

PART II (Portable ART analyzer) – development of a XRF spectrometer adapted for the study of artworks in the Kunsthistorisches Museum, Vienna

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A portable focused-beam X-ray fluorescence (XRF) spectrometer was designed and manufactured taking into account a huge variation in material, size and shape of museum objects. The spectrometer is equipped with a vacuum chamber enclosed with a Kapton-window allowing the detection of chemical elements from Na upwards, which enables the characterization of glass and enamel objects. Two low-power X-ray tubes, one with a Mo-anode the other with a Cr-anode, operating from 4 to 50 kV and 0 to 2.5 mA with a maximum power of 50 W and a point focus of about 180 μm can be used as excitation source alternatively. A polycapillary lens with a spot size of 150 μm is used for focusing the primary beam to access small details of the different objects, e.g. fine brush strokes in paintings. The vacuum chamber can be evacuated to about 1 mbar.

A miniature camera is installed inside the chamber for inspecting the analyzed area through the Kapton-window. Two laser pointers mounted inside the chamber coincide with the focal point of the polycapillary at the investigated spot. The excitation and X-ray fluorescence radiation paths in air are about 1 mm each, minimizing the absorption losses. The spectrometer was designed to maximize the accessibility to all parts of the investigated objects through the use of translation stages and an innovative design of the detection head, especially the vacuum chamber. This article shows the capability of the spectrometer to reach measuring positions in concave parts of objects and presents the determined detection limits of elements. Copyright © 2009 John Wiley & Sons, Ltd.

Introduction

X-ray fluorescence (XRF) spectrometry is a powerful tool for the elemental analysis. The most important advantage of this technology is that the analysis can be performed in a fully noninvasive and nondestructive way. Therefore, it became one of the most important techniques for studying the chemical composition of unique and valuable objects of art and history. Nevertheless, the investigation of objects containing low-Z elements is difficult because of the absorption of their characteristic radiation in air. For the detection of the low energy X-rays from the light elements the radiation path needs to be evacuated or a He-flush has to be installed. Many comparable systems are working in air, thus lacking the capability to measure the light elements.^[1–3]

At the International Atomic Energy Agency (IAEA) Laboratories in Seibersdorf, Austria, a portable XRF spectrometer was constructed which enabled *in situ* analysis of non-transportable, highly valuable objects without any restriction to the object size.^[4] To be also capable of detecting X-ray fluorescence radiation of low-Z elements, such as Na, Mg, Al, Si, P and S a vacuum chamber was designed and manufactured.^[5,6] In this paper the IAEA – instrument is called PART I (portable art analyzer I).

Portable instruments like the PART I^[7–11] are of primary importance for museums because of the possibility of performing noninvasive/nondestructive multielemental analysis *in situ*. The Conservation Science Department of the Kunsthistorisches Museum Vienna (KHM) had the opportunity to perform many investigations on objects of art^[12] with the PART I.

After these measurements, the KHM suggested several improvements in the instrument design in order to better fit special requirements given by various types and shapes of artworks. The main problems to be solved concerning the application of PART I in the museum are:

- The vacuum chamber is too bulky to reach also spots in concave parts of the objects.
- Difficulties in measuring pictures cause of collisions between the stand of the instrument and the easel.
- Application of vacuum for an extended period of time bends the Kapton-window inside the chamber whereby the air-path gains which causes problems with the absorption of the characteristic X-rays for the determination of low-Z elements.

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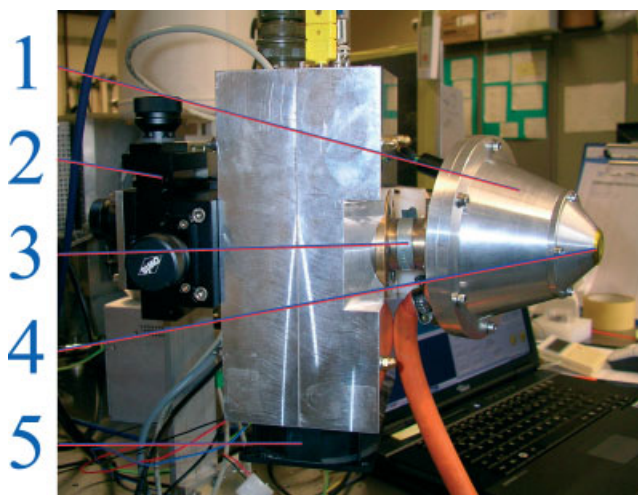


Figure 1. Spectrometer head. 1: vacuum chamber; 2: 3-dimensional manual stage; 3: flexible rubber hose; 4: Kapton-window; 5: 80 mm fan.

