



Development of a new portable X-ray powder diffractometer and its demonstration to on-site analysis of two selected old master paintings from the Rijksmuseum

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ABSTRACT

A portable X-ray powder diffractometer (p-XRD) PT-APXRD III has been developed for on-site analysis of paintings and archaeological samples. By using a Cu anode X-ray tube and a silicon drift diode (SDD) detector, diffraction patterns with a high signal-noise (S/N) ratio can be recorded. The X-ray tube can be operated at a maximum voltage of 60 kV, which makes it possible to simultaneously record X-ray fluorescence spectra up to the high-energy region. The total weight of this instrument is 16 kg, which can be carried anywhere and the goniometer unit (5.6 kg) can be placed on a tripod for analysis of mural paintings. We brought the instrument to the Rijksmuseum in the Netherlands to examine its applicability for the analysis of oil paintings. We successfully analyzed two seventeenth-century oil paintings by Johannes Vermeer and Jan Davidsz de Heem (copy after). Ultramarine blue, lead-tin yellow type I, and Naples yellow were identified from the diffraction patterns, demonstrating the high practicality of this instrument. Furthermore, it was found from the SEM-EDX analysis of a paint cross section that the yellow pigment was applied in separate layers rather than being mixed. This diffractometer will be commercially available in the near future and will have many applications in the field of material analysis.

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1. Introduction

1.1. Background of instrument development

X-ray powder diffraction (XRD) analysis is an essential tool for the identification of crystalline phases; is also among the most effective analytical methods for identifying art objects and archaeological crystalline substances such as pigments and minerals. Recently an advanced chemical imaging system, macroscopic X-ray diffraction (MA-XRD), suitable for two dimensional analysis of traditional oil paintings was developed [1]; however, this system imposes several constraints on the type of artworks/samples that can be analyzed. Since the instrument operates in transmission mode the material slab under investigation cannot be very thick or contain strongly X-ray absorbing elements, nor can this technique be used for mural paintings as the object under investigation needs to be moved during the scanning/imaging

experiment. Moreover, the instrument is not (very) portable, which is a key aspect of the present paper.

If destructive analysis is possible and a sample can be brought to an analytical facility, conventional powder diffractometers are suitable. However, in many cases, it is prohibited to transport samples outside archaeological sites or museums, and non-destructive analysis is a major premise. In addition, some paintings (canvas, panel or mural) are extremely large. The most effective solution to such problems unique to cultural properties is to bring portable analytical instruments directly to the archaeological site or the museum where the works are on display.

Recently, many efforts have been dedicated to the development of portable XRD instruments; so far several groups, such as NASA (DUETTO) and C2RMF (Louvre Museum, Paris France), have reported on portable devices [2–8]. The p-XRD instruments developed so far can be divided into two types. One type uses a conventional goniometer-based diffractometer in which data are obtained by scanning the detector and/or X-ray source such as the PT-APXRD III developed here; the other makes use of area detectors such as charge-coupled devices (CCDs) or imaging plates (IPs) and do not employ

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detector/tube movements. The devices developed by NASA and C2RMF are of the latter type. As described above, p-XRD systems are being developed by several manufacturers. The most recently developed instrument is the Surface Monitor by Assing [8]. However, the impact of portable X-ray powder diffractometers still significantly lags that of portable X-ray fluorescence (XRF) spectrometers, of which the hand-held type has been commercialized by many companies and is widely used [9,10]. For these reasons, since 2003 we have been developing a portable X-ray powder diffractometer with a view to commercialization [11–14]. Furthermore, we continue to improve the device by employing the resulting equipment for the characterization of various cultural artefacts, including the analysis of national treasures of Japan [15]. In the following section, the development process and improvements with regard to the previous model are explained.

1.2. History and progress of instrument development

The Development of the initial PT-APXRD I device began in 2001. The instrument was used for analysis in ancient ruins of the New Kingdom at Saqqarah (Egypt) immediately after its development [12]. We added the functionality of an X-ray fluorescence spectrometer to the diffractometer by utilizing a Silicon PIN Photodiode detector in 2007 [14]. As a result, simultaneous and complementary XRF and XRD analysis became possible in the PT-APXRD II instrument which allows to identify materials with high reliability. As there is no need to move the sample when switching between XRD and XRF analysis, a great advantage of this system is that it is possible to analyze exactly the same location on a large artefact. Please refer to references [10] to [12] for details of the previous instrumental improvements.

