

Feature Article

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Employing the Benefits of Atomic and Molecular Spectroscopy in a Combined X-ray Fluorescence/Raman Microanalyser

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X-ray fluorescence analysis (XRF) is a widely applied routine method for inorganic analysis of a variety of materials; compact ED-XRF equipment with microscopic analysis capabilities (μ -XRF) is available in different forms. Raman Spectroscopy (RS) is a highly specific method of molecular analysis that has shown itself to be admirably suitable for identification of many categories of inorganic and organic compounds. Also Raman instruments are becoming available under the form of increasingly compact apparatus. In order to combine the above-two spectroscopic methods into one compact combined XRF/Raman instrument, an irradiation/detection geometry was designed that allows to perform simultaneous XRF and Raman measurements at the same location on the surface of a sample. An illustrative example, highlighting the usefulness of the apparatus for pigment-related investigations in the cultural heritage sector is described.

Introduction

In the two last decades, many *instrumental analytical techniques* which previously only provided average information on a large sample have developed *microscopic equivalents* (e.g., IR microscopy). The drive for this development is twofold: (1) the increasing degree of material complexity (cf. micro-heterogeneous new materials) and (2) the growing need to investigate *local* changes in properties of natural and man-made materials (composition, stress, structure, colour, ...).

The most well-established method for *inorganic micro-analysis* is probably EPMA (electron probe microanalysis), sometimes denoted as SEM-EDX (scanning electron microscopy equipped with an energy-dispersive X-ray detector); however, this method only provides information on the major elemental constituents of a material.

FT-IR (Fourier Transform Infra-red Spectroscopy) is widely applied for microscopic characterization of organic materials but has only a limited use for analysis of crystalline and inorganic components.

On the other hand, in many disciplines, especially in those areas where material authentication, source identification or sample/source matching is of interest, more detailed data such as

- (a) the minor/trace-element fingerprint of a specific area of a material,
- (b) highly-specific molecular information, allowing to characterize complex mixtures of organic and inorganic compounds and to differentiate between materials with similar elemental but different molecular forms is often required ^[1].

Two fields having fairly similar requirements in this respect are forensic science and material research in the cultural heritage sector. Although the aims of both disciplines are quite different, the basic problems and operational limitations both disciplines are commonly faced with show a striking parallelism:

- authentication of a variety of materials [e.g., of documents (inks, paper analysis)];
- matching of 'unknown' samples to a series of 'library' materials by 'finger-print' comparison (e.g., glass fragments, pigmented materials such as car-paints or oil-paints, textile fibres, ...);
- non-destructive investigations are preferred (and often mandatory), allowing repeated analyses without damage/alteration to criminal evidence/valuable artefacts;
- often only minute samples are available, e.g., in case of

destructive sampling or analysis.

X-ray fluorescence analysis (XRF) is a widely applied routine method for inorganic analysis of a variety of materials. In this field, several technological breakthroughs have prompted the launch of compact ED-XRF equipment with microscopic capability as less expensive alternatives to traditional, large-scale wavelength dispersive XRF analysers. Inexpensive, low-power X-ray tubes, high-resolution, liquid nitrogen-free Si-PIN diode detectors and efficient X-ray focusing optics are currently available from various manufacturers and permit quantitative minor/trace level analysis at the 30-100 μm level of lateral resolution^[2].

Raman Spectroscopy is a highly specific method of molecular analysis that has shown itself to be admirably suitable for analysis of many categories of inorganic and organic compounds. Also here, the availability of cost-effective and compact laser sources, dispersive gratings and CCD detectors has led to smaller instruments. The use of fibre-optics to connect the excitation/detection system to a compact measuring head fitted with a microscope objective lens allows 'in-situ' and local analysis of macroscopic objects without the need for sampling or other destructive preparations^[3].

Both above-mentioned methods can be considered to be non-destructive, when used under the appropriate circumstances, and can provide highly-specific fingerprinting information but also feature inherent limitations:

- μ -XRF spectrometry yields relatively simple and systematic spectral data from which quantitative information on major, minor and trace elements can be derived, but does not offer any chemical/molecular specificity (such as, e.g., the distinction between sulphides and sulfates)
- μ -RAMAN spectroscopy is much more specific regarding the chemical form of the compounds constituting a sample but only provides information on the major composition while interpretation of the spectral information is non-trivial and usually is done on an empirical basis, by comparison of 'unknown' to 'library' spectra.

