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Technical note

A portable micro-X-ray fluorescence spectrometer with polycapillary optics and vacuum chamber for archaeometric and other applications ☆

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Abstract

A portable focused-beam XRF spectrometer was designed, constructed, and manufactured. The spectrometer allows to detect and perform analysis of chemical elements from Na upwards. The system is equipped with a compact vacuum chamber to reduce absorption of both the excitation and the fluorescence radiation in air. A low power Pd-anode tube operated up to 50 kV and 1 mA with a point focus of 400 μm is used as excitation source. A polycapillary lens with a spot size of about 160 μm, or a collimator with a 1 mm inner diameter can be used alternatively for either focusing or collimating the primary beam. The fluorescence radiation is collected by an Si drift detector with an active area of 10 mm^2 and equipped with an 8 μm Be entrance window.

A compact vacuum chamber was designed to house the X-ray beam optics and the detector snout. The chamber is attached to the X-ray tube and can be pumped down to 0.1 mbar. A Kapton™ window of 7.5 μm thickness allows to locate the investigated spot at about 1–2 mm distance outside of the chamber, thus minimizing absorption losses in the excitation and X-ray fluorescence radiation paths. Two lasers pointers are mounted inside the chamber. The laser beams cross at a point outside the chamber in front of the entrance window and coincide with the focal spot of the polycapillary.

This paper reports some preliminary results obtained from an in situ analysis of bronze samples as well as a comparison of these data with those given by other laboratory spectrometers and the reference values provided by the Italian bronze foundry Venturi Arte Bologna, Italy.

Keywords: Portable micro-X-ray spectrometer; Vacuum chamber; Polycapillary; In situ analysis

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1. Introduction

The aim of the study was to design and construct a portable X-ray Fluorescence (XRF) spectrometer which could enable performing on site, spot analysis of non transportable or highly valuable objects, e.g. outdoors or in museums without any restriction to the object size. Further, it should be capable of detecting X-ray fluorescence radiation of low-*Z* elements (Na, Mg, Al, Si, P, S, and Cl). Such portable instrument is of great interest to museums, archaeometry laboratories and other institutions involved in cultural heritage management. The non-destructiveness and multielemental capability of the XRF techniques are of primary importance in this field of applications.

The availability of liquid nitrogen-free high resolution semiconductor detectors prompted several research groups to design portable or transportable energy dispersive X-ray fluorescence spectrometers. Practically all systems designed up to now are working in air, thus lacking the capability to measure the light elements [1–4]. Also at the Agency's

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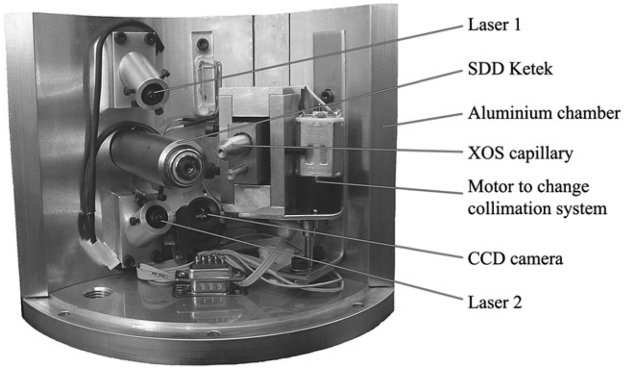

Fig. 1. Photograph of the vacuum chamber attachment showing the details of the arrangement inside the chamber.