- The small spot size of the capillary cannot be used properly because of the big size of the laser spots.

In a project of the Austrian Science Fund (FWF, project no. L430-N19; 'portable art analyzer – PART') based on the suggestions and experiences, in a collaboration between KHM, ATI (Atomic Institute of the Vienna University of Technology) and IAEA, an innovative portable focused-beam XRF spectrometer was designed and manufactured to fulfill the sophisticated needs of the KHM.

Experimental

The goal of the mechanical design was to build a transportable system which is able to fulfill all the needs to investigate the great variety of art objects of the KHM including the capability to detect low-Z elements. One of the most striking construction highlights of the new portable focused-beam XRF spectrometer (PART II) is the measuring head with the vacuum chamber. The design of the vacuum chamber is based on the need of good accessibility to the different parts of the museum objects. Therefore, a conical shape with a tip was employed (Fig. 1, No. 1). Internal details of the vacuum chamber are shown in Fig. 2.

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 micro-focus X-ray tube (XTF5011/high current),^[13] which is used as excitation source. The tube is cooled from the bottom by a forced air flow produced by an 80 mm fan (Fig. 1, No. 5) and it can be operated with 4–50 kV and 0–2.5 mA not exceeding 50 W power. The tube has a focal spot size of 180 μm for Mo-anode (120 μm for Cr-anode) at 50 W. The 125- μm thin Be-window of the tube allows the transmission of the Mo-L-lines around 2.3 keV leading to an efficient excitation of the low-Z elements (Na, Mg, Al, Si) but causes problems with the detection of characteristic radiation from P, S and Cl. Since the detection and quantification of these elements is often necessary another X-ray tube with a Cr-anode is available to cover the detection of the whole low-Z range without overlap problems with the source lines. The change between the X-ray tubes can be done fast and simple by four screws.

The collimation of the beam is achieved with a polycapillary X-ray lens (Fig. 2, No. 6) from X-Ray Optical Systems (XOS)^[14] with

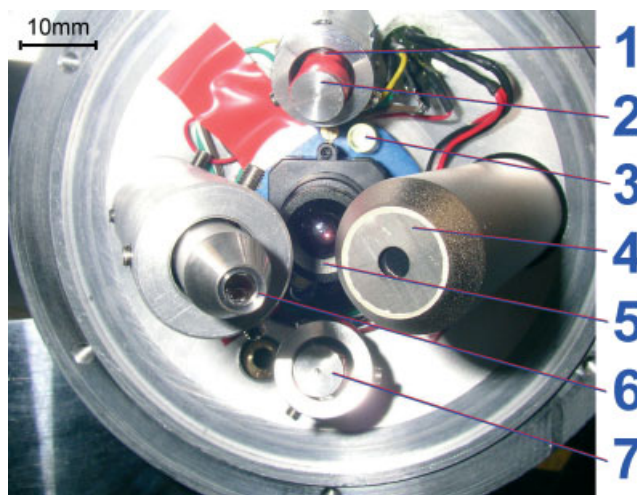


Figure 2. Internal details of the vacuum chamber. 1: laser; 2: collimator; 3: LED; 4: KETEK SDD; 5: color CCD camera; 6: polycapillary X-ray lens; 7: second laser with collimator.

an input focal point width of 400 μm at 5.41 keV (Cr $K\alpha$) and the output focal spot size of 145 μm at 5.41 keV (Cr $K\alpha$) in diameter. This small size allows microanalysis, e.g. of small details in paintings and other painted objects or small polished areas on bronzes. In the former prototype PART I, a change between two different collimation systems (polycapillary and cylindrical collimator) was possible. Because of the designated smaller size of the chamber in PART II this feature is not achievable any more but the installed capillary should be suitable for nearly all analytical problems in the KHM. If necessary, e.g. to get better flux of high energy photons, a change of the collimation system can be done manually by dismounting the capillary and mounting a cylindrical collimator instead.

