

Article

Design and Use of Portable X-ray Fluorescence Devices for the Analysis of Heritage Materials

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Abstract: X-ray fluorescence (XRF) is a successful technique often used for the elemental analysis of cultural heritage artefacts. It is non-invasive, the equipment can be miniaturized and made portable and it allows addressing crucial issues such as the fabrication technology, authenticity and provenance of the artefacts. Depending on the components' selection (e.g., the primary source, the detector and the focusing optics, if present), the analytical performance and the consequent suitability to investigate a given class of materials may vary significantly. The present paper discusses the analytical performance—with special regard to the limits of detection and the quantification uncertainty—of two portable XRF spectrometers developed within a collaboration between INFN-LNF-FISMEL and CNR-ISPC. The devices are expressly designed for heritage materials. In particular, one is equipped with focusing optics and it is intended to analyze small details on glasses and pigmented surfaces, whereas the other has a 70 kV X-ray tube, which greatly improves sensitivity for medium-Z elements, which is important in copper-based artefacts. Finally, this paper discusses two case studies to highlight the features of the instruments: one concerns Etruscan vitreous material beads and the other pre- and proto-historic copper-based artefacts from Tyrrhenian Central Italy. Thanks to the small size of the equipment, both investigations could easily be carried out in situ, namely, at the Museo Nazionale Etrusco in Rome and the Museo della Preistoria della Tuscia e della Rocca Farnese at Valentano.

Keywords: XRF; X-ray fluorescence; copper-based artefacts



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1. Introduction

X-ray fluorescence is a technique widely used for more than 60 years for the analysis of ancient materials [1,2]. Its success is due to the fortunate match between supply and demand. Given the crucial importance of elemental composition in addressing issues such as the manufacturing technology, provenance and authenticity of ancient artefacts, X-ray fluorescence can offer rapid, virtually non-invasive and multi-element analysis. The instrumentation lends itself to being miniaturized so that it can be used in the field, i.e., in museums and restoration laboratories, without the need to transfer the artefacts, which are often difficult to transport.

Depending on the design choices, and in particular the type of source and detector and the possible presence of focusing optics, the spectrometer has different characteristics and a different area of use. All this is particularly true in the case of portable instrumentation [3], for which, in addition to analytical performance, manageability and portability must be guaranteed.

In this paper, we discuss and compare the analytical performance, and in particular the limits of detection and the quantification uncertainties, of two portable spectrometers specifically developed within the framework of a collaboration between INFN-LNF-FISMEL

and CNR-ISPC for the analysis of ancient materials. We also discuss two case studies that highlight how the characteristics of each instrument match a specific type of artefact and/or the information to study.

The first case concerns research on the glass circulating in the Iron Age. The study is conducted through archaeometric data obtained by applying several analytical techniques on 40 glass beads (both fragments and whole beads), which have been found in the historical regions of Latium and Etruria in several burial sites. Nowadays, this region is named Central Italy. The samples under investigation were selected in order to represent different types of blue-green glass beads from funerary contexts dated to the first and second Early Iron Age (EIA), Early Orientalizing and Middle Orientalizing periods, i.e., from the 10th–9th to the 7th century B.C., with a prevalence of beads from EIA contexts. At present, the beads are kept and displayed in two archaeological museums: the “Museo delle Civiltà” and the “Museo Nazionale Etrusco di Villa Giulia” (both in Rome, Italy).

All beads have been thoroughly studied in order to identify their typology considering macroscopic evidences and to validate the discussion of the archaeometric data related to a period of peculiar relevance for archaeological glass studies. Indeed, glass-making recipes encountered evident changes in the Mediterranean and in the Near East areas, with new decorations and shapes (reflected in the typology of the beads) and materials (probably due to the chemical composition) appearing at the beginning of EIA.

