Abstract

X-ray fluorescence spectroscopy (XRF) is a common analytical technique found in many laboratories. The instrumentation for this technique is rather large and does not lend itself to on-site examinations. Recent innovations in solid-state technology make portable instruments available that can be used outside the laboratory in museum galleries or at archaeological sites. The use of such an instrument, however, has practical limitations that are different from laboratory models. This study relates experience with an Innov-X Systems portable X-ray fluorescence spectrum analyser and examines the practical limits of analysis done with that system. Selected glass, gold, and bronze objects from museum collections as well as standards and materials previously analysed using inductively coupled plasma mass spectrometry with laser ablation (LA–ICP–MS) were used in these tests. This study was meant not to present the theoretical limitations of XRF but to document the practical concerns of on-site XRF testing.

Keywords

X-ray fluorescence spectroscopy, non-destructive analysis, glass, metal, gold, bronze, paints, inductively coupled plasma mass spectrometry

Non-destructive elemental analysis: reliability of a portable X-ray fluorescence spectrometer for museum applications

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Introduction

Recent technological improvements have led to a reduction in size of X-ray fluorescence spectrometers (XRF), broadening the scope of investigation and opportunities for use, creating a tool for conservators and conservation scientists to inform and engage museum professionals in situ about cultural heritage.

This multi-elemental technique of analysis can be used to characterize the composition of many types of material as well as to reveal information about construction techniques, provenance, and historical alterations. It provides immediate results and allows non-invasive testing. The current investigation focuses on the usefulness of the portable XRF in diverse applications encountered in the fine arts rather than materials science.

A wide range of materials can be examined with the portable XRF. Our investigations have included the analysis of lead grounds in 19th century American oil paintings, metallic mordants in Native American textiles, pigments on 6th century Chinese stone sculptures and 15th century Italian painted panels, surface enrichment of 20th century United States Mint gold coin patterns, contaminants in bones, and original alloy compositions and restorations of diverse metal sculptures and objects.

Equipment

This study used the Innov-X Systems portable X-ray fluorescence spectrum analyser, a self-contained, lightweight (2 kg), portable model. Elements as light as phosphorus were detected with limits as low as hundreds of parts per million (ppm) depending on the element and the sample matrix. With a single measurement, it is possible to analyse for the presence of about 20 elements, from calcium to lead.

The Innov-X Systems analyser has an X-ray tube with a silver anode operating at a voltage ranging from 10 to 35 kV (5–50 μA). It has a thermoelectrically cooled Si-PIN diode detector with a resolution of 250 eV or less at full width of half maximum (FWHM) height of the peak at 5.9 keV (Kα for Mn). The acquisition window is 12 mm in diameter. Collimators with an aperture size of 5 mm are available but generally not used because it reduces signal output. Two modes of data processing are available: 'soil mode' described as useful for trace materials, and 'alloy mode' for metals. Analysis time can vary up to 1.5 min depending on the mode.

The penetration of the X-ray beam is dependent on the elements present (micrometres for heavier materials, millimetres for lighter elements). Corrosion or surface contamination can affect the results of the analysis by overemphasizing surface elements. Archaeological materials often have surface depletion of some elements because of corrosion and cleaning. Light elements ($Z < 15$) cannot be detected in the present configuration.

Results obtained using the handheld XRF and inductively coupled plasma mass spectrometry with laser ablation (LA–ICP–MS) are compared. Like XRF, LA–ICP–MS is a multi-elemental analytical method able to determine a wide range of elements over a large concentration range. The handheld XRF determines the composition of an object on a quite large surface (12 mm) with a depth of a few microns whereas LA–ICP–MS is used for sub-surface analysis. The

volume sampled is a cylinder, several tenths of a micron deep, with a diameter of 100 μm. A pre-ablation time of 20–40 s is used to minimize surface contamination. It is reasonable to compare XRF and LA–ICP–MS results as long as the material tested is reasonably homogeneous. LA–ICP–MS was used to compare the performance of the portable XRF within objects and to confirm the values from standards. ICP–MS is a destructive multi-elemental analytical technique easily sensitive to the range of parts per million. The sampling leaves a trace on the object almost invisible to the naked eye (the crater of ablation has a diameter of 100 μm) which makes this technique particularly suitable for the analysis of valuable artifacts. The ICP-MS used for this analysis was a Perkin Elmer Elan 6000 model with A Cetac LSX-200 Plus UV laser.