The energy dispersive detector from KETEK^[15] (Fig. 2, No. 4) is mounted close to the sample in order to ensure a large acceptance solid angle for the detection of the fluorescence X-rays. The detector is a silicon drift detector (SDD) with 20-mm² active area, 450 μm nominal thickness and 8- μm -thick Be entrance window, which allows the detection of X-rays from 1 keV upwards with an energy resolution of 140 at 5.9 keV.

The positioning of the spectrometer is done by a motorized three-dimensional stage mounted on a mobile stand. The objects to be analyzed in a museum vary a lot in size from small pigments to big statues and therefore the stages need to have long traverse paths but also good positioning sensitivities. The selected electric actuators have a positioning repeatability better than 50 μm and traverse path of 200 mm in x-direction, 300 mm in y-direction and 1000 mm in z-direction as shown in Fig. 3.

To position the spectrometer precisely with respect to the analyzed object/sample two laser pointers (Fig. 2, No. 1 and 7) are mounted in the chamber. The laser beams cross at a point outside the chamber approximately 1 mm from the Kapton-window and coincide with the output focal spot of the polycapillary and the point where the axes of the X-ray optics and the detector cross. To reduce the diameter of the laser spots on the object from about 1 mm to the required size of about 0.2 mm a collimator (Fig. 2, No. 2 and 7) with a pinhole is mounted in front of the lasers.

As a result of the small distance between the Kapton-window and the sample (~ 1 mm) the region in front of the chamber is not visible from outside. A color charge-coupled device (CCD) camera



Figure 3. Complete spectrometer with assigned axes.

and an LED (Fig. 2, No. 5 and 3) light source, both mounted inside the chamber, are used to observe the vicinity of the irradiated spot on the sample surface and help to perform the adjustment of the spectrometer.

The detector and the polycapillary mounted in the vacuum chamber are adjusted once and can be fixed in position after this procedure. The sensitive alignment of the polycapillary *versus* the

X-ray source is performed by moving the tube which is attached to a compact and robust three-dimensional manual stage (Fig. 1, No. 2). When the tube is adjusted, the stages are locked in their position and a flexible (rubber) hose (Fig. 1, No. 3) outside the adapter tightens the gap between the tube and the chamber. The X-ray beam leaves the chamber through a circular opening, 8 mm in diameter, covered by a Teflon inlay to avoid X-ray fluorescence radiation from the chamber material. To tighten the chamber the opening is covered by 8- μ m-thick Kapton-window (Fig. 1, No. 4) which is glued directly to the outside wall of the chamber, so that the air path between detector and sample is equal to about 1 mm. The reduced air gap leads to a drastic reduction in the absorption of low energy X-rays.

Results and Discussion

Several new and adapted features are available when comparing PART II with PART I.

Figure 4 shows two instruments positioned in front of a tea cup. Since the working distance of both spectrometers is ~ 1 mm in front of the Kapton-window, one can see that it is possible to access the inner bottom of the cup using PART II and that there is no possibility to reach this spot with PART I since the distance to the inner bottom is about 25 mm.

The elemental composition from the different colors at the tea cup is shown in Fig. 5.

The spectrum from the white part represents the composition of the bulk material, while the red pigment shows a higher amount of Fe so it is supposed to be red ochre. Since there is also a small amount of Zn to see in the spectra the cup seems to be from the last century. Looking at the spectrum the yellow color is obvious from Au.

In Fig. 6, X-ray spectra collected from the IAEA standard material Soil 7 with PART II in air and in vacuum conditions are presented. Especially in the range below 5 keV, a significant increase of intensity in vacuum is observed, note the logarithmic scale, thus allowing the detection of Al and Si.