After 15 years of experience with archaeometric analyses of cultural heritage materials, we have now developed an innovative portable diffractometer, the PT-APXRD III, which is especially designed for the analysis of paintings. A Moxtek® MAGPRO 60 kV 12 W Cu X-ray source and energy dispersive SDD detector were introduced to replace the 30 kV X-ray tube and Si-PIN detector of the previous model. As a result, a maximum operating voltage of 60 kV could be realized, enabling us to obtain diffraction patterns with high S/N ratio and XRF spectra up to the high-energy region (50 keV) due to white X-ray excitation. The specifications of this instrument are shown in Table 1 and are compared with those of the Surface Monitor [8], a recently developed commercially available diffractometer. As can be seen from Table 1, a relevant characteristic of the latter diffractometer is its lighter weight (3.5 kg) as compared to our instrument (5.6 kg). In addition, the Surface Monitor is equipped with powerful XRD pattern matching software based on ICDD database. In the following section, we outline the developed instrument.

Table 1
Specifications of the newly developed portable X-ray powder diffractometer PT-APXRD III compared with the Surface Monitor (Assing, Rome, Italy).

| | PT-APXRD III | Surface monitor |
|--|---|--------------------------------|
| Manufacturer | Techno-X, Japan | Assing S.p.A., Italy |
| Optic system | θ - θ goniometer | θ - θ goniometer |
| Minimum step | 0.01°/step | 0.1°/step |
| X-ray tube | Cu | Cu |
| Maximum tube voltage | 60 kV | 30 kV |
| Maximum output power | 12 W | 15 W |
| Detector | SDD | Si-PIN |
| Energy resolution (Mn-K α FWHM) | 140 eV | 260 eV |
| 2 θ resolution (20–30°) | 0.2–0.5°(selectable slit) | ? |
| Beam size | 1 mm Φ –1(W) \times 4(H) mm (selectable slit) | 9(W) \times 2.5(H) mm |
| Scan range (2 θ) | 0–90° | 0–90° |
| Wall surface scan range (2 θ) | 28–90° | 20–90° |
| Weight: goniometer (total) | 5.6 kg(16 kg) | 3.5 kg |
| Commercially available | Not yet | Yes |

1.3. Description of the instrument

The PT-APXRD III is composed of a goniometer unit, a measurement-controller unit, and a laptop computer. When carried, all of these can be placed in an aluminum case, and the total weight is 16 kg, which is excellent for portability. Fig. 1 shows a photograph of the setup for analyzing paintings with this system. Since the goniometer unit (weight 5.6 kg) can be set on a tripod, it can be used for studying large artworks and mural paintings. Fig. 2 shows a schematic diagram of the goniometer system. We adopted Cu as the target of the X-ray tube, and a SDD as a detector. Since Cu is used as a target of the X-ray tube, the background intensity becomes high when Cu containing materials are analyzed. However, past experiences show that, in general, crystalline compounds can be identified without serious problems.

X-rays from the tube are focused by a slit and collimator and are irradiated onto the sample. Since the detector can distinguish Cu-K α X-rays from others, it is unnecessary to monochromatize the primary X-rays by a filter or monochromator. Both the X-ray tube and the detector move along an arc-shaped rail on the base plate, around the θ -rotation axis of the goniometer. The operation of the goniometer, the generation of X-rays, the start and end of the measurement, etc., are controlled by dedicated software on a laptop computer.

In terms of mechanical development, the concept of the PT-APXRD III remains very similar to that of a conventional goniometer-type diffractometer. In order to increase the analytical accuracy and mobility of the goniometer, an optical encoder system was introduced into the device for the first time. Encoder signal processing improves the signal stability with a position error typically lower than 30 nm, leading us to a θ angle resolution of the order of 0.01° per step, which is 10 times better than with the earlier PT-APXRD II and the Surface Monitor instruments.

Previous X-ray sources for the PT-APXRD series were a side-window glass tube covered with radiation shielding, connected to a high voltage generator. The total weight of the X-ray source was about 4–5 kg, which is bulky and not suitable for wall painting analysis. In the most recent development phase, the X-ray tube and high voltage generator were replaced with an end-window mono-block Moxtek MAGPRO 60 kV 12 W X-ray generator. The tube has a built-in high voltage generator with a total weight of only 825 g. This significantly improved the instrument's portability and analytical flexibility. The compact design of the tube also allowed the thick high voltage cable of the glass tube to be replaced by a slim AC 110/220 V power cable and a USB control cable, further improving the portability of the instrument and making it more suitable for on-site analysis. The end-window X-ray tube allowed us to use a lower



Fig. 1. View of on-site analysis of Rembrandt, 'The Jewish Bride' (c. 1665–c. 1669) using the newly developed portable X-ray powder diffractometer on a tripod. Gallery of Honour, Rijksmuseum, Amsterdam, December 2015.

