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To cite this article: K Uhlig *et al* 2012 *IOP Conf. Ser.: Mater. Sci. Eng.* **37** 012008

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A newly developed, portable, vacuum-chamber equipped XRF-instrument, designed for the sophisticated needs of the Kunsthistorisches Museum, Vienna

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Abstract

In the analysis of artworks x-ray fluorescence (XRF) spectroscopy gains a high significance because of the non-destructiveness of the method. It can provide valuable information of technologies and materials and support conservation and restoration efforts. This method is especially suitable for the study of the collections of the Kunsthistorisches Museum Vienna (KHM) with its affiliated institutions, because of the great diversity of the materials and objects with different art historical and ethnological background. Within a research project in co-operation of the Conservation Science Department of the KHM with the ATI (Atomic Institute of the Vienna University of Technology) and the IAEA (International Atomic Energy Agency) a portable XRF instrument ("PART II") was designed and constructed, optimized to cope with the diverse analytical problems of a wide-spread museum collection as it is kept at the KHM.

Beneath some technical improvements concerning the optimization of the design of the new instrument (regarding stability and accessibility to objects) with respect to its precursor model, a special focus was laid on the detection of light elements to be able to analyze chemical elements from sodium (Na) onwards. In this way the palette of materials that can be analyzed could be expanded to matters like glass and enamel. In this paper the advantages of the new facility will be discussed.

Introduction

For the investigation of museum objects it is very important to apply a non-destructive analytical method. Additionally, as many objects are not moveable or too valuable for transportation to an external research facility, the investigations should be, as far as possible, done at the museum itself. Therefore, the instrument has to be portable to be applied in-situ in the exhibition spaces. Especially for the Kunsthistorisches Museum (KHM with its affiliated institutions: MVK – Museum of Ethnology, ÖTM – Austrian Theatre Museum, Treasury, Neue Burg with Ephesos Museum - Collection of Ancient Musical Instruments - Collection of Arms and Armour, Museum of Carriages and Department of Court Uniforms and Ambras Castle), which holds many objects of different materials and different art historical background, problems of a great diversity have to be considered. An analytical method which is employed very successfully for the investigation of cultural heritage objects and that can fulfill all the above mentioned needs, is the energy-dispersive x-ray fluorescence (XRF) analysis. Valuable information about materials and pigments used in art and ethnological objects, which are of great interest for restoration and conservation purposes, can be obtained using XRF. Additionally, an integral description of the objects in an art historical and ethnological background is possible. For these reasons also the KHM was interested in the application of this technique in its institutions.

A prototype XRF instrument (PART I – *Portable Art Analyzer I*) [1, 2] developed by the IAEA (International Atomic Energy Agency, Laboratories Seibersdorf) and the ATI (Atomic Institute of the Vienna University of Technology) could be applied and tested at the museum [3]. After this testing phase some ideas for an improvement of the instrument were born [4], which could be put into practice by the construction of an enhanced XRF instrument, funded by the Austrian Science Fund (FWF, project no. L430-N19; „Portable Art Analyzer – PART“).

Experimental

The goal of the mechanical design of the new portable focused beam XRF spectrometer was to build a transportable system with improvements in the accessibility to the different parts of the objects and in the positioning of the instrument in front of an object as well as an enhancement in the detection of low-Z elements.



Fig. 1 Portable Art Analyzer II (PART II)

One of the most striking construction highlights of PART II is the measuring head with the vacuum chamber (fig. 2). It is mounted rotatable (horizontal) for better accessibility to the objects and can be locked in the desired position. 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. Both, incident and fluorescent beams pass through a Kapton™ window of 8 μm thickness, which is applied at the tip of the vacuum chamber. In contrast to PART I [1, 2], the Kapton™ window is pre-stressed and glued directly on the outside of the chamber, which leads to less bending of the window when the vacuum is applied. The air gap between chamber and sample is about 1 mm, minimizing absorption losses in the excitation and x-ray fluorescence radiation paths and enhancing the sensitivity for light elements.