Performance claims

Even if the portable XRF is theoretically able to give quantitative results, the software provided with the instrument does not easily take into account the variation in surface and matrix effects encountered in museum or archaeological specimens. At this time, portable XRF analysis is considered capable of qualitative measurements or at best, semi-quantitative ones.

Using different kinds of commonly available reference materials: glass standards, gold and copper alloys, the limits of detection of the instrument in the different analytical modes were defined. We have tested 'alloy mode', which is able to detect major and minor elements and 'soil mode' designed to determine trace elements in a low Z matrix. Owing to matrix effects and interference, the limits of detection that were determined for the specific applications are in the range down to hundreds of parts per million. The absence of a particular element must be cautiously interpreted as either below the sensitivity of the instrument, obscured by other elements, or in fact, absent.

Materials tested

Glass

To evaluate the performance of the portable XRF for glass, standard reference materials 610 and 612 manufactured by the National Institute of Standard and Technology were selected. These two pellet-shaped reference materials had a bulk composition of 72 per cent silica, 12 per cent calcium, 14 per cent sodium, and 2 per cent aluminium. Moreover, these standards contain about 50 different trace elements. The concentration of these trace elements in standard 610 is about 500 ppm and in standard 612, 50 ppm. Certified concentrations are provided for only eight of the elements. The other elements have target values. For the other elements in SRM 610 values published by Pearce et al. (1997) were also references. The use of multi-element standards may lead to some complex problems in the evaluation of the limits of detection (peak overlap for example) but more closely resembles the realities of working with museum or 'real world' specimens.

Comparisons were made with the results obtained with the portable XRF both for standards and for excavated historic glass. Our glass samples were 19th century European and Chinese glass beads that were used in trade with Native Americans and currently housed in the collection of the Smithsonian Institution's National Museum of Natural History. The beads were of different shapes and sizes and varied widely in composition. Some were lead glass while others were alkaline glasses. Their colour and opacity were due to the presence of particular elements such as chromium, copper, arsenic, cobalt, manganese, or iron. Their composition, including major, minor and trace elements was determined first using LA–ICP–MS and then analysed using the portable XRF. For the smallest beads, a number of them were grouped together to maximize the intensity of the signal measured by the instrument.

Innov-X Systems' 'soil mode' method analyses trace elements in a matrix composed at 95 per cent of light elements ($m < 48$ uma). When using this mode, the instrument assumes that the concentration of an element is directly

proportional to the measured signal for this element (corrected of the background and normalized). A sampling time of 90–180 s was used.

Limits of detection

Using the standard reference materials 612 and 610, the limits of detection were found to be better than 50 ppm when the corresponding element was detected in both standards. When not detected in standard reference material 612 but detected in standard reference material 610, the elements have a limit of detection between 50 and 500 ppm. If for a given element no signal was detected whichever standard was tested, the limit of detection (lod) is presumed to be over 500 ppm in that matrix (Table 1).

Some elements were detected in the historic glass samples at a concentration below the limits of detection determined using the glass standards. This could relate to the large number of elements (more than 50) in the standard reference materials. Such composite material is likely to have an X-ray spectrum with multiple overlapping peaks that will effect the determination of some of the elements. On the other hand, some elements had poor limits of detection in the archaeological samples in comparison with the standards. The standard's pellet shape provided a flat surface, in contrast to the irregular shape of the sample beads, and may have contributed to scattering and interference.

