

# The use of a European coinage alloy to compare the detection limits of mobile XRF systems. A feasibility study<sup>†</sup>

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The investigation of archaeological and historical materials makes use of techniques that, though borrowed from other fields of research and industrial production, frequently have to be ‘re-invented’ because of peculiar characteristics of the analysed objects. Artistic relevance, limited movability, compositional and structural heterogeneity radically change the experimental approach and often require *ad hoc* designed equipment. These considerations also apply to x-ray fluorescence, especially regarding mobile systems. The extensive development and use of mobile spectrometers has produced an extremely diversified context and created the need for common criteria to evaluate their performances as well as the advisability of a survey on the existing equipment.

This paper shows the feasibility of such an idea through a demonstrative survey that was carried out among users of different mobile x-ray fluorescence spectrometry (XRF) systems in the areas of Rome, Italy and Valencia, Spain. The experimental protocol was based on measuring spectrometer detection limits with the single standard method. The standard was the 50 eurocent coin, whose alloy is made of 89% Cu, 5% Al, 5% Zn, 1% Sn; the large spread of the European currency guarantees maximum availability. The experimental data show that the use of different x-ray tubes and detectors results in detection limits that may differ from each other by a factor of 6 for Zn and almost 100 for Sn; despite the large number of variables that in principle affect the performance, it was observed that the high voltage of the x-ray tube is the most important parameter. Copyright © 2007 John Wiley & Sons, Ltd.

## INTRODUCTION

The investigation of archaeological and historical materials uses techniques that are, in most cases, borrowed from other fields of research. What makes the difference is the object of the analysis: its artistic relevance, limited movability, fragility, compositional and structural heterogeneity radically change the experimental approach. Nondestructive aspect of the investigation and portability of the equipment become a priority and require such a heavy work of adaptation—both in hardware and in procedures—so that even well established techniques have, in fact, to be ‘re-invented’.

These considerations also apply to x-ray fluorescence, which is one of the most widely used techniques in this field. This is due to the peculiarities of the technique itself, but also

due to the importance that compositional information has for investigation of the type, provenance, fabrication technique and authenticity of archaeological and historical materials.

One of its most attractive aspects, since long explored,<sup>1,2</sup> is the possibility of reducing weight and size of the system to obtain an easily transportable device for *in situ* operation. However, since minimum weight and size is only one of the requirements, to avoid exclusion of instruments otherwise very effective for the investigation of cultural materials, the adjective *mobile* instead of *portable* is used in this paper to identify such devices. Also one has to consider that the spectrometer has to be suitably supported, according to the dimensions of the object and the aim of the investigation; the stand becomes therefore an integral part of the system and may affect portability more than the spectrometer itself.

As new types of sources and detectors have become available, a number of different devices, both ‘home-made’ and commercial, have been and are still being developed and used, thus proving the interest for these instruments. Such a diversified field brings forward the need for common

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criteria to evaluate mobile XRF systems; this applies not only to portability but also to analytical performance.

In this regard, it is observed that among several commercial sites<sup>3–11</sup> found on the Internet<sup>12</sup> with the keywords 'portable XRF', only one reported detection limits of the equipment. This confirms that a simple, operative method to evaluate the analytical performance of mobile XRF equipment would be important not only for a survey on the existing equipments, but also to compare different devices in view of a possible purchase.

The present paper suggests a protocol and a reference material suitable for these purposes. The strength of the method, as we consider, relies on extreme simplicity, in favor of which a bit of metrological strictness can be sacrificed. It was therefore arbitrarily decided to consider elemental detection limits as indicators of the spectrometer's analytical capabilities and to measure them by the single standard method.<sup>13</sup>

Following the same general principle of simplicity and feasibility, the 50 eurocent coin was used as reference material because of its widespread availability. Besides, it is particularly attractive because the alloy contains tin, which is also present in cultural materials such as metals, paintings and glasses.<sup>14</sup> Furthermore, given the frequent use of low-power x-ray tubes and small dimension detectors (Si-PIN or Si-Drift), the detection limit for the K-lines of this element becomes particularly suited to highlight the limitations and the field of use of the spectrometer itself.