In order to combine the above-two spectroscopic methods into one compact combined XRF/Raman instrument, equipped with a remote measuring head, that allows non-destructive and local analysis of microscopic samples with high elemental sensitivity and outstanding molecular specificity but that also can be used as a table-top unit in a laboratory environment, a irradiation/detection geometry was designed that allows to perform

simultaneous XRF and Raman measurements at the same location on the surface of a macroscopic sample.

In what follows, the design of the combined instrument is briefly outlined, followed by the description of a few illustrative examples, highlighting the usefulness of the apparatus for investigations in the cultural heritage sector.

Design and Construction of a Combined XRF/ Raman Microanalyser

The conventional irradiation/detection geometry of μ -XRF spectrometers usually involves the irradiation of the materials to be investigated under an angle close to 45°, while the emitted X-ray fluorescence radiation is detected under a similar angle. On the other hand, (confocal) Raman irradiation and detection usually is carried out by means of an optical system that involves an objective lens that both focuses the primary laser beam and collects the Raman scattered radiation in a geometry perpendicular to the sample surface. Thus it was possible to design a combined XRF/Raman irradiation/detection geometry as shown in Figure 1(a). In this figure, the primary X-ray photons reach the sample from the left, originating from a micro-focus X-ray tube (T) and focused into a spot of ca 50 μm diameter by a polycapillary lens (P) having a focal length of 10 mm. Element-specific X-ray fluorescence signals are recorded by means of a carefully collimated Silicon drift chamber detector (D). The detector collimator is fitted with tubing allowing the flushing of the path between the sample surface and the detector window with He-gas in order to reduced absorption of low-energy radiation. In between the X-ray tube and the detector, a remote Raman probe is positioned, connected via fibre optics to a primary laser source and a Czerny-Turner type optical spectrograph. The primary laser light reaches the sample surface via a strongly focusing objective lens with a 20 mm ultra long working distance; this lens is also employed to collect the scattered Raman light and to guide it towards the spectrograph. The remote Raman head includes a optical video system for sample observation that allows to position the sample surface at the focal distance of the objective lens. Figure 1(b) shows a photograph of the total system, indicating that all components of the combined XRF/Raman measurement head fit in a relatively small volume, of ca. 30x40x50 cm^3 ; the total mass of the measurement head is ca. 10 kg, i.e. sufficiently small to allow positioning of the entire head above or (after rotation over 90° around a horizontal axis) in front of a large work of art or other artefact.