The second case study concerns the analysis of pre- and proto-historic metallic objects found in Tyrrhenian Central Italy, in particular in the areas in the provinces of Viterbo and Rome. The artefacts’ typology and group size are affected by archaeological research vicissitudes and also from events that may have led to the diffusion in different museums of unitary contexts. Therefore, the objects are not geographically homogeneously distributed: currently, most of the artefacts come from an area between the River Fiora Middle Valley and the Lake Bolsena, for the north, and an area among the Tyrrhenian Coast, the Tolfa mountains and the Lake Bracciano, for the south. The objects under study cover a chronological period that conventionally ranges from the Eneolithic beginning (mid-fourth millennium B.C.) to the EIA (XIth–VIIIth century B.C.). The present paper does not intend to discuss the artefacts’ chronological attribution.

2. Instruments

The XRF systems discussed here were developed in-house according to specific requirements. The first of them, hereinafter identified as Frankie (Figure 1, left), is a portable spectrometer weighing approximately 3 kg. It is equipped with an X-ray tube with a front window and a tungsten anode, with a maximum voltage of 50 kV, a polycapillary lens and a silicon-drift type detector. Given these components, it is clear that the feature that we wanted to enhance is the minimum size of the primary beam and therefore the ability to analyze small details (with dimensions of the order of tens of μm) with no interference from the surrounding materials, providing a focus size of 300 μs . Against the excellent spatial resolution due to the narrow focal spot (see Table 1), the polycapillary lens attenuates the high energy component of the primary spectrum and consequently limits the excitation efficiency of high-energy lines, such as the K lines of silver, tin, antimony and barium. The best materials to analyze with Frankie are painted surfaces, vitreous materials and enameled metals.

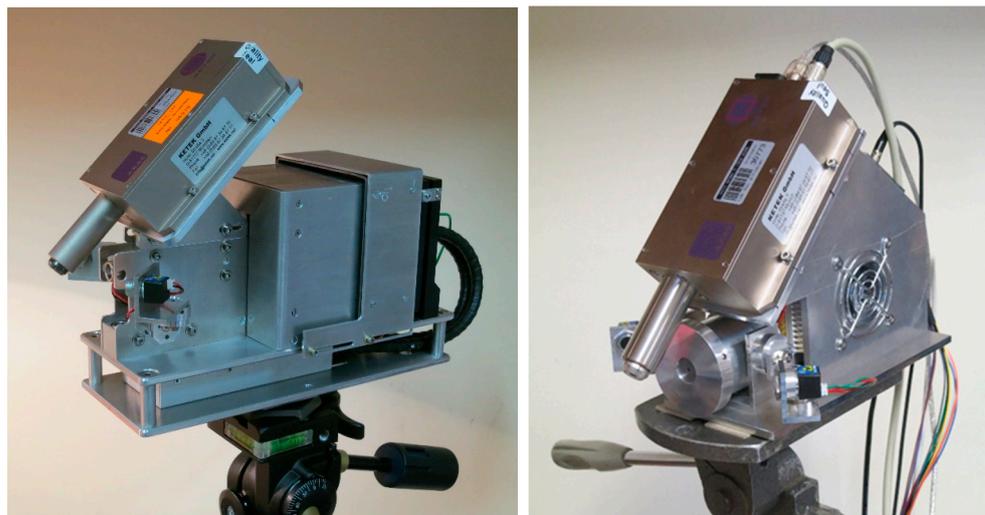


Figure 1. Picture of the two spectrometers compared in this paper: Frankie on the left and F-70 on right.

Table 1. Technical specifications of the two spectrometers.

Spectrometer	Frankie	F-70
X-ray tube	Front window, W anode Max high voltage = 50 kV Max current = 200 μ A	Front window, W anode Max high voltage = 70 kV Max current = 170 μ A
Detector	Si-Drift Area = 20 mm ² Thickness = 450 μ m	Si-Drift Area = 20 mm ² Thickness = 450 μ m
Focusing optics	Polycapillary lens Focal spot = 300 μ m	None

