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Abstract. X-ray fluorescence (XRF) is a technique frequently used for the elemental analysis of cultural heritage materials. Depending on components selection (i.e. the primary source, the detector and the focusing optics, if present), the analytical performance of the spectrometer, and its consequent suitability for a given purpose, may vary considerably. In this paper, we compare the analytical performance of four different devices, two commercial and two expressly designed by the authors, and we consider two figures of merit: the limit of detection (LOD) and the standard error of regression (SER). The measurements are performed on a set of 19 copper alloy standards.

1. Introduction

The long-lasting success that X-ray fluorescence (XRF) has had in the field of cultural heritage [1] is not only due to the importance of elemental analysis to address issues such as provenance, fabrication technology and authenticity of the artefacts, but also to the fact that this is a non-invasive technique and it can be performed through portable systems. For the purpose of this paper, only energy-dispersive spectrometers will be considered.

The core of any XRF spectrometer is made of a source of electromagnetic radiation (usually an X-ray tube) and a detector (usually a thermoelectrically-cooled detector, such as the Si-drift or Si-PIN type [2][3]). Depending on the use for which the system is intended, the source may be equipped with focusing optics to have small beam spot-sizes (usually few tens of microns) and high beam intensities [4][5]. Moreover the measuring head may be mounted on an automatic displacement system to perform two-dimensional scans of flat surfaces, such as paintings [6][7][8].

Miniaturization of the components has led to produce spectrometers that can be used by a single hand (hand-held or HH-XRF) and almost completely automatized. This has contributed to spread the technique among non-specialists, such as art historians, archaeologists and restorers [9] and, perhaps, to form the misperception that XRF is simple [10].

The design of an XRF system is the result of a trade-off among different needs, sometimes conflicting with one another. For example, enhancing portability and reducing radiation hazard would suggest to use X-ray tubes with the lowest possible power, whereas enhancing analytical sensitivity and precision would require to do the opposite.

The present paper aims at discussing the effect of two aspects of the design, i.e. the high-voltage of the X-ray tube and the presence/absence of X-ray optics, on the analytical performance of an XRF device. We chose two figures of merit to quantitatively describe the analytical performance. Both of them will be defined in the next section: the limit of detection (LOD), i.e. the lowest concentration of a given element detectable by the device, and the standard error of regression (SER), i.e. the overall absolute uncertainty with which a given element is quantified.

The LOD and the SER of four spectrometers, two of which are commercial and two designed by the authors, were measured on a set of copper alloy standards. Copper-based alloys were chosen because they are particularly challenging for XRF applications, besides being widely represented in Italian heritage.

A general consideration is that copper-based artifacts are in most cases covered by corrosion products that preclude accurate measurement of the "true" alloy composition, even after restoration. As abrading the surface is not always allowed, one tries to at least reduce the relative weight of the surface in the overall fluorescent signal by using high energy lines. This leads to prefer the K over the L-lines and the L over the M-lines, which also allows to ignore some spectral interferences, such as those occurring among the L-lines of Ag, Sn and Sb.

Ancient copper alloys are characterized by a number of unintentional minor elements, such as Fe, Co, Ni, As, Ag, Sb, Bi, usually present in the metal with concentrations below 1 wt%. In principle these are powerful discriminators to distinguish among different alloys, because their variation range is larger compared to that of Sn, Zn and Pb, which are intentional and therefore more controlled. Indeed, It is possible to take advantage from this occurrence only if detection limits are sufficiently low that is, if the net peak intensities and the peak-to-background ratios are sufficiently high. Efficient excitation of the K-lines of Ag, Sn and Sb requires the X-ray tube to work above 60 kV, whereas commercial systems do not work beyond 50 kV. This is why one of the tested devices, named F-70, was expressly designed to meet this requirement, enhance the analytical performance for elements ranging from Ag to Sb and make the device particularly suitable, in order to investigate copper-based artifacts.

2. Experimental data and discussion

The LOD is the minimum concentration of an element necessary for its fluorescent lines to be distinguished from the background with a given confidence level (here 95%). It is measured on a reference material and expressed by the following relationship [11]:

$$LOD = \frac{2.33 \cdot C_{std} \cdot \sqrt{B}}{P} \tag{1}$$

where:

- C_{std} is the concentration of the element in the reference material, included between 10 and 100 times the LOD;
- B is the background area;
- P is the net peak area.