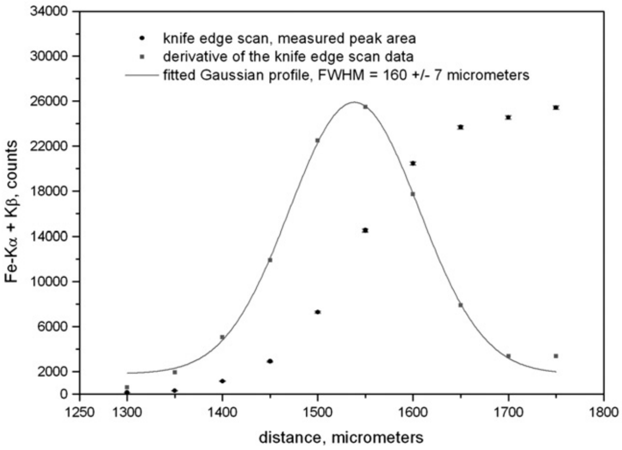

Fig. 2. The X-ray beam spot size, focused by polycapillary lens.

Seibersdorf Laboratories such system was designed a few years ago [5]. In a recent project, this portable system was used to determine the chemical composition of modern bronzes and bronze sculptures by performing the measurements in air [6]. In this project, a vacuum chamber was designed in order to extend the measurement capability of the portable system to light elements.

If the measurements are carried out in air, a drastic absorption of the low energy characteristic radiation of the low-*Z* elements occurs. An approach to significantly reduce such absorption effect is to evacuate the beam paths between the X-ray source — sample and between the sample-detector.

2. Experimental

The vacuum chamber attachment and its internal design are shown in Fig. 1. The incidence and exit angles of radiation, measured with reference to the sample surface, are both equal to 67.5°. The vacuum chamber is attached to a low power (50 W), Pd-anode, micro-focus X-ray tube [7], which is the excitation source. The tube is cooled by forced air flow. The tube can be operated up to 50 kV and 1 mA and has a focal spot size of 400 µm at 50 W. The 127 µm thin Be window of the Pd–anode tube allows transmission also of the Pd L-lines around 2.8 keV, thus leading to an efficient excitation of the low Z elements.

The collimation of the beam is achieved with a cylindrical brass collimator of 0.7 mm inner diameter, resulting in a spot size diameter of about 1 mm on the object. Alternatively, a polycapillary X-ray lens (XOS [8]) can be inserted. The input focal point width is in the range of 400 µm (390 µm at 17.5 keV and 470 µm at 8 keV) which fits perfectly to the focal spot size of the tube. The achieved focal spot size was about 160 µm in diameter. The spot size has been estimated by the "knife edge" scan approach, and the results are presented in Fig. 2. This small size allows micro analysis of pigments in paintings, transition zones of material in statues of bronze or other metals, etc. The exchange between the two collimators in their vertical positions is accomplished with a motorized control device, thus assuring a reproducible alignment.

The energy dispersive detector itself is mounted close to the sample in order to insure a large acceptance solid angle for the detection of the fluorescent X-rays. The detector is an Si drift detector with 10 mm^2 active area, 300 µm nominal thickness (KETEK [9]), and 8 µm thick Be entrance window. This allows the detection of X-rays from 1 keV upwards. For the Na Kα line with energy of 1.024 keV the intrinsic detection efficiency is around 25%. The detector enables the collection of low energy characteristic photons emitted by elements such as Na, Mg, Al, Si, and P.

A precise positioning of the spectrometer with respect to the analyzed object/sample is facilitated by the use of two laser pointers. The spectrometer, or alternatively the object investigated, is moved to a point where the two laser beams cross each other at the spot to be analyzed. This defines the correct point of analysis on the object of interest. The laser pointers are pre-adjusted with a luminescence screen (ZnS) to cross precisely at the X-ray beam spot.

As a result of the small space between the chamber wall and the sample (1–2 mm), the laser spots cannot be seen from an outside observer. The visual observation of the region in front of the window on the object is important and is therefore