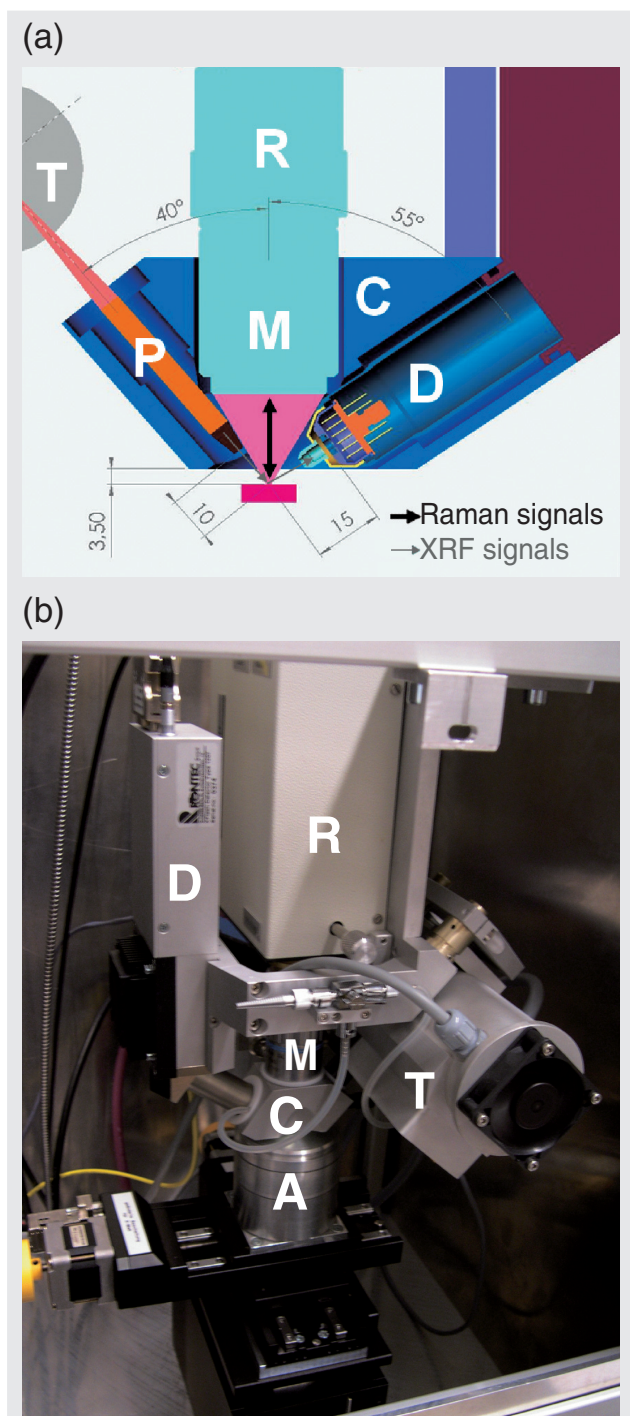


Figure 1 Schematic layout and photograph of the combined μ -XRF/ μ -Raman spectrometer

- (a) Schematic layout of the combined μ -XRF/ μ -Raman spectrometer
 T: X-ray tube, P: polycapillary X-ray lens
 R: remote Raman head
 M: ULWD microscopic objective (with 2 cm working distance)
 D: energy dispersive X-ray detector, C: central mounting block
 (b) Photograph of the combined μ -XRF/ μ -Raman spectrometer

Here shown positioned above a motorized sample stage; in this case, the sample is mounted on top of an Al cylinder A in order to increase its height. Total width x depth x height of the measurement head is ca. 30 x 40 x 50 cm³; total mass is ca 10 kg. The central block C is equipped with tubing to allow flushing of the space between the sample surface and the X-ray detector window with a stream of He in order to improve the sensitivity for low Z-elements.

Monochromatic light (e.g. with a wavelength of 632 nm or of 785 nm) from a laser source reaches the measurement head via a fibre optic cable while the Raman scattered light leaves the head for a dispersive spectrometer via a second fiber optic cable. Via exchange of the Raman notch filters that are present in the measurement head it is possible to switch between different primary laser sources. The laser source(s) and CCD-based dispersive spectrometer are mounted in an easily moveable 19" rack in which also the high voltage supply for the X-ray tube, its interface electronics and the electronics of the energy-dispersive detector are present. Finally a computer, responsible for (a) control of the Raman spectrometer parameters (grating selection, position and size of the spectral window being detected, spectrum collection time and number of repeat acquisitions) and of the X-ray tube parameters (voltage, current), (b) simultaneous or sequential data-acquisition of the Raman and X-ray spectra, (c) display of optical video images, Raman and X-ray spectra, line-scans and two-dimensional Raman and/or XRF-intensity maps and (d) sample movement in three dimensions, completes the instrument.

Results and Discussion

As an example of the use of the combined μ -XRF/ μ -Raman spectrometer, the investigation of the pigments used to paint a number of heraldic shields in a 16th C family register, a historical document that is part of the collection of the City Archives of Antwerp (Belgium) is described below. The register belonged to the "Pot" Family, of which several generations were active in mercantile activities in post-medieval Antwerp. Each time a member of the family married, the event was recorded by inserting small paintings the heraldic shields of bride and bridegroom in the register.

Four examples of such heraldic shields are shown in

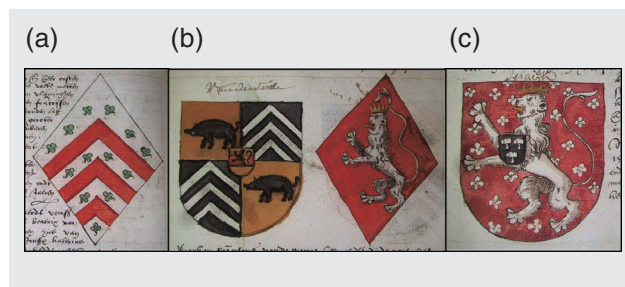


Figure 2 Four examples of heraldic shields painted on the pages of the 16th C. Register of the Antwerp "Pot" Family (a:left, b:centre, c:right)

Figure 2, revealing that different shades of red/orange were used to render them. While the broad bands of the shield in Figure 2(a) is rendered in a bright orange-red shade, the red background of the lion shield of Figure 2(c) is rendered with a significantly darker tone of red paint. Finally, the lozenge-shaped shield in Figure 2(b) features an intermediate colour.