Accuracy

To evaluate accuracy, certified or recommended concentrations for standard reference material 610 and concentration using the portable XRF were compared. We noticed an overestimation when using the portable XRF for many elements with a certified concentration of about 500 ppm (Figure 1). For copper, cobalt and nickel, the values given by XRF are more than twice what was expected.
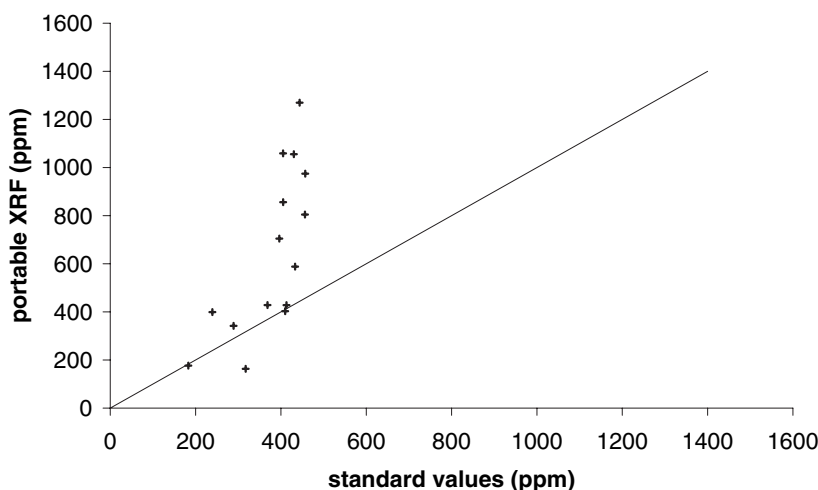
Table 1. Portable XRF results for limits of detection (lod) in glass

	Glass standard (612, 610)	Excavated glass sample
Cr	50 < lod <500 ppm	> 2000 ppm
Mn	50 < lod <500 ppm	180 < lod < 500 ppm
Fe	lod < 50 ppm	250 < lod < 500 ppm
Co	lod < 50 ppm	not measured
Ni	lod < 50 ppm	160 ppm
Cu	lod < 50 ppm	35 ppm
Zn	lod < 50 ppm	20 ppm
As	lod < 50 ppm	42 ppm
Se	lod < 50 ppm	not measured
Rb	no reading	13 ppm
Sr	no reading	36 ppm
Zr	no reading	20 ppm
Mo	lod < 50 ppm	not present in tested samples
Ag	lod < 50 ppm	not present in tested samples
Cd	lod < 50 ppm	not present in tested samples
Sn	lod < 50 ppm	500
Sb	50 < lod <500 ppm	> 1000 ppm
Te	50 < lod <500 ppm	not measured
Ir	50 < lod <500 ppm	not measured
Hg	50 < lod <500 ppm	not measured
Pb	50 < lod <500 ppm	200 ppm

Figure 1. For standard reference material 610, comparison between certified and measured concentrations

As far as historic glass samples are concerned, results obtained using LA–ICP–MS and XRF were reported in different graphs (Figure 2). From a general point of view, the concentrations provided by the XRF are of the same order of magnitude as the ones provided by LA–ICP–MS. There is variation over the elements but no specific trend.

