Comparison of matrix effects on portable and stationary XRF spectrometers for cultural heritage samples

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Abstract In this work, we compare the matrix effects for two different X-ray fluorescence spectrometers, a portable and a stationary one, in order to evaluate their performances in terms of scattering radiation for different matrices. Five reference materials were analyzed: orchard leaves (NBS-1571), clay (ISE-954), bone ash (NIST-1400), 70% copper alloy (BCR-691) and 22 ct gold alloy (Fisher).

The results obtained showed similar behavior for both spectrometers. The lowest background was obtained for the light matrix and an increase was observed for intermediate atomic number matrices, reaching a maximum for copper and gold alloys.

In spite of that the lowest background had been obtained for the light matrix, the portable system presents a tremendously high background when compared to the stationary one. For this matrix, some of the trace elements were almost not detected by the portable spectrometer, which makes difficult their characterization with this system. For medium Z matrices there is an increase on the Compton peak and a decrease on the Rayleigh one, reaching a similar intensity. Finally, for heavy matrices, the Compton peak almost disappears and the Rayleigh effect takes the lead. Three case studies were also performed in order to appraise the behavior of the spectrometers: a paper document from the XVIII century, a sample of archaeological bone from the Middle Ages and a Portuguese coin from the XIX century.

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1 Introduction

Scientific studies of art works are common practice in many museums and institutions dedicated to study and protect cultural heritage. Applied physics and chemistry provide the scientific data necessary to characterize and understand the environment in which the art work was created. Multidisciplinary teams are formed where restorers, curators and scientists merge their knowledge together in order to obtain better and more accurate results [1–5].

The major requirement for an analytical technique employed in the study of objects of important historical value is the ability to perform non-destructive analysis.

In field of Cultural Heritage, numerous objects cannot be moved from the original location due to their weight and dimensions or to their value. The requirement of analyzing such objects gave rise to the development of portable energy dispersive X-ray fluorescence spectrometers (PXRF) that allow in situ analysis, which are of common use nowadays [6–12]. However, the sensitivity of these portable spectrometers, for some kinds of samples, is limited by the high Bremsstrahlung radiation emitted by the X-ray tube. The intensity and energy distribution of this scattered radiation very much depends on the atomic number of the matrix. Regardless of the matrix composition, strong reduction of the scattered radiation can be obtained making use of polarized radiation and monochromatic radiation, but in these situations, the spectrometers are not portable in most of the cases. The use of polarized X-rays to improve the detection limits have already been very well studied [13–18]. In these works, much attention has been paid to comparison of different excitation methods and geometrical improvements in order to achieve scattered radiation reduction. The maximum improvements in the signal to background ratios were

obtained for triaxial geometry spectrometers. In other studies [18, 19] Rao et al. obtained coherent and incoherent cross sections for a few pure elements, ranging from Al to Pb. No results have been obtained for trace element detection in different sample compositions.

In a recent review publication Margaret West et al. give an overview on most X-ray fluorescence spectrometry [20]. Concerning PXRF systems they refer to the most innovative applications and developments in instrumentation.

Aceto et al. [21] used a Mo anode to study with success the ink composition of an ancient manuscript from 4th A.D. A remote controlled PXRF system equipped with Rh and W anodes [22] was used to identify the elemental composition of pigments in wall paintings. Cesareo et al. [23] used a PXRF with a silver tube to identify gilded copper objects from Peru. Zarkadas and Karydas [24] used a PXRF with a gold anode to identify metallic objects. Ferreti [25] proposed some solutions in cases that spurious lines originated from the X-ray spectrometer or collimators come out, which could interfere or misrepresent the elements present in the sample. Craig et al. [26] presented a comparison between laboratory XRF and PXRF for the analysis of obsidians from Peru.

The sample matrix is the main responsible for the diffusion effects, and the total amount of scattered radiation by Compton and Rayleigh effects is strongly dependent on the matrix composition, even under the best geometrical improvements.

For light matrices, the predominant effect is Compton scattering, while for heavy matrices the Rayleigh effect takes the lead [27].

If the sample is excited with an unpolarized source, then the differential cross section for Compton scattering in the non-relativistic limit, the total incoherent (Compton) collision cross section per atom is a function of Z.

Rayleigh scattering is a process originating in bound atomic electrons. The differential cross section for unpolarized photons is a function of $|F(x, Z)|^2$.

In the forward direction $|F(x, Z)| = Z^2$, hence Rayleigh scattering must become appreciable for high-Z materials.

The aim of this work is to evaluate the effect of the scattered radiation in the analytical process for several types of matrices (different Z) currently studied in art works. Furthermore, we intend to preview the analytical capabilities of two common spectrometers, with and without secondary target, in terms of detection limits for different types of matrices. From these results, we can assess the limitations of the portable equipment when compared with stationary ones for a large number of sample matrix compositions.

