Quantitative criteria to configure and characterise portable X-ray fluorescence spectrometers

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Abstract – **The emergence of hand-held X-ray fluorescence devices (HH-XRF) has changed the cultural approach to the analysis of ancient materials. These instruments are characterised by highly miniaturised hardware and powerful software and much of the designer's effort is devoted to encourage users to consider the device as a black box. This makes archaeologists, art historians and restorers virtually autonomous about materials analysis. However, there are specific applications, such as the investigation of copper-based artefacts, for which the user needs to go deeper into the functioning of the instrument. This paper discusses the experiments carried out to reconfigure from scratch a hand-held Bruker Tracer 5g, to compare it with an in-house developed portable spectrometer and to prepare both devices for field use. In particular, we address the optimisation of the primary filters and the calibration of the devices by considering two quantitative parameters: the limit of quantification and the relative uncertainty of quantification.**

I. INTRODUCTION

The analysis of ancient materials by X-ray fluorescence (XRF) has a long history: first articles date back to 65 years ago [1] and portable XRF systems are being used since at least 50 years [2] [3]. Nevertheless, only in relatively recent times the cultural approach towards the technique has changed substantially. Operation of the instruments and, most important, interpretation of data has no more been an exclusive prerogative of users with natural sciences background. The change occurred when the so-called hand-held XRF devices (HH-XRF) [4] came into common use. They have a gun-like form (see Fig. 1 right)

and are fully self-consistent, thus meaning that they are battery operated, automatically controlled by an on-board computer and capable to provide the results of the analysis with no need of external connections or off-line data processing. Their features including the user-friendly form, which suggests the idea that XRF could be as easy as taking aim and shooting, have fostered an enfranchisement of archaeologists, art historians and restorers about materials analysis and made them virtually autonomous in performing measurements and interpreting data.

Discussing whether this approach is always beneficial for a deeper knowledge of ancient material cultures is beyond the scope of this paper. Rather, it focuses on assessing to what extent the general-purpose configuration of a HH-XRF device provided by the manufacturer is suitable for specific purposes, namely the analysis of archaeological copper-based alloys. It will be clear in the following that such an assessment requires a deep understanding of the spectrometers working principles, so that it can be no more considered as a black box. We used two devices, i.e. a hand-held Bruker Tracer 5g and an in-house developed portable spectrometer, referred to as F-70. The latter was specifically designed for the analysis of copper-based alloys and works here as a basis of comparison. We discuss the experiments carried out to prepare the instruments for field use. In particular, we address two crucial issues – i.e., the filtration of the primary beam and the calibration of the device – by considering two parameters: the limit of quantification (LOQ) and the relative uncertainty of quantification (RUOQ).

II. MATERIALS AND METHODS

A. Instruments

This work considers two portable XRF spectrometers: a Bruker Tracer 5g and an in-house designed device identified as F-70 (see Fig.1). The working conditions were kept as close as possible to what we assume required for fieldwork: maximum high voltage to provide effective excitation of the K-lines of Ag, Sn and Sb; a beam size not larger than 3 mm and a dead time not larger than 20%. Being in-house developed, F-70 has more room for adjustment than the Tracer 5g, which is only provided with 2 collimators (3 and 8 mm) and 4 filters. Moreover, the Tracer 5g has a maximum high voltage of 50 kV (whereas F-70 has 70 kV) and automatic limitations on the tube current depending on the high voltage. The working conditions of each device are summarised in Table 1.

Fig. 1. XRF devices used for the experiments: F-70 (left) and Bruker Tracer 5g (right).

Table 1. Bruker Tracer 5g and F-70 working conditions.

Device	Source	Collimator
Bruker Tracer 5g	Rh anode HV=49kV i=39.31µA	3 mm
F-70	W anode HV=70 kV i=55 µA	2 mm

B. Reference materials

A group of 26 certified standards, compositionally significant of heritage copper-based artefacts, was used for the experiments. Part of them is from the Charm Set [5].

C. Data processing

All the spectra, including those of Tracer 5g, were quantified by PyMCA, an external software package based on the Fundamental Parameters method [6]. This is the only exception to the general criterion adopted of operating each device in its field working conditions. Regarding Tracer 5g, it would have implied using the on-board quantification algorithms, whose functioning at the time of the work still had to be fully understood. Considering Tracer 5g alone and comparing different on-board and external quantification algorithms will be the focus of a future paper [7]. Once the quantification had been performed, the spectra were subjected to calibration. The purpose is to remove systematic deviations due to possible inaccurate description of the primary beam and to make the results virtually comparable with other results obtained in another laboratory using another device. It consists of the linear transformation:

$$c_{cal} = a \cdot c_{meas} + b \qquad (1)$$

where:
c_{cal} is the calibrated concentration;
c_{meas} is the measured concentration as provided by PyMCA and a and b are the slope and the intercept derived from the linear weighted regression of the measured concentrations, considered as independent variables, versus the corresponding nominal concentrations c_{nom}, considered as dependent variables.

