Case Study

Nondestructive identification of gemstones by using a portable XRF–XRD system: an illuminating study for expanding its application in museums

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Abstract

Nine gemstone samples were analysed by using a portable X-ray fluorescence–X-ray diffraction (XRF–XRD) system without any destructive preparation processes. The samples were measured by groups based on the transparency and the complexity of molecular structure. The XRF and the XRD measurements for each sample were performed simultaneously. The key experimental parameters were optimized in order to obtain XRD patterns acceptable for phase identification in a limited time. The XRF spectrum of each sample was analysed first to acquire the elemental composition qualitatively, and the information was then applied to refining possible phases. The phase analysis process of each sample was described in detail and the most likely phases were determined. Normal XRD experiments were conducted in order to verify the results. Advantages, disadvantages and applicable range of the system were analysed. The results indicate that the portable XRF–XRD system can be applied to identifying particular gemstones effectively, while single-crystal gems may not be identified very well. Wider recognition and application of the portable XRF–XRD system in cultural heritage and gemological fields call for hardware development, software updating and more real application cases.

Keywords Nondestructive testing · Gem · XRF–XRD coupled technique · Portable apparatus · Museum · Cultural heritage

1 Introduction

Gems are always of special meaning on both human's material life and spiritual world. Some gems are either rarely found [1–3] or of amazing scale [4–6] so that the museums conserve them as priceless collections. Undoubtedly, it is important for museums or private collectors to evaluate the authenticity before reserving the objects. Due to the preciousness and the unique character, destructive methods are usually not applied to identifying the gems. Instead, the nondestructive methods play predominant roles. Traditionally, the physical characteristics

or phenomena for differentiating gemstones include [7]: colour, gloss, transparency, hardness, cleavage, density, thermal conductivity, refractivity, birefractivity, reflectivity, spectral selective absorption, chromatic dispersion, pleochroism, polarised light, fluorescence, phosphorescence, and special optical effects, etc. Some of these methods are based on general characters of bulk materials, such as colour and hardness, while some others are only applicable for particular kinds of gemstones. Along with the development of science and technology, modern analytical techniques have more actively participated in the gem identification field and have played significant

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roles. The most widely recognised instrumental methods are infrared (IR) and Raman spectroscopies. Both the transmittance and the reflectance modes of IR spectroscopy are applicable [8, 9]. The former mainly provides the spectral information about the shortwave region (wavenumber $> 2000\text{ cm}^{-1}$) such as the existence of constitution water, organic inclusion and other organic matters for gem optimisation [8, 10–12], while the latter is useful for getting the spectral information about the long wave region (wavenumber $= 2000\text{--}400\text{ cm}^{-1}$), which is an effective method for determining the gem species [8, 13]. Thus, the complete IR spectra information about gems can be obtained by the combination of transmittance and reflectance measurements. The advantages of IR spectroscopy are also reflected by the high availability of instruments and the mature and complete database of standard materials [14]. On the other hand, as a rising technique, Raman spectroscopy has been commonly introduced into gemmology for only about 20 years, but with the advantages like quick measurement, low sample content requirement and high sensitivity, it is appreciated by museums [15]. Raman spectroscopy is applied to identifying different gems [15], determining the chemical composition [16, 17], and deducing the origin [18–20]. Both IR and Raman methods are regarded as nondestructive provided that appropriate working modes and parameters are adopted. However, different gems may have similar IR absorption peaks at certain positions [9]; meanwhile, IR spectroscopy is a method for detecting chemical groups rather than phases. These points indicate that IR spectroscopy cannot be singly employed as an absolute method for identifying gems. Compared with IR, the Raman method is weak in the scale of standard spectra database, the repeatability of measurement results, and the availability of instruments. Therefore, searching for other instrumental methods with higher reliability is a major issue in gemmology.