Five reference materials were analyzed: orchard leaves (NBS-1571), of which major composition is C, H and O, on a total of 90%; clay material (ISE-954), of which composition is mainly Al (11%), Fe (5%), C (2.5%), Ca, K, Mg

(2–2.5% each). Bone ash (NIST-1400), of which composition is mainly Ca (38%) and P (18%); copper alloy (BCR-691) (Cu 70%) and gold alloy 22 ct (Fisher). These standard materials were chosen considering that they represent light matrices (orchard leaves); intermediate matrices (bone ash and clay) and heavy matrices (copper and gold alloy).

Furthermore, these kinds of matrices are common in most art works: paper documents, human remains (bones and teeth), ceramics, jewellery and metallic artefacts.

Three case studies were also performed in order to assess the behavior of the spectrometers in the most representative matrices on art works: a paper document from XVIII century, a sample of archaeological bone from the Middle Ages and a Portuguese coin from the XIX century mechanically coined [28].

2 Experimental

2.1 Stationary spectrometer

The stationary spectrometer used in this work for XRF analysis in the laboratory consists on a commercial X-ray tube (Philips, PW 1140; 100 kV, 80 mA), equipped with a molybdenum (Mo) changeable secondary target. With this system it is possible to obtain a nearly monochromatic source, with Kα and Kβ lines of Mo, energies 17.44 and 19.60 keV respectively.

The X-ray tube, the secondary target and the sample are in a triaxial geometry [29]. With this arrangement, we decrease the background, taking advantage of the effect of the polarization of the incident X-ray beam from the tube and the nearly monochromatic radiation. Both the X-ray beam emitted by the secondary target and by the sample are collimated throughout two silver apertures, in order to reduce the scattered radiation and improve the detection limits. The distance between the sample and the detector is 27 mm. The incident X-ray spot has an elliptic form, with a horizontal axis of approximately 20 mm and a vertical axis of approximately 15 mm.

The characteristic radiation emitted by the elements present in the sample is detected by a Si(Li) detector, with a 30 mm^2 active area and 8 μm beryllium window. The energy resolution is 138 eV at 5.9 keV and the acquisition system is a Nucleus PCA card. The pulse processing and dead time corrections are automatically adjusted by a commercial pulse processor (Oxford). The operating conditions of this system for all analyzed spectra were 50 kV and 20 mA.

2.2 Portable spectrometer

The spectrometer used consists on an Eclipse III Amptek X-Ray tube (30 kV, 100 μA,) with a silver anode. The ra-

diation is highly collimated by a tantalum collimator allowing a 5 mm diameter beam on the sample, placed at 7 mm distance from the tube and the detector. The detector is an Amptek XR-100CR Si(Li) with a 7 mm^2 detection area and 300 μm thick, and a 12.5 μm Be window [30]. The system is equipped with two laser points to identify the local point of analysis. The energy resolution is 190 eV at 5.9 keV and the acquisition system is Amptek PMCA. The operating conditions of this system for all analyzed spectra were 30 kV and 100 μA. The angle between the incident and emitted beam is 90°. This geometry allows for a minor background reduction due to Compton scattering. Samples were analyzed directly on air at room temperature. This spectrometer is prepared to work under helium flux, to allow for better detection conditions for low elements. Due to the difficulty to transport the helium system into museums or situations of difficult access, normally the measurements outside laboratory are carried out on air; hence the measurements undertaken in this work tried to reproduce the worse situations of analysis.

All spectra analyses were performed using the AXIL-QXAS (Analysis of X-ray spectra by iterative least-squares fitting) software package by the International Atomic Energy Agency [31].

2.3 Sample preparation

Samples of the reference material were obtained in the form of powder, except for copper and gold alloys. For analysis the powdered samples were pressed into pellets 2.0 cm in diameter, of 1 mm thickness, without any chemical treatment. Each sample was pressed under 10 ton for 1 min and glued on a carbon scotch on a sample holder and placed directly on the X-ray beam, for elemental determination. A minimum of three pellets for each sample was used. The copper metallic alloys were discs (about 2 mm thick and 35 mm in diameter) and the gold samples were squares of 100 mm^2 and approximately 1 mm thick. These standard materials were glued directly on carbon scotch on the sample holder.

2.4 Detection limits

The detection limits (DL), were determined according to $DL = \frac{3C_i\sqrt{N_b}}{N_p}C_i$, where C_i is the concentration of the element i; N_b is the counting rate for the background and N_p is the counting rate for the corresponding peak.

