for sure influence the applicability of XRF in the environmental field in the upcoming years.

Authors contribution statement

Eva Marguí: Conceptualization, data curation, writing- original draft; writing-review & editing.

Ignasi Queral: Writing-review & editing.

Eduardo de Almeida: Conceptualization, data curation, writing-original draft; writing-review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Aboh, I.J.K., Henriksson, D., Laursen, J., Lundin, M., Pind, N., Lindgren, E.S., Wahnström, T., 2007. EDXRF characterisation of elemental contents in PM_{2.5} in a medium-sized Swedish city dominated by a modern waste incineration plant. *X Ray Spectrom.* 36, 104–110. <https://doi.org/10.1002/xrs.947>.
- Adebisi, F.M., Asubiojo, O.I., 2008. Assessment of element accumulation from bitumen deposit by vegetation using Energy Dispersive X-ray Fluorescence (EDXRF) spectroscopy technique. *Chem. Ecol.* 24, 423–435. <https://doi.org/10.1080/02757540802497467>.
- Akhmetzhanov, T.F., Pashkova, G.V., Chubarov, V.M., Labutin, T.A., Popov, A.M., 2021. Three calibration techniques combined with sample-effective design of experiment based on Latin hypercube sampling for direct detection of lanthanides in REE-rich ores using TXRF and WDXRF. *J. Anal. At. Spectrom.* 36, 224–232. <https://doi.org/10.1039/D0JA00264J>.

- Aldrian, A., Ledersteger, A., Pomberger, R., 2015. Monitoring of WEEE plastics in regards to brominated flame retardants using handheld XRF. *Waste Manag.* 36, 297–304. <https://doi.org/10.1016/j.wasman.2014.10.025>.
- Alexandre, T.L., Bueno, M.I.M.S., 2006. Classification of some species, genera and families of plants by x-ray spectrometry. *X Ray Spectrom.* 35, 257–260. <https://doi.org/10.1002/xrs.900>.
- Allegretta, I., Gattullo, C.E., Renna, M., Paradiso, V.M., Terzano, R., 2019. Rapid multi-element characterization of microgreens via total-reflection X-ray fluorescence (TXRF) spectrometry. *Food Chem.* 296, 86–93. <https://doi.org/10.1016/j.foodchem.2019.05.187>.
- Almeida, E. de, Nascimento Filho, V.F. do, Menegário, A.A., 2012. Paper-based diffusive gradients in thin films technique coupled to energy dispersive X-ray fluorescence spectrometry for the determination of labile Mn, Co, Ni, Cu, Zn and Pb in river water. *Spectrochim. Acta B Atom Spectrosc.* 71–72, 70–74. <https://doi.org/10.1016/j.sab.2012.05.006>.
- Almeida, M.I.G.S., Catrall, R.W., Kolev, S.D., 2017. Polymer inclusion membranes (PIMs) in chemical analysis - a review. *Anal. Chim. Acta* 987, 1–14. <https://doi.org/10.1016/j.aca.2017.07.032>.
- Amosova, A.A., Panteeva, S.V., Chubarov, V.M., Finkelshtein, A.L., 2016. Determination of major elements by wavelength-dispersive X-ray fluorescence spectrometry and trace elements by inductively coupled plasma mass spectrometry in igneous rocks from the same fused sample (110 mg). *Spectrochim. Acta B Atom Spectrosc.* 122, 62–68. <https://doi.org/10.1016/j.sab.2016.06.001>.
- Aslan, A., Apaydin, G., Yazici, K., Cengiz, E., Aylikci, V., Tirasoglu, E., 2010. Analysis of trace element concentrations of some lichens of Turkey. *Asian J. Chem.* 22, 389–400.
- Bahadır, Z., Torrent, L., Hidalgo, M., Marguí, E., 2018. Simultaneous determination of silver and gold nanoparticles by cloud point extraction and total reflection X-ray fluorescence analysis. *Spectrochim. Acta B Atom Spectrosc.* 149, 22–29. <https://doi.org/10.1016/j.sab.2018.07.016>.
- Baranik, A., Gagor, A., Queralt, I., Marguí, E., Sitko, R., Zawisza, B., 2018. Ceria nanoparticles deposited on graphene nanosheets for adsorption of copper(II) and lead(II) ions and of anionic species of arsenic and selenium. *Microchim. Acta* 185, 264. <https://doi.org/10.1007/s00604-018-2806-6>.
- Barua, A.G., Hazarika, S., Pathak, J.S., Kalita, C., 2008. Spectroscopic investigation of the seeds of chilli (*Capsicum annum* L.). *Int. J. Food Sci. Nutr.* 59, 671–678. <https://doi.org/10.1080/09638280701623810>.
- Batchu, N.K., Regadio, M., 2019. Methodologies and developments in the analysis of REEs. In: *Critical and Rare Earth Elements*. CRC Press, pp. 365–373. <https://doi.org/10.1201/9780429203545-19>.
- Beckhoff, B., Kanngießer habil, B., Langhoff, N., Wedell, R., Wolff, H. (Eds.), 2006. *Handbook of Practical X-Ray Fluorescence Analysis*. Springer Berlin Heidelberg, Berlin, Heidelberg. <https://doi.org/10.1007/978-3-540-36722-2>.
- Bilo, F., Borgese, L., Cazzago, D., Zacco, A., Bontempi, E., Guarnieri, R., Bernardello, M., Attuati, S., Lazo, P., Depero, L.E., 2014. TXRF analysis of soils and sediments to assess environmental contamination. *Environ. Sci. Pollut. Control Ser.* 21, 13208–13214. <https://doi.org/10.1007/s11356-013-2203-y>.
- Bilo, F., Borgese, L., Dalipi, R., Zacco, A., Federici, S., Masperi, M., Leonasio, P., Bontempi, E., Depero, L.E., 2017. Elemental analysis of tree leaves by total reflection X-ray fluorescence: new approaches for air quality monitoring. *Chemosphere* 178, 504–512. <https://doi.org/10.1016/j.chemosphere.2017.03.090>.
- Bilo, F., Borgese, L., Pardini, G., Marguí, E., Zacco, A., Dalipi, R., Federici, S., Bettinelli, M., Volante, M., Bontempi, E., Depero, L.E., 2019. Evaluation of different quantification modes for a simple and reliable determination of Pb, Zn and Cd in soil suspensions by total reflection X-ray fluorescence spectrometry. *J. Anal. At. Spectrom.* 34, 930–939. <https://doi.org/10.1039/C9JA00040B>.
- Borgese, L., Zacco, A., Bontempi, E., Colombi, P., Bertuzzi, R., Ferretti, E., Tenini, S., Depero, L.E., 2009. Total reflection of x-ray fluorescence (TXRF): a mature technique for environmental chemical nanoscale metrology. *Meas. Sci. Technol.* 20, 084027. <https://doi.org/10.1088/0957-0233/20/8/084027>.