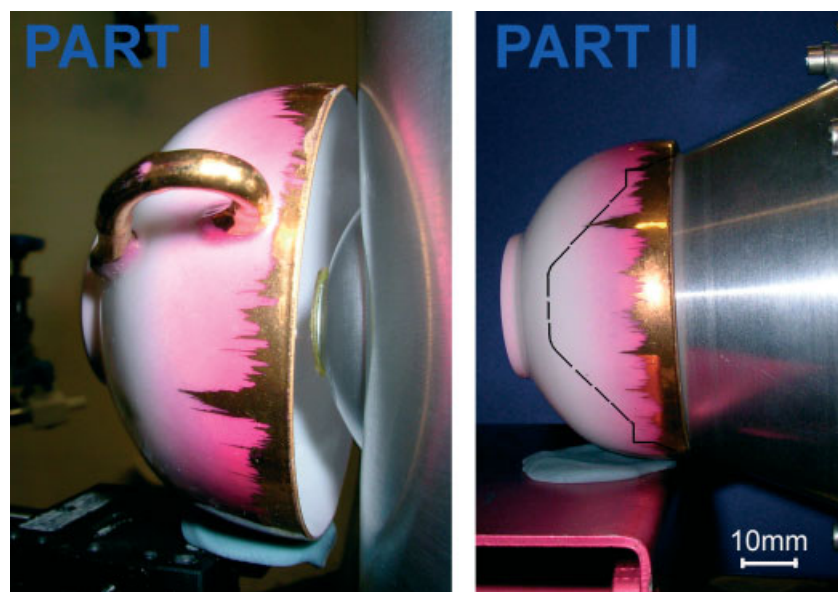


Figure 4. Accessibility comparison PART I–PART II showing the spectrometers in front of a tea cup and overlaid a sketch with the shape from PART II.

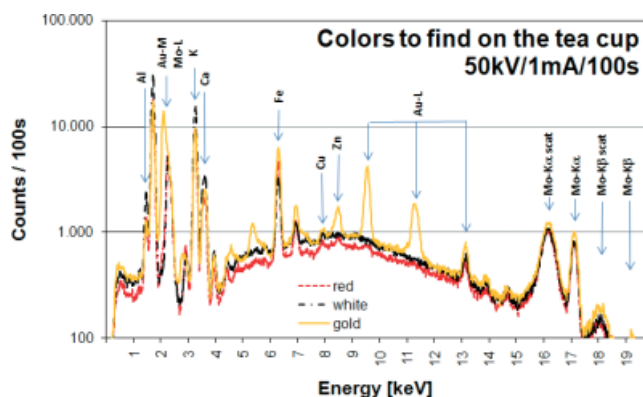


Figure 5. Spectra of the different colors to find on the tea cup.

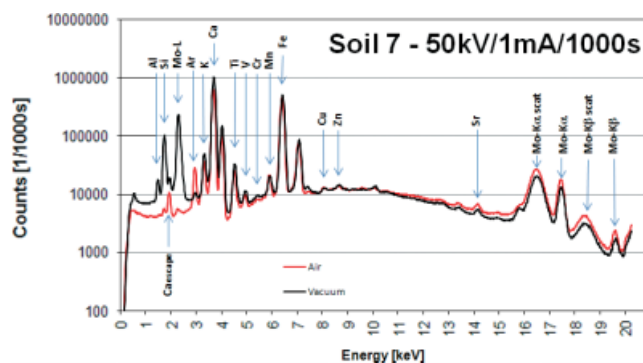


Figure 6. Comparison of spectra from Soil 7 measured in air and vacuum atmospheres with PART II.