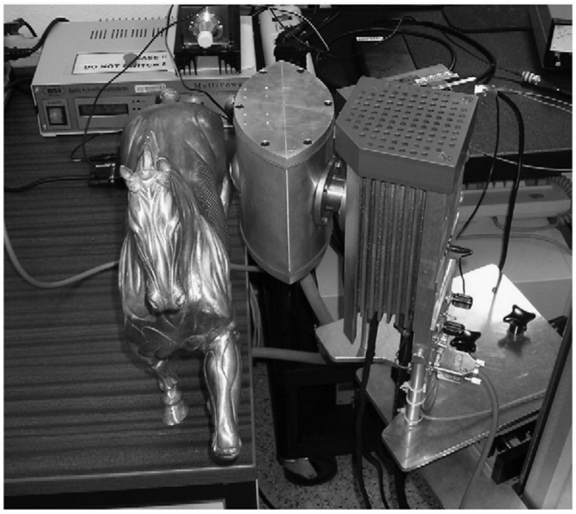

Fig. 3. Photograph of the portable XRF spectrometer in operating position.

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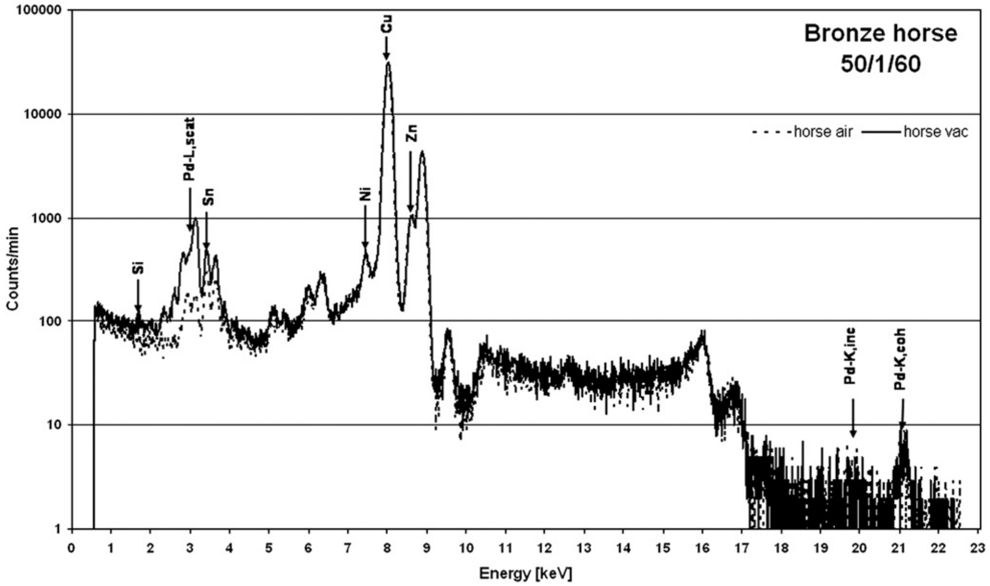

Fig. 4. Spectrum of a bronze horse measured in vacuum (-) and in air (...).

controlled by a CCD camera mounted inside the chamber. The obtained camera image is displayed on a monitor. The signal is also shown on the PC used for data acquisition.

The X-ray tube exit window is situated in the centre of a flange with an O-ring groove. To this flange, the vacuum chamber is attached. The X-ray lens/brass collimation holder is also attached to this side of the vacuum chamber. The holder position is controlled by a motor which brings into the beam either the X-ray lens or the brass collimator. The switching between the X-ray lens/brass collimator can be done remotely without opening the chamber. The X-ray beam leaves the chamber through an 8 μm thick Kapton window, which is mounted in the centre of the vacuum chamber front wall. An air gap of about 1–2 mm between the sample and the Kapton window is the remaining radiation path length in air. Such a drastic reduction of the air path length alleviates significantly the problem due to the absorption of low energy X-rays.

The goal of the mechanical design was to keep the system light weighted and transportable, so a compact vacuum chamber looking like an American Football was the resulting shape.