- Borgese, L., Bilo, F., Tsuji, K., Fernández-Ruiz, R., Marguí, E., Strelci, C., Pepponi, G., Stosnach, H., Yamada, T., Vandenabeele, P., Maina, D.M., Gatari, M., Shepherd, K. D., Towett, E.K., Bennun, L., Custo, G., Vasquez, C., Depero, L.E., 2014. First Total Reflection X-Ray Fluorescence round-robin test of water samples: preliminary results. *Spectrochim. Acta B Atom Spectrosc.* 101, 6–14. <https://doi.org/10.1016/j.sab.2014.06.024>.
- Borgese, L., Bilo, F., Zacco, A., Federici, S., Mutahi, A.W., Bontempi, E., Trzepla, K., Hyslop, N., Yatkin, S., Wobruschek, P., Prost, J., Ingerle, D., Depero, L.E., 2020. The assessment of a method for measurements and lead quantification in air particulate matter using total reflection X-ray fluorescence spectrometers. *Spectrochim. Acta B Atom Spectrosc.* 167, 105840. <https://doi.org/10.1016/j.sab.2020.105840>.
- Böttger, S., Kolny-Olesiak, J., Fittschen, U.E.A., 2020. A comparison of different nanoscopic silver species with respect to their capacity to bind mercury from the gas-phase using total reflection X-ray fluorescence. *Spectrochim. Acta B Atom Spectrosc.* 170, 105903. <https://doi.org/10.1016/j.sab.2020.105903>.
- Bruker, 2022. S2 Picofox.
- Bull, A., Brown, M.T., Turner, A., 2017. Novel use of field-portable-XRF for the direct analysis of trace elements in marine macroalgae. *Environ. Pollut.* 220, 228–233. <https://doi.org/10.1016/j.envpol.2016.09.049>.
- Campos, J.A., Tejera, N.A., Sánchez, C.J., 2009. Substrate role in the accumulation of heavy metals in sporocarps of wild fungi. *Biomaterials* 22, 835–841. <https://doi.org/10.1007/s10534-009-9230-7>.
- Carr, R., Zhang, C., Moles, N., Harder, M., 2008. Identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyser and GIS. *Environ. Geochem. Health* 30, 45–52. <https://doi.org/10.1007/s10653-007-9106-0>.
- Chao, J., Liu, J., Yu, S., Feng, Y., Tan, Z., Liu, R., Yin, Y., 2011. Speciation analysis of silver nanoparticles and silver ions in antibacterial products and environmental waters via cloud point extraction-based separation. *Anal. Chem.* 83, 6875–6882. <https://doi.org/10.1021/ac201086a>.
- Charlier, B., Skår, Ø., Korneliussen, A., Duchesne, J.-C., Vander Auwera, J., 2007. Ilmenite composition in the Tellnes Fe–Ti deposit, SW Norway: fractional crystallization, postcumulus evolution and ilmenite–zircon relation. *Contrib. Mineral. Petrol.* 154, 119–134. <https://doi.org/10.1007/s00410-007-0186-8>.
- Chen, Z., Williams, P.N., Zhang, H., 2013. Rapid and nondestructive measurement of labile Mn, Cu, Zn, Pb and as in DGT by using field portable-XRF. *Environ. Sci. J. Integr. Environ. Res.: Process. Impacts* 15, 1768. <https://doi.org/10.1039/c3em00250k>.
- Chou, J., Elbers, D., Clement, G., Bursavich, B., Tian, T., Zhang, W., Yang, K., 2010. In situ monitoring (field screening) and assessment of lead and arsenic contaminants in the greater New Orleans area using a portable X-ray fluorescence analyser. *J. Environ. Monit.* 12, 1722. <https://doi.org/10.1039/c0em00012d>.
- Chuparina, E.V., Aisueva, T.S., 2011. Determination of heavy metal levels in medicinal plant *Hemerocallis minor* Miller by X-ray fluorescence spectrometry. *Environ. Chem. Lett.* 9, 19–23. <https://doi.org/10.1007/s10311-009-0240-z>.
- Clark, H.F., Brabander, D.J., Erdil, R.M., 2006. Sources, sinks, and exposure pathways of lead in urban garden soil. *J. Environ. Qual.* 35, 2066–2074. <https://doi.org/10.2134/jeq2005.0464>.
- Dalipi, R., Marguí, E., Borgese, L., Depero, L.E., 2017. Multi-element analysis of vegetal foodstuff by means of low power total reflection X-ray fluorescence (TXRF) spectrometry. *Food Chem.* 218, 348–355. <https://doi.org/10.1016/j.foodchem.2016.09.022>.
- Dalipi, R., Borgese, L., Tsuji, K., Bontempi, E., Depero, L.E., 2018. Elemental analysis of teas, herbs and their infusions by means of total reflection X-ray fluorescence. *J. Food Compos. Anal.* 67, 128–134. <https://doi.org/10.1016/j.jfca.2018.01.010>.
- de Almeida, E., Montanha, G.S., Pereira de Carvalho, H.W., Marguí, E., 2020. Evaluation of energy dispersive X-ray fluorescence and total reflection X-ray fluorescence spectrometry for vegetal mass-limited sample analysis: application to soybean root and shoots. *Spectrochim. Acta B Atom Spectrosc.* 170, 105915. <https://doi.org/10.1016/j.sab.2020.105915>.
- Desideri, D., Meli, M.A., Roselli, C., 2010. Determination of essential and non-essential elements in some medicinal plants by polarised X ray fluorescence spectrometer (EDPXRf). *Microchem. J.* 95, 174–180. <https://doi.org/10.1016/j.microc.2009.11.010>.
- Dhara, S., Misra, N.L., 2011. Application of total reflection X-ray fluorescence spectrometry for trace elemental analysis of rainwater. *Pramana* 76, 361–366. <https://doi.org/10.1007/s12043-011-0035-1>.
- dos Santos, F.R., de Oliveira, J.F., Bona, E., dos Santos, J.V.F., Barboza, G.M.C., Melquiades, F.L., 2020. EDXRF spectral data combined with PLSR to determine some soil fertility indicators. *Microchem. J.* 152, 104275. <https://doi.org/10.1016/j.microc.2019.104275>.
- dos Santos, F.R., de Oliveira, J.F., Barbosa, G.M.C., Melquiades, F.L., 2021. Comparison between energy dispersive X-ray fluorescence spectral data and elemental data for soil attributes modelling. *Spectrochim. Acta B Atom Spectrosc.* 185, 106303. <https://doi.org/10.1016/j.sab.2021.106303>.
- Dunlea, A.G., Murray, R.W., Tada, R., Alvarez-Zarikian, C.A., Anderson, C.H., Gilli, A., Giosan, L., Gargas, T., Hennekam, R., Irino, T., Murayama, M., Peterson, L.R., Reichart, G., Seki, A., Zheng, H., Ziegler, M., 2020. Intercomparison of XRF core scanning results from seven labs and approaches to practical calibration. *G-cubed* 21. <https://doi.org/10.1029/2020GC009248>.