As a technique for determining the existence of elements, X-ray fluorescence (XRF) spectrometry has been widely used in scientific researches and engineering fields [21–24]. XRF spectrometry can be divided into wavelength-dispersive XRF (WD-XRF) and energy-dispersive XRF (ED-XRF). WD-XRF is developed for qualitative and quantitative analyses of elements with atomic number ≥ 4 (Be), which features the quantitative function provided that samples are properly prepared and calibration is strictly operated; while ED-XRF is applicable for qualitative and semi-quantitative analyses of elements from atomic number 9 (F) to 92 (U) in principle [25], which features quick and sensitive measurement without pretreating or touching samples, just fitting in with the needs of the museum field [24]. The metallic elements in alloy-based artefacts [26, 27], antique polychromy [28], paintings [29, 30] and porcelains [31, 32] were all successfully detected

by different types of XRF measurement. Compared with WD-XRF, ED-XRF is commoner in the museum field due to lower cost, simpler structure and easier operation as well. However, ED-XRF is not a rigorously quantitative method, which means the data measured are only used for reference. Moreover, XRF instruments are weak in detecting light elements; also, the elemental measurement results only characterise one face of the samples, while for the other face, the phase composition of particular samples (such as patinas), the XRF spectrometry is basically incapable. These points indicate that XRF spectrometry has some intrinsic limitations as a characterisation method for cultural objects. In recent years, the occurrence of portable XRF analysers has further expanded the application of XRF spectrometry in various walks of life [33]. Especially, their cultural heritage applications have attracted even more attentions [24, 33]. Higher portability makes them more suitable for field detection, which is just a special demand of museums [33, 34]. Nevertheless, the higher portability is at the expense of function or measurement precision in a sense, showing the two sides museums have to think about when they purchase the instruments.

Differing from element-measuring XRF, X-ray diffraction (XRD) is a method for detecting material phases. According to the principles of crystallography, solid materials are generally divided into three types based on the ordered degree of their microscopic structures or crystalline modes, as single-crystal, poly-crystal, and amorphous solid [35]. XRD is the most reliable method for identifying crystalline materials [36], while amorphous solids tend to form widened dispersive peaks in XRD patterns. The working mode of XRD instruments is divided into two types, as the single-crystal XRD and the powder XRD, which are respectively suitable for the analyses of single-crystals and poly-crystals in principle. The powder XRD is commoner and has a wider application range. In fact, single-crystal materials can also be identified by powder XRD provided that they are ground to powders as well as that the condition of the Bragg's Law is met while the systematic absence does not occur [37, 38]. On the other hand, nondestructive identification of single-crystal materials by powder XRD is also realisable, but some specific conditions must be met [37]. Sampling is not an essential process in powder XRD experiments for poly-crystal materials as well, but it is the guarantee of getting high-quality standard diffraction patterns [37]. The nondestructive mode is useful for getting diffraction data from bulk materials unsuitable for breaking or sampling, but the pattern quality may not be very satisfactory. Thus, performing powder XRD through sampling is usually the primary choice, while the nondestructive mode is a favourable complement. As a mature method, XRD is equipped with a huge database supplied by International Centre for Diffraction Data (ICDD). Users

compare their own patterns with 672,313 reference data to determine the most likely material phases [36]. XRD plays an irreplaceable role in chemistry, material science and engineering fields. As for the cultural heritage field, the application of XRD is far less popular than that of XRF due to the sampling process which is prohibited in principle [36]. Moreover, the sample volume demand also limits its wider application in the cultural heritage field. Therefore, XRD is traditionally applied to identifying corrosion products of metallic objects [39], bulk objects with suitable sizes [40], or objects less valuable which can be sampled carefully [41, 42], but a very cautious approach is always taken concerning the priceless [43]. Along with the development of science and technology, more powerful apparatuses and smarter programs are introduced to the XRD method constantly, favouring its wider and deeper application in the cultural heritage field. One of the main advances is the realisation of portable analysers, which lowers the threshold of XRD experiments and makes it more suitable for museum use [36]. Portable XRD analysers with nondestructive feature are welcomed by museums at present, but their applications in the research and conservation of cultural heritages seem limited to several object types such as ancient coloured pottery [44] and paintings [45, 46], which may be associated with the inherent demand of the XRD measurement, as samples having flat surfaces are preferred.