2.5 Results and discussion

The detection limits obtained for the analyzed standard reference materials are presented in Table 1 for both spectrom-

Table 1 Detection Limits (μg g^{-1}) for standard reference materials: orchard leaves (NBS-1571), bone ash (NIST-1400), clay (ISE-954), copper alloy (BCR-691) and gold alloy 22 ct (Fischer) obtained by two spectrometers, a stationary one with secondary target and a portable one

	Portable					Stationary				
	Orchard leaves	Clay	Bone ash	Copper alloy	Gold alloy	Orchard leaves	Clay	Bone ash	Copper alloy	Gold alloy
P			1014					*		
Si		5950					*			
K	287	900	84			60	225	47		
Ca	212	250	154			35	98	74		
Ti		116					41			
Cr		*					21			
Mn	14	34				3	12			
Fe	13	64	17			2	10	5		
Ni	*	*				1	6			
Cu	2	7			300	1	3			67
Zn	6	19	23	515		1	3	3	60	
As	*	*		100		1	3		40	
Se	*					1				
Br	*					1				
Rb	*	25				1	1			
Sr	*	31	20			1	1	1		
Ag					2500					4466
Sn				5100					1635	
Ba		*					66			
Au					1600					86
Pb	*	*	*	2010		1	5	2	54	

*Not detected

Fig. 1 Spectra of orchard leaves (NBS-1571) obtained by two spectrometers, a stationary one with secondary target and a portable one
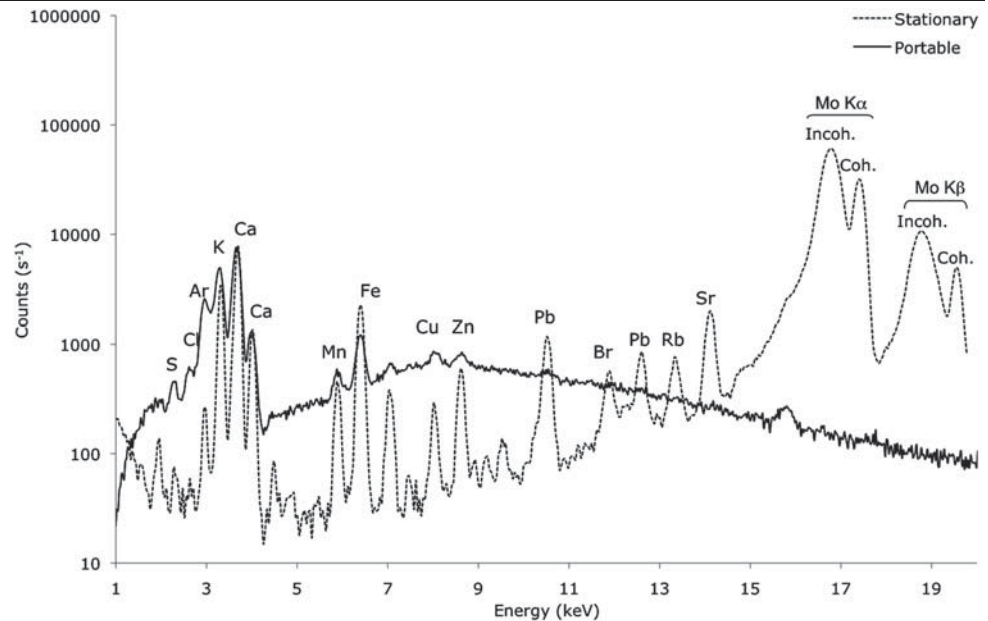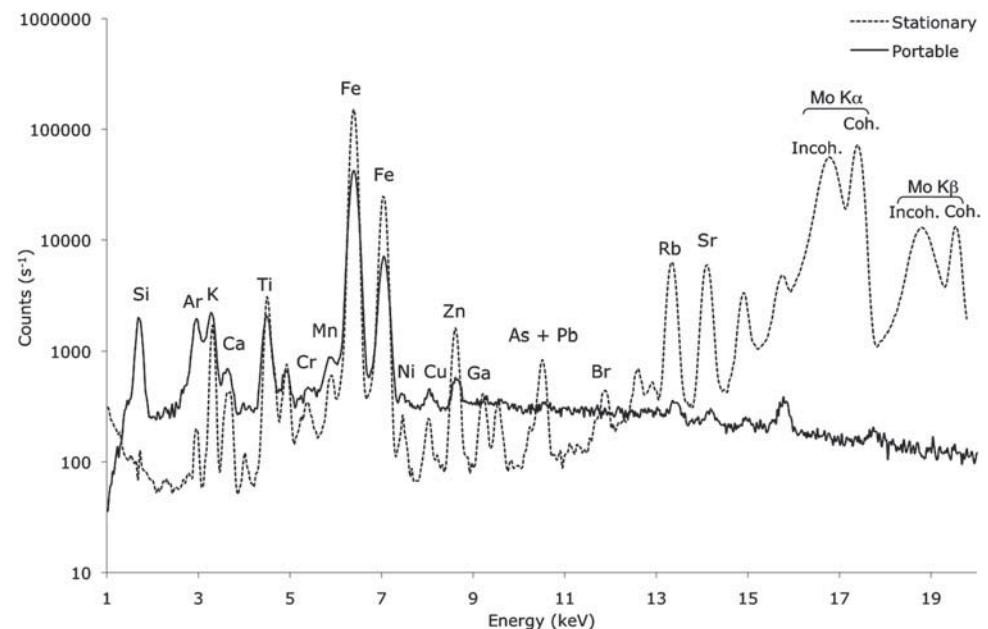