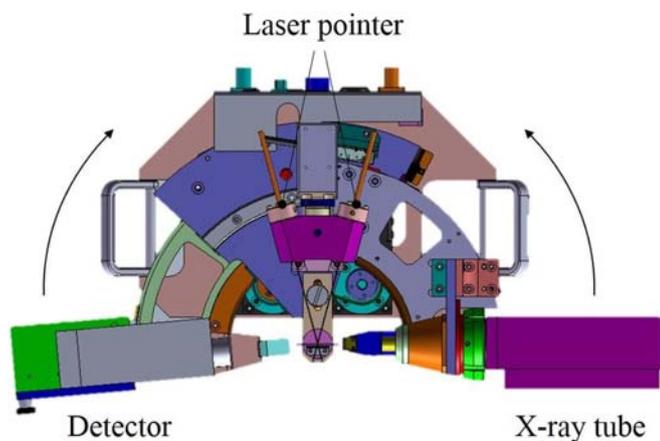


Fig. 2. Schematic diagram of the goniometer.

starting 2θ angle, which means that more complete XRD patterns can be collected. The most important advantage point of using a MAGPRO X-ray tube for this XRD instrument is its adaptability, with an easy-to-remove and switchable instrumental design, allowing to instantly exchange X-ray tubes with different X-ray target materials on an archaeological site or in a museum. This gives us more flexibility when XRD data in a wider 2θ range and a higher XRF excitation efficiency. In terms of software development, a package including several essential XRD and XRF spectral inspection and manipulation tools was developed.

In the case of a sample coated on a glass plate, the sample is fixed to the mechanical θ zero point using a dedicated sample holder. When analyzing an irregularly shaped sample, we remove this holder and determine the sample position with two laser pointers. Therefore, non-invasive analysis is possible even for large-sized artifacts such as easel paintings and murals. However, in the case of an irregularly shaped object/surface, shifts of the diffraction angle 2θ are inevitable. To correct for such a shift of the diffraction angle, as in the case of the apparatus we developed in the past, we estimate the offset amount $\Delta 2\theta$ from the deviation between the literature 2θ values of particular compounds, known to be present in the analyzed objects, and their measured values. This constant value is then subtracted from the measured 2θ values of the XRD peaks of the unknown compounds in the analyzed material [14].

The standard measurement conditions of PT-APXRD III are shown in Table 2. For the analysis of actual paintings, these measurement conditions are adopted.

The difficulty with on-site analysis of a painting is that it is obligatory to orient the instrument towards a vertical surface such as the wall painting is hanging on. In order to obtain sufficient information with one measurement, the measurement must begin from the lowest possible 2θ angle, implying that the instrument should approach the surface to be analyzed very closely. Great care must be taken to cautiously approach the precious artwork. In order to do so, we set the goniometer unit up on a horizontal stage and operated it so that it can be positioned more safely and precisely by laser pointers relative to the painting surface. In this instrument, it is in practice possible to measure starting from $2\theta = 25^\circ$ when analyzing a painting, making it possible to detect the major diffraction peaks of most pigments. When the measurement is started from 25° with a step width of 0.1° , the time required for one measurement is about 30 min.

1.4. Purpose of the analysis

In order to evaluate the performance of the developed instrument, spectral data were recorded from standard samples in both the XRD and XRF modes. Moreover, in order to verify the practicality, we brought this device to the Rijksmuseum in Amsterdam, Netherlands and

Table 2
Typical measurement conditions of PT-APXRD III.

| | XRD | XRF |
|---------------------------------------|---|-------------------|
| X-ray tube | Cu target | |
| Detector | SDD | |
| Maximum exciting voltage/tube current | 60 kV/0.2 mA | |
| Exciting X-ray | Cu $K\alpha$ | Cu |
| Angular range | $5^\circ < 2\theta < 70^\circ$ $25^\circ < 2\theta < 70^\circ$ (Wall surface) | – |
| Step width | 0.1° | – |
| Scattering angle | – | 90° |
| Measurement time | 1–3 s/step | 100 s (live time) |
| Atmosphere | Air | Air |

conducted non-destructive on-site analyses of paintings. The Rijksmuseum has about 8000 works by painters from the Dutch Golden Age of the 17th-century, such as Johannes Vermeer and Rembrandt van Rijn. For two of these paintings, analyses were performed that reveal the pigments and techniques used by the painters [16,17].