Non-destructive analysis with both XRF spectrometry and Raman spectroscopy in the combined μ -XRF/ μ -Raman spectrometer described above allows to identify the pigments employed here. In Figure 3 the XRF spectra obtained by irradiating small areas of the shields of Figure 2 are shown.

From the presence of characteristic Hg-L $_{\alpha}$, Hg-L $_{\beta}$ and S-K $_{\alpha}$ X-ray lines in the spectrum of Figure 3(c) and the (dark) red colour of the paint, one can straightforwardly deduce the presence of the red mineral cinnabar (HgS). However, to determine the source of the red colour in Figure 2(a) by using the information from the associated XRF spectrum of Figure 3(a) is not so straightforward. This spectrum shows the presence of Pb (indicated by the characteristic Pb-M, Pb-L $_{\alpha}$ and Pb-L $_{\beta}$ lines) but since in the 16th C. several Pb-containing pigments are known (such as lead white, PbCO $_3$, Pb(OH) $_2$; red lead or minium, Pb $_3$ O $_4$; and litharge, PbO (red)) while the observed colour might also have been obtained by covering a lead white base with a transparent layer of a red organic dye, it is not possible to unequivocally identify the pigment or pigment combination used. Clearly no cinnabar was employed to create this particular shade of orange-red as the XRF

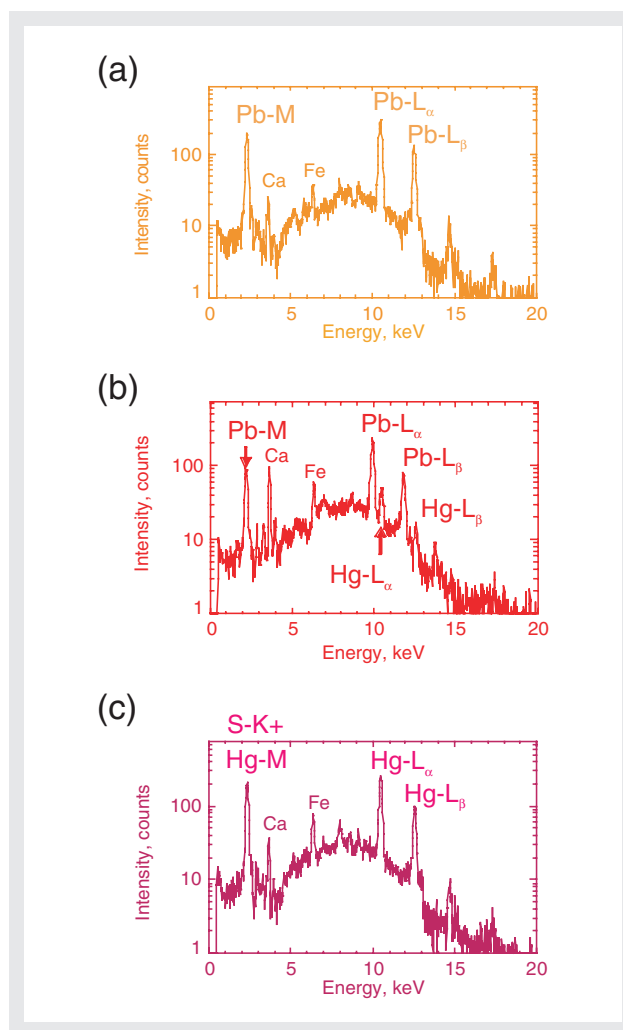


Figure 3 XRF spectra the red areas of the heraldic shields
 (a) Figure 2(a) (orange-red bands)
 (b) Figure 2(b) (orange-red background)
 (c) Figure 2(c) (dark red background area)