- Elias, G., Marguí, E., Díez, S., Fontàs, C., 2018. Polymer inclusion membrane as an effective sorbent to facilitate mercury storage and detection by X-ray fluorescence in natural waters. *Anal. Chem.* 90, 4756–4763. <https://doi.org/10.1021/acs.analchem.7b05430>.
- Espinoza-Quiones, F.R., Módenes, A.N., de Pauli, A.R., Palácio, S.M., 2015. Analysis of trace elements in groundwater using ICP-oes and TXRF techniques and its compliance with Brazilian protection standards. *Water, Air, Soil Pollut.* 226, 32. <https://doi.org/10.1007/s11270-015-2315-8>.
- Fernández-Ruiz, R., Friedrich, K.E.J., Redrejo, M.J., Pérez-Aparicio, R., Saiz-Rodríguez, L., 2020. Quantification of recycled rubber content of end-of-life tyres in asphalt bitumen by total-reflection X-ray fluorescence spectrometry. *Spectrochim. Acta B Atom Spectrosc.* 166, 105803. <https://doi.org/10.1016/j.sab.2020.105803>.
- Fittschen, U.E.A., Kunz, H.-H., Höhner, R., Tyssebotn, I.M.B., Fittschen, A., 2017. A new micro <sc>X-ray</sc> fluorescence spectrometer for *in vivo* elemental analysis in plants. *X Ray Spectrom.* 46, 374–381. <https://doi.org/10.1002/xrs.2783>.
- Gallardo, H., Queralt, I., Tapias, J., Candelá, L., Marguí, E., 2016a. Bromine and bromide content in soils: analytical approach from total reflection X-ray fluorescence spectrometry. *Chemosphere* 156, 294–301. <https://doi.org/10.1016/j.chemosphere.2016.04.136>.
- Gallardo, H., Queralt, I., Tapias, J., Guerra, M., Carvalho, M.L., Marguí, E., 2016b. Possibilities of low-power X-ray fluorescence spectrometry methods for rapid multielemental analysis and imaging of vegetal foodstuffs. *J. Food Compos. Anal.* 50, 1–9. <https://doi.org/10.1016/j.jfca.2016.04.007>.
- Gazulla, M.F., Vicente, S., Orduña, M., Ventura, M.J., 2012. Chemical analysis of very small-sized samples by wavelength-dispersive X-ray fluorescence. *X Ray Spectrom.* 41, 176–185. <https://doi.org/10.1002/xrs.2381>.
- Genna, D., Gaboury, D., Moore, L., Mueller, W.U., 2011. Use of micro-XRF chemical analysis for mapping volcanogenic massive sulfide related hydrothermal alteration: application to the subaqueous felsic dome-flow complex of the Cap d'Ours section, Glenwood rhyolite, Rouyn-Noranda, Québec, Canada. *J. Geochem. Explor.* 108, 131–142. <https://doi.org/10.1016/j.gexplo.2010.12.001>.

- Gupta, D., Chatterjee, J.M., Ghosh, R., Mitra, A.K., Roy, S., Sarkar, M., 2010. Radioisotope-induced EDXRF investigation of elemental uptake in cauliflower grown at MSW-contaminated site. *X Ray Spectrom.* 39, 364–371. <https://doi.org/10.1002/xrs.1276>.
- Haschke, M., 2014. *Laboratory Micro-X-Ray Fluorescence Spectroscopy*. Springer International Publishing, Cham. <https://doi.org/10.1007/978-3-319-04864-2>.
- Hatzistavros, V.S., Kallithrakas-Kontos, N.G., 2011. Determination of trace perchlorate concentrations by anion-selective membranes and total reflection X-ray fluorescence analysis. *Anal. Chem.* 83, 3386–3391. <https://doi.org/10.1021/ac103295a>.
- Hatzistavros, V.S., Kallithrakas-Kontos, N.G., 2014. X-ray fluorescence mercury determination using cation selective membranes at sub-ppb levels. *Anal. Chim. Acta* 809, 25–29. <https://doi.org/10.1016/j.aca.2013.11.045>.
- Hoefler, H., Strelci, C., Wobrauschek, P., Óvári, M., Záray, G., 2006. Analysis of low Z elements in various environmental samples with total reflection X-ray fluorescence (TXRF) spectrometry. *Spectrochim. Acta B Atom Spectrosc.* 61, 1135–1140. <https://doi.org/10.1016/j.sab.2006.07.005>.
- Hu, W., Huang, B., Weindorf, D.C., Chen, Y., 2014. Metals analysis of agricultural soils via portable X-ray fluorescence spectrometry. *Bull. Environ. Contam. Toxicol.* 92, 420–426. <https://doi.org/10.1007/s00128-014-1236-3>.
- Hürkamp, K., Raab, T., Völkel, J., 2009. Two and three-dimensional quantification of lead contamination in alluvial soils of a historic mining area using field portable X-ray fluorescence (FPXRF) analysis. *Geomorphology* 110, 28–36. <https://doi.org/10.1016/j.geomorph.2008.12.021>.
- Ichikawa, S., Onuma, H., Nakamura, T., 2016. Development of undersized (12.5 mm diameter) low-dilution glass beads for X-ray fluorescence determination of 34 components in 200 mg of igneous rock for applications with geochemical and archeological silicic samples. *X Ray Spectrom.* 45, 34–47. <https://doi.org/10.1002/xrs.2652>.
- Kilbride, C., Poole, J., Hutchings, T.R., 2006. A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP-OES and ex situ field portable X-ray fluorescence analyses. *Environ. Pollut.* 143, 16–23. <https://doi.org/10.1016/j.envpol.2005.11.013>.
- Kim, S.-M., Choi, Y., 2019. Mapping heavy metal concentrations in beach sands using GIS and portable XRF data. *J. Mar. Sci. Eng. T.* 7, 42. <https://doi.org/10.3390/jmse7020042>.
- Kim, N., Kim, J., Ahn, K., Lee, B., 2007. Use of field-portable X-ray fluorescence (FPXRF) analyzer to measure airborne lead levels in Korean workplaces. *J. Occup. Health* 49, 493–498. <https://doi.org/10.1539/joh.49.493>.
- Klockenkämper, R., von Bohlen, A. (Eds.), 2014. *Total-Reflection X-Ray Fluorescence Analysis and Related Methods*. John Wiley & Sons, Inc., Hoboken, New Jersey <https://doi.org/10.1002/9781118985953>.
- Kocot, K., Zawisza, B., Marguí, E., Queralt, I., Hidalgo, M., Sitko, R., 2013. Dispersive micro solid-phase extraction using multiwalled carbon nanotubes combined with portable total-reflection X-ray fluorescence spectrometry for the determination of trace amounts of Pb and Cd in water samples. *J. Anal. At. Spectrom.* 28, 736. <https://doi.org/10.1039/c3ja50047k>.