The combination of XRF and XRD is a revolutionary idea which may not only expand the application range of XRF, but also provide people with reliable information to refine the possible phases. In a word, the advantages of XRF, like the nondestructive feature and the qualitative and semi-quantitative functions for elemental analysis, can be combined with the phase identification function of XRD, which may convert the traditionally destructive XRD to a nondestructive method suitable for specific objectives. Several research groups' work jointly advances the establishment and development of the relevant theories, the practical systems and the actual applications [36, 47–60]. According to a review, five systems are especially noteworthy [36]: the PT-APXRD system designed by Japanese researchers for identifying pigments on ancient Egyptian potteries [47]; the Assing S. p. A. commercial system installed at the Laboratorio di Analisi Non Distruttive In Situ (LANDIS), Laboratori Nazionali del Sud, Istituto Nazionale di Fisica Nucleare, Italy, for characterising pigments present in ancient Roman frescos [48]; the CheMin instrument developed for National Aeronautics and Space Administration (NASA)'s Mars Science Laboratory mission [49]; the Duetto instrument employed by the Getty Conservation Institute for characterising art objects and antiquities [50]; and the system used in the Louvre Museum for identifying pigments on a mural painting [51]. In addition to reviewing

and comparing the characteristics of different portable XRF–XRD systems, the authors of the article also pointed out the key factors for evaluating the practicability of the portable XRF–XRD systems for museum use, such as availability, safety of the measurement process, power, pattern resolution, measurement range, software function, and mobility [36]. It is easy to find that the applications of the systems mainly concentrated on analysing pigments on ancient artworks, manuscripts or different kinds of painting, which ran through the researches by a Japanese group [47, 52, 53] and a French group [51, 54–57]. With their efforts, this integrated technique is popularly recognised in Japan and Europe for museum use currently. Moreover, Assing S. p. A. (Italy) also makes significant efforts to develop and spread this technique [48, 58–60].

As for the identification of gems, it is significantly advantageous to apply the nondestructive XRF–XRD technique. Compared with traditional indirect methods, the XRF–XRD coupled method measures the elemental and phase composition of gems, which is unique for each sample. Also, the identification task can be finished with less time compared with conducting a series of experiments. On the other hand, XRD is superior to IR due to higher uniqueness of pattern characteristics; while the Raman spectroscopy is not equal to XRD because of less comprehensive database, higher difficulty in spectrum interpretation, and the laser which may destroy the sample surface if the energy is not set correctly [36]. Undoubtedly, the nondestructive XRF–XRD technique can be recognised as a valuable method in the gem identification field if the XRF and the XRD functions work in coordination efficiently. However, the applications of similar systems are focused on cultural objects like paintings at present, while that on gemmological field has not been studied adequately, as few relevant works have been reported so far [36]. In fact, analysing gemstones using XRF and XRD apparatuses separately is more commonly seen [61–63], indicating that availability, option, function, practicability, and operation of the XRF–XRD integrated systems are the main considerations when people try to find the best methods for gem identification.

In this work, the author designed a series of experiments to analyse the elemental and phase composition of several gemstone samples by using an Assing Surface Monitor portable XRF–XRD system. The system is composed of a removable apparatus, a controlling laptop and a multifunctional case, which are connected by cables. The appearance of the whole system, and the surface of the operation software, are respectively shown in Figs. 1 and 2. The samples were analysed without any destructive sample preparation processes. The XRF and the XRD measurements were performed on the system simultaneously. The XRF results were analysed first and then applied to

Fig. 1 The whole system including a controlling laptop (left), a removable apparatus (middle) and a multifunctional case (right)

Fig. 2 The initial surface of the software

refining the possible phases recognised by the system. The phase identification results were verified by conducting normal XRD experiments. The study shows great potential for further applying the XRF–XRD integrated method to more real cases of gem identification.

2 Materials and methods

2.1 Materials

The gemstones analysed in this study were purchased online. The sellers claimed that they were artificial emerald, chrysoprase, hematite, larimar, lazurite, nephrite, serpentine, sugilite and yttrium aluminium garnet (YAG), respectively. Artificial emerald and YAG are single-crystals in theory, while

the others are polycrystalline. All of them had at least one flat surface. Hematite, larimar, lazurite and sugilite were opaque; chrysoprase, nephrite and serpentine were translucent; and artificial emerald and YAG were transparent. The appearances of them are shown in Fig. 3.