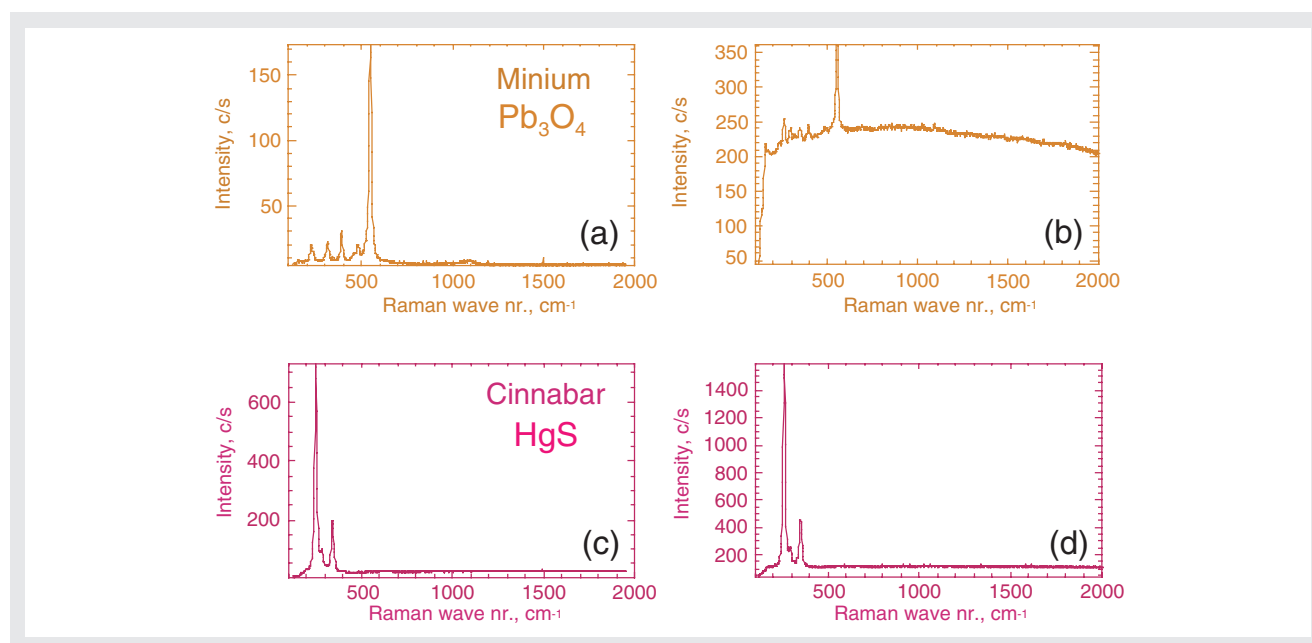


Figure 4 Raman spectra
 (a) minium
 (b) the red areas of the heraldic shield shown in Figure 2(a) (orange-red bands)
 (c) cinnabar
 (d) the red area of the heraldic shield shown in Figure 2(c) (dark red background area)
 Raman spectra are not background corrected.

spectrum does not reveal the presence of Hg. By comparing the Raman spectrum (Figure 4(b)) obtained from an individual pigment grain inside the red/orange shield of Figure 2(a) with that of minium (Figure 4(a)) and cinnabar (Figure 4(c)), it follows that in this case, the orange-red pigment minium was employed. Raman and XRF measurement performed at different locations within the band of this shield do not reveal any significant difference. Thus, the red bands of this shield are likely to have been painted with minium only.

The situation is different in the lozenge-shaped heraldic shield of Figure 2(b). Here, in the corresponding XRF spectrum (Figure 3(b)) intense Pb-lines are present, but also less intense Hg- L_{α} and Hg- L_{β} lines are visible, pointing to the presence of a 10:3 mixture of Pb:Hg. XRF spectra collected at various locations show only a slight variation (<10 %) of this mass ratio, suggesting the use of a mixture of cinnabar and another, Pb-containing pigment or the use of a relatively thick Pb-rich base layer (e.g. containing lead white) covered by a thinner red cinnabar-layer. Again the information in the XRF spectra is insufficient to permit an unambiguous pigment identification. By considering the Raman spectra obtained

from different grains and adjacent positions in the red layer of this shield, on the other hand, it is possible to identify the pigments used here. While in some points, the Raman spectra of pure minium (Figure 5(a)) or of quasi-pure cinnabar (Figure 5(c)) are observed, at a significant number (about 30%) of the locations examined, Raman spectra are obtained where the characteristic Raman lines of both pigments are visible. An example is shown in Figure 5(b). Careful observation of the red paint layer in the shield of Figure 2(b) at 50x magnification reveals the presence of grains of different colour and having diameters smaller than 10 μm . Apparently, when the laser beam simultaneously illuminates two or more adjacent minium and cinnabar grains, a Raman spectrum will result in which both characteristic signatures are visible. It should be noted that the Raman spectra shown in Figure 4 and Figure 5 are not background corrected and thus, the presence of the paper below the paint and/or the remains of the binding medium (possibly arabic gum or another type of polysaccharide) give rise to a background continuum due to electronic excitation of these materials. With single paint layers of this type, painted with a water-based paint to which only a limited amount of binding medium was