The second instrument (Figure 1, right), named F-70, weighs approximately 3 kg and it is also portable. It is equipped with a front window X-ray tube with a tungsten anode and with a maximum voltage of 70 kV. The detector is a silicon-drift one. The high energy of the primary radiation allows the efficient excitation of intermediate-atomic-number elements, such as silver, tin, antimony and barium. Furthermore, the use of appropriate filters guarantees an adequately low background in the energy range of analytical interest. In addition to the X-ray tube's own filtration, a 200 μ m thickness of copper and a 105 μ m thickness of an iron-chromium-nickel alloy were inserted. The need to keep the intensity of the primary radiation high does not allow the beam collimation to be reduced below one millimeter. We therefore have a spatial resolution that is not comparable to Frankie. F-70 was expressly designed for copper-based artefacts, for which the analysis of the minor elements—such as arsenic, silver and antimony—is particularly important. The efficient excitation of these elements requires an X-ray energy above 60 kV, while commercial systems' typical high voltage (HV) is below 50 kV [4]. This is the reason why F-70 has been expressly designed to meet this demand. The higher HV allows improving analytical performance for elements with atomic numbers ranging from Ag to Sb and, furthermore, makes the device particularly suitable for investigating copper-based artefacts.

Table 1 summarizes the characteristics of the two custom designed systems. Moreover, a detailed review of the analytical performances of the two presented X-ray fluorescence devices, in comparison with additional commercial systems, is reported in [5].

Figure 2 compares the primary spectra of the two spectrometers, with information concerning the energy distribution of the primary beams, which is a relevant aspect for the results' discussion. Both spectra have been acquired using a highly scattering material as

a sample (with a low atomic number). Even if the representation of the primary spectra is rough, it is still useful to appreciate the effect of polycapillary optics. The spectra's irregularities are due to the intrinsic detectors efficiency, the Compton shift and the presence of fluorescent lines from the surrounding materials. It is clear that the excitation conditions are completely different. Consequently, the analytical performance will differ as well.

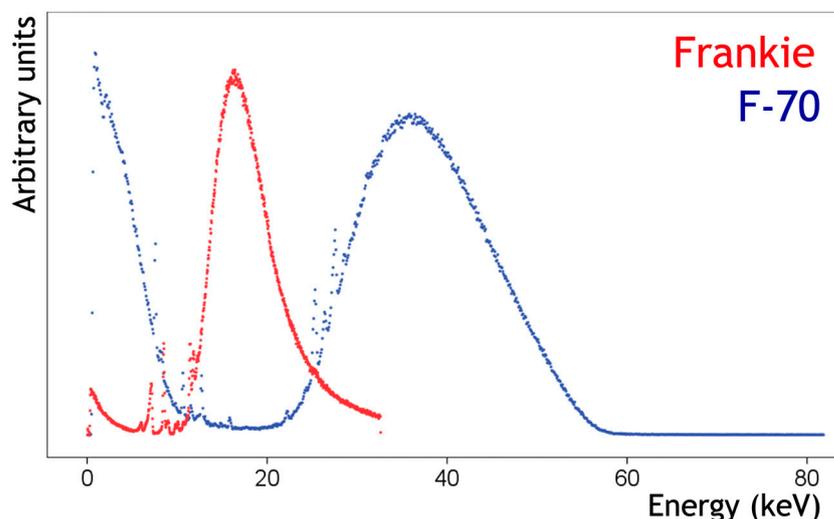


Figure 2. Comparison of the two devices' spectra acquired by using a highly scattering sample (i.e., a low-Z material).

From a radioprotection point of view, these instruments are authorized for transport as mobile radiation sources. Therefore, they can be used in museums without moving the artefacts. The precautions to be taken by operators are to direct the beam on the target, not in the direction of the operator, and maintain a distance of 2 m during irradiation, using chains to delimit the measurement area. Furthermore, their transport must be accompanied by fire extinguishers.

3. Analytical Performance

Two parameters were chosen to quantify the analytical performance: the limits of detection (LOD) and the quantification uncertainty. These parameters are part and parcel of the calibration procedure, which was carried out using a set of reference copper alloys (details are reported in [5,6]). All parameters discussed will therefore refer to copper matrices. The spectra were acquired for 200 s and quantified by using the PyMCA Fundamental Parameters software (version 5.9.2) [7], and the calibrations were carried out following the procedure indicated in [8,9].