2. Material and methods

2.1. Standard sample

To evaluate the performance as a diffractometer, standard silicon powder (NIST SRM 640c) was applied on a glass plate by a smear mount method. The measurement conditions were: tube voltage of 50 kV, tube current of 0.24 mA, and step width of 0.1° . A NIST SRM 610 standard glass sample was used to evaluate the XRF functionality of the instrument. The same tube conditions were used as for the XRD measurements.

2.2. Oil painting

2.2.1. Johannes Vermeer, 'Woman Reading a Letter', c. 1663, oil on canvas (Rijksmuseum SK-C-251).

This work was created in c.1663 by the Dutch painter Johannes Vermeer (1632–1675). It is painted in oil on canvas measuring 46.5×39 cm. We focused on the blue areas in this painting. Vermeer favored the blue pigment called ultramarine blue, and used it in many works [18,19]. This pigment is sometimes called "Vermeer blue." XRD and XRF analyses were performed by means of the PT-APXRD III instrument at four points including the blue jacket (P1, blue area) shown in Fig. 3 (a). The other analysis points were in the tablecloth (P2, gray area); tablecloth (P3, dark blue area); upholstery of the chair (P4, blue area).

2.2.2. Jan Davidsz de Heem (copy after), 'Still Life with Fruit and a Lobster', 1640–1700, oil on canvas (Rijksmuseum SK-A-139)

This is a work created in the period 1640–1700. It is a presumed copy of a work by the Dutch painter Jan Davidsz de Heem (1606–1684), 'Still Life with a Lobster', c. 1669, in the Gemäldegalerie Alte Meister in Dresden (Gal.-Nr. 1260), Germany. It is painted in oil paint on canvas, measuring 70×39 cm. This painting is worked up in various colors, and we focused on the yellow pigments. In the 17th century, when this picture was created, many kinds of yellow pigments such as orpiment, lead-tin yellow, Naples yellow, and lead-tin-antimony yellow were available [20–23]. XRD and XRF analyses were performed on the yellow part of the peach shown in Fig. 3(b).

2.3. SEM-EDX

From 'Still Life with Fruit and a Lobster,' a micro paint sample was taken and prepared as a cross section, on which light microscopy and two dimensional microbeam analysis with a SEM-EDX instrument were carried out. The sample was analyzed under low vacuum (80 Pa)

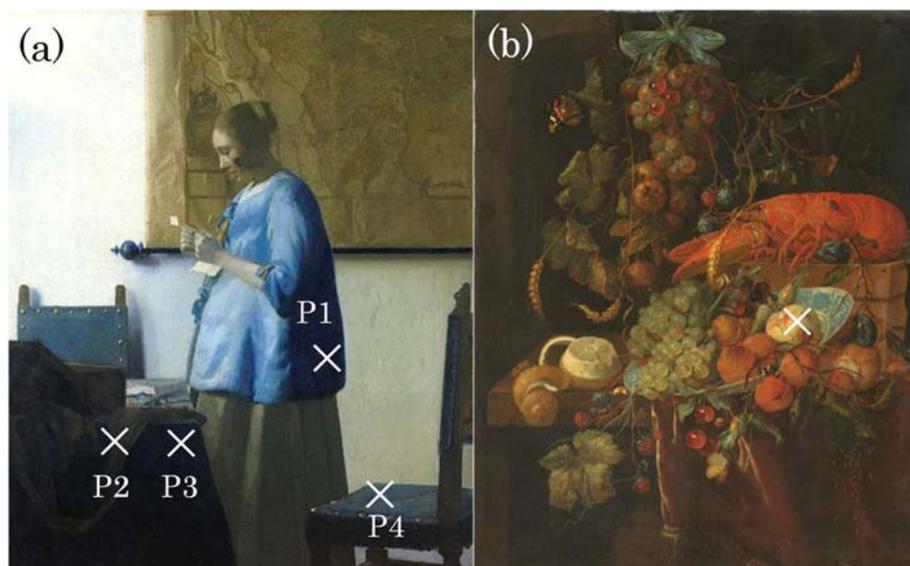


Fig. 3. Analyzed points by X-ray powder diffractometer: (a) Johannes Vermeer, *Woman Reading a Letter*, c. 1663, Rijksmuseum, Amsterdam, and (b) Jan Davidsz. de Heem (Copy after), *Still Life with Fruit and a Lobster*, 1640–1700, Rijksmuseum, Amsterdam.

using a FEI Nova NanoSEM 450 variable pressure electron microscope at an accelerating voltage of 20 kV. The SEM was outfitted with a Thermo EDX system to obtain the elemental composition of the pigments within the paint layers.