2.2 XRF and XRD measurements

Several glass slides were stacked up to play the role as a sample carrier. The stones were placed on the glass slides in turn to perform the XRF and XRD experiments. The flat surface of each sample was placed up to receive the X-ray beams. A small ball of plasticine was applied to fixing the samples and keeping the flat surfaces as horizontal as possible. After these preparation procedures, the parameters of XRF and XRD experiments were set as shown in Fig. 4. The acceptable working distance from the laser interferometer to the sample surface is 94.85 ± 0.20 mm, but in this study the distance was more strictly set as 94.85 ± 0.05 mm to prevent detection process from occasional vibration more effectively. The measurement scene and the laser spot are shown in Figs. 5 and 6, respectively.

The experimental order of the stones was hematite, larimar, sugilite, lazurite, chrysoprase, nephrite, serpentine, artificial emerald and YAG based on both the transparency and the complexity of their theoretical molecular structures.

The X-ray penetration depth can be calculated using Eq. 1:

$$Z_m = 0.033m_a \cos \alpha (E_i^{1.7} - E_k^{1.7}) / \rho Z \quad (1)$$

In Eq. 1, Z_m is the X-ray penetration depth (μm); m_a is the average atomic mass of the bombarded area; α is the tilt ($^\circ$); E_i is the energy of the incident electron beam

Fig. 3 The appearances of the gemstone samples. **a** Artificial emerald. **b** Chrysoprase. **c** Hematite. **d** Larimar. **e** Lazurite. **f** Nephrite. **g** Serpentine. **h** Sugilite. **i** YAG

Fig. 4 The parameter setting surface. For XRF, the main parameters included step acquisition time (10 s), pre-heating time (0 s), tube angle (45°) and detector angle (45°). For XRD, the main parameters included working voltage (50 kV), tube current (75 μ A), XRD energy (9.71 keV, Au target), start angle (20°), stop angle (70°) and step angle (0.1°)

Fig. 5 The experimental scene. The left arm was the Newton Scientific Inc. Mini-X X-ray tube (50 kV, 75 μ A), the right arm was the Amptek X-123 SDD X-ray spectrometer, and the middle was the hematite sample fixed at the plasticine with glass slides

(keV); E_k is the critical excitation energy of the target material (keV); ρ is the density of the bombarded area (g/cm^3); Z is the average atomic number of the bombarded area. In the case of the hematite sample, for instance, $m_a = 32$, $\alpha = 45^\circ$, $E_i = 50$ keV, $E_k = 9.71$ keV, $\rho = 5.2$ g/cm^3 , $Z = 15.2$, thus the theoretical $Z_m = 6.85$ μm when the XRF experiment was performed. This simulation is more valuable for further studies on polycrystalline inhomogeneous samples.

For determining the optimal conditions, the step angle was also adjusted to 0.05° and 0.02° (2θ), and the voltage

Fig. 6 The laser spot illuminated on the hematite sample (spot diameter = 2 mm)

was adjusted to 40 kV and 30 kV when the first sample (hematite) was tested.

For comparing the pattern appearances and verifying the phase identification results, normal XRD experiments were performed on all the gemstone samples by using a Rigaku SmartLab XRD analyser (Cu K α , 40 kV, 100 mA).

All the raw data are given in the online electronic supplementary material (ESM).

2.3 Analysis of the XRF spectra

Once the measurement of a sample was finished, the XRF spectrum was analysed. First, buttons "Analysis", "XRF Analysis" and "Qualitative XRF" on the operation panel were clicked in turn to access into the XRF match surface. Then, possible elements were selected manually by considering both the characteristic lines and the detected peaks. The elemental selection range is in principle from atomic number 11 (Na) to 100 (Fm) at the XRF match surface.

2.4 Analysis of the XRD patterns

Once the analysis of XRF spectrum of a sample was done, analysis of its XRD pattern was performed. First, buttons "Analysis", "XRD Analysis" and "XRD Match" on the operation panel were clicked in turn to access into the XRD match surface. Then, buttons "Search" and "Search Match" were clicked in turn to enter the XRD search match surface (see Fig. 7). At this surface "Mineral" was selected from the database options. The possible elements detected by XRF were selected from the periodic table (in green); the "AUTO" button can be used to automatically rule out the heavy elements and inert elements not present (in red); other cells corresponded to light elements not detected or out of the application of XRF, and they can be selected, removed or left without operation according to the operator's experience. The two options, either "At least one must be present" or "All must be present", can be selected