For each device and each element, the LOD was calculated as the average of the individual values obtained for all the standards, with C_{std} between 10 and 100 times the LOD.

Analytical practice is usually concerned about the limit of quantification (LOQ), which represents the minimum measurable concentration, rather than about the LOD. However, the designers point of view is different: we need an easy-to-calculate figure of merit to evaluate and compare different excitation conditions. The LOD is suitable for this purpose and fast to calculate. However, in the following it will be clear that the LOD and the LOQ (better: the LOD and the SER, which are the figures measured in this work) are not always closely related.

A detailed discussion of the SER starts from quantification. In the present work it is implemented by the Fundamental Parameters software package PyMCA [12]. Calibration consists of analyzing a group of standards and applying to the measured concentrations, as provided by PyMCA, a linear transformation defined by the least square regression line of the measured versus the nominal concentrations of the standards. It aims at correcting the output of PyMCA with respect to possible errors in the description of the primary beam and improving accuracy and reproducibility [13]. Three spectra were acquired on each standard. The resulting measured concentrations were all used to build the calibration lines, thus taking into account the overall uncertainty of the measured concentrations.

In light of the above, the SER is the standard error of the least square regression of the measured versus the nominal concentration, defined as the root mean square distance of the data points from the line. It is an estimate of the deviation from the regression line expected for an unknown value. As systematic errors are supposed to be removed by calibration, the SER accounts for the remaining random errors and it represents the overall uncertainty of the calibrated concentrations.

The identification and the main characteristics of the four X-ray spectrometers are provided in Figure 1 and Table 1, respectively. The measurements were performed on nineteen standards including the Charm Set [14], with the configuration and in the working conditions normally used for routine measurements.

Further informations concerning the energy distribution of the primary beams and the photon flux integrated over the measuring time are reported in Figure 2. These are also relevant for the results discussion. The spectra were acquired by using a low-Z and highly scattering material as a sample. The total areas have been normalized to 1. The representation of the primary spectra is rough (due to the Compton shift, the intrinsic efficiency of the detectors and the presence of fluorescent lines from the surrounding materials),but still useful to appreciate the effect of polycapillary optics. Figure 2 (right) shows the integrated flux of Unisantis is at least 10 times lower compared to other devices, which means that the measuring time should be at least 10 times longer. On the other hand, the comparison concerns the devices in normal operative conditions. So that, we decided to keep the measuring time of 200 s.

In Figure 3, the average LODs of each spectrometer versus the atomic number Z are reported on a logarithmic scale. Three groups of elements are considered: those with $24 \leq Z \leq 33$ (Mn, Fe, Co, Ni, Zn, As) and $47 \leq Z \leq 51$ (Ag, Cd, Sn, Sb), for both of which the K-lines are used and those with $82 \leq Z \leq 83$ (Pb, Bi), for which the L-lines are used.

The first consideration is Unisantis is less performing for all the elements, excepting Pb and Bi, if compared to the other devices. The main reason is the low integrated flux.

For the elements of the first group (Mn, Fe, Co, Ni, Zn and As), the other devices show similar performances, with values scattered between 0.002 wt% and 0.02 wt%, approximately.
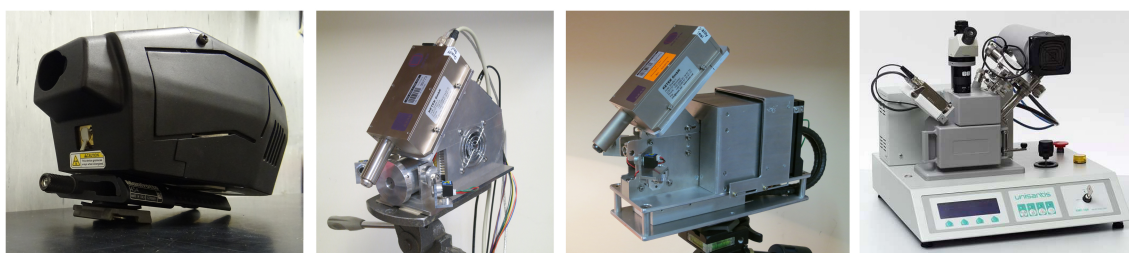

Figure 1. The four spectrometers compared in this work. From left to right: Elio, F-70, Frankie and Unisantis.