The LOD is the minimum concentration of a given element that can be distinguished from the background with a certain level of confidence (in this case, 95%). This value is significant of the excitation conditions and can be measured by the single standard method through the relationship [10,11]:

$$LOD = \frac{2.33 \cdot c_{std} \cdot \sqrt{B}}{P};$$

where:

- P is the net peak area;
- B is the background area;
- c_{std} is the element concentration in the reference material.

Figure 3 shows the LODs in semi-logarithmic scale for all the elements considered and for each instrument. The performances are comparable for the elements between manganese and arsenic. For the intermediate elements, F-70 performs better and that is the

purpose for which it was designed: to have a system particularly suitable for detecting the minor elements typical of ancient copper alloys.

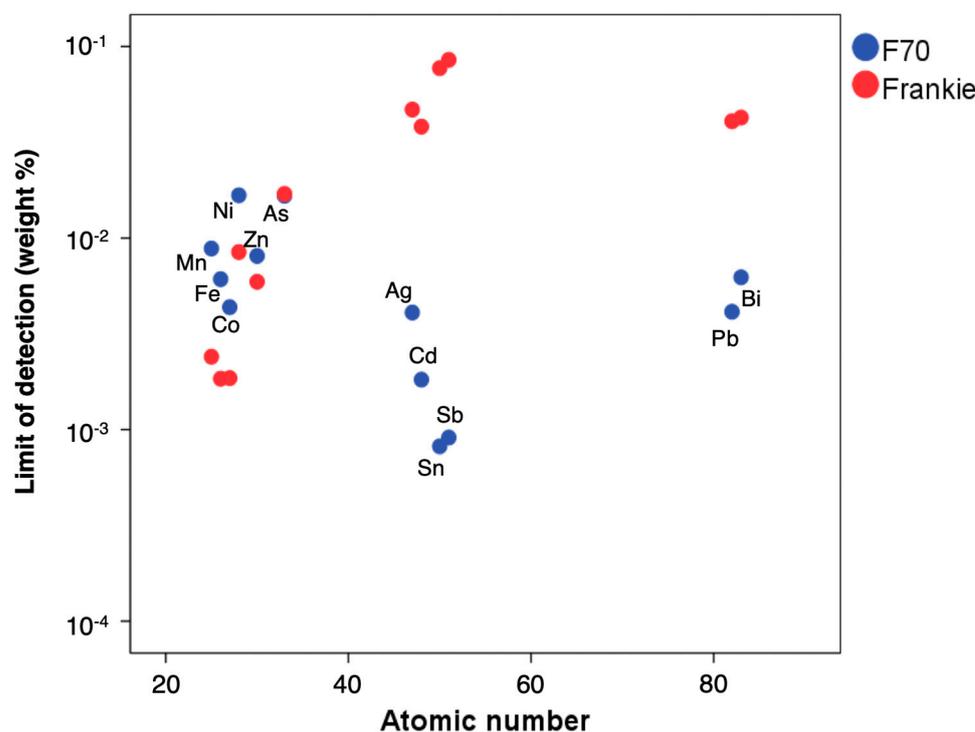


Figure 3. Scatterplot of the LOD in percentage in a semi-logarithmic scale versus the atomic number, Z , for both XRF systems.

The final step of the calibration procedure involves the calibration proper. This operation consists in applying a linear transformation to the measured concentrations, as provided by PyMCA, which corrects any errors made in the assignment of the spectrum and intensity of the primary radiation. The parameters of the transformation are obtained from the regression line in which the concentrations measured on the standards are the independent variable and the corresponding nominal values are the dependent variable [12]. Among the characteristics of the regression, the standard error of regression (SER), defined as the points' mean square deviation from the best-fit line, is of particular interest. Since systematic errors are supposedly eliminated by calibration, the SER is an estimate of the overall uncertainty of the analysis. An estimate of the corresponding relative uncertainty is obtained by dividing the SER with the concentration average of each element. Figure 4 shows the SER and the relative uncertainty for major and minor constituents for each instrument. The results follow the trend of the LODs in most cases. Among the main constituents, lead shows the highest relative uncertainty. For both instruments, it is around 15%. The others are under 5%, with the exception of tin, which Frankie measures (not surprisingly) with an uncertainty of about 10%. Concerning the minor elements, the relative uncertainties do not significantly exceed 20%, with the exception of cobalt. The differences between the two instruments are particularly apparent for silver, cadmium and antimony for the already discussed reasons.