- Kunimura, S., Kawai, J., 2010. Polychromatic excitation improves detection limits in total reflection X-ray fluorescence analysis compared with monochromatic excitation. *Analyst* 135, 1909. <https://doi.org/10.1039/c0an00009d>.
- Lammel, G., Baumgardner, D.G., Fittschen, U.E.A., Peschel, B., 2007. Evolution of anthropogenic aerosols in the coastal town of Salina Cruz, Mexico: part III size-segregated elemental composition analysed by total-reflection X-ray fluorescence spectrometry. *Int. J. Environ. Anal. Chem.* 87, 659–672. <https://doi.org/10.1080/03067310701321967>.
- Lawryk, N.J., Feng, H.A., Chen, B.T., 2009. Laboratory evaluation of a field-portable sealed source X-ray fluorescence spectrometer for determination of metals in air filter samples. *J. Occup. Environ. Hyg.* 6, 433–445. <https://doi.org/10.1080/15459620902932119>.
- Leroux, I.N., Ferreira, A.P.S. da S, Silva, J.P. da R., Bezerra, F.F., da Silva, F.F., Salles, F. J., Luz, M.S., de Assunção, N.A., Cardoso, M.R.A., Olympio, K.P.K., 2018. Lead exposure from households and school settings: influence of diet on blood lead levels. *Environ. Sci. Pollut. Control Ser.* 25, 31535–31542. <https://doi.org/10.1007/s11356-018-3114-8>.
- Linak, W.P., Yoo, J.-I., Wasson, S.J., Zhu, W., Wendt, J.O.L., Huggins, F.E., Chen, Y., Shah, N., Huffman, G.P., Gilmour, M.I., 2007. Ultrafine ash aerosols from coal combustion: characterization and health effects. *Proc. Combust. Inst.* 31, 1929–1937. <https://doi.org/10.1016/j.proci.2006.08.086>.
- Liu, Y., Imashuku, S., Kawai, J., 2013. Multi-element analysis by portable total reflection X-ray fluorescence spectrometer. *Anal. Sci.* 29, 793–797. <https://doi.org/10.2116/analsci.29.793>.
- Löwemark, L., Jakobsson, M., Mörth, M., Backman, J., 2008. Arctic Ocean manganese contents and sediment colour cycles. *Polar Res.* 27. <https://doi.org/10.3402/polar.v27i2.6169>.
- Maltsev, A.S., Ivanov, A.V., Chubarov, V.M., Pashkova, G.V., Panteeva, S.V., Reznitskii, L.Z., 2020. Development and validation of a method for multi-element analysis of apatite by total-reflection X-ray fluorescence spectrometry. *Talanta* 214, 120870. <https://doi.org/10.1016/j.talanta.2020.120870>.
- Maltsev, A.S., Ivanov, A.V., Pashkova, G.V., Marfin, A.E., Bishaev, Y.A., 2021. New prospects to the multi-elemental analysis of single microcrystal of apatite by total-reflection X-ray fluorescence spectrometry. *Spectrochim. Acta B Atom Spectrosc.* 184, 106281. <https://doi.org/10.1016/j.sab.2021.106281>.
- Mans, C., Hanning, S., Simons, C., Wegner, A., Janßen, A., Kreyenschmidt, M., 2007. Development of suitable plastic standards for X-ray fluorescence analysis. *Spectrochim. Acta B Atom Spectrosc.* 62, 116–122. <https://doi.org/10.1016/j.sab.2007.02.001>.
- Marcó Parra, L.-M., 2011. Determination of total As in onion plants growing in contaminated substrates by total reflection X-ray fluorescence. *J. Radioanal. Nucl. Chem.* 287, 479–484. <https://doi.org/10.1007/s10967-010-0834-8>.
- Marguí, E., 2013. *X-Ray Fluorescence Spectrometry and Related Techniques*. Momentum Press. <https://doi.org/10.5643/9781606503935>.
- Marguí, E., Hidalgo, M., Queralt, I., 2005. Multielemental fast analysis of vegetation samples by wavelength dispersive X-ray fluorescence spectrometry: possibilities and drawbacks. *Spectrochim. Acta B Atom Spectrosc.* 60, 1363–1372. <https://doi.org/10.1016/j.sab.2005.08.004>.
- Marguí, E., Padilla, R., Hidalgo, M., Queralt, I., Van Grieken, R., 2006. High-energy polarized-beam EDXRF for trace metal analysis of vegetation samples in environmental studies. *X Ray Spectrom.* 35, 169–177. <https://doi.org/10.1002/xrs.890>.
- Marguí, E., Queralt, I., Carvalho, M.L., Hidalgo, M., 2007. Assessment of metal availability to vegetation (*Betula pendula*) in Pb-Zn ore concentrate residues with different features. *Environ. Pollut.* 145, 179–184. <https://doi.org/10.1016/j.envpol.2006.03.028>.
- Marguí, E., Jurado, A., Hidalgo, M., Pardini, G., Gispert, M., Queralt, I., 2009a. Application of small-spot energy dispersive X-ray fluorescence instrumentation in phytoremediation activities around metal mines. *Appl. Spectrosc.* 63, 1396–1402. <https://doi.org/10.1366/00037020979019021>.
- Marguí, E., Queralt, I., Hidalgo, M., 2009b. Application of X-ray fluorescence spectrometry to determination and quantitation of metals in vegetal material. *Trac. Trends Anal. Chem.* 28, 362–372. <https://doi.org/10.1016/j.trac.2008.11.011>.
- Marguí, E., Floor, G.H., Hidalgo, M., Kregsamer, P., Roman-Ross, G., Strelci, C., Queralt, I., 2010a. Applicability of direct total reflection X-ray fluorescence analysis for selenium determination in solutions related to environmental and geochemical studies. *Spectrochim. Acta B Atom Spectrosc.* 65, 1002–1007. <https://doi.org/10.1016/j.sab.2010.10.002>.
- Marguí, E., Floor, G.H., Hidalgo, M., Kregsamer, P., Román-Ross, G., Strelci, C., Queralt, I., 2010b. Analytical possibilities of total reflection X-ray spectrometry (TXRF) for trace selenium determination in soils. *Anal. Chem.* 82, 7744–7751. <https://doi.org/10.1021/ac101615w>.
- Marguí, E., Kregsamer, P., Hidalgo, M., Tapias, J., Queralt, I., Strelci, C., 2010c. Analytical approaches for Hg determination in wastewater samples by means of total reflection X-ray fluorescence spectrometry. *Talanta* 82, 821–827. <https://doi.org/10.1016/j.talanta.2010.05.066>.
- Marguí, E., Tapias, J.C., Casas, A., Hidalgo, M., Queralt, I., 2010d. Analysis of inlet and outlet industrial wastewater effluents by means of benchtop total reflection X-ray fluorescence spectrometry. *Chemosphere* 80, 263–270. <https://doi.org/10.1016/j.chemosphere.2010.04.027>.