Fig. 2 Spectra of clay sample (ISE-954) obtained by two spectrometers, a stationary one with secondary target and a portable one

eters. The dominant feature in these results is the strong dependence on the matrix material. For light matrices, represented here by orchard leaves, of which the matrix is 90% constituted by C, H and O, most of the trace elements are only detected by the stationary spectrometer. This is better emphasized in Fig. 1 where the spectra obtained by the two equipments are overlapped. It is remarkable that we see the effect of the nearly monochromatic radiation, especially in the region 4–13 keV, where the peak height to background ratio is improved by a factor of the order of 10. This allows us to detected elements like As, Br, Sr and Pb, which are normally extremely important in characterizing not only art

works, but also biological samples for trace elements determination in medical applications. For these spectra it is clear that the intensity of Compton peaks for $K\alpha$ and $K\beta$ are predominant over the Rayleigh ones.

For medium Z materials like bone ash (NIST-1400), of which composition is mainly Ca (38%) and P (18%) and clay material (ISE-954), of which composition is mainly Al (11%), Fe (5%), C (2.5%), Ca, K, Mg (2–2.5% each), most of the elements are detected by both equipments, except for those in concentrations lower than 30 $\mu g\,g^{-1}$ (Table 1). In Figs. 2 and 3 a comparison of the spectra is plotted, which clearly illustrates the results. An improvement in

Fig. 3 Spectra of bone ash (NIST-1400) obtained by two spectrometers, a stationary one with secondary target and a portable one
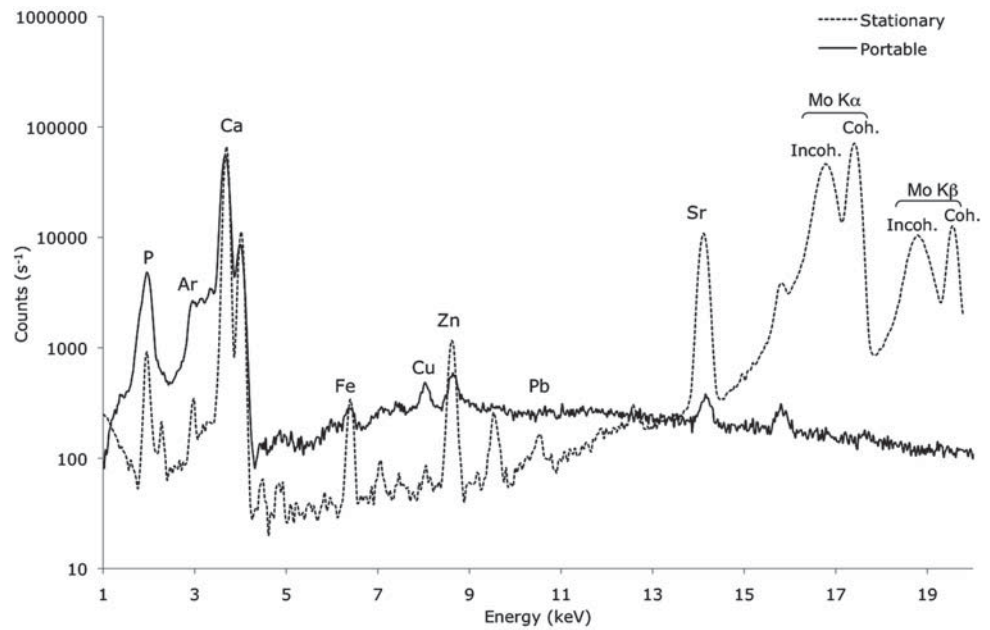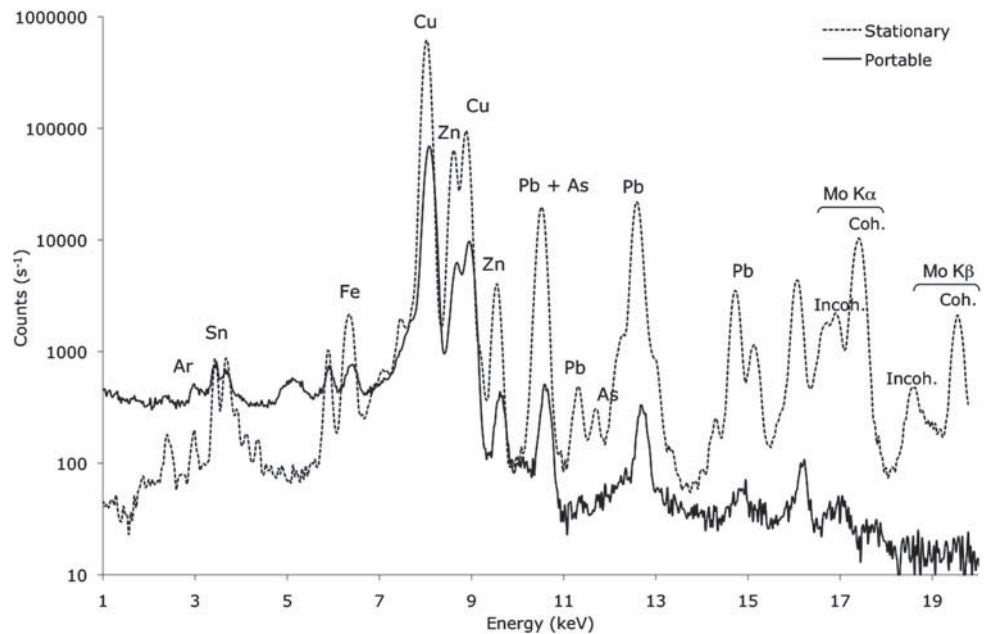
Fig. 4 Spectra of Cu alloy (BCR-691) obtained by two spectrometers, a stationary one with secondary target and a portable one