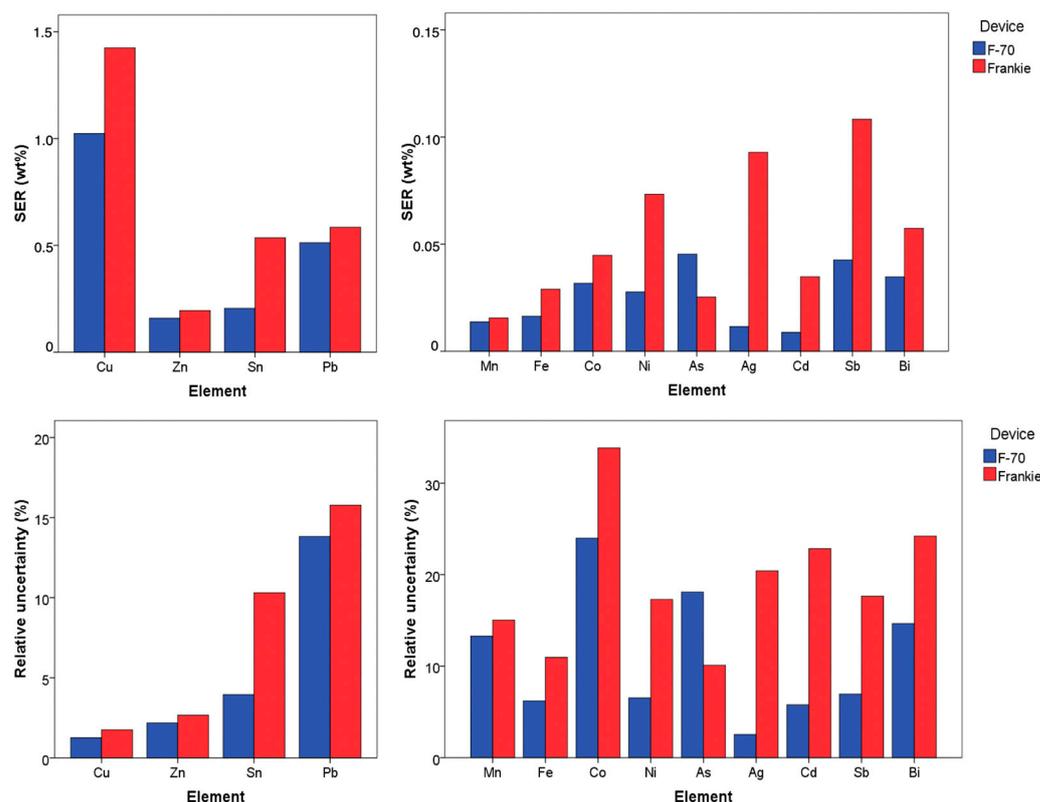


Figure 4. Histograms of the SER (**top**) and relative uncertainties (**bottom**), both for major elements (**left**) and minor elements (**right**) for the two devices.

4. Applications

4.1. Vitreous Material Beads from the Iron Age in Central Italy

Figure 5 shows some of the analyzed materials from the Villa Giulia Museum. These are several types of (mostly) blue-green glass beads dating back to the Iron Age and coming from archaeological sites in Central Italy, and which were studied and investigated using several spectroscopic techniques: fiber optics reflectance spectroscopy [13], micro-Raman spectroscopy and laser ablation inductively coupled plasma mass spectrometry [14], scanning electron microscopy with energy-dispersive X-ray spectrometry [15], and portable XRF spectrometry. A detailed discussion of the materials can be found in [16]. Each technique provided complementary information, which was then discussed in the frame of the artefacts' archaeological typology. The measurements' systematic evaluation allowed the researchers to derive conclusions on raw materials used for primary production and to point out some relevant glass indicators for the provenance. Some beads from Iron Age contexts were preliminarily attributed to the Final Bronze Age (FBA) production, considering their typology. And the compositional results obtained within this work confirmed that these elements were high-potassium low-magnesium glass [17–19], typical of FBA in the Italian peninsula. Instead, other beads were considered to be high-magnesium glass or low-magnesium glass, providing more information on the fluxing agents typically used in the EIA and beyond.