It is clear that detection limits strongly depend on the matrix, whereas copper alloys, though common, are only part of the huge variety of archaeological and historical materials. In this respect, it should be pointed out that the aim of this work is to provide a common ground to compare different systems, but not to measure actual detection limits with different types of materials.

In order to test the method, a demonstrative survey was carried out among frequent users of mobile XRF (see authors and affiliations) in the field of archaeometry and conservation science. As only feasibility is investigated here, the choice of the systems is simply related to their availability in the participants' laboratories. The spectrometers are mostly home-made and tailored to user-specific needs. They are however representative of different design approaches, as they range from small 35 kV x-ray tubes combined with SiPIN detectors to heavy 60 kV radiographic tubes combined with planar Ge detectors.

Large differences were found among the measured detection limits, especially with respect to Sn. Although qualitatively predictable, the results confirm the importance of experimental assessment of these parameters.

## EXPERIMENTAL PROTOCOL AND RESULTS

All participants in survey complied with an experimental protocol based on the single standard method, according to which the minimum detectable limit is given by:

$$C_{MDL} = 2.33 \cdot C_{std} \frac{\sqrt{B}}{P}$$

where:

$C_{MDL}$  [mg/kg] is the minimum detectable limit of the analyte at 95% confidence level;

$C_{std}$  [mg/kg] is the mass fraction of the analyte in the standard (or reference material);

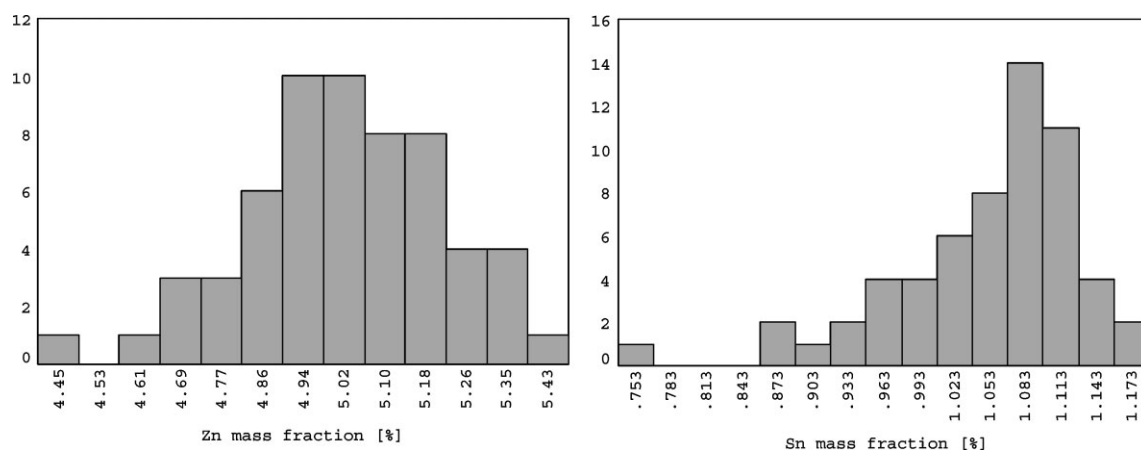
P is the net peak area;

B is the background area.