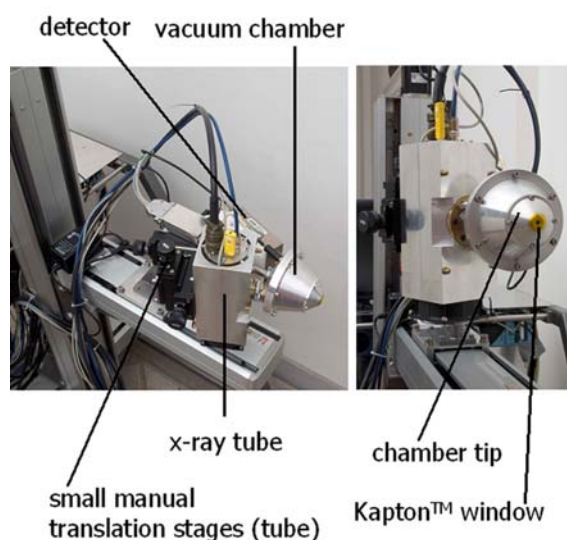


Fig. 2 The measuring head of PART II

The internal design of the vacuum chamber [4] is shown in fig. 3. The x-ray optic used is a polycapillary (focal spot size 145 μm for Cr K_{α} , 5.41 keV). The detector is a Si Drift Detector (SDD) with an improved efficiency in comparison to PART I [1, 2, 4]. The alignment of the incidence and take-off angles of radiation allows an acute-angled design of the vacuum chamber [4]. Inside also a camera for the positioning of the instrument in front of an object and an LED for the illumination is incorporated [4]. Additionally, two collimated laser pointers cross in 1 mm distance outside the Kapton™ window (focal point of the capillary) [4].

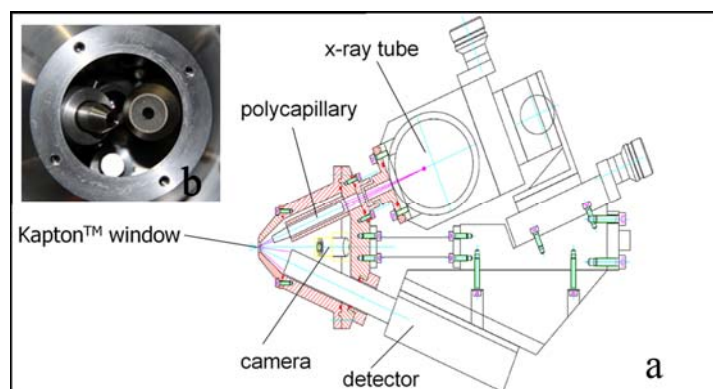


Fig. 3 Sketch of the internal design of the vacuum chamber (a) and a frontal look inside the chamber (b)

Using PART II with the Mo-tube the detection limits could be raised compared to PART I (equipped with a Pd-tube) [4]. The analysis of the NIST glass standard reference material 620, measured using both instruments (measuring conditions: 50 kV, 1 mA, 1000 s), shows an overall enhancement of intensity with PART II, doubling the intensity of the Na-peak from 914 to 2010 counts (fig. 4). For comparison all peak intensities of the two spectra are listed in tab. 1. For fitting the WinQXAS program of the IAEA was used.

Using PART II with the Cr-tube, due to an overload of the detector, no spectrum with the conditions 50 kV and 1 mA could be obtained. Therefore, the values of a spectrum obtained with 50 kV, 0.6 mA and 1000 s (fig. 5) were extrapolated for comparison (tab. 1).

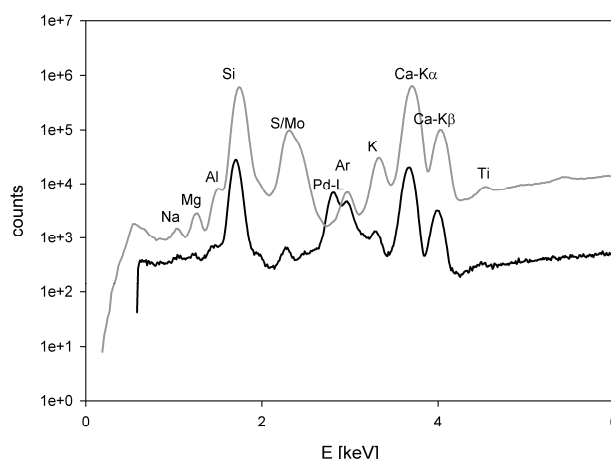


Fig. 4 Two spectra of NIST SRM 620 collected with PART I (black) and PART II with Mo-tube (grey). The energy-range up to 6 keV is shown. Measuring conditions for both spectra: 50 kV, 1 mA, 1000 s