Table 1. Technical specification of the 4 spectrometers, named Unisantis, Frankie, Elio, F-70.

Device Id	Source	Detector	Beam focusing	Design
Unisantis	Side-window X-ray tube Mo anode HV = 50 kV I = 100 μA	Si-PIN area = 7 mm2 thickness = 300 μm	Polycapillary lens focal spot of 80 μm	Commercial
Frankie	Front-window X-ray tube W anode HV = 50 kV I = 200 μA	SDD area = 20 mm2 thickness = 450 μm	Polycapillary lens focal spot of 300 μm	Ad hoc
Elio	Front-window X-ray tube Rh anode HV = 50 kV I = 50 μA	SDD area = 25 mm2 thickness = 500 μm	None	Commercial
F-70	Front-window X-ray tuee W anode HV = 70 kV I = 170 μA	SDD area = 20 mm2 thickness = 450 μm	None	Ad hoc

The elements of the second group (Ag, Cd, Sn and Sb) are the most visibly affected by the different excitation conditions. The F-70's X-ray tube works till 70 kV and it has a large part of the primary spectrum available to excite the K-lines, if compared to Elio's 50 kV tube. Frankie works in a different conditions, due to the polycapillary lens, which acts as a low-pass filter and cuts almost completely the high-energy part of the spectrum. Consequently, F-70 is the best performing device for copper alloys studies, with average values of approximately 0.002 wt%, followed by Elio with 0.01 wt% and Frankie with 0.06 wt%.

As regards the elements of the third group (Pb and Bi), again F-70 has a larger part of the primary spectrum above the absorption edges, compared to Elio and Frankie. For this group analysis, the performances are not so different among devices, which are 0.006 wt%, 0.02 wt%, and 0.04 wt%, respectively.
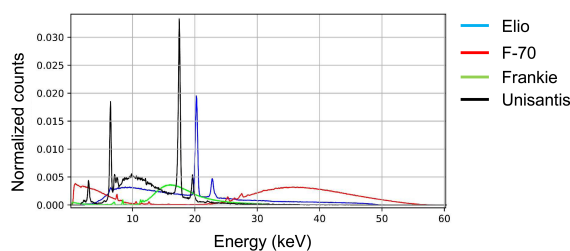
Device Id	Flux (photons/s)	Live time (s)	Integrated flux (photons)
Unisantis	5.0×10^6	200	1.0×10^9
Frankie	7.5×10^7	197	1.5×10^{10}
Elio	1.2×10^8	138	1.7×10^{10}
F-70	1.2×10^8	116	1.4×10^{10}

Figure 2. Left: Primary spectra of the four devices. The total areas are normalized to 1. Right: photon flux, live time and integrated flux of the four devices.
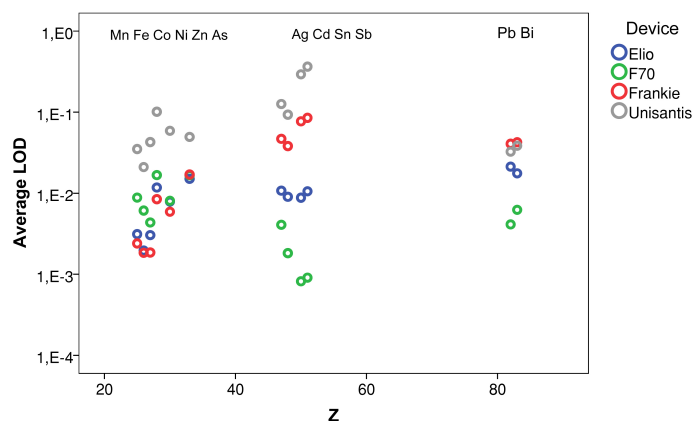
Figure 3. Semi-logarithmic scatterplot of the average LOD versus the atomic number Z for each spectrometer.