It is not important here to find out whether the data obtained with the single standard method are more or less realistic with respect to other methods. As previously stated,

**Table 1.** Number of coins investigated by XRF for each country and issue; n.i means that no coins were issued in the corresponding country and year

Country	Mint	Issue							
		1999	2000	2001	2002	2003	2004	2005	
Austria	Vienna	n.i	n.i	n.i	2	1	—	—	
Belgium	Brussels	2	—	—	1	—	1	—	
Finland	Vanda	2	1	—	—	—	—	—	
France	Pessac	2	1	2	—	—	—	—	
Germany	Berlin (A)	n.i	n.i	n.i	2	—	—	—	
	Munich (D)	n.i	n.i	n.i	2	—	—	—	
	Stuttgart (F)	n.i	n.i	n.i	2	—	—	—	
	Karlsruhe (G)	n.i	n.i	n.i	2	—	—	—	
	Hamburg (J)	n.i	n.i	n.i	2	—	—	—	
Greece	Halandri	n.i	n.i	n.i	1	—	—	—	
	Pessac	n.i	n.i	n.i	2	n.i	n.i	n.i	
Ireland	Dublin	n.i	n.i	n.i	2	—	—	—	
Italy	Rome	n.i	n.i	n.i	2	2	2	2	
Luxemburg	Utrecht	n.i	n.i	n.i	1	1	1	—	
Netherlands	Utrecht	1	2	2	2	—	—	—	
Portugal	Lisbon	n.i	n.i	n.i	2	—	—	—	
Spain	Madrid	2	2	1	—	2	—	—	



**Figure 1.** Histograms of the mass fractions of Zn (left) and Sn (right) measured by XRF on 59 coins from different countries and issues.

**Table 2.** Results of XRF analyses carried out on 59 coins from different countries and issues; the precisions are one standard deviation; relative instrumental precision includes positioning errors and is estimated through a significant number of measurements carried out on the same sample; relative composition precision is obtained by quadratically subtracting the instrumental relative precision from the relative standard deviation of the measured mass fractions

Element	Mean of measured mass fractions (%)	Relative standard deviation of measured mass fractions (%)	Relative instrumental precision (%)	Relative composition precision (%)
Zn	5.02	4.1	1.2	3.9
Sn	1.05	7.7	1.4	7.6

our aim is to provide a simple means of comparing different spectrometric systems, thus fulfilling the requirements of the present work.

The reference material was the 50 eurocent coin, whose nominal composition is of 89% Cu, 5% Al, 5% Zn, 1% Sn. In order to estimate the precision of these figures, 59 coins from different countries and issues (Table 1) were nondestructively analysed by a mobile XRF system, whose sensitivity is 165 kg/s·dg for Zn and 365 kg/s·dg for Sn; the measurement point was on the background over the '5' on the reverse. Figure 1 shows the histograms of measured mass fractions for Zn and Sn, respectively. For the purposes of this paper, the distribution can be approximated to a normal curve and the interval  $mean \pm 2 standard deviation$  can be taken as the 95% confidence interval of the measurements. For each element, Table 2 gives the values of the concerned statistical parameters, i.e. the mean values and relative standard deviations of the measured mass fractions, the instrumental relative precision (this includes positioning errors and was estimated through a significant number of measurements, carried out on the same sample) and, finally, the relative precision of the alloy composition, given by quadratic subtraction of instrumental precision from the standard deviation of the measured mass fractions. Our estimate of precision concerned with the composition of the 50 eurocent coin is therefore 7.8% relative for Zn and 15.2% relative for Sn at 95% confidence level; these figures are larger than those of reference materials commonly used for calibration and metrological purposes, however, it will be

shown that the possibility of distinguishing different systems remains essentially unaffected, as the ranges of variation of detection limits are by far larger.

According to Ref. 13, the analyte concentration in the standard used to determine  $C_{MDL}$  should be 10–100 times the expected  $C_{MDL}$ . Although for the most sensitive systems it is out of this range, this does not affect much the results and has to be however accepted, given the necessity of using the same standard for all systems.

Five, 300 s each, measurements of a 50 eurocent coin were taken on system tested. The spectra collected were then converted to the '.spe' file format and processed with the IAEA software WinQXAS,<sup>15</sup> in order to calculate the net peak areas and the background areas. The choice of the software was dictated by its acceptance and availability free of charge. The minimum detectable limits were measured for Zn and Sn  $K\alpha$ -lines.