- Marguí, E., Van Grieken, R., Fontàs, C., Hidalgo, M., Queralt, I., 2010e. Preconcentration methods for the analysis of liquid samples by X-ray fluorescence techniques. *Appl. Spectrosc. Rev.* 45, 179–205. <https://doi.org/10.1080/05704920903584198>.
- Marguí, E., Hidalgo, M., Queralt, I., Van Meel, K., Fontàs, C., 2012. Analytical capabilities of laboratory, benchtop and handheld X-ray fluorescence systems for detection of metals in aqueous samples pre-concentrated with solid-phase extraction disks. *Spectrochim. Acta B Atom Spectrosc.* 67, 17–23. <https://doi.org/10.1016/j.sab.2011.12.004>.
- Marguí, E., Queralt, I., Hidalgo, M., 2013a. Determination of cadmium at ultratrace levels in environmental water samples by means of total reflection X-ray spectrometry after dispersive liquid–liquid microextraction. *J. Anal. At. Spectrom.* 28, 266–273. <https://doi.org/10.1039/C2JA30252G>.
- Marguí, E., Zawisza, B., Skorek, R., Theato, T., Queralt, I., Hidalgo, M., Sitko, R., 2013b. Analytical possibilities of different X-ray fluorescence systems for determination of trace elements in aqueous samples pre-concentrated with carbon nanotubes. *Spectrochim. Acta B Atom Spectrosc.* 88, 192–197. <https://doi.org/10.1016/j.sab.2013.07.004>.
- Marguí, E., Zawisza, B., Sitko, R., 2014. Trace and ultratrace analysis of liquid samples by X-ray fluorescence spectrometry. *Trac. Trends Anal. Chem.* 53, 73–83. <https://doi.org/10.1016/j.trac.2013.09.009>.
- Marguí, E., Queralt, I., Van Grieken, R., 2016. Sample preparation for X-ray fluorescence analysis. In: *Encyclopedia of Analytical Chemistry*. John Wiley & Sons, Ltd, Chichester, UK, pp. 1–25. <https://doi.org/10.1002/9780470027318.a6806m.pub3>.
- Mazzei, F., D'Alessandro, A., Lucarelli, F., Nava, S., Prati, P., Valli, G., Vecchi, R., 2008. Characterization of particulate matter sources in an urban environment. *Sci. Total Environ.* 401, 81–89. <https://doi.org/10.1016/j.scitotenv.2008.03.008>.
- McComb, J.Q., Rogers, C., Han, F.X., Tchounwou, P.B., 2014. Rapid screening of heavy metals and trace elements in environmental samples using portable X-ray fluorescence spectrometer, A comparative study. *Water, Air, & Soil Pollut.* 225, 2169. <https://doi.org/10.1007/s11270-014-2169-5>.
- McGladdery, C., Weindorf, D.C., Chakraborty, S., Li, B., Paulette, L., Podar, D., Pearson, D., Kusi, N.Y.O., Duda, B., 2018. Elemental assessment of vegetation via portable X-ray fluorescence (PXRF) spectrometry. *J. Environ. Manag.* 210, 210–225. <https://doi.org/10.1016/j.jenvman.2018.01.003>.
- Melquades, F.L., Parreira, P.S., Appoloni, C.R., Silva, W.D., Lopes, F., 2011. Quantification of metals in river water using a portable EDXRF system. *Appl. Radiat. Isot.* 69, 327–333. <https://doi.org/10.1016/j.apradiso.2010.09.021>.
- Menzel, M., Fittschen, U.E.A., 2014. Total reflection X-ray fluorescence analysis of airborne silver nanoparticles from fabrics. *Anal. Chem.* 86, 3053–3059. <https://doi.org/10.1021/ac404017u>.
- Moore, N.E., Grunder, A.L., Bohrsen, W.A., 2018. The three-stage petrochemical evolution of the Steens Basalt (southeast Oregon, USA) compared to large igneous provinces and layered mafic intrusions. *Geosphere* 14, 2505–2532. <https://doi.org/10.1130/GES01665.1>.

- Natali, Marco, Zanella, Augusto, Rankovic, Aleksandar, Banas, Damien, Cantaluppi, Chiara, Abbadie, Luc, Lata, Jean Christophe, 2016. Assessment of trace metal air pollution in Paris using slurry-XRF analysis on cemetery mosses. *Environ. Sci. Pollut. Res.* 23, 23496–23510.
- Neves, V.M., Heidrich, G.M., Rodrigues, E.S., Enders, M.S.P., Muller, E.I., Nicoloso, F.T., Carvalho, H.W.P. de, Dressler, V.L., 2019. La 2 O 3 nanoparticles: study of uptake and distribution in *Pfaffia glomerata* (speng.) pedersen by LA-ICP-MS and μ -XRF. *Environ. Sci. Technol.* 53, 10827–10834. <https://doi.org/10.1021/acs.est.9b02868>.
- Niu, J., Rasmussen, P.E., Wheeler, A., Williams, R., Chénier, M., 2010. Evaluation of airborne particulate matter and metals data in personal, indoor and outdoor environments using ED-XRF and ICP-MS and co-located duplicate samples. *Atmos. Environ.* 44, 235–245. <https://doi.org/10.1016/j.atmosenv.2009.10.009>.
- Omote, J., Kohno, H., Toda, K., 1995. X-Ray fluorescence analysis utilizing the fundamental parameter method for the determination of the elemental composition in plant samples. *Anal. Chim. Acta* 307, 117–126. [https://doi.org/10.1016/0003-2670\(95\)00033-V](https://doi.org/10.1016/0003-2670(95)00033-V).
- Óvári, M., Strelci, C., Wobruschek, P., Zárny, G., 2009. Determination of carbon in natural freshwater biofilms with total reflection X-ray fluorescence spectrometry. *Spectrochim. Acta B Atom Spectrosc.* 64, 802–804. <https://doi.org/10.1016/j.sab.2009.05.022>.
- Ozdemir, T., Apaydin, G., Mendil, D., Bulut, V.N., E.C, Ayilicci, A.G., V, 2010. Determination of some elements in moss samples from north eastern Anatolia, Turkey. *Asian J. Chem.* 22, 346–352.
- Parsons, C., Marguí Grabulosa, E., Pili, E., Floor, G.H., Roman-Ross, G., Charlet, L., 2013. Quantification of trace arsenic in soils by field-portable X-ray fluorescence spectrometry: considerations for sample preparation and measurement conditions. *J. Hazard Mater.* 262, 1213–1222. <https://doi.org/10.1016/j.jhazmat.2012.07.001>.
- Pashkova, G.V., Revenko, A.G., 2015. A review of application of total reflection X-ray fluorescence spectrometry to water analysis. *Appl. Spectrosc. Rev.* 50, 443–472. <https://doi.org/10.1080/05704928.2015.1010205>.