oxide in NIST SRM 620	E (keV)	nominal concentration (oxides) NIST SRM 620	peak area [counts]		
	$K_{\alpha 1}$		PART I (Pd-tube)	PART II (Mo-tube)	PART II (Cr-tube)
Na ₂ O	1.041	14.39 %	914 ± 104	2010 ± 149	1380 ± 178
MgO	1.254	3.69 %	1858 ± 112	9206 ± 181	6270 ± 226
Al ₂ O ₃	1.487	1.80 %	4864 ± 125	44395 ± 277	33415 ± 347
SiO ₂	1.74	72.08 %	272897 ± 535	3869057 ± 1979	305277 ± 2293
SO ₃	2.307	0.28 %	3912 ± 118	725827* ± 852	4087 ± 398
	2.957	Ar (air)	64660** ± 264	28966 ± 292	235950 ± 745
K ₂ O	3.313	0.41 %	10043 ± 160	191945 ± 519	857517 ± 1301
CaO	3.691	7.11 %	225817 ± 456	4390572 ± 1967	19658823 ± 5305
TiO ₂	4.509	0.018 %	1620 ± 106	24944 ± 409	111550 ± 648
Fe ₂ O ₃	6.399	0.043 %	11024 ± 169	151944 ± 683	15926 ± 357

Tab. 1 Comparison of the elemental peak intensities in the spectra of NIST SRM 620, collected with PART I and PART II. Measuring conditions for PART I and PART II with Mo-tube: 50 kV, 1 mA, 1000 s, PART II with Cr-tube: 50 kV, 0.6 mA, 1000 s extrapolated to 1 mA, * Mo L-lines subtracted, **Pd L-lines subtracted

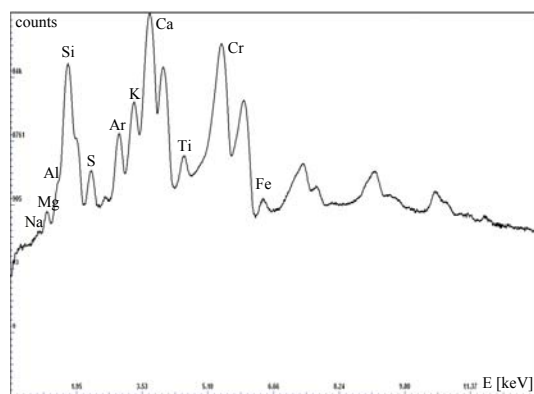


Fig. 5 Spectrum of NIST SRM 620 collected with PART II, Cr-tube (50 kV, 0.6 mA, 1000 s)

The detection limit for the PART II device using the Mo-tube could be calculated to 7.7 % Na [4], equaling 10.4 % Na_2O . Experimentally, the three glass reference materials NIST 1831 (13.32 wt% Na_2O), NIST 620 (14.39 wt% Na_2O) and V5 (19.00 wt% Na_2O) were analyzed using the measuring conditions 50 kV, 1 mA, 500 s. The spectra were fitted with the WinAxil program and the counts of the Na-peaks are plotted versus the Na_2O concentration in fig. 6. For the lowest Na-content in NIST 1831 417 counts could be found (fig. 6). A Na-peak of 13 wt% Na_2O is detectable properly. Unfortunately, a reference material with approximately 10 wt% Na_2O was not available.

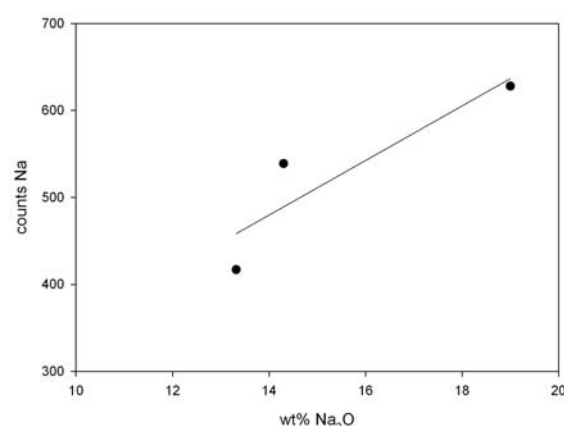


Fig. 6 Counts of the Na-peaks of the reference materials NIST 1831, NIST 620 and V5