This is the same procedure discussed by Heginbotham *et al.* [8], except that ours is a weighted regression with:

$$weight = \frac{1}{(c_{nom})^2} \qquad (2)$$

This corresponds to minimising the relative deviations instead of absolute ones. Only data points with c_{nom} above the limit of quantification (see the following) are used in the regression. The advantage of using weights is that a weighted regression ensures that relative deviations are approximately constant all over the concentration range, whereas a non-weighted one is mainly controlled by high concentration values and remains almost unaffected by low-concentration data points.

The limit of quantification (LOQ) is the minimum concentration of a given element that can be measured with a given uncertainty. If we set at $B+10*\sigma(B)$ the limit above which the fluorescent signal is considered quantifiable [9], LOQ is calculated as follows:

$$LOQ = \frac{10 \cdot c \cdot \sqrt{B}}{P} \qquad (3)$$

where:
c is the concentration of the element in the sample;
B is the background area and
P is the net peak area.

Strictly speaking, LOQ depends, besides other variables, on spectral interferences and is therefore specific of a given sample. For the purpose of the present work, however, it is calculated only for the standards having the analyte concentration at approximately 1% and is considered approximately constant. It closely relates to the excitation conditions, in particular to the spectral features of primary radiation. In the present work, it is used for two purposes: 1) as a figure of merit to optimise the filtration of the primary beam and 2) to select the data points to be used for the calibration and the calculation of quantification uncertainties (see the following). Concerning the first point, it is a common practice to put absorbers on the path of the primary beam to selectively attenuate parts of the primary spectrum, thus reducing the background and improving the detection conditions of specific elements. The selection of the appropriate filter is often performed by visual inspection of the spectrum. This method, however, may result in overlooking the effects that the filter may have on other parts of the spectrum and other elements. Our proposal is to identify all significant elements and use the corresponding LOQ's to quantitatively evaluate the effect of a given filter. The optimum filter is the one achieving the best compromise among all the considered elements.

The relative uncertainty of quantification (RUOQ) is the relative uncertainty associated to the calibrated concentration. It is calculated for $c_{nom}>LOQ$ and equals the standard deviation of relative residuals $(c_{cal}-c_{nom})/c_{nom}$. It will be clear in the following that it crucially depends on LOQ, as an underestimation of the latter may produce an overestimation of the former. Fig.2 summarises the meaning of the quantities discussed in this section.
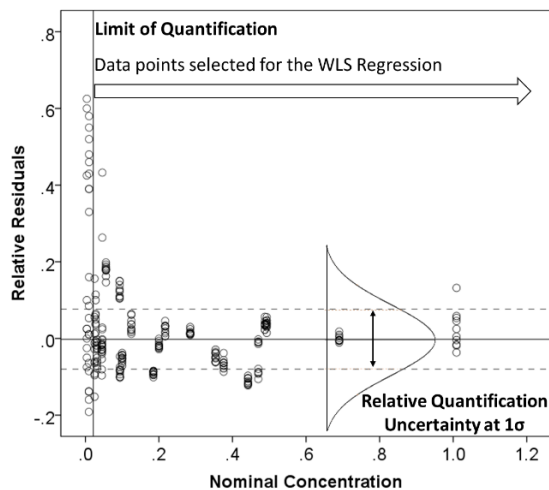

Fig. 2. Synoptic graph of the quantities (limit of quantification and relative quantification uncertainty) discussed in this section.

III. EXPERIMENTS AND DISCUSSION

The measurements concern a group of 26 certified Cu-based alloys. For each device, a first series of measurements was performed on the whole group of standards, then a second one and so on until the 10th series was completed. The data set of each device is therefore made of 260 records. The measuring time is 100 s for F-70 and 30 s for Tracer 5g, with a dead time of approximately 20%. Given the importance, for the analysis of copper-based alloys, of efficiently exciting the K-lines of Sn, tube voltage was always kept at maximum.