The color variations among beads is linked to their chemical composition, with several beads' typologies colored in a certain manner. In some cases, it was possible to establish different origins for the coloring raw materials. On the other hand, the artefacts' provenance was difficult to define, but the chemical study raised a subdivision for the raw glass employed for the beads' production: a local origin of the glass could be hypothesized for one set of samples, whereas several manufacturing sites in the Near East were identified for most of the beads under consideration. Some preliminary clues were highlighted for one typological group too, for the local working of imported glass.



Figure 5. Some of the Iron Age vitreous materials beads investigated at Villa Giulia museum.

Part of these analyses was conducted with Frankie and it allowed to identify differences in composition mainly due to different manufacturing contexts. More interesting for the purposes of this research is the effectiveness of the spectrometer to analyze different colors on beads smaller than one centimeter thanks to its excellent spatial resolution. Table 2 illustrates the identified chromophores and opacifiers. These data are important for reconstructing the manufacturing technologies of colored vitreous materials during the Iron Age.

Table 2. Chromophores and opacifiers of the vitreous materials detected using XRF [20].

	Samples	Chromophore(s)/Opacifier	Technique for Confirmation
RED	VG24, 25, 26, 29	Cu ⁰	FORS, p-XRF
DARK-GREEN	VG25	Cu ²⁺ , Fe ³⁺	FORS, p-XRF, LA-ICP-MS
BLUE	VG28	Cu ²⁺ , Fe ³⁺	FORS, p-XRF, LA-ICP-MS
Co-Cu BLUE	VG106	Co ²⁺ , Cu ²⁺ , Fe ³⁺ , Fe ²⁺	FORS, p-XRF, LA-ICP-MS
DARK	VG22, 2359	Co ²⁺ , Fe ²⁺ , Fe ³⁺	FORS, p-XRF, LA-ICP-MS
WHITE 1	VG 106	CaSb ₂ O ₆	p-XRF, SEM-EDS, u-Raman, LA-ICP-MS
WHITE 2	VG25, 26, 29	Fine bubbles	OM, D-XRF, u-Raman, LA-ICP-MS

4.2. Copper-Based Artefacts from Pre- and Proto-Historic Central Italy

Some of the analyzed artefacts are shown in Figure 6. The XRF analysis was conducted using F-70 and a detailed discussion can be found in [20]. The study objective was to define the elemental composition of copper-based artefacts dating from the Copper Age to the EIA and found on the Tyrrhenian side of the Italian peninsula, which is the area that corresponds to the Lazio region. The objects under study had various functions and belong to different archaeological contexts.



Figure 6. Pre- and proto-historic metallic findings from archaeological sites in Tyrrhenian Central Italy (from [20]).

Artefacts measurements were performed using the XRF technique on the surface areas where corrosion products were previously removed. The experimental condition was

established to satisfy both efficient excitation requirements and the well-resolved detection of crucial elements, such as Ag, Sn and Sb. In this manner, the LODs evaluated with the single standard method [13] were approximately 50 mg/kg for Ag, 250 mg/kg for Zn, Sn, Sb and 300 mg/kg for Pb, and 400 mg/kg for Fe and Ni. For each element, the overall relative accuracy is of about 5–10%. The accuracy is evaluated as the mean deviation between the measured concentration and the nominal one, through calibration standards.

Most of the considerations and hypotheses that were made on metallurgical technologies and production contexts are based not only on the main constituents of the alloys, but also on the minor ones. It makes therefore sense to design an XRF device with the excellent analytical performance and the low limits of detection of F-70.