Fig. 3 shows an overall view of the portable XRF spectrometer. The spectrometer is positioned in front of a bronze sculpture. One

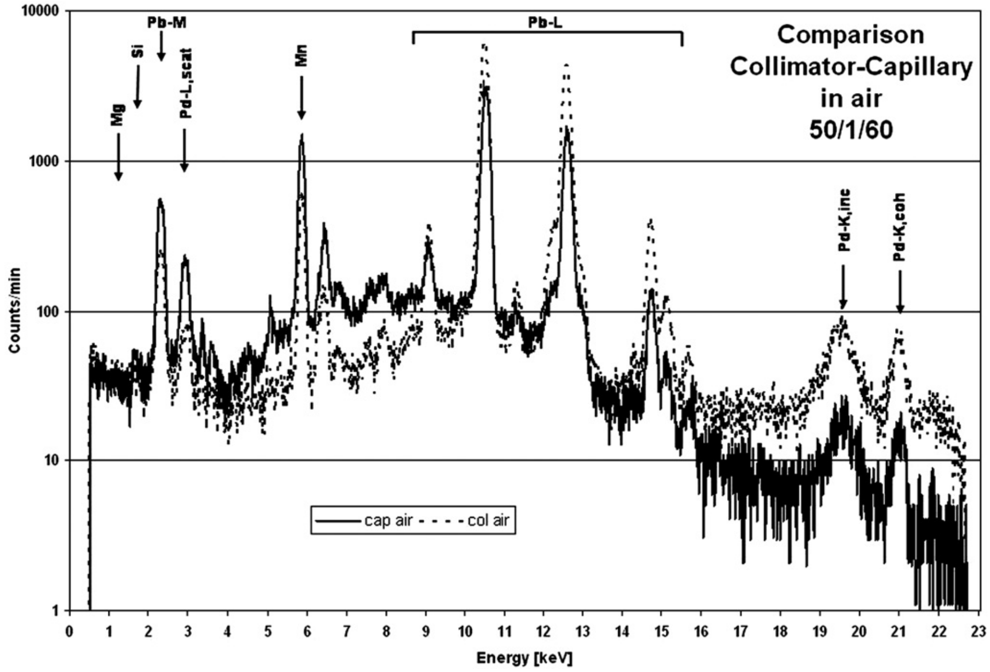

Fig. 5. Spectrum of a multielement sample measured with the collimator in comparison to the polycapillary in air.

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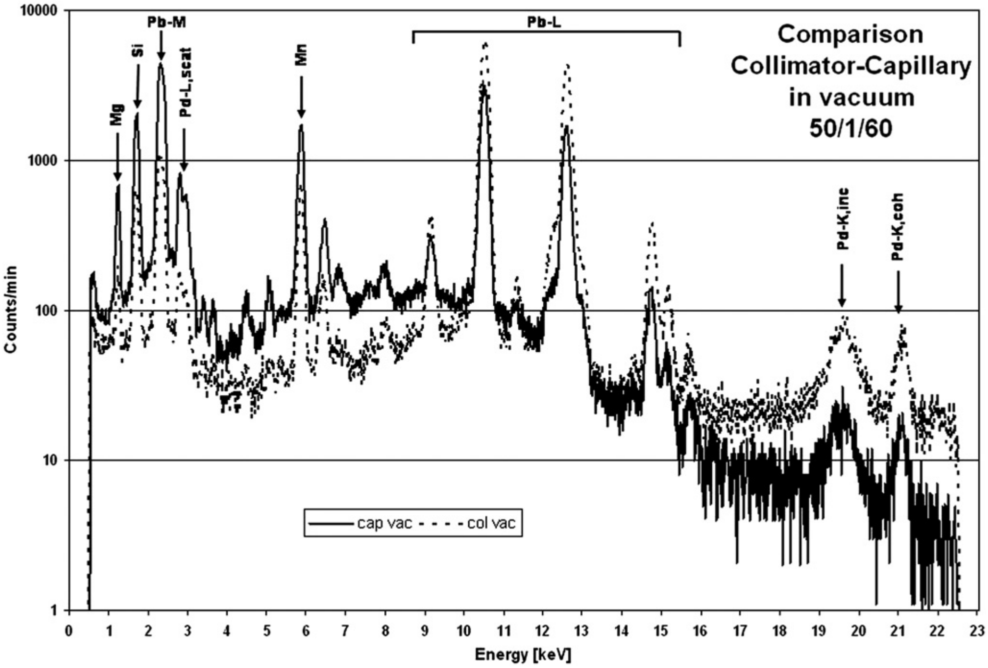

Fig. 6. Spectrum of a multielement sample measured with the collimator in comparison to the polycapillary in vacuum.

can note the short distance between the chamber exit window and the bronze horse sculpture. Also visible is the vacuum-tight brass tube connecting the chamber with the X-ray tube housing.