- Pashkova, G.V., Aisueva, T.S., Finkelshtein, A.L., Ivanov, E.V., Shchetnikov, A.A., 2016. Analytical approaches for determination of bromine in sediment core samples by X-ray fluorescence spectrometry. *Talanta* 160, 375–380. <https://doi.org/10.1016/j.talanta.2016.07.059>.
- Pashkova, G.V., Aisueva, T.S., Finkelshtein, A.L., Cherkashina, T.Y., Shchetnikov, A.A., 2018. Quantitative approaches to the determination of elements in lake sediments by total reflection X-ray fluorescence. *Microchem. J.* 143, 264–271. <https://doi.org/10.1016/j.microc.2018.08.020>.
- Peinado, F.M., Ruano, S.M., González, M.G.B., Molina, C.E., 2010. A rapid field procedure for screening trace elements in polluted soil using portable X-ray fluorescence (PXRF). *Geoderma* 159, 76–82. <https://doi.org/10.1016/j.geoderma.2010.06.019>.
- Peng, Y.-Z., Huang, Y.-M., Yuan, D.-X., Li, Y., Gong, Z.-B., 2012. Rapid analysis of heavy metals in coastal seawater using preconcentration with precipitation/Co-precipitation on membrane and detection with X-ray fluorescence. *Chin. J. Anal. Chem.* 40, 877–882. [https://doi.org/10.1016/S1872-2040\(11\)60554-9](https://doi.org/10.1016/S1872-2040(11)60554-9).
- Peng, L., Li, X., Sun, X., Yang, T., Zhang, Y., Gao, Y., Zhang, X., Zhao, Y., He, A., Zhou, M., Cao, Y., Mielke, H.W., 2020. Comprehensive Urumqi screening for potentially toxic metals in soil-dust-plant total environment and evaluation of children's (0–6 years) risk-based blood lead levels prediction. *Chemosphere* 258, 127342. <https://doi.org/10.1016/j.chemosphere.2020.127342>.
- Pessanha, S., Marguí, E., Carvalho, M.L., Queralt, I., 2020. A simple and sustainable portable triaxial energy dispersive X-ray fluorescence method for in situ multielemental analysis of mining water samples. *Spectrochim. Acta B Atom Spectrosc.* 164, 105762. <https://doi.org/10.1016/j.sab.2019.105762>.
- Prost, J., Wobruschek, P., Strelci, C., 2015. Comparison of different excitation modes for the analysis of light elements with a TXRF vacuum chamber. *Powder Diffr.* 30, 93–98. <https://doi.org/10.1017/S088571561500024X>.
- Prost, J., Wobruschek, P., Strelci, C., 2017. Quantitative total reflection X-ray fluorescence analysis of directly collected aerosol samples. *X Ray Spectrom.* 46, 454–460. <https://doi.org/10.1002/xrs.2752>.
- Radulescu, C., Stihl, C., Busuioac, G., Popescu, I.V., Gheboianu, A.I., Cimpoa, V.G., 2010. Evaluation of essential elements and heavy metal levels in fruiting bodies of wild mushrooms and their substrate by EDXRF spectrometry and FAA spectrometry. *Romanian Biotechnol. Lett.* 15, 5444–5456.
- Rai, P., Furger, M., El Haddad, I., Kumar, V., Wang, L., Singh, A., Dixit, K., Bhattu, D., Petit, J.-E., Ganguly, D., Rastogi, N., Baltensperger, U., Tripathi, S.N., Slowik, J.G., Prévôt, A.S.H., 2020. Real-time measurement and source apportionment of elements in Delhi's atmosphere. *Sci. Total Environ.* 742, 140332. <https://doi.org/10.1016/j.scitotenv.2020.140332>.
- Ramos, I., Pataco, I.M., Mourinho, M.P., Lidon, F., Reboredo, F., Pessoa, M.F., Carvalho, M.L., Santos, J.P., Guerra, M., 2016. Elemental mapping of biofortified wheat grains using micro X-ray fluorescence. *Spectrochim. Acta B Atom Spectrosc.* 120, 30–36. <https://doi.org/10.1016/j.sab.2016.03.014>.
- Ravansari, R., Wilson, S.C., Tighe, M., 2020. Portable X-ray fluorescence for environmental assessment of soils: not just a point and shoot method. *Environ. Int.* 134, 105250. <https://doi.org/10.1016/j.envint.2019.105250>.
- Rawal, A., Chakraborty, S., Li, B., Lewis, K., Godoy, M., Paulette, L., Weindorf, D.C., 2019. Determination of base saturation percentage in agricultural soils via portable X-ray fluorescence spectrometer. *Geoderma* 338, 375–382. <https://doi.org/10.1016/j.geoderma.2018.12.032>.
- Remoundaki, E., Bourliva, A., Kokkalis, P., Mamouri, R.E., Papayannis, A., Grigoratos, T., Samara, C., Tsezos, M., 2011. PM10 composition during an intense Saharan dust transport event over Athens (Greece). *Sci. Total Environ.* 409, 4361–4372. <https://doi.org/10.1016/j.scitotenv.2011.06.026>.
- Rodrigues dos Santos, F., de Almeida, E., da Cunha Kemerich, P.D., Melquiades, F.L., 2017. Evaluation of metal release from battery and electronic components in soil using SR-TXRF and EDXRF. *X Ray Spectrom.* 46, 512–521. <https://doi.org/10.1002/xrs.2784>.
- Rodrigues, E.S., Gomes, M.H.F., Duran, N.M., Cassanji, J.G.B., da Cruz, T.N.M., Sant'Anna Neto, A., Savassa, S.M., de Almeida, E., Carvalho, H.W.P., 2018. Laboratory microprobe X-ray fluorescence in plant science: emerging applications and case studies. *Front. Plant Sci.* 9. <https://doi.org/10.3389/fpls.2018.01588>.
- Rodrigues, E.S., Montanha, G.S., de Almeida, E., Fantucci, H., Santos, R.M., de Carvalho, H.W.P., 2021. Effect of nano cerium oxide on soybean (*Glycine max* L. Merrill) crop exposed to environmentally relevant concentrations. *Chemosphere* 273, 128492. <https://doi.org/10.1016/j.chemosphere.2020.128492>.
- Rothwell, R.G., Cloude, I., 2015. *Micro-XRF Studies of Sediment Cores: Applications of a Non-destructive Tool for the Environmental Sciences*, 1a Edition. Springer.
- Rouillon, M., Taylor, M.P., Dong, C., 2017. Reducing risk and increasing confidence of decision making at a lower cost: in-situ pXRF assessment of metal-contaminated sites. *Environ. Pollut.* 229, 780–789. <https://doi.org/10.1016/j.envpol.2017.06.020>.
- Rousseau, R.M., Willis, J.P., Duncan, A.R., 1996. Practical XRF calibration procedures for major and trace elements. *X Ray Spectrom.* 25, 179–189. [https://doi.org/10.1002/\(SICI\)1097-4539\(199607\)25:4<179::AID-XRS162>3.0.CO;2-Y](https://doi.org/10.1002/(SICI)1097-4539(199607)25:4<179::AID-XRS162>3.0.CO;2-Y).