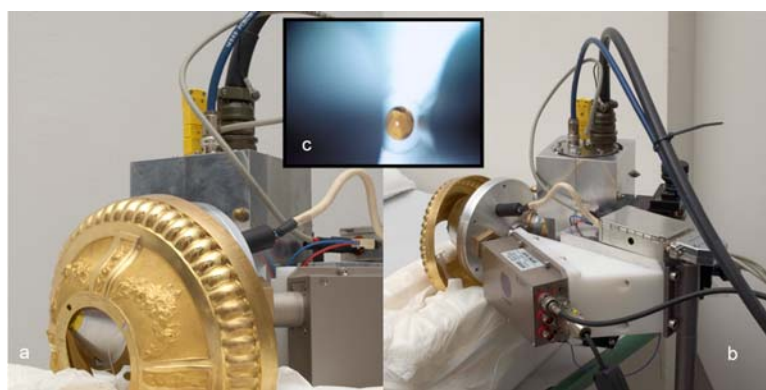


Fig. 7 The vacuum chamber of PART II positioned to measure in the inner part of the pedestal shown from the front (a) and the backside (b). The view of the camera through the KaptonTM window is also shown (c).

In fig. 7 an example for the potential of positioning is shown. The instrument is placed to analyze the gold-composition in the inner side of the pedestal of an Étagère, created in 1755 by Peter Josef Fonson. This object is made of red (or rose) gold, which was chemically etched to leach out the base metals copper and silver from the surface to achieve a golden appearance. Because XRF is a surface sensitive method, polishing of a small area is necessary to perform a quantitative investigation of the base alloy. Of course the polishing has to be done at a very inconspicuous part, like in the inner part of the pedestal.

Due to the improved design of the measurement head of the PART II instrument and even though the distance to the Kapton entrance window has to be 1 mm, measurements in the inner part of the object were possible. The delicate positioning is shown from the front and the backside in fig. 7. The view of the camera mounted inside the vacuum chamber looking through the Kapton window is also inserted in Figure 7. The two laser pointers cross in the focal point of the capillary (1 mm outside the chamber). Evaluation of the analysis, carried out using

tht Mo-tube, 50 kV, 0.3 mA and 200 s measuring time, showed an alloy composition of approximately 70 wt% Au, 20 wt% Cu and 10 wt% Ag. One selected spectrum is presented in fig. 8, clearly showing the signals for Au, Ag and Cu. As expected, the analysis of metal alloys could be performed without major complications. Only between approximately 4 and 7.5 keV some diffraction peaks, due to the acute-angled design of the vacuum chamber, appear. For reducing these diffraction peaks (if they overlap with the peaks of important elements) an aluminum filter can be used.