Fig. 7 The XRD search match surface

Fig. 8 The XRD pattern fitting surface

Fig. 9 Patterns of the hematite sample. **a** XRF spectrum. **b** XRD pattern (voltage = 50 kV, step angle = 0.1°)

based on the operator's judgment as well. After these, the "NEXT" button was clicked to access into the pattern fitting surface (see Fig. 8). In this stage, the "Peaks" button was clicked first to enable the selection of characteristic peaks. Then, the "Peak Mode" button was clicked, and "MANUAL" was selected. The significantly intense peaks were selected by directly clicking on the peak positions using the mouse. The manually selected peaks can be modified by clicking the "ADD" or "DEL" buttons according to the operator's judgment. After that, the "Gauss" button was clicked to enable the Gauss fit. By clicking the "Gauss Fit" button, the selected peaks were connected by a smooth fitting curve (in blue). Other buttons were left without operation. Finally, the "SEARCH" button was clicked to enable the search for possible phases.

On the other hand, the XRD patterns acquired by normal XRD experiments were analysed by using the Materials Data Inc. (MDI) Jade 5.0 software. The standard phase data were based on the built-in database ICDD PDF-2(2004).

3 Results and discussion

3.1 Analysis of the hematite sample

Since hematite has only a single phase composition ($\alpha\text{-Fe}_2\text{O}_3$) in theory, as well as that the molecular structure of $\alpha\text{-Fe}_2\text{O}_3$ is simple, the hematite sample was selected as the first to be examined. From Fig. 9a it can be seen that the peaks for Fe were predominant while other elements could be ignored, which means only Fe should be considered when selecting the possible elements at the XRD search match surface.

The XRD search match results showed that there were 1007 possible phases when Fe was regarded as the only heavy element present, which might cost too much time for preliminary screening. For improving the analysis efficiency, a strategy was employed, as adding O, the

commonest element forming rocks, to the potential element list to see if highly matched phases can be recognised among fewer candidates. Based on this, 903 possible phases were recognised, which was still a large number for screening. In this case, the position of the measured diffraction peaks coincided with the Hematite (ICDD 24-0072) very well when the whole pattern was moved to the low angle direction for 0.37° (2θ) (see Fig. 9b). The pattern shift is caused by the inclining of sample surface. Although the samples were placed very carefully before the experiments, it is hard to make the selected surfaces absolutely horizontal by naked-eye observation and operation. Nevertheless, the pattern shift generally does not increase the difficulty of pattern analysis if the sample is put carefully, as it usually can be offset by the system ($\pm 3^\circ$, 2θ). The phenomenon was commonly observed in this study and is not further discussed below. On the other hand, the intensity of peaks seemed different from the standard, which is

Fig. 10 Normal XRD pattern of the hematite sample

probably caused by the difference between bulk sample and powder sample. Since the stones are bulk materials, their XRD patterns are different from the standard patterns acquired from powder samples [37]. In general, the combination of XRF and XRD is successful in the nondestructive identification of the hematite crystal, but it cost time to eliminate those unlikely phases by artificial comparison and judgment.

The above phase identification result was confirmed by normal XRD analysis (see Fig. 10). It can be found that the background noise was considerable when the nondestructive measurement was performed by using a normal XRD instrument. Also, the measured intensity of diffraction peaks did not coincide with the standard.

3.2 Determination of the optimal experimental parameters

In normal XRD experiments, 0.02° (2θ) is commonly selected as the step angle [41, 64–66]. For the identification of unknown gems by XRD, it is certainly favoured if samples can be measured as careful as possible so that the unobvious information like impurity and locality may be found or deduced. In this study, the step angle was also switched to 0.05° and 0.1° (2θ) to improve the pattern resolution and find out if possible to acquire the additional information. As shown in Fig. 11a, when the step angle was lowered, the patterns became more similar to normal XRD patterns in resolution. However, the cost was that it needed about 8.5 h to finish the whole measurement (0.02° , 2θ). Meanwhile, other information cannot be simply obtained due to the limitation of pattern quality. Considering the balance between pattern resolution and experimental efficiency, the author selected 0.1° (2θ) as the step

Fig. 11 XRD patterns of the hematite sample. **a** Voltage = 50 kV, step angle = 0.1° , 0.05° and 0.02° . **b** Step angle = 0.1° , voltage = 50 kV, 40 kV and 30 kV

angle because the intensity of main characteristic peaks was high enough to play the XRD search match while the weak peaks were not quite important in this search, as well as that the whole test period (about 100 min) was acceptable for preliminary identification of crystal phases in a sample.