Reproducibility

Reproducibility was calculated for standard reference material 610 by obtaining the relative standard deviation for five analyses done over the course of several days. For most of the elements detected in this standard, the reproducibility error
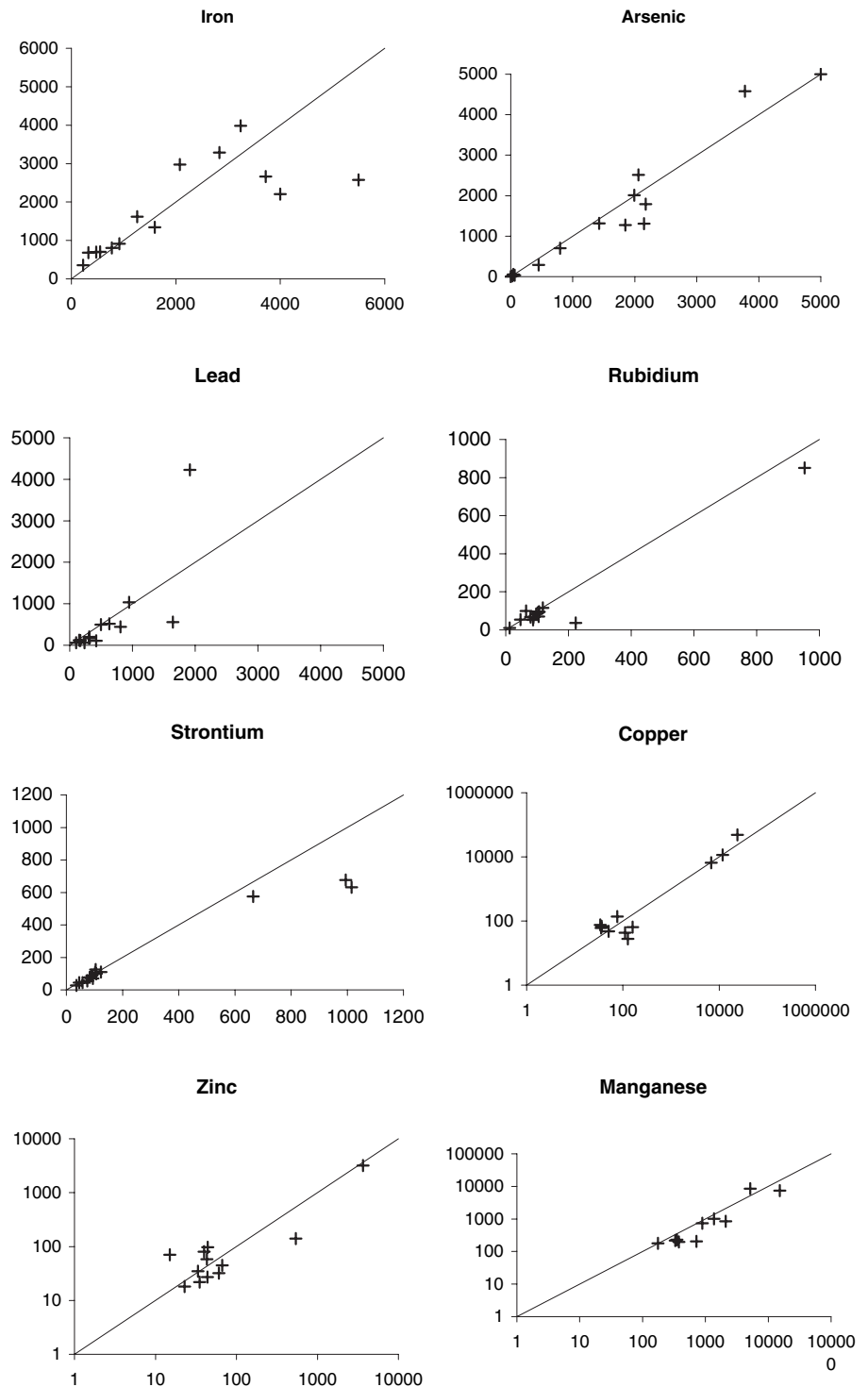
Figure 2. Comparison of the results for different elemental components of excavated glass with LA–ICP–MS (x-axis) and XRF (y-axis). The compositions are listed in parts per million

is below 5 per cent (Figure 3). Two elements within the standard, tellurium and manganese, have reproducibility errors greater than 10 per cent. This may be a result of approaching the limits of detection within the matrix.

Though the portable XRF is able to discriminate lead glass from non-lead glass without ambiguity (Figure 4), the presence of lead jeopardizes the measurement of any other elements.

Leaded glasses gave peaks that could not be resolved to give unequivocal identification of elements and in some cases implied elements that were not actually present in the glass. It also produced an overestimation of the concentration of some elements. For example, cadmium was systematically
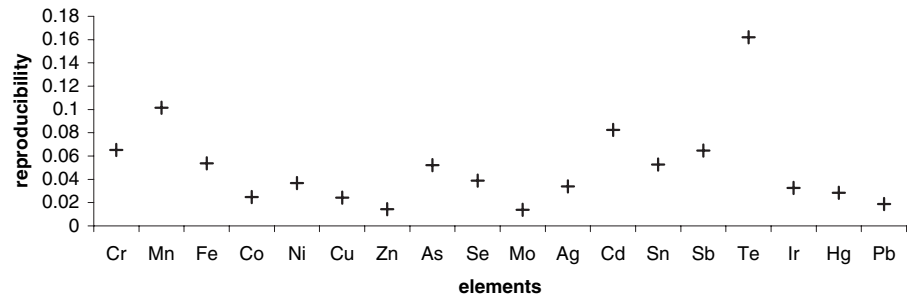
Figure 3. Reproducibility of the measurement of standard reference material 610 with portable XRF
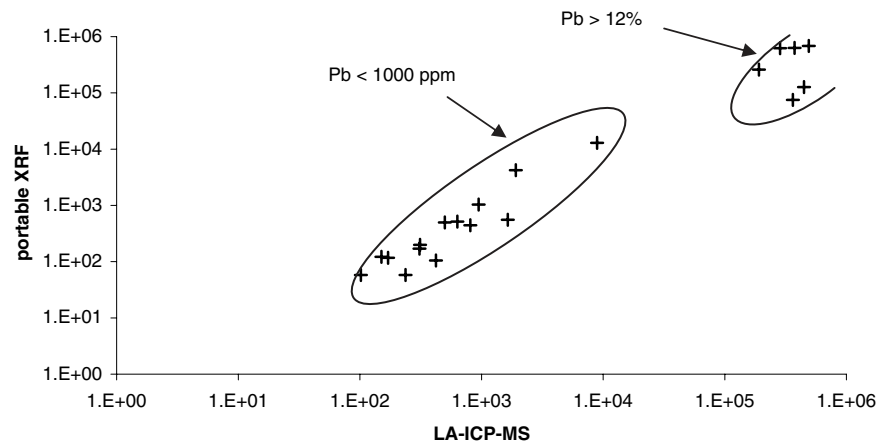