signal to background ratios is visible especially in Fig. 2 for the portable equipment. This supports the dependence of the background with the matrix main composition, which for clay is Fe and for bone ash is Ca. In addition, in the spectra obtained with the stationary spectrometer the intensity of Compton scattered radiation peaks is identical to Rayleigh peaks, evidencing for this spectrometer the dependence on Z of the material to scattered radiation.

Finally, heavy matrices, copper alloy (BCR-691) (Cu 70%) and gold alloy 22 ct (Fisher), present detection limits ranging from 50 $\mu g\, g^{-1}$ to 0.5%, as can be observed in Table 1. Nevertheless, these are good results taking into ac-

count that these kinds of matrices contain elements that can reach more than 50%. In Figs. 4 and 5 a comparison of the two overlapped spectra is displayed. It must be emphasized that all elements are detected with both spectrometers. Furthermore, in these, the strong reduction on the Compton scattering peaks when compared to the Rayleigh peaks is impressive, confirming that under the same ionization conditions the incoherent scattering is predominant for low Z elements, while for high Z materials the predominant effect is the coherent interaction. These conclusions are similar to the ones obtained by Craig for analysis of 68 obsidian from Peru [26] with a portable XRF similar to the one used in this

Table 2 Characteristics and other significant experimental parameters for the portable and stationary XRF equipments

	Portable	Stationary
X-ray generator	Amptek-Eclipse III	Philips PW 1140, 100 kV, 80 mA
X-ray tube	Ag	W
Secondary target	–	Mo
Detector	Amptek XR-100CR; 7 mm^2	Si(Li)—Oxford; 30 mm^2
Resolution at 5.9 keV	190 (eV)	138 (eV)
Collimator	Ag	Ta
Cooling	Water	Air
Spot	Diameter (5 mm)	Elliptic form (20 mm × 15 mm)
Distance sample-detector	5 mm	27 mm
Working conditions		
H.V. (kV)	30	50
Intensity	100 μA	20 mA

Fig. 5 Spectra of gold 22 ct (Fisher) obtained by two spectrometers, a stationary one with secondary target and a portable one
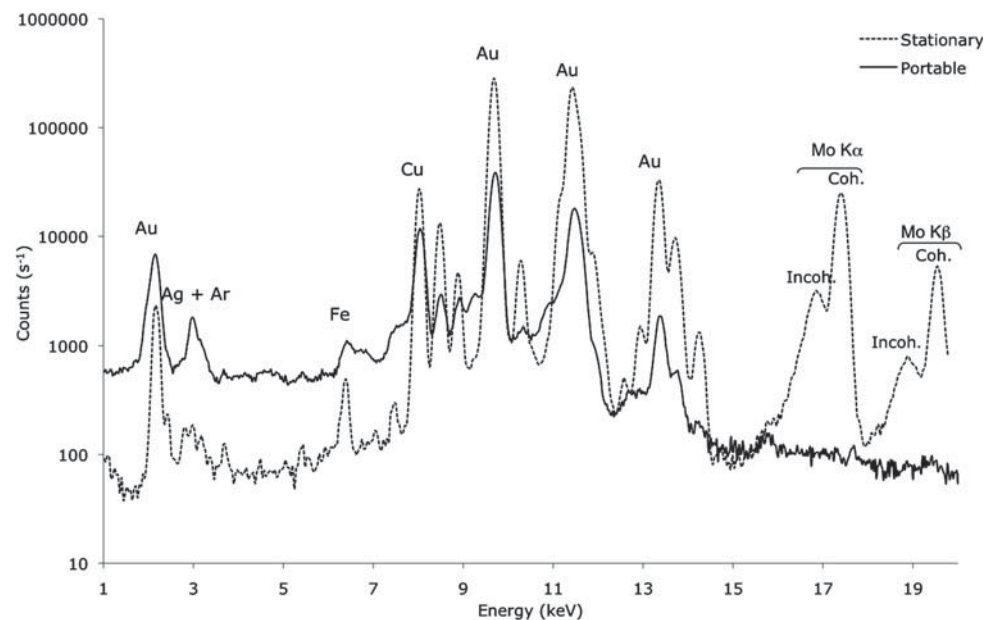
work and a stationary spectrometer with a Cu X-ray target. The results obtained by both spectrometers arrived at identical conclusions and allowed one to identify the origin of the obsidian, in spite of the fact that some elements could not be detected by the PXRF spectrometer.