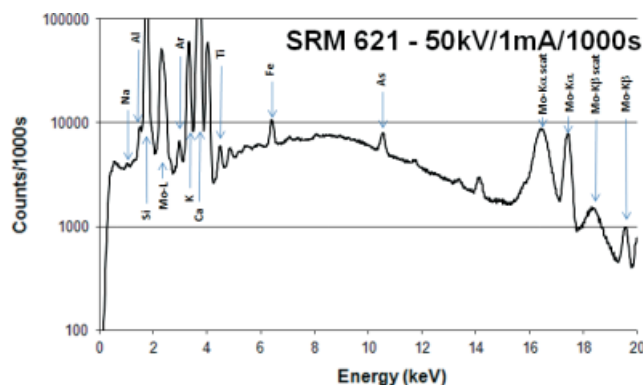


Figure 7. Spectra collected from the glass standard material NIST-SRM 621 with PART II in vacuum conditions.

Figure 7 shows a spectrum collected from the glass standard material NIST-SRM 621 with PART II in vacuum conditions which shows the ability of the spectrometer to detect low-Z elements from Na upwards. The detection limits (DL_{1000} measured with 50 kV, 1 mA for 1000 s) for Na and the other detectable elements of SRM 621 are listed in Table 1.

To obtain the net intensities of the characteristic peaks from the measured spectra, a 'peak-fitting' routine has been performed with AXIL-QXAS spectrum evaluation software. The detection limits (DL) obtained from the measurement in vacuum conditions are shown

Table 1. Detection limits for Na (in %) and the other elements (in ppm) of NIST-SRM 621 (50 kV/1 mA/1000 s)

Element	Na	Al	Si	K	Ca	Ti	Fe	As
DL_{1000} PART II [ppm]	7.69%	452	205	39	28	4	6	6

in Table 2. The following formula had been used for the calculation:

$$DL = \frac{3 \times \sqrt{N_B}}{N_N} \times m \quad (1)$$

A comparison of the DLs for PART I and PART II, both operated with 50 kV and 1 mA and measured for 1000 s, is shown in Table 2. The obtained improvement for the low-Z elements is a result of the shorter air path between the window and the sample achieved by a better fixation of the Kapton-window. The dramatic improvement of the detection limits for medium Z elements can be explained by the larger detector area of 20 mm² and the increase of the photoelectric absorption coefficient for Mo-K radiation in comparison to the Pd-K radiation used in PART I. The detector has also a thicker Si-crystal (450 μm) which leads to an improvement in the detection limits because of the better efficiency of the detector in the high energy region.

Conclusions

The first investigations show that the objectives of the project have successfully been achieved:

- The design of a portable XRF spectrometer performing *in situ*, spot analysis even for concave parts of art objects was performed by designing a vacuum chamber with a conical shape and a tip, accepting a disadvantage of losing the possibility to easily change the collimation system.
- The new design of a stable stand combined with the possibility of moving the measuring head in a very flexible way, allowing an overhang up to 400 mm, enables measurements with fewer restrictions to the size and shape of the objects. Also the mounting of paintings on an easel for the measurements is possible as a result of the overhang.
- The spectrometer nose has an 8 mm diameter opening to enable the passage of the primary radiation outside and the fluorescence radiation inside the chamber. To tighten this opening a prestressed Kapton-foil is glued on the chamber tip with commonly available 'fast glue' and a specially designed application device. Owing to the prestressing, the foil does not bend into the chamber as much as it was observed for PART I. Therefore, the air path is minimized even after long use. To be able to exchange the window very fast two tips were manufactured to have always a new window in stock.
- The attachment of pinhole collimators to the laser diodes gives a spot size of about 0.2 mm on the sample which is in the range of the size of the X-ray beam at the output focal distance of the capillary. As a result a precise positioning even to very small details on an object is possible.

The results obtained for PART II are in a good agreement with the expectations of a redesign of PART I. It is expected that the practical applications will also confirm the advantages and capabilities of this new device.

Table 2. Detection limits of soil 7 – comparison PART I–II (50 kV/1 mA/1000 s)

Element	Al	Si	K	Ca	Ti	V	Cr	Mn	Fe	Cu	Zn	Rb	Sr
DL ₁₀₀₀ PART I [ppm]	623	352	107	64	26	28	30	19	16	n.d.	13	n.d.	37
DL ₁₀₀₀ PART II [ppm]	599	258	33	19	12	5	5	6	7	4	4	7	9
n.d. – Not detected.													

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