A. Filtration of the primary beam

The elements whose LOQ's were used to optimise the filter are Ni, Zn, Pb and Sn. Being F-70 more flexible, fine tuning of the filter was easier than for Tracer 5g, for which only the filters provided by the manufacturer could be used. Figs. 3 and 4 show, for F-70 and Tracer 5g respectively, the LOQ's of Ni, Zn, Pb and Sn for different filters. The LOQ's of F-70 are initially controlled by the count-rate. Consequently, they improve for decreasing absorbing powers until 72 μm of Cu, which provides the best results. If the absorbing power decreases further, the background takes control and LOQ's get larger. Regarding Tracer 5g, the few collimators available and the automatic reduction of the current in fact reduce to four the viable configurations. At present, it is not clear why applying maximum high voltage results in a current reduction much exceeding the one required to keep the power constant. The best results are obtained with 25 μm of Ti plus 300 μm of Al and high voltage set at 49kV. Surprisingly, increasing high voltage from 40 to 49 kV does not improve significantly the LOQ of Sn. We suspect that it is precisely because of the mentioned current reduction.
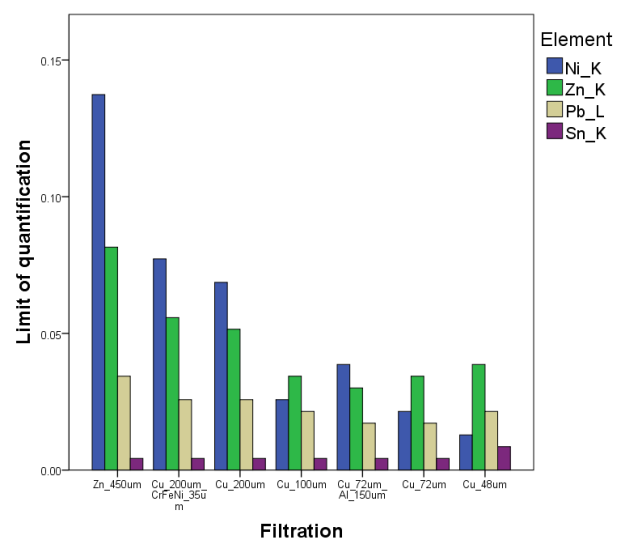

Fig. 3. Optimisation of the primary filter for F-70: limits of quantification of Ni, Zn, Pb and Sn for different filters.
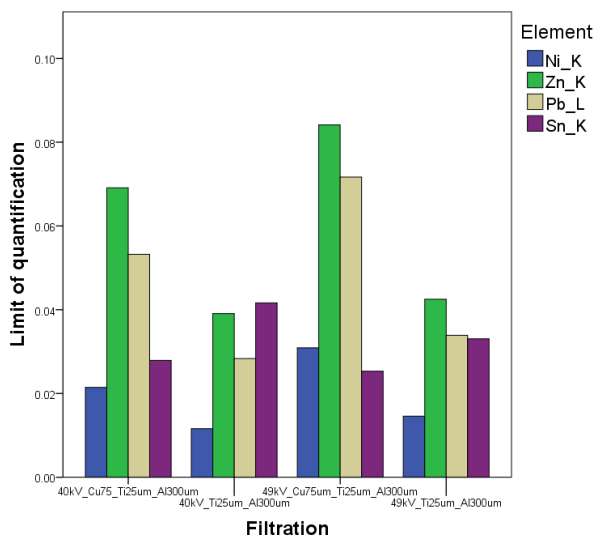
Fig. 4. Optimisation of the primary filter for Tracer 5g: limits of quantification of Ni, Zn, Pb and Sn for different filters and voltage.

B. Calibration and relative uncertainty of quantification

The other important use of LOQ it to establish a minimum value of c_{nom} above which a standard can be included in the calibration regression. Fig. 5 compares the LOQ's of the two devices calculated for all the analysed elements. In general, F-70 performs better than Tracer 5g due to the higher primary intensity. The difference in performance is especially noticeable for Ag, Cd, Sn and Sb, elements that are crucial for the investigation of copper-based alloys [10]. This is due the possibility of operating the tube of F-70 at 70 kV, whereas the maximum voltage of most hand-held devices, including Tracer 5g, does not exceed 50 kV.
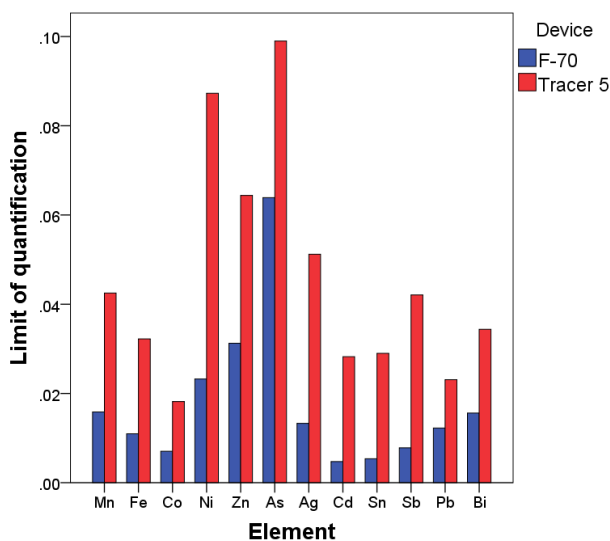

Fig. 5. LOQ's of the analysed elements for F-70 and Tracer 5g.