- Rydberg, J., 2014. Wavelength dispersive X-ray fluorescence spectroscopy as a fast, non-destructive and cost-effective analytical method for determining the geochemical composition of small loose-powder sediment samples. *J. Paleolimnol.* 52, 265–276. <https://doi.org/10.1007/s10933-014-9792-4>.
- Sabatini, S.E., Juárez, Á.B., Eppis, M.R., Bianchi, L., Luquet, C.M., Ríos de Molina, M. del C., 2009. Oxidative stress and antioxidant defenses in two green microalgae exposed to copper. *Ecotoxicol. Environ. Saf.* 72, 1200–1206. <https://doi.org/10.1016/j.ecoenv.2009.01.003>.
- Schlummer, M., Vogelsang, J., Fiedler, D., Gruber, L., Wolz, G., 2015. Rapid identification of polystyrene foam wastes containing hexabromocyclododecane or its alternative polymeric brominated flame retardant by X-ray fluorescence spectroscopy. *Waste Manag. Res.: J. Sustain. Circul. Econ.* 33, 662–670. <https://doi.org/10.1177/0734242X15589783>.
- Schramm, R., 2016. Use of X-ray fluorescence analysis for the determination of rare earth elements. *Phys. Sci. Rev.* 1. <https://doi.org/10.1515/psr-2016-0061>.
- Seeger, S., Osan, J., Czömpöly, O., Gross, A., Stosnach, H., Stabile, L., Ochsenkuehn-Petropoulou, M., Tsakanika, L.A., Lymperopoulou, T., Goddard, S., Fiebig, M., Gaie-Levrel, F., Kayser, Y., Beckhoff, B., 2021. Quantification of element mass concentrations in ambient aerosols by combination of cascade impactor sampling and mobile total reflection X-ray fluorescence spectroscopy. *Atmosphere* 12, 309. <https://doi.org/10.3390/atmos12030309>.
- Serranti, S., Capobianco, G., Malinconico, S., Bonifazi, G., 2020. Micro X-ray fluorescence imaging coupled with chemometrics to detect and classify asbestos fibers. In: *DEMOLITION WASTE*. Detritus, pp. 150–159. <https://doi.org/10.31025/2611-4135/2020.14007>.
- Sharma, A., Weindorf, D.C., Wang, D., Chakraborty, S., 2015. Characterizing soils via portable X-ray fluorescence spectrometer: 4. Cation exchange capacity (CEC). *Geoderma* 239–240, 130–134. <https://doi.org/10.1016/j.geoderma.2014.10.001>.
- Silva, V.M., Boleta, E.H.M., Lanza, M.G.D.B., Lavres, J., Martins, J.T., Santos, E.F., dos Santos, F.L.M., Putti, F.F., Junior, E.F., White, P.J., Bradley, M.R., Carvalho, H.W. P., Reis, de, dos, A.R., 2018. Physiological, biochemical, and ultrastructural characterization of selenium toxicity in cowpea plants. *Environ. Exp. Bot.* 150, 172–182. <https://doi.org/10.1016/j.envexpbot.2018.03.020>.
- Sitko, R., Kocot, K., Zawisza, B., Feist, B., Pytlakowska, K., 2011. Liquid-phase microextraction as an attractive tool for multielement trace analysis in combination with X-ray fluorescence spectrometry: an example of simultaneous determination of Fe, Co, Zn, Ga, Se and Pb in water samples. *J. Anal. At. Spectrom.* 26, 1979. <https://doi.org/10.1039/c1ja10143a>.
- Sitko, R., Janik, P., Zawisza, B., Talik, E., Marguí, E., Queralt, I., 2015. Green approach for ultratrace determination of divalent metal ions and arsenic species using total-reflection X-ray fluorescence spectrometry and mercapto-modified graphene oxide nanosheets as a novel adsorbent. *Anal. Chem.* 87, 3535–3542. <https://doi.org/10.1021/acs.analchem.5b00283>.
- Siyabol, W.O., Fasasi, A.Y., Funtua, I.I., Fasasi, M.K., Tubosun, I.A., Pelemo, D.A., Adesiyun, T.A., 2005. Energy dispersive X-ray fluorescence analysis of samples of the Nigerian Zircons. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 239, 426–432. <https://doi.org/10.1016/j.nimb.2005.05.043>.
- Skupio, R., 2020. Portable XRF spectrometer with helium flow as a tool for lithological interpretation. *Geol. Geophys. Environ.* 46, 315–320. <https://doi.org/10.7494/geol.2020.46.4.315>.
- Sotiriou, M., Ferguson, S.F., Davey, M., Wolfson, J.M., Demokritou, P., Lawrence, J., Sax, S.N., Kourtrakis, P., 2008. Measurement of particle concentrations in a dental office. *Environ. Monit. Assess.* 137, 351–361. <https://doi.org/10.1007/s10661-007-9770-7>.
- Sun, T., Liu, Z., Li, Y., Ma, Y., Wang, G., Zhu, G., Xu, Q., Lin, X., Luo, P., Pan, Q., Liu, H., Teng, Y., Ding, X., 2011. Size-resolved source apportionment of aerosol particles with a confocal micro X-ray fluorescence spectrometer. *Appl. Spectrosc.* 65, 1398–1402. <https://doi.org/10.1366/11-06354>.
- Swanhart, S., Weindorf, D.C., Chakraborty, S., Bakr, N., Zhu, Y., Nelson, C., Shook, K., Acree, A., 2014. Soil salinity measurement via portable X-ray fluorescence spectrometry. *Soil Sci.* 179, 417–423. <https://doi.org/10.1097/SS.000000000000088>.
- Tarsoly, G., Óvári, M., Zárny, G., 2010. Determination of fluorine by total reflection X-ray fluorescence spectrometry. *Spectrochim. Acta B Atom Spectrosc.* 65, 287–290. <https://doi.org/10.1016/j.sab.2010.02.019>.

- Tavares, T.R., Nunes, L.C., Alves, E.E.N., Almeida, E. de, Maldaner, L.F., Krug, F.J., Carvalho, H.W.P. de, Molin, J.P., 2019. Simplifying sample preparation for soil fertility analysis by X-ray fluorescence spectrometry. *Sensors* 19, 5066. <https://doi.org/10.3390/s19235066>.
- Tavares, T.R., Molin, J.P., Javadi, S.H., Carvalho, H.W.P. de, Mouazen, A.M., 2020. Combined use of vis-NIR and XRF sensors for tropical soil fertility analysis: assessing different data fusion approaches. *Sensors* 21, 148. <https://doi.org/10.3390/s21010148>.
- Thermo Fisher Scientific Inc, 2012. WDXRF as an Investigative and Analytical Tool Using Small Spot/Mapping and Thermo Scientific UniQuant.