3. Results and discussion

3.1. Performance evaluation by standard sample

The calculated and measured d values and relative intensity obtained by measuring the NIST SRM 640c silicon standard sample are shown in Table 3 together with the corresponding PDF data (Silicon: PDF 27-1402). Table 3 shows that both the d values and intensity match well with the PDF data, and that the diffraction angle 2θ can be measured with sufficient accuracy. The calculated lattice parameter $a = 5.472$ (2) Å is in a good agreement with SRM640c data of 5.4311946(9) Å and the PDF data of $a = 5.441$ Å.

To evaluate the XRF detection capability, we used NIST standard glass sample SRM 610 and estimated the lower limits of detection (LLD) by means of the following equation:

$$LLD = 3 \frac{C}{I_{\text{net}}} \sqrt{\frac{I_{\text{back}}}{T}}$$

C is the certified concentration of the standard sample, I_{net} is the peak intensity, I_{back} is the background intensity, and T is the measurement time in seconds (here, 100 s). The XRF spectrum obtained for SRM 610 is shown in Fig. 4, and Table 4 shows the LLD calculated from the $K\alpha$ ray of Ti, Fe, Sr, Sb, and Ba. The LLD's of the Surface Monitor instrument are 65 ppm for Fe, 250 ppm for Sr and 200 ppm for Ba when 1 mm slit is used [8]. From these results, it can be observed that the PT-APXRD III instrument has a suitable XRF detection capability in

both the low-energy and the high-energy region, superior to that of the Surface Monitor instrument.

3.2. Application to onsite analysis of two selected old master paintings from the Rijksmuseum

3.2.1. 'Woman Reading a Letter'

The X-ray diffraction pattern of the blue area of the female jacket (P1) and the gray part of the tablecloth (P2) is shown in Fig. 5. Lazurite ($\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{S}_x$), hydrocerussite (lead white, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and calcite (CaCO_3) were identified at both measurement points. It should be noted that the diffraction peaks in Fig. 5 show significant broadening, which is typical for diffraction peaks of the pigment in a painting because of the thickness of the paint layer. The diffraction data of P1 Lazurite is shown in Table 5 together with the PDF data (Lazurite-C: PDF 17-0749). From Table 5, it can be seen that the d values of both are very close. On the other hand, regarding the intensity, a 222 reflection was observed as the strongest line, while the other diffraction lines were several tens of percent different from the PDF data. This is thought to be caused by overlapping of peaks with other pigments. However, this degree of variation in intensity does not become a significant problem in practical identification.

The lattice parameter of lazurite was calculated to be $a = 9.093$ (7) Å, which is very close to the literature value of $a = 9.090$ Å. Since lazurite is the main component of ultramarine blue, it is possible to

Table 3
X-ray powder diffraction data of silicon, standard reference material NIST-SRM640c.

| NIST-SRM640c | | | Silicon (PDF:27-1402) | | |
|--------------|----------------------------|------|----------------------------|--------------|------|
| hkl | $d_{\text{meas}}/\text{Å}$ | Int. | $d_{\text{meas}}/\text{Å}$ | $d/\text{Å}$ | Int. |
| 111 | 3.173 | 100 | 3.1356 | 3.1355 | 100 |
| 220 | 1.936 | 52 | 1.9201 | 1.9201 | 55 |
| 311 | 1.649 | 28 | 1.6375 | 1.6375 | 30 |

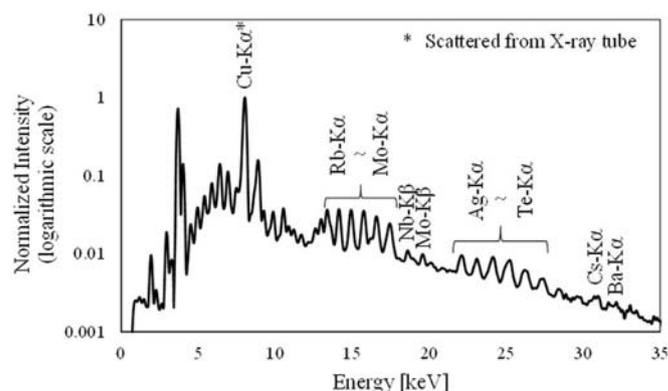


Fig. 4. X-ray fluorescence spectrum of glass standard reference material NIST-SRM610.