In Table 2 we summarize the X-ray tube features, the detector characteristics and the experimental conditions used in the present work.

3 Case studies

3.1 Document paper of XVIII century

The reduction of scattering in an X-ray fluorescence spectrum and the outcome on a document paper identification

was performed. The obtained results are displayed in Fig. 6. It is noticeable that Ni, As, Rb and Sr are not detected with the portable system, while Mn, Cu, Zn and Br are hardly detected, which originates in the low accuracy for quantitative calculation. These results are important to identify and characterize documents [32]. This is an example where the superiority of the stationary equipment is remarkable.

3.2 Human bone from the Middle Ages

The results obtained for this sample are presented in Fig. 7. Most of the trace elements have been detected. However, as concerns Pb, it is hardly visible with the portable equipment, making quantitative calculations almost impossible. This element can be extremely important in identification procedure, mostly if contamination by Pb ante mortem

Fig. 6 Spectra of a paper document from XVIII century, obtained by two spectrometers, a stationary one with secondary target and a portable one
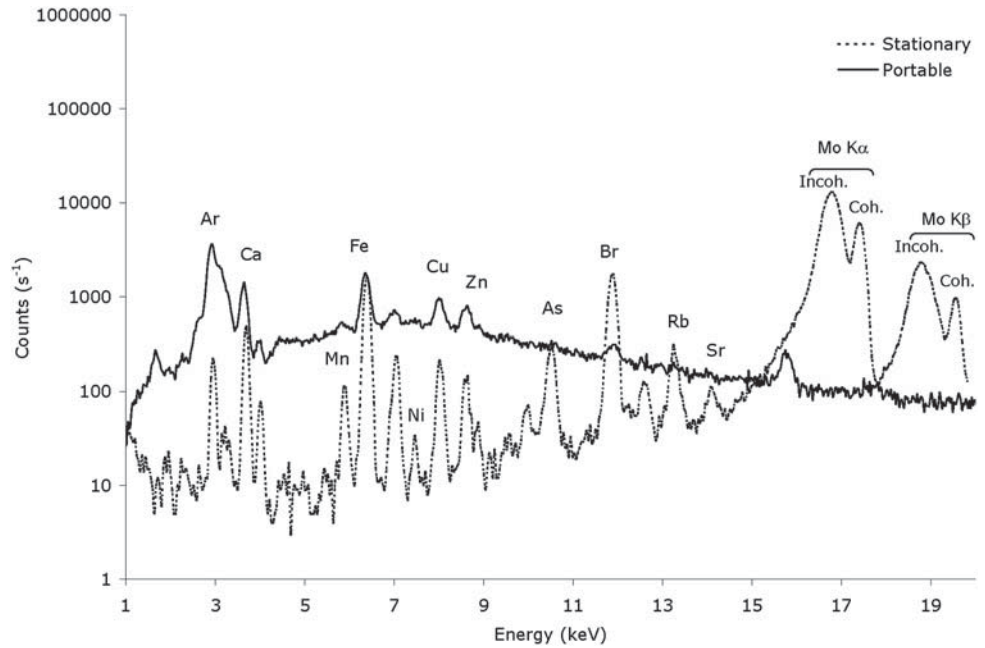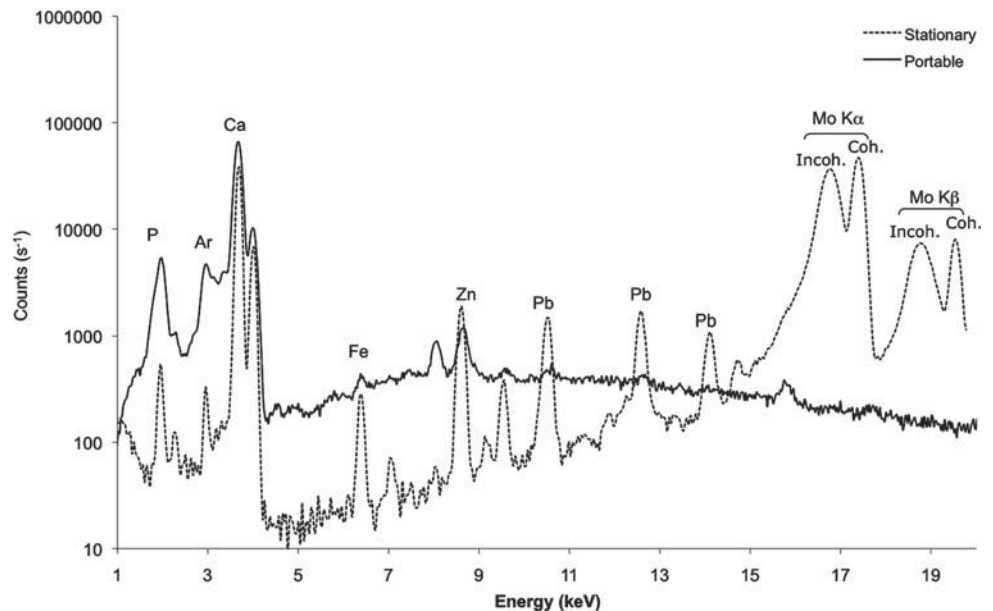

