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Analytical characterization of a new mobile X-ray fluorescence and X-ray diffraction instrument combined with a pigment identification case study

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ABSTRACT

A new, commercially available, mobile system combining X-ray diffraction and X-ray fluorescence has been evaluated which enables both elemental analysis and phase identification simultaneously. The instrument makes use of a copper or molybdenum based miniature X-ray tube and a silicon-Pin diode energy-dispersive detector to count the photons originating from the samples. The X-ray tube and detector are both mounted on an X-ray diffraction protractor in a Bragg–Brentano θ:θ geometry. The mobile instrument is one of the lightest and most compact instruments of its kind (3.5 kg) and it is thus very useful for in situ purposes such as the direct (non-destructive) analysis of cultural heritage objects which need to be analyzed on site without any displacement. The supplied software allows both the operation of the instrument for data collection and in-depth data analysis using the International Centre for Diffraction Data database.

This paper focuses on the characterization of the instrument, combined with a case study on pigment identification and an illustrative example for the analysis of lead alloyed printing letters. The results show that this commercially available light-weight instrument is able to identify the main crystalline phases non-destructively, present in a variety of samples, with a high degree of flexibility regarding sample size and position.

1. Introduction

Analysis of cultural heritage objects and their environment with the application of archeometry can teach us not only much about the objects themselves, but also about history as well as past behavior and interactions of people. Archeometric studies often involve the analysis of unique and vulnerable, fragile objects that must be preserved without any damage as a result of the analysis. Therefore, in situ non-destructive qualitative and quantitative elemental/structural analyses are often required [1–3]. Currently, there is a large number of commercial portable instruments available allowing the analysis of objects on site. Hence, analytical measurements are not restricted to investigations during which researchers have to get the permission to relocate the cultural heritage objects to the lab, and to objects which are sufficiently small to fit into the analytical instruments [4–6]. Among currently used mainstream methods, analytical techniques based on X-ray fluorescence (XRF) are among the most appropriate to examine the elemental composition. In most cases, however, not only elemental information is required, but also structural data on the detectable crystalline phases [7,8]. X-ray (powder) diffraction (XRD) has proven to be a powerful tool for identifying crystal structures with very useful applications in the analysis of objects of art or archeological artifacts containing crystalline materials [9–14]. Starting from the early 1990s, the first prototypes of mobile XRD instruments were developed at NASA. A few commercial companies (e.g. CHEMIN and MOXTEK) started manufacturing portable X-ray fluorescence/X-ray diffraction (XRF/XRD) instruments starting from 2000 and the development of their own, improved, instruments is still ongoing [15–17]. Recently, a number of companies (e.g. Olympus, Assing) made mobile instruments available combining XRF and XRD, providing powerful tools for the comprehensive in situ characterization of materials in several research fields. However, until now, almost no information on these commercially available instruments can be found in the literature. Concerning non-commercial XRF/XRD instruments, the latest developments on such instrumentation can be found in e.g. [11,18].

In this paper, a commercially available mobile X-ray fluorescence/X-ray diffraction instrument (Surface Monitor, Assing S.p.A, Italy) is characterized [19]. It is a new mobile device for simultaneous determination of the elemental constituents by XRF and of the mineral phases

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by XRD. The surface monitor works on a broad range of surfaces, without the need of any sample preparation. The instrument adopts an innovative data acquisition strategy allowing the exploitation of the entire energy range provided by the X-ray sources. The novelty of this mobile XRF/XRD instrumentation is due to a combination of energy-dispersive XRF spectroscopy with goniometry based XRD data collection. This is different from most other commercially available systems, which rely on a charge coupled device based non-dispersive XRD methodology. Also, the very low weight of the entire instrument is unique and allows a straightforward way of working on site. Beside the characterization of the instrument, also an application example is discussed demonstrating the applicability of the mobile XRF/XRD instrument for pigment and preparation layer identification in different paint layers.

During the analytical characterization and testing of the surface monitor using model pigment samples in the lab, we also applied the instrument for the non-destructive, in situ study of the famous painting "Mad Meg" by Pieter Bruegel the Elder. The analysis of pigments present on the painting using the XRD method gives valuable information on the underlying preparation layer where the XRD fingerprint matches with calcite. The results of this study were described in detail elsewhere [20].

2. Experimental

The surface monitor is equipped with a Cu (maximum voltage 30 kV/current 500 μA) or Mo (maximum voltage 30 kV/current 300 μA) anode based X-ray tube in combination with an Amptek X-123 Si-Pin diode detector (260 eV energy resolution at 5.9 keV, 6–25 mm^2 detector area depending on collimation conditions and 25 μm Be window thickness). Both the X-ray tube and the detector are mounted on an XRD protractor applying the Bragg–Brentano θ:θ geometry [15,21]. The θ:θ protractor is integrated in a motorized probe head which is equipped with a laser interferometer for beam positioning as shown in Fig. 1. The tube and the detector can be respectively equipped with (pairs of) pinholes or vertical slits, with internal diameters ranging from 0.5 mm to 2.0 mm (in steps of 0.5 mm).