Table 6
X-ray powder diffraction data of 'Still Life with Fruit and a Lobster': yellow part of peach.

| Yellow pigment | | Pb ₂ SnO ₄ (PDF:24-0589) | | | Bindheimite (PDF:42-1355) | | |
|----------------|------|--|------|-----|---------------------------|------|-----|
| d/Å | Int. | d/Å | Int. | hkl | d/Å | Int. | hkl |
| 3.30 | 100 | 3.323 | 100 | 211 | | | |
| 3.02 | 77 | | | | 3.004 | 100 | 222 |
| 2.76 | 67 | 2.762 | 20 | 310 | | | |
| 2.61 | 87 | | | | 2.603 | 30 | 400 |
| 2.00 | 47 | 2.008 | 8 | 411 | | | |
| 1.85 | 69 | | | | 1.840 | 30 | 440 |
| 1.80 | 34 | 1.795 | 14 | 402 | | | |
| 1.72 | 31 | 1.724 | 17 | 332 | | 24 | |
| 1.57 | 37 | | | | 1.569 | | 622 |

cross-section(s). From this, it was found that the paint was built up of three layers, with two yellowish paint layers applied on top of the gray ground. From the EDX spectra of the two yellow layers shown in Fig. 8, we can see that Pb and Sn are present in layer 3, and Pb and Sb in layer 2. Together with the results of XRD, it was found that the two yellow pigments were not mixed, but that lead-tin yellow was superimposed on top of Naples yellow. From these results we found that we must be careful to interpret X-ray fluorescence analytical data of paintings when pigments are layered because of the larger penetration depth of the X-rays used for XRF can cause a simultaneous detection of different layers. In this case, as discussed above, a combination of X-ray diffraction and SEM-EDX, which is a surface analysis technique, of a cross section provides the most reliable result.

4. Conclusion

We recently developed a new goniometer-type portable X-ray powder diffractometer PT-APXRD (being the third model of this instrument), aiming for research applications on cultural heritage objects. By using a high power Cu X-ray tube and SDD as a detector with high energy resolution, a maximum voltage of 60 kV was realized and enabled us to obtain a diffraction pattern with a high S/N ratio and an X-ray fluorescence spectrum with high energy resolution up to the high-energy region. This was proven by evaluating the performance of the instrument on standard samples and its application to painting analysis. In Vermeer's 'Woman Reading a Letter,' the p-XRD instrument revealed the use of Vermeer's most preferred pigment, ultramarine blue. We also found that two types of yellow pigment were used in 'Still Life with Fruit and a Lobster,' demonstrating that it is a highly practical

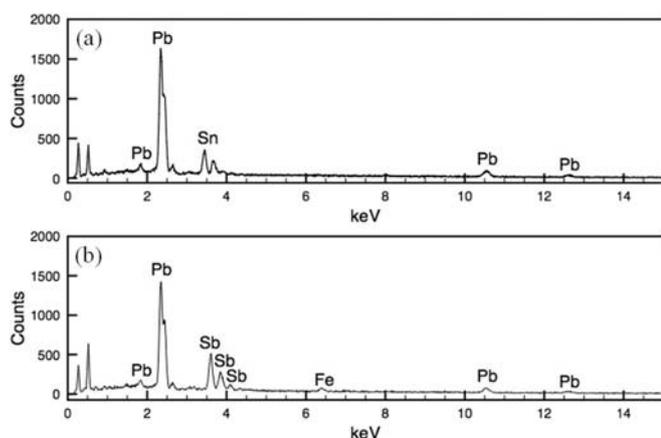


Fig. 8. EDX spectra of yellow part of peach: (a) layer 3 and (b) layer 2.

instrument with sufficient portability. XRD has drawbacks in that it is unsuitable for elucidating the layer structure because information in the depth direction overlaps. If the purpose of the analysis is to reveal the layer structure, it is desirable to use this instrument in combination with a cross-sectional analysis of a micro-sample with SEM-EDX. This field portable diffractometer has unlimited applications not only in painting studies, but also in archaeology, environmental science, geological sciences etc. and will be commercially available in the near future.

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