Figure 4. Comparison of the lead concentration in excavated glass samples detected with LA–ICP–MS and portable XRF

detected in glass containing lead even though cadmium is rarely present in glass except when involved in specific colouring processes. The presence of an anomalous cadmium peak is somewhat inexplicable but may be the result of a 'pile up' peak from lead fluorescence as suggested by an anonymous reviewer. When lead was present in the bead, the iron concentration was also exaggerated by the portable XRF, sometimes measuring four times greater than values indicated by LA–ICP–MS. The 'soil mode' software is designed to handle lower concentrations of elements than have been found in the leaded glasses and does not take into account the inter-elemental effects.

Even though barium can in theory be detected by portable XRF, the instrument could not detect barium with a concentration as high as 9 per cent in lead–barium glass.

As far as the unleaded glass was concerned, it was not possible to differentiate between the different alkaline glasses because sodium ($Z = 11$) is a too light an element to be detected in an air based system. Modification of the XRF to helium or vacuum-based systems may resolve this problem.

Metals

Metallic museum or archaeological objects can be of very different natures. Two types of metallic object were tested using the portable XRF: gold and the copper alloys. For these materials, the 'alloy mode' was selected. This mode is designed for the analysis of metal alloys. The algorithm that is used to calculate concentrations in this mode takes into account the nonlinearity of the response of the instrument over a range of concentrations by using empirical factors and fundamental parameter calculations. A sampling time of 30 s was chosen.

GOLD ALLOYS
For metallic objects, we tested standards as well as antique objects. Gold–silver–copper alloys manufactured by the Royal Canadian Mint with certified concentrations for gold and silver (NIST SRM 8068, 8077, and 8074)
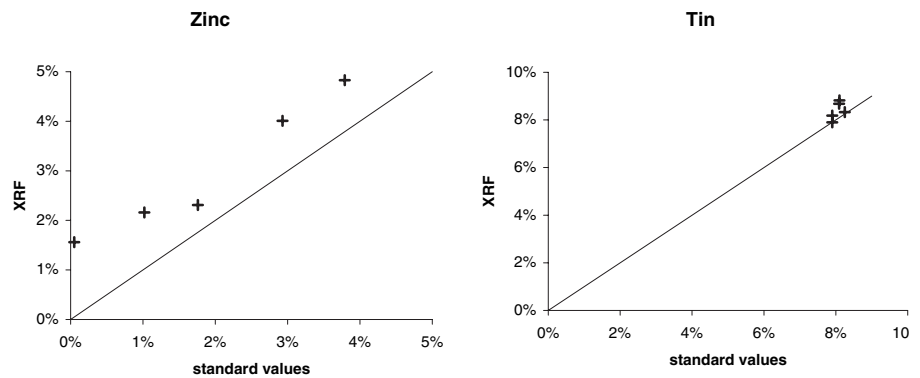
Figure 5. Comparison between portable XRF and LA–ICP–MS results
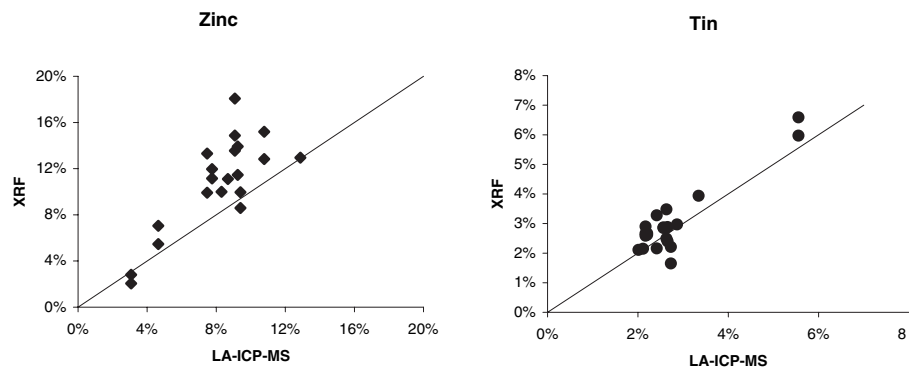

