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Development and optimisation of a portable micro-XRF method for in situ multi-element analysis of ancient ceramics

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Abstract

Non-destructive analysis of cultural objects by micro-XRF spectrometry is an advantageous multi-element technique that has rapidly developed during the past few years. Portable instruments contribute significantly to the in situ analysis of valuable cultural objects, which cannot be transported to the laboratory. Ancient ceramics are the most common archaeological findings and they carry a significant historical content. Their analysis often presents certain particularities due to surface irregularities and heterogeneity problems. In the present work, the analytical characteristics (beam spot size, geometry effect and detection limits) of a compact and portable micro-XRF instrument with a monocapillary lens are presented in details. The standard reference materials SARM 69, SRM 620, NCS DC 73332 and the reference materials AWI-1 and PRI-1 were analysed for the determination of the detection limits (DL's) and the evaluation of the accuracy of the micro-XRF. Emphasis is given on the critical parameters, which should be monitored during measurements and influence the final results in the analysis of ancient ceramics. A quantitative analysis of ancient ceramic samples from Abdera (North Greece) is also presented.

Keywords: Micro-XRF; In situ analysis; Ancient ceramics; Portable instruments; Non-destructive analysis

1. Introduction

The potential of using X-rays in the qualitative and quantitative analysis of several different samples was appreciated soon after their discovery. Since then, a large variety of instrumental techniques, employing the use of X-rays, have been developed and can be successfully applied for the study and conservation of cultural objects [1,2]. Among these, X-ray fluorescence spectroscopy is the most widely used technique due to a number of favorable analytical characteristics, such as multi-element analysis, non-destructive analysis, high sensitivity and applicability to a wide range of samples (solids, liquids and gases) [3–5]. These features have made XRF a very popular analytical technique in several archaeometric studies [1,5–8].

Micro-X-ray fluorescence spectroscopy, the microscopic equivalent of bulk XRF, is one of the most modern and promising branches of XRF, which permits the precise, accurate, non-destructive and localized analysis of small objects or of details on larger ones [9,10]. The implementation of capillary optics for focusing X-ray beams, which was introduced in the mid-80s, has contributed significantly to the development of several new scientific instruments [11–14]. The ability to obtain point spectra and elemental maps have lead to numerous applications of micro-XRF on the analysis of different types of materials, including metallic objects, industrial materials, forensic samples, gold artifacts, bronze statuettes, paint layers, etc. [15–19]. More recently, the need to perform in situ analysis of cultural objects, which cannot be transported to the laboratory, has lead to the development of portable micro-XRF spectrometers [20–22]. This was facilitated by the development of small-sized Peltier-cooled energy dispersive detectors and X-ray optics [20,21].

Information on the applicability of the portable micro-XRF instruments and thorough examination of their analytical characteristics is useful for their evaluation but is rarely found in the literature. Such integrated information concerning the analytical characteristics of a portable micro-XRF with monocapillary

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optics and its application for the in situ analysis of ancient ceramics is presented in this paper with emphasis on the effect of certain critical parameters on the analysis.

Quantitative measurements were performed on ceramic and glass standard reference materials. Similar measurements were performed for the quantitative analysis of ancient ceramics, which represent a large class of cultural objects with important historical content.

2. Experimental

2.1. Instrumentation

The micro-XRF spectrometer (SPECTRO, COPRA model) used in this work includes a side-window X-ray tube with Mo anode (Oxford Instruments, Series 5011 XTF), a straight monocapillary lens and a solid state Si(Li) Peltier-cooled detector (8 μm Be window, 3.5 mm^2 active area, 300 μm nominal thickness). The maximum tube voltage is 50 kV and its maximum current 1 mA. The nominal energy resolution of the detector for Mn K_a is 149 eV at a count rate of 1 kcps, while the measured resolution is 151, 154, 190, 151 and 171 eV for the K K_a, Ca K_a, Ca K_b, Fe K_a and Fe K_b lines, respectively, at a total count rate of 1.3 kcps.