The participants provided additional information, summarized in Table 3, concerning (1) detector characteristics and measurement conditions, (2) x-ray tube cooling and (3) weight of the whole system and of the mobile part alone.

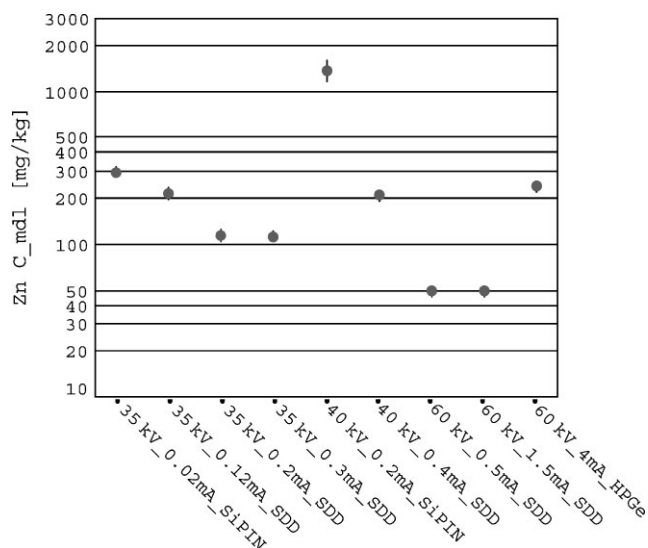
Figures 2 and 3 show, on a logarithmic scale and for each system, the minimum detectable limits for Zn and Sn, respectively, averaged for each spectrometer over five measurements. Error bars account for both instrumental and compositional relative uncertainties and are given at 95% confidence level. They are around 8% relative (with one outlier at 15%) for Zn and around 15–20% relative (with one outlier at 40%) for Sn. The minimum detectable limit

**Table 3.** Specifications of the spectrometers participating in the survey

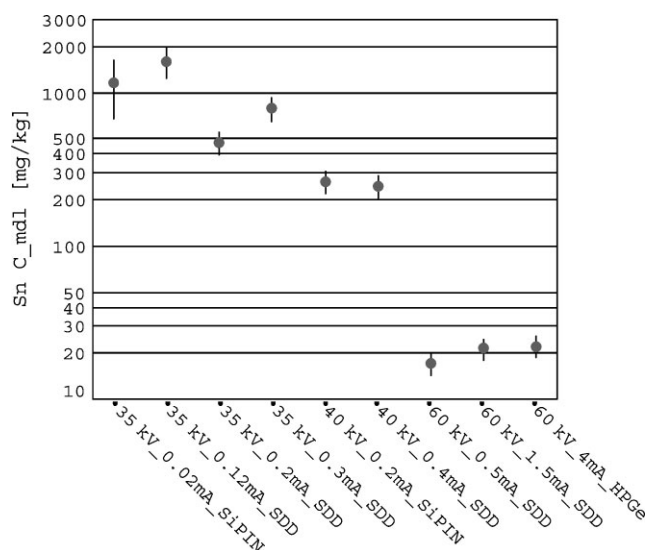
Detector	Spectrometer's Identification											
	35kV_0.02 mA_SiPIN	35 kV_0.12 mA_SDD	35 kV _0.2mA_SDD	35 kV_0.3 mA_SDD	40 kV_0.2 mA_SiPIN	40 kV_0.4 mA_SDD	60kV_0.5 mA_SDD	60kV_1.5 mA_SDD	60kV_4 mA_HPGe			
Manufacturer	Amptek	EIS-Ketek	EIS-Ketek	Röntec	Amptek	EIS-Ketek	Ketek	Ketek	EG&G ORTEC			
Model	Si-PIN XR-100CR			SDD XFlash	Si-PIN XR-100CR		SDD 10 mm <sup>2</sup>	SDD 5 mm <sup>2</sup>	GLP-16195/10			
FWHM [eV]	175	150	160	160	170	160	160	170	195			
Area [mm <sup>2</sup> ]	5	5	5	5	7	5	7	5	200			
Thickness [µm]	500	300	300	300	300	300	450	300	10 000			
Shaping time [µs]	20	1	1	1	20	1	2	1	3			
Internal collim.	Ag	Zr	Zr	Zr	none	Zr	Zr	Zr	none			
Manufacturer	EIS	EIS	EIS	EIS	EIS	EIS	Italstructures	Italstructures	Gilardoni			
Anode	Pd	W	W	Pd	W	W	W	W	W			
High voltage [kV]	35	35	35	35	40	40	60	60	60			
Current [mA]	0.02	0.12	0.2	0.3	0.2	0.4	0.5	1.5	4			
Collim. diam. [mm]	3	2	2	3	3	4	4	6	1			
Filter	0.15 mm Be	2 mm Al	2 mm Al	0.15 mm Be	0.2 mm Cu	4mm glass	0.4 mm Cu	0.4 mm Cu	0.5 mm Cu			
Total [kg]	20	10	10	20	20	20	30	30	200			
Mobile [kg]	4	3	3	4	4	4	9	9	18			
Cooling	Air	Air	Air	Air	Air	Air	Water	Water	Water			
Weight + Cooling												