Figure 6. Comparison between XRF and LA–ICP–MS results for tin and zinc

were selected as well as Islamic gold coins dated from the 8th century, the 10–11th and 12–13th centuries AD. The gold coins were also previously analysed using LA–ICP–MS. To compare the composition determined by XRF with certified composition or the composition obtained using LA–ICP–MS, we calculated the correlation parameters, for some elements, between results obtained by either technique on a series of samples. The two series of values are consistent as the slope and the R^2 value of the correlation curve are close to 1. For both standards and historic gold samples, the agreement was quite good for gold, copper, and silver, the most common constituents in gold alloys.

LA–ICP–MS showed that one coin contained 1500 ppm of copper whereas the portable XRF did not record the presence of copper at all, suggesting that the limit of detection for this element in a gold alloy is over 1500 ppm or, alternatively, that the composition at the surface varies from the bulk composition, a phenomenon not unusual in cleaned coins.

COPPER ALLOYS

Investigations of bronze alloys were made starting with industrial bronzes (Tymetal bronze). The recommended compositions were available and used for comparative purposes. The overestimation of zinc occurred in every sample. For example, the measured concentration of zinc in a bronze with a known concentration of 0.05 per cent of this element was 1.56 per cent. It seems, when looking at Figure 7, that the portable XRF will have the same response whatever the quantity of zinc when the concentrations of this element range from hundreds of parts per million to 1 or 2 per cent. This observation was confirmed by analysing other types of bronze where zinc was not actually present in the composition. This overestimation does not affect the tin concentrations. The same phenomenon was observed with bronze sculptures from the collection of the Baltimore Museum of Art, which were tested with the portable XRF and in some cases by LA–ICP–MS. LA–ICP–MS was performed on metal shavings saved from the drilling of mounting bolts whereas the portable XRF analysis examined the flat surface on the underside of the base of each sculpture.

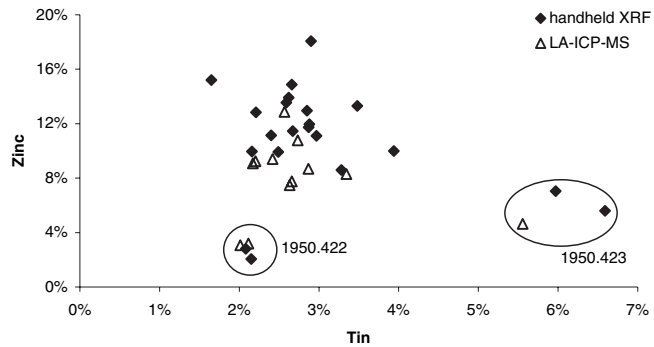In general, the portable XRF overestimated the concentration of zinc

Figure 7. Comparison between zinc and tin determined with the portable XRF and LA–ICP–MS

compared with the results obtained from LA–ICP–MS. However, the difference in composition can be due to a heterogeneous distribution of zinc within the bronze, and specifically to a surface enrichment. Alternatively, the software may not adequately separate the smaller energy peaks from the larger peaks, in this case the low energy Cu peak from the Zn peak, and this would overestimate the zinc concentration.

Individual bronze sculptures were grouped according to their zinc and tin contents. Figure 7 shows that, even if there are slight differences in the composition determined using both methods, the results are similar overall. As the minimum zinc content in bronze is about 3 per cent, the results are not affected by the problem encountered by the portable XRF in providing reliable values for zinc contents below 2 per cent.