In Figure 4, the SER values for major (Cu, Zn, Sn and Pb) and minor elements (Fe, Co, Ni, As, Ag, Sb, Bi) are reported for each device under consideration. Unisantis is less performing w.r.t. other spectrometers for most of the elements. However, the differences are not as large as those of the LOD. Concerning the LOD, the ratio between the best and the worst performance is in the range of tens or hundreds. For the SER, the same ratio is in the range of units or, at most, tens. This is due to the fact the LOD is just controlled by parameters related to the excitation conditions. Instead, the SER is affected by the excitation conditions and by other parameters, including X-ray tube instabilities and electronics drifts. They may combine in different ways so that the best SER does not necessarily correspond to the best LOD. Elio, F-70 and Frankie are characterized by SER values in the range of a few wt% for Cu (the most abundant element in all samples), tenths of wt% for the other major elements (Zn, Sn and Pb) and hundreds of ppm for the minor elements. An estimate of the relative uncertainties is provided in Figure 4 (bottom). These are calculated dividing the SER by the average nominal concentration of the element. With the exception of Unisantis, results are below 15% for all major elements, with Pb reaching the highest values, and below 30% for minor elements, with the exception of Frankie.

3. Conclusions

Four spectrometers, routinely used to investigate heritage materials, were quantitatively compared with regard to the limits of detection and the quantification uncertainty. The former parameter is just controlled by the excitation conditions and it accounts for the capability of detecting small amounts of a given element. The reported measurements shown that it is not sufficient to describe the analytical capabilities of a device, a reason why it is necessary to consider the quantification uncertainties, which are of greater interest in the analysis. Quantification uncertainty results from a complex combination of effects, including X-ray tube instabilities and drifts of the electronics, besides the excitation conditions. The overall effect is that one can have acceptable quantification uncertainties, even with high limits of detection, provided by sufficiently stable hardware components, highlighted by the performance of the spectrometer Unisantis.

The measurements also highlighted that polycapillary optics are essential to obtain intense primary beams with focal spot sizes of tens to hundreds of μm but they are detrimental for the limits of detection of elements with absorption edges beyond 20 keV. For instruments not using polycapillary optics, the parameter that mostly affects the limits of detection is the tube

voltage, especially for elements with Z∼50 (i.e. Ag, Cd, Sn, Sb). The good performance of F-70 shows the use of X-ray tubes working above 60 kV may improve the excitation conditions to analyze copper alloys.
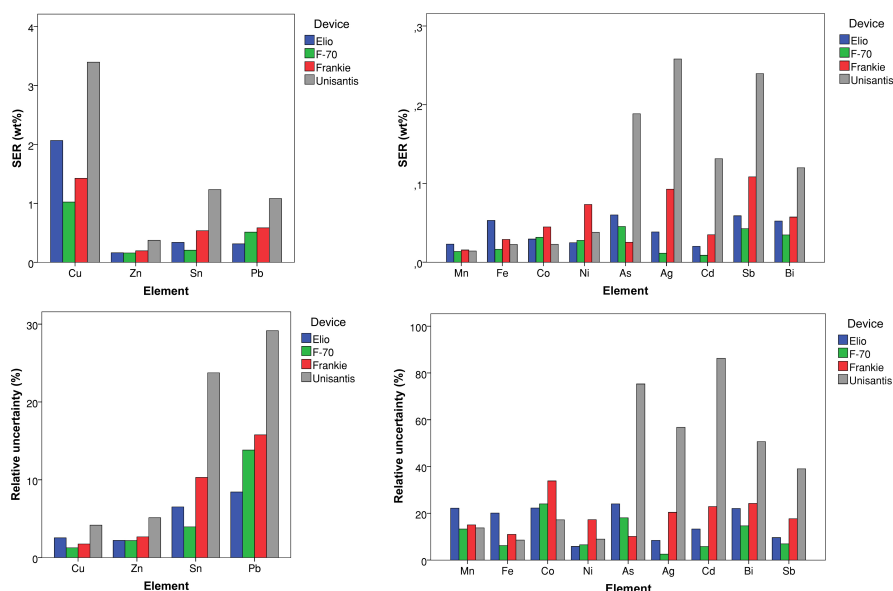

Figure 4. Bar chart of the SER (top) and relative uncertainties (bottom) for major elements (left) and minor elements (right) for each device.

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