of Zn varies between 50 and 300 mg/kg, except one figure at 1370 mg/kg. The situation for Sn is different: depending on the tube characteristics, the minimum detectable limit is approximately few tens of mg/kg for systems working at 60 kV, few hundreds of mg/kg at 40 kV and, except for one case, more than several hundreds of mg/kg at 35 kV. Given these variation ranges, it is apparent that, though quite large, uncertainties in alloy composition (to which errors are mostly related) do not prevent from clearly distinguishing differently performing systems.

A general consideration is that the systems have to be taken 'as such', as they are tailored to user-specific needs and therefore differently optimised. For instance, collimator diameters range from about 1 mm, used for paintings to



**Figure 2.** Logarithmic scatterplot of Zn minimum detectable limits for each system; error bars are given at 95% confidence level; the figures refer to a Cu matrix and a counting live-time of 300 s.



**Figure 3.** Logarithmic scatterplot of Sn minimum detectable limits for each system; error bars are given at 95% confidence level; the figures refer to a Cu matrix and a counting live-time of 300 s.

about 6 mm, used for bronze statues. It comes out that the effect on detection limits of such parameters as detector speed and efficiency, decisive other things being equal, may be completely hidden by differences in collimator diameter.

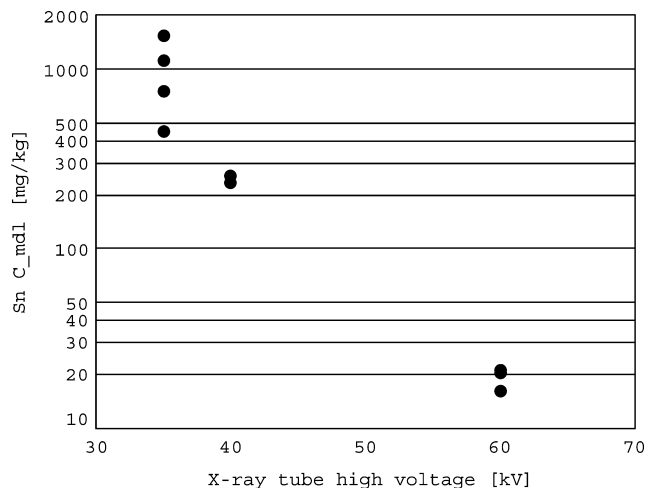
As regards Zn C<sub>MDL</sub>'s, this element is well within the optimum detection range of all instruments. Hence, the system components are not driven to show their limitations. For this reason, Zn detection limits do not vary much within the group, although, relatively speaking, the best performing systems are all equipped with Si-Drift detectors. Clearly this is due to their low shaping time and to the consequent capability to take advantage of intense primary beams.