In addition to the industrial copper alloys previously described, three standards manufactured and controlled by Le Centre Technique des Industries de la Fonderie in France (B10, B12, and 4763) were tested. The results are shown in Figure 8. The values measured are always of the same order of magnitude as the recommended or certified values.
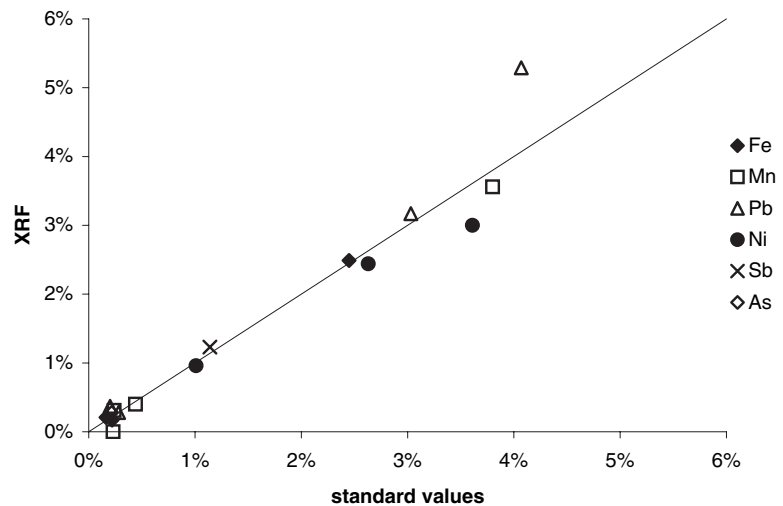

Figure 8. Comparison between XRF and LA–ICP–MS results for various elements of interest from standards B10, B12, and 4763

Arsenic was successfully detected in quantities as low as 0.22 per cent, whereas the portable XRF provides no reading for nickel when concentrations are in the range of the thousands of parts per million.

Conclusion

The Innov-X Systems portable X-ray fluorescence spectrum analyser is a lightweight (2 kg) portable system that can be used for the analysis of museum or archaeological materials. In the 'alloy' mode, the instrument is quite suitable for

determining the bulk composition of metals and, within limits, certain trace materials. In the 'soil' mode, analysis of glass and similar materials can be made for most constituents but again, detection of trace elements must be viewed with caution. The technique is useful as a qualitative indicator of composition and often useful as a semi-quantitative technique.

The reproducibility of the measurements evaluated on glass standards is satisfactory, because for most elements the relative standard deviation for five analyses is better than 5 per cent. The accuracy of the concentrations was shown to be dependent on the matrix of the material tested, and therefore appropriate standards become more important as the concentration of the measured element becomes smaller, that is, it gets closer to the limits of detection. The system does not easily allow for interference corrections that would determine some elements in the presence of other interfering elements. For example, for arsenic, the best spectral line of measurement is the Kα line (10.5 keV), whereas lead has an Lα line at the same energy. The presence of lead will obscure detection of arsenic, and other elements. High concentrations of lead in glasses are then problematic for some elements.

The matrix will also affect the limits of detection. According to the type and the number of elements, the spectrum provided by the portable XRF will be more or less complex. A complex spectrum will lead to higher background noise, overlapping peaks, and other artifacts altering both the identification and quantification of elements. When metallic alloys were tested, the 'alloy mode' was used whereas 'soil mode' was selected for trace elements in light element matrices. The second mode provides a better sensitivity but issues of reabsorbtion and possibly saturation remain.

Our experience showed that the suitability of the portable XRF for museum survey applications depends greatly on the experience of the operator. The instrument is designed for quick investigations, for determining the nature of materials, for comparing the composition of materials of similar nature, and for sorting. After separation of lead from unleaded glass, it is possible to identify elements of interest such as those involved in the colouring process for non-lead glass. For the bronze sculptures evaluated in the present study, distinctions in the composition matched changes in production and led to classifications of sculptures by foundry and date.

It is advisable that the portable XRF be used in tandem with another technique such as ICP–MS to confirm the absence of certain elements or to quantify these elements.

Acknowledgements

Reference

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