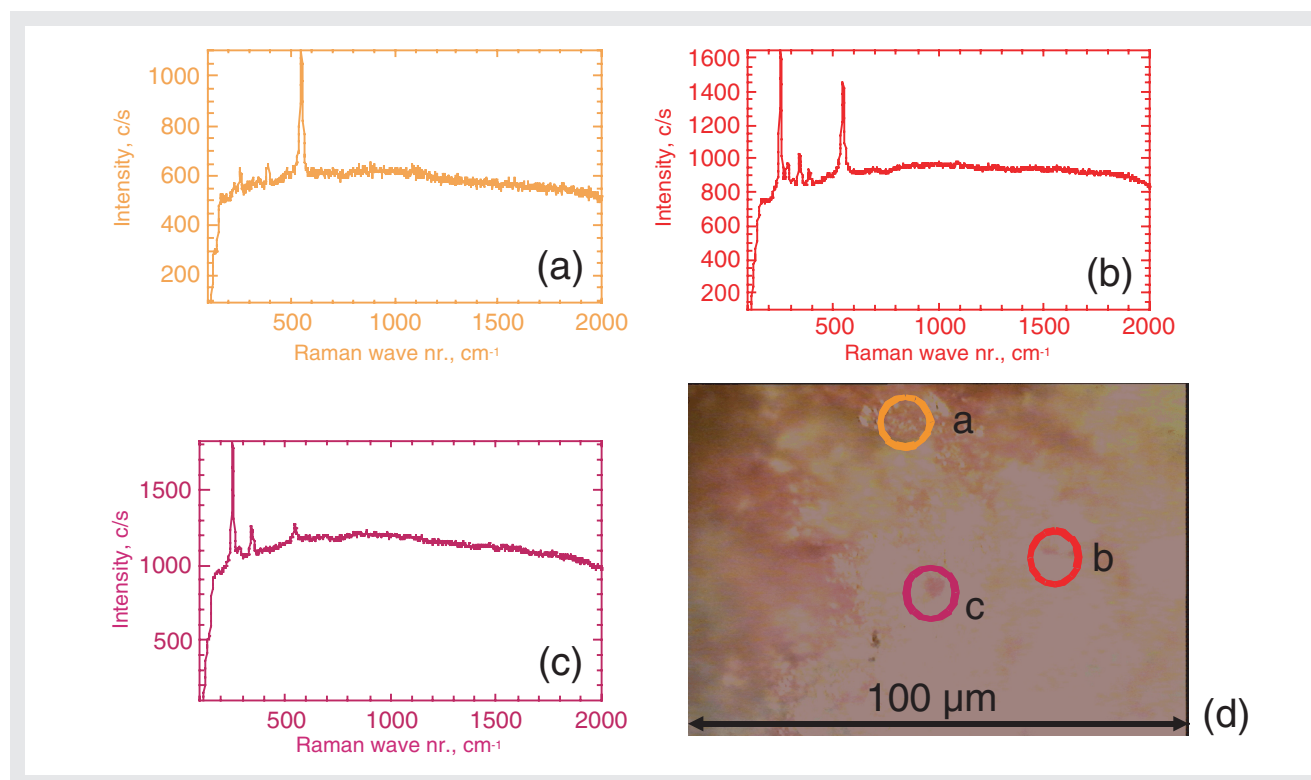


Figure 5 Raman spectra from different locations in the orange-red areas of the shield shown in Figure 2(b) (a) mainly minium, (b) mixture of cinnabar and minium and (c) mainly cinnabar, but with the main Raman line of minium still visible at 548 cm^{-1} . In set: high magnification optical photograph of a small area of the orange-red area indicating the measurement positions. In all spectra a fluorescence background due to the presence of the paper and the pigment binding medium can be observed.

added, the Raman analysis of individual pigments grains is relatively straightforward. Experience with the analysis of oil paintings or of samples taken from oil paintings shows that also from these more binding medium-rich materials, XRF and Raman spectra can be obtained by means of the combined μ -XRF/ μ -Raman spectrometer^[4].

Conclusion

In this paper, the usefulness of a combined μ -XRF/ μ -Raman instrument, which combines the advantages of fast elemental analysis provided by the X-ray fluorescence part of the apparatus with the highly specific fingerprinting capabilities of Raman spectroscopy, has been illustrated for identification of pigments in the cultural heritage investigations. The instrument is able to analyze a large work of art or other artifact without destruction, since its measurement head is sufficiently small. The instrument will also be used in other fields that the cultural heritage area, for example to gather objective evidence in criminal investigations or for soil analysis.

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Reference

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