On the other hand, the influence of the working voltage was also evaluated. The working voltage of the apparatus is limited to 50 kV, and the power cannot exceed 4 W due to safety consideration. Thus, the maximum tube current is 80 μ A in theory, but in fact the upper limit is set as 76 μ A by the manufacturer. In view of this, the tube current was fixed at 75 μ A while the working voltage was reduced to 40 kV and 30 kV in turn to observe the differences. As shown in Fig. 11b, the pattern was very similar to that at 50 kV and it remained most details when the voltage was set as 40 kV, but several platforms were observed especially in the valleys, which means the XRD pattern cannot be exhibited adequately at 40 kV. Moreover, when the voltage was further reduced to 30 kV, the platform-like peaks were commonly observed, and more significantly, it was obvious that even the intense peaks were not recorded adequately. The results indicate that lower voltages may lead to distortion of the XRD patterns. Hence, 50 kV was set as the standard working voltage in this study.

3.3 Analysis of the larimar, lazurite and sugilite samples

These three samples shared a common point, as the opacity. Also, they were theoretically more complicated than hematite in molecular structure. Thus, the cases are discussed in the same section.

The XRF spectrum of the larimar sample showed that Ca was the predominant element in the sample, while traces of Mn and Fe may also exist (see Fig. 12a). The Au peaks belonged to the Au target, while the occurrence of

Cu and Zn peaks was caused by the brass material installed in the X-ray tube for shielding testers from extra beams. These foreign peaks are ignored in the following discussion. Since three metallic elements were detected, two cases were considered when the possible elements were selected at the XRD search match surface: (1) selecting Ca, Mn and Fe as three coexisted elements in a single phase, or (2) regarding them as existed in different phases. As for case (i), 128 possible phases were recognised by the system. Considering the significant differences among the three elements' XRF peak intensities, and the fact that the measured pattern did not fit any of the 128 possible phases very well, the author believes that it is not quite possible for the three elements to be coexisted in a phase. Rather, inputting them separately is closer to the reality. When Ca was selected as the only element present, 1287 possible phases were shown by the system. For improving the analysis efficiency, O and Si, the two commonest elements forming the earth's crust, were added to the potential element list to see if highly matched phases can be recognised among fewer candidates. The two elements were input separately. In the "Ca + O" case, 1221 possible phases were found, while in the "Ca + Si" case the number was 731. When Ca, O and Si were all selected, the possible phase number was also 731, indicating that the combination of Ca and Si cannot be stable without the participation of O. In this case, the author found that the measured pattern was fairly similar to the Pectolite-1A phase (ICDD 33-1223, $\text{NaCa}_2\text{HSi}_3\text{O}_9$) (see Fig. 12b). However, although possible phases were found by the system when the combinations "Mn + O", "Mn + Si", "Fe + O" and "Fe + Si" were input, it was hard to affirm their existence and species due to the low content of elements Mn and Fe, as well as the inadequacy of pattern resolution. The analysis process indicates that users may need to consider different elemental combinations at the XRD search match surface when they want to identify a multi-elemental stone by the system efficiently.

Fig. 12 Patterns of the larimar sample. **a** XRF spectrum. **b** XRD pattern

The above phase identification result was verified by normal XRD analysis (see Fig. 13). Compared with this pattern, it is clear that several characteristic lines (in red) were absent in Fig. 12b, which may be a software defect. It is necessary for the developer to eliminate bugs like this to prevent users from regarding a single phase as multiple phases.