This work refers only to copper-based alloys. Objects with a main component of lead, silver and antimony are not considered. It is clear that the measured compositional differences are related to the evolution of metallurgical know-how and, consequently, to the artefacts' chronology.

One of the most interesting aspects is to replace tin with antimony as a major alloy constituent. This is observed only in the fragmentary objects from the Selvicciola Hoard, dating back to the early Iron Age (see Figure 7). A hypothesis to explain this evidence is that there were multiple production lines, aimed at different commercial targets which also included a demand for cheaper materials (copper-antimony instead of copper-tin alloys).

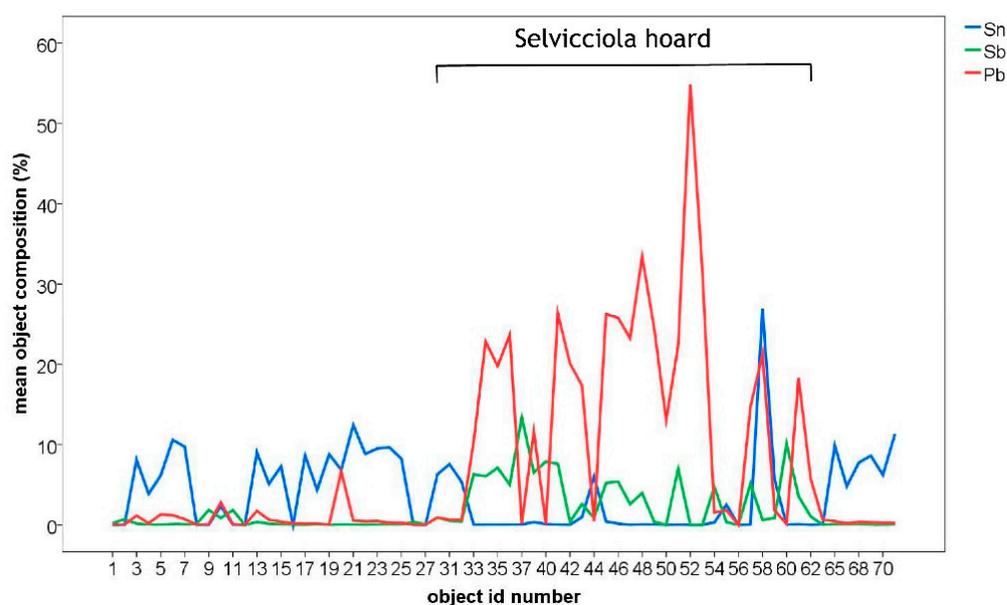


Figure 7. Mean concentration of tin, antimony and lead as a function of the object identification number (from [20]).

5. Conclusions

The investigation of the great variety of materials that form the tangible cultural heritage requires a dedicated design of instrumentation. X-ray fluorescence is no exception.

Among the requirements that XRF instruments ideally have to comply with are portability, spatial resolution and, of course, analytical performance. Often, these requirements are in contrast with each other. This is why the designer has to clearly identify the type of artefacts that the device will be dedicated to.

This article compares the analytical performance and discusses the strengths of two portable XRF spectrometers developed within a collaboration between INFN-LNF-FISMEL and CNR-ISPC for the analysis of ancient materials. These are Frankie, a portable spectrometer equipped with a polycapillary lens, and F-70, a portable spectrometer equipped with a 70 kV tube with no focusing optics.

One of the case studies reported here shows the great effectiveness of polycapillary optics for analyzing small details (for example, the polychromy in vitreous material beads) with no interference from the surrounding materials. On the other hand, polycapillary lenses attenuate the high energy component of the primary beam and worsen the analytical performance, in particular the LOD and quantification uncertainties, for elements with atomic number around 50.

It follows that different types of artefacts ideally require different spectrometers. The second case study presented in this work concerns pre- and proto-historic bronzes. Given the size of the objects, spatial resolution is not important while the superior analytical performance of F-70 (LOD and quantification uncertainties) is crucial for quantifying major and minor alloy constituents and developing considerations and hypotheses on prehistoric metallurgy.

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