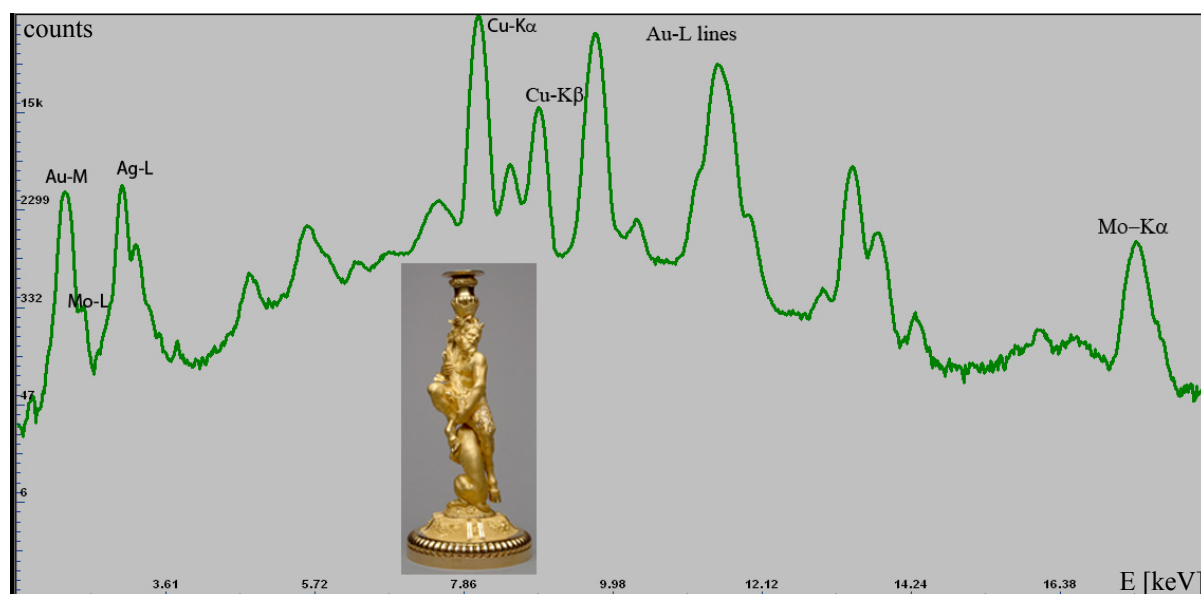


Fig. 8 Spectrum of the red gold alloy of the candelabra, Inv. No. KK_1283, also shown in this figure

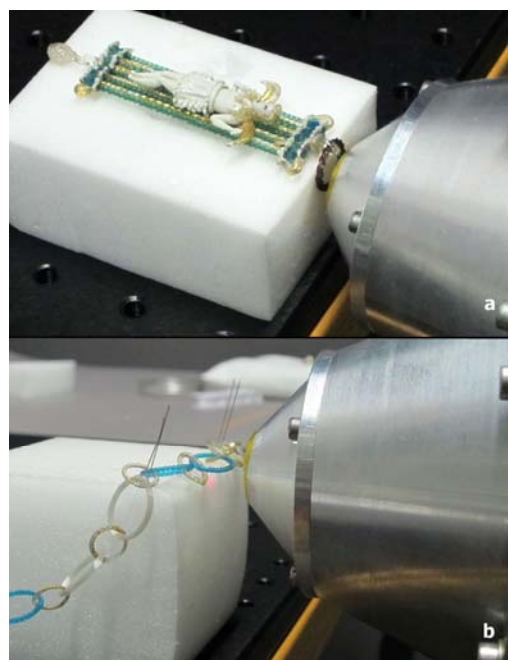


Fig. 9: Illustration of the positioning of small and very fragile glass objects in front of PART II: glass figurine Inv. No. KK_2801 (a) and glass chain Inv. No. KK_3042 (b).

One project concerning light elements was the analysis of 16th century glass jewelry (a unique glass jewelry collection held by the Collection of Sculpture and Decorative Arts, so-called “Kunstammer”, of the Kunsthistorisches Museum Vienna). Originally the pieces were part of Archduke Ferdinand’s II “Kunst- und Wunderkammer”, located at Ambras Castle near Innsbruck, Tyrol, Austria. For producing these outstanding objects he employed glass-makers from Murano, a very unique privilege, so the manufacturing technique should be based on Venetian recipes. In a first study around 80 objects made of differently colored transparent and opaque glasses were analysed. Representative for the whole collection two pieces will be presented here: a figurine (fig. 9a, Inv. No. KK_2801), where three differently colored glasses could be analyzed, and a glass chain (Fig. 9b, Inv. No. KK_3042). Positioning of these glass objects was often difficult due to their brittleness and different shapes. The mostly thin and highly varying thicknesses of the glass-parts as well as often unfavorable measurement geometries are the main problems for the quantitative evaluation of the data. Therefore, as a first step, only classifications of the glass types used were made.

The measurements were carried out using the Cr-tube (30 kV, 1 mA and 100 s measurement time per point, vacuum) to avoid any overlap in the low-energy region, taking into account that the identification of manganese (Mn) is problematic because of the overlap of Cr K_{β} and Mn K_{α} . Additionally, the presence of Na is not always assured, because of the necessity of applying short measuring times to get an overview of a vast number of objects within a very limited period of time available for analysis. Also corrosion plays a big part in the detectability of Na. Nevertheless, the K and Ca intensities can give an indication of the glass type used.