As for the case of the sugilite sample, Fe, Ca, Mn and K were detected in the XRF measurement (see Fig. 14a). Considering the peak intensity, the author regarded Fe as the key element in the phase identification stage. When Fe was selected singly, 630 possible phases were found. Since the other three elements present were much lower than Fe in peak intensity, they were considered secondary to the possibility of O and Si. When both Fe and O were input, 583 possible phases were recognised; when the combination of Fe and Si were selected, 266 possible phases were found; and the number further decreased to 260 when Fe, O and Si were all selected. Among the 260 possible phases, the most likely one was Sugilite (ICDD 29-0824) (see Fig. 14b). According to the built-in database, the chemistry of Sugilite (ICDD 29-0824) is (K,Na)

$(\text{Na,Fe})_2(\text{Li,Fe})_3\text{Si}_{12}\text{O}_{30}\cdot\text{H}_2\text{O}$ which does not contain Ca and Mn, indicating that calcium and manganese compounds may be too scarce to be detected by the portable XRD, while the presence of Na and Li is out of the regular detection range of the portable XRF. On the other hand, when at least two elements were selected from Fe, Ca, Mn and K without considering O and Si, any possible phases found did not actually fit the measured pattern very well except Sugilite (ICDD 29-0824).

According to the normal XRD result, the measured pattern also coincided with the phase Sugilite (ICDD 29-0824) (see Fig. 15).

As for the case of the lazurite sample, both the elemental and the phase compositions are more complicated in theory. As shown in Fig. 16a, the major elements in the sample were Ca and Fe, while Mn, K, Ti, Ni, Cr and S were regarded as trace elements. Similar to the cases discussed above, Ca was solely selected first, which led to 927 possible phases. When the “Ca + O” case was considered, 846 possible phases remained; when the “Ca + Si” strategy was tried, 418 possible phases were

Fig. 13 Normal XRD pattern of the larimar sample

Fig. 15 Normal XRD pattern of the sugilite sample

Fig. 14 Patterns of the sugilite sample. **a** XRF spectrum. **b** XRD pattern

Fig. 16 Patterns of the lazurite sample. **a** XRF spectrum. **b** XRD pattern

listed; when Ca, O and Si were all selected, the number was still 418. Among these possible phases, three members were especially notable, as Lazurite-C (ICDD 17-0749), Diopside (ICDD 09-0460) and Augite (ICDD 02-0676), which fitted the measured pattern best (see Fig. 16b). The three phases have a theoretical chemistry as $\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)_2$, $\text{CaMg}(\text{SiO}_3)_2$ and $\text{N}[\text{CaO} \cdot (\text{Mg}, \text{Fe}) \text{O} \cdot 2\text{SiO}_2] \cdot (\text{Al}, \text{Fe})_2\text{O}_3$, respectively, according to the built-in database. Therefore, the presence of Ca, Fe and S can be clearly explained. On the other hand, when Fe was selected singly, 1363 possible phases were found. When the “Fe + O” case was considered, 1074 possible phases remained; when the “Fe + Si” strategy was tried, 462 possible phases were found; when Fe, O and Si were all selected, the number further decreased to 405. Among these candidates, the phase Augite (ICDD 02-0676) also accorded with the measured pattern best. Also, when both Ca and Fe were selected, 180 possible phases were listed, among which Augite (ICDD 02-0676) was present again. However, as for Mn, K, Ti, Ni and Cr, no reliable phases were identified by trying the relevant searches, indicating that the compounds were not sufficient to meet the demand of the phase identification.

The normal XRD measurement indicates that the lazurite sample is composed of at least three phases, as mentioned above (see Fig. 17). Moreover, it still remained several diffraction peaks which cannot be definitely identified.

In general, as for the above four opaque samples, the relation between the XRF results and the phase identification results can be classified as four modes:

- (i) Only a single element is detected by XRF, and the element can be directly applied to searching the possible phases, and actually the sample is composed of only a single phase;
- (ii) At least two elements are detected by XRF, and the elements are located in a single phase composing the sample;

Fig. 17 Normal XRD pattern of the lazurite sample

- (iii) At least two elements are detected by XRF, and the elements are located in different phases which can be identified;
- (iv) At least two elements are detected by XRF, and the elements are located in different phases which cannot be identified completely.