The entire systems weighs only 3.5 kg, which is a considerable improvement compared to other mobile instruments available from the early 2010s [11]. During analysis, the instrument is installed on a tripod which allows easy and safe positioning of the device probe-head at the position of interest, covering a suitable height range and, if needed, compensating for the inclination angle to the artifact's surface. This allows for in situ measurements without a need for repositioning the artwork, as typically requested by the museum. A camera, mounted on a flexible arm, was added to provide an inclined top-view of the probe head and the sample to monitor all movements (by means of a controlling portable PC) so that the operator can work from a safe distance (at least two meters) from the X-ray instrument.

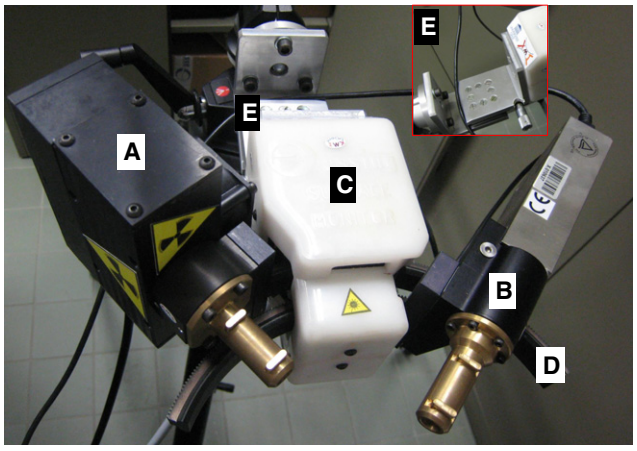

Fig. 1. Photograph of the surface monitor, a portable XRF/XRD system: (A) X-ray tube, (B) detector, (C) laser interferometer, (D) protractor for Bragg–Brentano θ:θ methodology, (E) micromanipulator for the fine adjusting step relative to the sample surface, zoom out in small photograph right top.

In the experiments described below, the Cu X-ray tube was used for the characterization and application of the instrument. The Cu anode, providing lower energy characteristic lines, is preferable for X-ray diffraction experiments compared to Mo. In general, the procedure for swapping the available X-ray tubes (Mo, Cu) is not straightforward. In case of a tube replacement, the entire procedure of calibration and characterization needs to be repeated. The Mo tube is preferable when XRF measurements have priority over XRD due to the higher excitation energy represented by its characteristic lines. X-ray tubes with targets of lower characteristic energy allow carrying out diffraction analysis with larger diffraction angles, resulting in a better separation of diffraction peaks. In all measurements described below, a start angle ($2\theta_i$) of 20° was used with an end angle ($2\theta_f$) of 70° or 90° (which is below the instrumental limit of 92.1°), with a step size of either 0.1° or 0.2°. The detector dwell (live) time per angular step was 5 s or 30 s. In all cases, the exact parameters of data acquisition are given in the text or figure.

3. Result and discussion

3.1. Characterization of the mobile surface monitor

When using the surface monitor in practice, the final step of setting up the instrument before starting the analysis is to measure and adjust the distance between the surface of the sample and the analytical head. When characterizing the mobile XRF/XRD instrument, it was of utmost importance to know the optimal distance between the object and the sensor of the probe head. Therefore, a laser interferometer is built in the analytical head (between the X-ray tube and detector) to measure the sample distance and to ensure the correct positioning of the X-ray beam on the area of interest (C on Fig. 1). A micromanipulator has been added between the mounting points of the tripod and the surface monitor in order to enhance the accuracy of the longitudinal positioning of the analytical head in the direction of the sample (E on Fig. 1).

To obtain XRD patterns with optimal quality, the surface monitor has to be positioned with the main axis perpendicular toward the sample and the distance between the instrument head and the sample should be between 94.5 mm and 95.0 mm. This optimal distance was determined by measuring a NIST SRM 660b lanthanum hexaboride (LaB_6) powder diffraction standard between 20° (start-angle = $2\theta_i$) and 45° (end-angle = $2\theta_f$), using a step size of 0.2°, over different distances and corresponding interferometer read-out values (ranging from 92.0 to 98.0 mm) between the probe head and the standard. Table 1 shows the area under the most intense diffraction peak and the difference in the 2θ-angle between this peak and the corresponding certified value (30.385° — [110]). Based on these results, the optimal distance is reached when maximal intensity and minimal angular deviation is obtained. This optimum is observed in the distance read-

Table 1
Numerical values defining the optimal distance of the surface monitor with respect to the sample using a NIST standard (SRM 660b–LaB_6), obtained by measuring the intensity and the deviation from the certified value ($2\theta = 30.385°$) of the most intense diffraction [110] peak.

Distance (mm)	Counts	Deviation (°)
92.80	832	3.613
94.04	1727	1.618
94.56	1807	0.612
94.95	1683	0.215
96.03	894	−1.385
97.03	139	−3.185
98.07	/	/