As discussed in section II.C calibration is performed by a weighted linear least squares fit. The standard deviation of the relative residuals of the fit provides an estimate of the relative uncertainty of quantification (RUOQ) that can be reasonably extended to any copper-based alloy analysed in the same conditions. Fig. 6 shows the RUOQ's at 1σ confidence level for each device and for all the analysed elements. There are no significant differences between F-70 and Tracer 5g: most elements are in the range of 10% or less. The important difference concerns the range of concentrations to which uncertainties refer. If we consider Sn, for example, uncertainties are similar (3% relative versus 4.5%), but F-70 retains this figure down to concentrations of 0.005%, whereas for Tracer 5g the limit is 6 times higher. The high As uncertainty of F-70 is probably due to the underestimation of LOQ and to the consequent inclusion in the fit of highly uncertain data points.
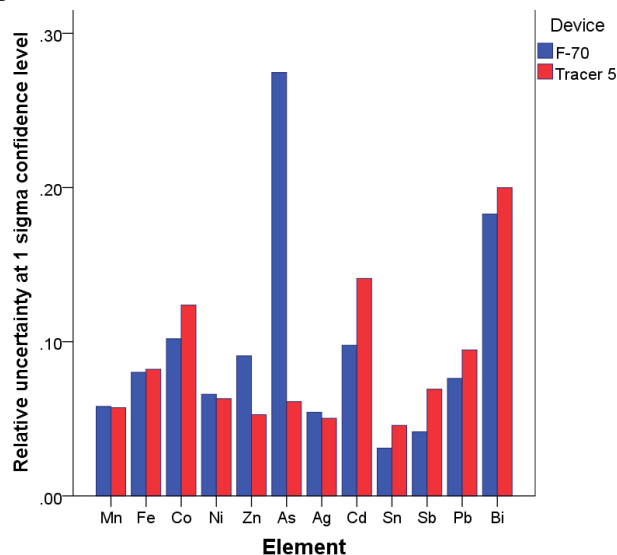

Fig. 6. Relative uncertainty of quantification (RUOQ) at 1σ confidence level for the analysed elements. It is calculated as the standard deviation of the regression relative residuals.

IV. CONCLUSIONS

The paper has discussed quantitative methods to configure and characterise portable XRF spectrometers. The experiments were carried out on two devices: an in-house developed spectrometer (identified as F-70) expressly designed to investigate copper-based artefacts and a commercial hand-held device, namely a Bruker Tracer 5g. Although it was virtually ready for use since the very moment it entered the laboratory, we preferred to reconfigure it from scratch and characterise it by comparison with the more "transparent" F-70. This paper discusses the optimisation of the primary spectrum and the calibration of the instruments, required to get them ready for field use.

Optimisation of the primary spectrum consists in placing different filters on the path of the primary beam and considering the corresponding limits of quantification, that we used as a figure of merit to quantitatively evaluate the detection conditions. Ideally, the optimum filter is the one that minimises the limits of quantification. In fact, it is a compromise solution among elements with absorption edges at different energies. The filters that we selected are 72 μm of Cu for F-70 and 25 μm of Ti plus 300 μm of Al for Tracer 5g.

We also used the limits of quantification to select the standards to be used in the calibration regression: those with c_{nom} above the limit of quantification were included. Different from reference [8], we introduced the weighs $1/c_{nom}^2$ in the regression to reduce the weight of data points with high c_{nom} and improve accuracy at low concentrations.

The standard deviation of the regression residuals was taken as an estimate of the relative quantification uncertainty (RUOQ) at 1σ confidence level.

A comparison of the two devices shows that the limits of quantification of F-70 are significantly lower, due to the higher tube voltage and current. They range from 0.005% for Sn to 0.06% for As, whereas those of Tracer 5g range from 0.02% for Co to 0.1% for As. Conversely, the relative uncertainties of quantification are similar, around 10% or less. Due to lower limits of quantification, however, F-70 retains these figures down to concentrations considerably lower than those of Tracer 5g.

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