Quite different is the situation for Sn C<sub>MDL</sub>'s, as this element highlights the system limitations concerning both tube high voltage and detector efficiency. The results show that the overall effect is dominated by the tube high voltage, beyond any difference in system optimisation. As it appears from Fig. 4, there is a strong inverse relation of this parameter with Sn detection limits; the scatter at 35 kV being mainly due to different current used (Table 3). This behavior is consistent with the equation that describes the line intensity as a direct function of the 'overvoltage'  $V - \phi$ .<sup>13</sup>

$$I_i = Ki(V - \phi)^n$$

- $I_i$  [ $s^{-1}$ ] is the intensity of the analyte line,
- $K$  is a proportionality constant,
- $i$  [mA] is the tube current,
- $V$  [kV] is the tube high voltage,
- $\phi$  [keV] is the absorption edge of the analyte line,
- $n$  is a number between 1 and 2, 1.6 is commonly chosen.

As regards detection efficiency, comparison with the system equipped with HPGe detector shows that this parameter is important but not essential: other systems working with Si-Drift detectors at 60 kV perform equally well or even better. In fact, low detection efficiency can be offset by more intense primary beams, provided the detector is sufficiently fast to bear the much higher count rate at low energy.



**Figure 4.** Semilogarithmic scatterplot showing the inverse relation of Sn C<sub>MDL</sub> with the x-ray tube high voltage ( $t = 300$  s).

## CONCLUSIONS

A survey was carried out among a limited number of mobile XRF systems used in the field of art and archaeology; the aim was to provide a common ground to *compare* detection limits, that we consider significant of the spectrometer's performance. The investigated systems represent different compromises between portability and analytical performance; they range from small 35 kV x-ray tubes equipped with SiPIN detectors to heavy 60 kV radiographic tubes equipped with HPGe detectors. The results demonstrate that a larger scale survey would not only be feasible, but also very informative.

Maximum feasibility was the guiding principle of the whole work and was achieved through:

- simplicity of procedures: detection limits were measured by the single standard method;
- availability of the reference material: 50 eurocent coins were used as standard;
- availability of software: the spectra were processed with WinQXAS program, downloadable free of charge from the IAEA's website.

Precision in coins composition was measured on coins from different countries and issues and found to be 7.8% relative for Zn and 15.2% relative for Sn at 95% confidence level; though larger than those usually accepted for reference materials, these figures produce an overall uncertainty that is still small with respect to the variation range of measured detection limits. It can be concluded that 50 eurocent coins, used as a standard, are suitable to clearly distinguish differently performing systems.

The relevance of information provided is not only related to the fact that elements in the ranges  $Z \approx 30$  and  $Z \approx 50$  are important in archaeological and historical materials, but also to the results, that show differences not *a priori* predictable. The minimum detectable limits of Zn are relatively similar among the spectrometers and range between 50 and 300 ppm ( $t = 300$  s); on the other hand Sn shows much larger variations, ranging from 20 to 1500 ppm ( $t = 300$  s). Among the parameters that should, in principle, affect these figures—type, area, thickness, speed of the detector, working conditions of the tube—the tube high voltage was found to be the most important, and only for Sn, whereas the effect of the other parameters is much smaller, hidden in fact by the different optimisations of the systems. The observed inverse relation of Sn detection limits with the high voltage (and obviously with the weight) confirms that portability and sensitivity have opposite requirements and tend to push the system design in opposite directions; this contrast is marked at present, but will presumably fade as miniature x-ray tubes of 50–60 kV come into common use.

The results also lead to conclusion that a larger scale survey would be advisable for several reasons. Such a survey would be suited:

- to describe the state of the art in the field;
- to contribute to the ongoing European standardization activities, namely, those of CEN/TC 346/WG 2, with regard to both measurement procedures and qualification of equipment;
- to stimulate the development of new x-ray tubes, more suitable for portable XRF spectrometers.

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