Fig. 7 Spectra of a femur bone sample from the Middle Ages, obtained by two spectrometers, a stationary with secondary target and a portable one

or post mortem is under study. This is another example where the advantage of the stationary equipment is significant.

3.3 Portuguese coin from the XIX century

Metallic artefacts are one of the most important fields of X-ray spectrometry applications. A Portuguese coin was analyzed by both spectrometers and it was possible to identify and characterize all the present elements: Fe, Cu, Zn, Sn and Pb. This coin is a copper alloy made of brass a Cu–Zn alloy with Fe, As, Sn and Pb. In Fig. 8 the obtained

spectra are overlapped, and the background is similar for both spectrometers, allowing for identification of all the elements.

4 Conclusions

We have measured the most common used matrix samples with a portable spectrometer with direct and unfiltered radiation and a stationary one with a secondary target and triaxial geometry.

From our results it has been confirmed experimentally that there is influence of the matrix composition on the back-

Fig. 8 Spectra of a Portuguese coin of XIX century, obtained by two spectrometers, a stationary one with secondary target and a portable one
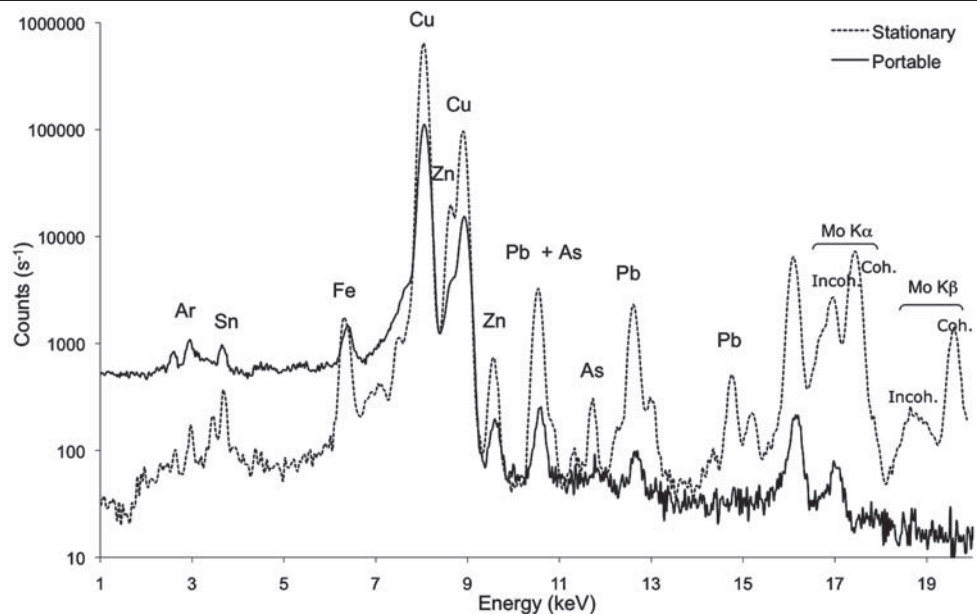
ground radiation due to Compton and Raleigh effects. Furthermore, also was confirmed the big advantage of the background reduction by the secondary target in the stationary equipment. Light matrices are the most critical. We demonstrated that the high background makes difficult the characterization of biological samples or paper documents by portable systems.

Concerning samples of medium Z atomic number like bone and soils, the portable spectrometer can identify practically all the elements present in the sample and both spectrometers can reach equivalent conclusions.