A long-distance optical microscope located on the detector and X-ray tube plane is used in order to select the points of interest over the surface of the sample (Fig. 1). The samples which are placed on a rotating holder mounted on a motorized *XYZ* stage, consisting of three linear stages by NewPort (PRL-12) featuring 0.1 mm step size, travel distance of 5 cm in the *X*–*Y*-direction and 2.5 cm in the *Z*-direction are moved so that the points of interest lie in the focal plane of the long-distance optical microscope. At this position, the angle of incidence of the primary beam is 48°, while the angle between the sample and the detector is 42°. All measurements are performed in air and no filters were used. The micro-XRF experimental set-up and the respective geometry are shown in Fig. 1. The angle between the primary beam and the detector axis with respect to the surface of the sample can be changed by rotation of the sample. The relative angle between the X-ray tube and the detector is fixed by the manufacturer at 90° and remained unchanged during the measurements. All measurements are performed in air and no filters were used.

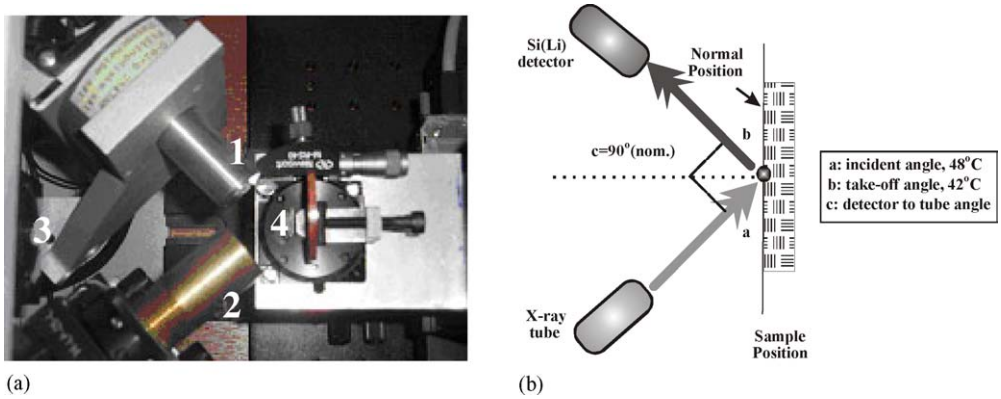
All micro-XRF measurements were performed in a point scan mode. X-ray spectra were deconvoluted by a dedicated software package (WinAxil v 4.0.1). In particular, spectral data are processed by the method of non-linear least squares fitting, where the optimum values of χ^2 (the weighted sum of squares of the differences between a chosen model and the measured spectrum) are found iteratively (Marquardt algorithm).

2.2. Samples and standard reference materials

The investigated ceramic sherds were excavated in the ancient cemetery of Abdera (North Greece) and they date back to the 5th and 7th century B.C. Quantitative analysis was performed for the samples coded A45, A46, A47, A48, A51, A53, A56, A57, A58, A78, A118 and A119. According to the archaeological information, samples A57, A58, A118 and A119 are suspected to be imported products, while the remaining samples are regarded as local products. All samples were cleaned by distilled water and oven-dried at 105° C until constant weight before analysis.

The effect of the incident angle of the primary X-ray beam on the elemental peak area was investigated for three ancient ceramic sherds each representative of a different grain size distribution (fine, medium and coarse texture). The characterization fine, medium and coarse was assigned after the investigation of the three sherds under a polarizing microscope without any further quantitative justification, since this exceeded of the scope of the present work.

Three standard reference materials and two reference materials were used. The standard reference material SARM 69 is prepared and distributed by MINTEK South Africa and the Department of Geology, University of Free State, the SRM 620 (soda lime flat glass) is prepared by the National Institute of Standards and Testing and the SRM NCS DC 73332 is prepared by China's National Analysis Center for Iron and Steel. The reference materials AWI-1 and PRI both from Group of Instrumental Geochemistry, Fonds National de la Recherche Scientifique/Nationaal Fonds Voor Wetenschappelijk, FNRS-NFWO were also used. All standards (except for SRM 620 which is in the form of a wafer) were analysed in the form of pressed



(a) (b)

Fig. 1. (a) Micro-XRF spectrometer: (1) X-ray tube and monocapillary system; (2) Si(Li) detector; (3) optical microscope; (4) sample holder and sample. (b) Schematic diagram of the experimental micro-XRF geometry.