- Tighe, M., Bielski, M., Wilson, M., Ruscio-Atkinson, G., Peaslee, G.F., Lieberman, M., 2020. A sensitive XRF screening method for lead in drinking water. *Anal. Chem.* 92, 4949–4953. <https://doi.org/10.1021/acs.analchem.9b05058>.
- Torrent, L., Iglesias, M., Hidalgo, M., Marguí, E., 2018. Determination of silver nanoparticles in complex aqueous matrices by total reflection X-ray fluorescence spectrometry combined with cloud point extraction. *J. Anal. At. Spectrom.* 33, 383–394. <https://doi.org/10.1039/C7JA00335H>.
- Turnau, K., Ostachowicz, B., Wojtczak, G., Anielska, T., Sobczyk, Ł., 2010. Metal uptake by xerothermic plants introduced into Zn-Pb industrial wastes. *Plant Soil* 337, 299–311. <https://doi.org/10.1007/s11104-010-0527-7>.
- Turner, A., Comber, S., Rees, A.B., Gkiokas, D., Solman, K., 2015. Metals in boat paint fragments from slipways, repair facilities and abandoned vessels: an evaluation using field portable XRF. *Talanta* 131, 372–378. <https://doi.org/10.1016/j.talanta.2014.08.012>.
- Turner, A., Arnold, R., Williams, T., 2020. Weathering and persistence of plastic in the marine environment: lessons from LEGO. *Environ. Pollut.* 262, 114299. <https://doi.org/10.1016/j.envpol.2020.114299>.
- USEPA, 2007. Method 6200. EPA, Washington, DC.
- Üstündağ, Z., 2009. Polarized energy dispersive X-ray fluorescence applications of spice samples. *Spectrosc. Lett.* 42, 7–11. <https://doi.org/10.1080/00387010802428450>.
- Van Meel, K., Smekens, A., Behets, M., Kazandjian, P., Van Grieken, R., 2007. Determination of platinum, palladium, and rhodium in automotive catalysts using high-energy secondary target X-ray fluorescence spectrometry. *Anal. Chem.* 79, 6383–6389. <https://doi.org/10.1021/ac070815r>.
- Vanhoof, C., Holschbach-Bussian, K.A., Bussian, B.M., Cleven, R., Furtmann, K., 2013. Applicability of portable XRF systems for screening waste loads on hazardous substances as incoming inspection at waste handling plants. *X Ray Spectrom.* 42, 224–231. <https://doi.org/10.1002/xrs.2485>.
- Vanhoof, C., Bacon, J.R., Fittschen, U.E.A., Vincze, L., 2021. Atomic spectrometry update – a review of advances in X-ray fluorescence spectrometry and its special applications. *J. Anal. At. Spectrom.* 36, 1797–1812. <https://doi.org/10.1039/D1JA90033A>.
- Vijayan, P., Willick, I.R., Lahlali, R., Karunakaran, C., Tanino, K.K., 2015. Synchrotron radiation sheds fresh light on plant research: the use of powerful techniques to probe structure and composition of plants. *Plant Cell Physiol.* 56, 1252–1263. <https://doi.org/10.1093/pcp/pcv080>.
- Wagner, A., Mages, M., 2010. Total-Reflection X-ray fluorescence analysis of elements in size-fractionated particulate matter sampled on polycarbonate filters — composition and sources of aerosol particles in Göteborg, Sweden. *Spectrochim. Acta B Atom Spectrosc.* 65, 471–477. <https://doi.org/10.1016/j.sab.2010.02.007>.
- West, M., Ellis, A.T., Potts, P.J., Strelci, C., Vanhoof, C., Wegryzneck, D., Wobruschek, P., 2010. Atomic spectrometry update—X-ray fluorescence spectrometry. *J. Anal. At. Spectrom.* 25, 1503. <https://doi.org/10.1039/c005501h>.
- Westerhold, T., Röhl, U., 2009. High resolution cyclostratigraphy of the early Eocene – new insights into the origin of the Cenozoic cooling trend. *Clim. Past* 5, 309–327. <https://doi.org/10.5194/cp-5-309-2009>.
- Wienold, J., Recknagel, S., Scharf, H., Hoppe, M., Michaelis, M., 2011. Elemental analysis of printed circuit boards considering the ROHS regulations. *Waste Manag.* 31, 530–535. <https://doi.org/10.1016/j.wasman.2010.10.002>.
- Woodward, C.A., Gadd, P.S., 2019. The potential power and pitfalls of using the X-ray fluorescence molybdenum incoherent: coherent scattering ratio as a proxy for sediment organic content. *Quat. Int.* 514, 30–43. <https://doi.org/10.1016/j.quaint.2018.11.031>.
- Yadav, V.B., Jha, S.K., 2013. Status of trace and toxic elements pollution in creek ecosystem using TXRF method. *J. Radioanal. Nucl. Chem.* 295, 1759–1762. <https://doi.org/10.1007/s10967-012-2095-1>.
- Yamasaki, S., Takeda, A., Watanabe, T., Tagami, K., Uchida, S., Takata, H., Maejima, Y., Kihou, N., Tsuchiya, N., 2015. Bromine and iodine in Japanese soils determined with polarizing energy dispersive X-ray fluorescence spectrometry. *Soil Sci. Plant Nutr.* 61, 751–760. <https://doi.org/10.1080/00380768.2015.1054773>.
- Yanada, Y., Hokura, A., Matsuda, K., Mizuhira, M., Nakai, I., 2007. High-sensitive determination of inorganic elements in spinach leaves by X-ray fluorescence analysis and its application to identification of their production area. *Bunseki Kagaku* 56, 1053–1061. <https://doi.org/10.2116/bunsekikagaku.56.1053>.
- Yatkin, S., Trzepla, K., White, W.H., Hyslop, N.P., 2018. Generation of multi-element reference materials on PTFE filters mimicking ambient aerosol characteristics. *Atmos. Environ.* 189, 41–49. <https://doi.org/10.1016/j.atmosenv.2018.06.034>.
- Zereini, F., Alt, F., Messerschmidt, Jü, Wiseman, C., Feldmann, I., von Bohlen, A., Müller, Jü, Liebl, K., Püttmann, W., 2005. Concentration and distribution of heavy metals in urban airborne particulate matter in Frankfurt am main, Germany. *Environ. Sci. Technol.* 39, 2983–2989. <https://doi.org/10.1021/es040040t>.
- Zhang, Y., Sakurai, K., 2009. Inter-correlation of impurity trace elements in bloodstone rock: X-ray fluorescence mapping studies. *J. Anal. At. Spectrom.* 24, 1579. <https://doi.org/10.1039/b909667a>.
- Zhu, Y., Weindorf, D.C., 2009. Determination of soil calcium using field portable X-ray fluorescence. *Soil Sci.* 174, 151–155. <https://doi.org/10.1097/SS.0b013e31819c6e1b>.