The X-ray tube is located inside a radiator-like aluminum enclosure, which is cooled by an air flow forced by fan mounted on its top, under the plastic grid. The whole setup is installed on a movable stand, which is also equipped with *xyz*-translation stages used for positioning the spectrometer in front of the object investigated.

3. Results and discussion

In Fig. 4, the X-ray spectra collected from a bronze horse sample cast with a new type of alloy are presented. The same figure shows a comparison of a spectrum obtained in air with one obtained under vacuum conditions. It can be seen that, especially in the range up to 5 keV, an increase of intensity under vacuum is observed, thus allowing the detection of Si.

Figs. 5 and 6 show the spectra collected from a multielement sample in 4 different excitation modes with the brass collimator vacuum – air and polycapillary vacuum – air operating conditions 50 kV, 1 mA, 60 s.

The spectra of a multielement sample collected in vacuum and in air show an increase of intensity in the low energy range for the polycapillary as compared to the collimator, while in the high energy region the opposite behavior is observed.

To obtain the net intensities of the characteristic lines from the measured spectra, a "peak-fitting" routine has been performed with AXIL-QXAS spectrum evaluation software. The concentrations of elements in the analyzed sample are calculated using the fundamental parameters obtained from a series of measurements of a set of standards.

A comparison of quantitative results obtained with different spectrometers from the same reference sample (bronze #5) is given in Table 1.

4. Conclusions

The project goals, namely the design of a portable XRF spectrometer performing on site, spot analysis of objects, capable of detecting low-*Z* elements, have been successfully achieved. Measurements can be carried out outdoors or in museums with no restrictions of the size of the objects investigated.

A technical solution to the problem of analyzing light elements with a portable EDXRF spectrometer was implemented. A vacuum chamber with compact excitation/detection geometry has been designed and constructed. Reduction of the air path to a few

Table 1
Values of a bronze measured with various EDXRS spectrometers (Atominstitute uses Thermo TN5000, IAEA Lab. uses Spectrolab2000) and the new portable System

Elements in bronze no. 5.	Reference values Venturi [wt.%]	Values obtained at the Atominstitut [wt.%]	Values obtained at the IAEA Laboratories [wt.%]	Values obtained with the portable XRF in air [wt.%]	Values obtained with the portable XRF in vacuum [wt.%]
Si	3	2.86	3.94	–	3.17
Ni	n.a.	0.18	0.073	0.40	0.42
Cu	89	86.61	89.54	91.14	88.74
Sn	8	10.71	7.75	7.40	7.47
Pb	n.a.	0.16	0.148	0.16	0.19

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mm extended the applicability of the portable XRF spectrometer towards low-*Z* elements. The low-*Z* elements sensitivity has been improved by the use of the Pd L-series excitation and of an 8 µm Be detector entrance window.

The effectiveness and ease of aligning the spectrometer to find the proper position of analysis on the object with 2 lasers was demonstrated, without restriction to the size and shape of the object investigated. The possibility of performing micro-analysis with a spot size of ~160 µm, depending on the energy range, was achieved with the use of a polycapillary.

The quantification procedures, as known from the analytical application of Energy Dispersive XRF (EDXRF) to thick samples were applied here. The results obtained from the portable spectrometer were in good agreement with those obtained with the stand-alone laboratory spectrometers using the standards with the reference values provided by the Italian bronze foundry Venturi Arte Bologna, Italy.

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