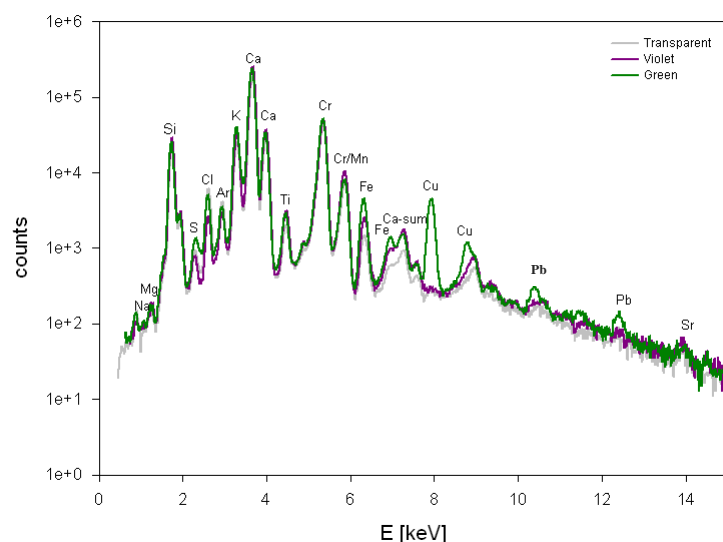


Fig. 10 Spectra for different areas on the figurine KK_2801 (see Fig. 9a) showing the characteristic elements for the specific colors.

The spectra of the differently colored glasses of the figurine KK_2801 are compared in fig. 10. As expected for these items, the three differently colored glasses show a similar composition for the base glass used. The applied technique of lamp working requires glasses with very similar physical characteristics. Therefore, the coloring elements were added to the same base glass - oxides of copper and iron for green, of manganese for violet. Soda-lime-silica glass could be identified for the base glass composition.

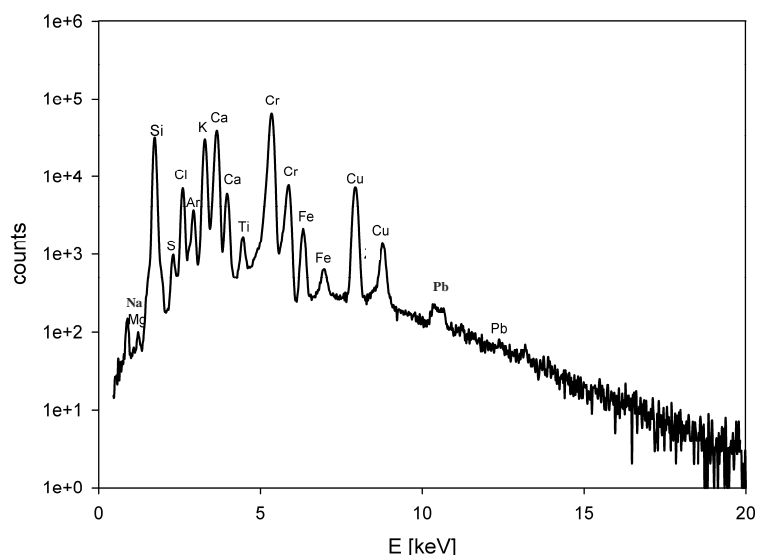


Fig. 11: Spectrum of the transparent blue glass of the glass chain KK_3042 (see Fig. 9b).

The spectrum of the blue glass of the glass chain KK_3042 is displayed in fig. 11. It can be seen that the Ca-concentration is very low compared to the spectra in fig. 10. These low concentrations of stabilizer can be found in the so-called Venetian *cristallo* glass, which was obviously used for some blue hues in the analyzed items. This seems also to be the reason why these glasses are more affected by corrosion. The coloring in this blue part is due to copper oxide.

Conclusion

In summary it can be stated that the portable XRF spectrometer ("PART II") was successfully designed to meet the needs that arise within the miscellaneous collections of the KHM: optimization of the vacuum chamber (minimization in size and conical form), minimization of the pathways of the excitation and fluorescence beam in air due to a better fixation of the KaptonTM window of the vacuum chamber, high efficiency of the detector and optimization of the positioning of the measurement head by the use of three electronically controllable translation stages. As could be shown, the qualitative analysis of elements down to Na is definitely possible, although the Cr-tube, acquired with regard of a better excitation of the light elements, did not fulfill the expectations. Nevertheless, following the first measurements on standards, it is very likely that with the Mo-tube semi-quantitative studies of glass and enameled objects will be possible using the PART II.

Acknowledgements

The authors gratefully thank A. Markowicz and his team from the International Atomic Energy Agency (IAEA), Seibersdorf Laboratories, for their invaluable support in constructing the PART instrument and the Austrian Science Fund (FWF) for financing the project "Portable ART Analyser (PART)", project no. L430-N19. Special thanks to Eva Putzgruber for the excellent collaboration regarding the analysis of the 16th century glass jewelry.

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