Finally, metallic samples are the less affected by the portable system and both spectrometers can lead to similar conclusions.

Considering these aspects, the portable equipment is useful when in situ analysis is required and the results obtained by this system should be perceived as a starting point or as a complement to other studies whenever trace elements are critical to identify some kinds of samples.

References

1. D. Barilaro, G. Barone, V. Crupi, D. Majolino, P. Mazzoleni, M. Triscari, V. Venuti, Vibr. Spectrosc. **42**, 381 (2006)
2. R. Padilla, P. Van Espen, P.P. Godo Torres, Anal. Chim. Acta **558**, 283 (2006)
3. M. Brai, M. Camaiti, C. Casieri, F. De Luca, P. Fantazzini, Magn. Reson. Imaging **25**, 461 (2007)
4. N. Grassi, L. Giuntini, P.A. Mandó, M. Massi, Nucl. Instrum. Methods B **256**, 712 (2007)
5. M. Pérez-Alonso, K. Castro, M. Álvarez, J.M. Madariaga, Anal. Chim. Acta **524**, 379 (2004)
6. M. Mantler, M. Schreiner, X-Ray Spectrom. **29**, 3 (2000)
7. M. Manso, M.L. Carvalho, J. Anal. At. Spectrom. **22**, 164 (2007)
8. L. Pappalardo, A.G. Karydas, N. Kotzamani, G. Pappalardo, F.P. Romano, Ch. Zarkadas, Nucl. Instrum. Methods B **239**, 114 (2005)
9. A.G. Karydas, N. Kotzamani, R. Bernard, J.N. Barrandon, Ch. Zarkadas, Nucl. Instrum. Methods B **226**, 15 (2004)
10. J.L. Ferrero, C. Roldán, D. Juanes, J. Carballo, J. Pereira, M. Ardid, J.L. Lluch, R. Vives, Nucl. Instrum. Methods B **213**, 729 (2004)
11. R. Cesareo, Nucl. Instrum. Methods B **211**, 133 (2003)
12. C. Caneva, M. Ferretti, in *Proceedings of 15th World Conference on Nondestructive Testing*, Rome (2000)
13. K.P. Champion, R.N. Whittem, Nature **199**, 1082 (1963)
14. T.G. Dzubay, B.V. Jarrett, J.M. Jaklevic, **115**, 297 (1974)
15. R.H. Howell, W.L. Pickles, J.L. Cate Jr., **18**, 265 (1975)
16. R.W. Ryon, J.D. Zahrt, P. Wobrauschek, H. Aiginger, Adv. X-Ray Anal. **25**, 63 (1982)
17. R.B. Strittmatter, Adv. X-Ray Anal. **25**, 75 (1982)
18. D.V. Rao, R. Cesareo, G. Gigante, Phys. Scr. **53**, 332 (1996)
19. D.V. Rao, R. Cesareo, G. Gigante, Phys. Scr. **50**, 314 (1994)
20. M. West, A.T. Ellis, P. Kregsamer, P.J. Potts, C. Streli, C. Vanhoof, P. Wobrauschek, J. Anal. At. Spectrom. **23**, 149 (2008)
21. M. Aceto, A. Agostino, E. Boccaleri, A.C. Garlanda, X-Ray Spetrom. **37**, 286 (2008)
22. F.-P. Hocquet, H.-P. Garnir, A. Clar, C. Oger, D. Strivay, X-Ray Spetrom. **37**, 304 (2008)
23. R. Cesareo, A. Brunetti, S. Ridolfi, X-Ray Spetrom. **37**, 309 (2008)
24. Ch. Zarkadas, A.G. Karydas, Spectrochim. Acta B **59**, 1611 (2004)
25. M. Ferreti, Nucl. Inst. Methods B **226**, 453 (2004)
26. N. Craig, R.J. Speakman, R. Popelka-Filcoff, M.D. Glascock, J. David Robertson, M. Steven Shackley, M.S. Aldenderfer, J. Arch. Sci. **34**, 2012 (2007)
27. R. Van Grieken, A. Markowicz (eds.), *Handbook of X-Ray Spectrometry* (Dekker, New York, 1993)
28. The Imprensa Nacional-Casa da Moeda website http://www.incm.pt. Accessed 10 May 2008

29. P.J. Custódio, M.L. Carvalho, F. Nunes, J. Trace Elem. Med. Biol. **19**, 151 (2005)

30. A. Guilherme, A. Cavaco, S. Pessanha, M. Costa, M.L. Carvalho, X-Ray Spectrom. **37**, 444 (2008)

31. G. Bernasconi, A. Tajani, P. Kregsamer, Manual for QXAS/AXIL, in *Version 3.5* (IAEA, Vienna, 2000)

32. M. Manso, M.L. Carvalho, J. Anal. At. Spectrom. **22**, 164 (2007)