It is easy to deal with case (i). In fact, it is also possible for the only element present in the XRF result to form different phases in a sample, but this case did not occur in the present study. As for other three cases, it is necessary to employ reasonable strategies to save the time spent on screening. When all the elements present are metals, it is natural to primarily consider O or Si the possible coexisted elements in the minerals. The main reason is that O and Si are the primary elements forming the earth's crust, but it is unable to detect O by the ED-XRF system, while the peak intensity for Si are necessarily much weaker compared with those for heavy elements, which in fact makes it difficult to identify Si definitely. Another reason is that light non-metallic elements are either not active enough

to directly form chemical bonds with most metallic elements in common conditions (such as H, He, B, C, N, Ne, Si, P and Ar), or so active (F and Cl) that most of their simple compounds (salts) tend to be dissolved in water bodies and therefore reduce the occurrence of them on land; the exceptions are O and S, as they can combine with many metallic elements directly, and the products often feature poor water solubility, which makes them commoner on land; the valences of O (−II) and S (−II, +IV and +VI) indicate the complex structures of their compounds, which are just the origin of numerous minerals. Accordingly, in the cases no non-metallic elements are detected definitely by XRF, the coexistence of O can be considered first, then Si and S. The metallic elements with high XRF peak intensity are usually considered prior to the trace elements. The difference of XRF peak intensities for measured metallic elements is sometimes useful for judging the location of metallic elements (coexisted in one phase or located in different phases), but the difference between light and heavy elements in detection sensitivity should also be considered. If both metallic and non-metallic elements are present, it is natural to consider the combination of them first, and then the involvement of O or Si. Since most gems are regarded as composite oxides, silicates, or the composites of them, correct identification needs several times of search trying different strategies on the system, which calls for experience and carefulness when the XRF results are complex.

3.4 Analysis of the chrysoprase, nephrite and serpentine samples

The common characteristic of these three samples was their translucency. Meanwhile, they are all regarded as the members of the jade family in Chinese culture. Therefore, it is of great meaning to identify these samples with similar appearances and Chinese names.

Only Ni was observed in the XRF spectrum of the chrysoprase sample (see Fig. 18a), which means either Ni was the predominant element in the sample, or that the XRF detector was not quite sensitive to the other elements. When Ni was solely selected at the XRD search match surface, 118 possible phases were found. However, the pattern did not fit them, implying that light elements may also be present, but they cannot be detected by XRF effectively, while nickel compounds may not occupy a predominant position in real contents. In this case, elements O and Si were considered primarily. When O was solely selected, 545 possible phases were recognised; when Si was considered singly, the number was 266; and the number further decreased to 222 when both O and Si were input. As shown in Fig. 18b, the pattern fitted the featured peaks for a kind of Quartz (ICDD 05-0490) very well, but no indication of nickel compounds was found. The result indicates that the essence of the chrysoprase sample is a kind of quartz, while Ni is probably the colour-causing element doped in the crystal as the form of Ni^{2+} , or the key element forming traces of coloured compounds.

The normal XRD pattern of the chrysoprase sample clearly accorded with the Quartz phase (ICDD 05-0490) very well, verifying the above result (see Fig. 19).

In the XRF spectrum of the nephrite sample, Fe, Ca, Ni, Cr and Mn were recognised (see Fig. 20a). Among them, Fe and Ca were more significant and they were primarily considered in the following phase identification. When both Fe and Ca were selected at the XRD search match surface, 379 possible phases were found. When the coexistence possibility of O was considered, the possible phase number was still 379; when the combination of Fe, Ca and Si was tried, the number was 282; and when Fe, Ca, O and Si were all selected, the number was still 282. As shown in Fig. 20b, the measured pattern fitted the phase Actinolite (ICDD 04-0594) best in peak position among the 282 possible phases. According to the built-in database, the molecular structure of Actinolite (ICDD 04-0594) is simply

Fig. 18 Patterns of the chrysoprase sample. **a** XRF spectrum. **b** XRD pattern

Fig. 19 Normal XRD pattern of the chrysoprase sample

written as $\text{Ca}(\text{Mg}, \text{Fe}^{2+})(\text{SiO}_2)\text{OH}$, in which Mg was not obviously detected by the XRF due to its poor applicability in light elements. On the other hand, when one, two or three elements from Ni, Cr and Mn were selected and considered together with Fe, Ca, “Fe + Ca”, O, Si, or “O + Si”, the possible phases found did not actually accord with the measured pattern in peak position. Therefore, the presence of Ni, Cr and Mn implies the existence of their compounds, but the low contents limited further identification.

The normal XRD pattern verified the above identification result (see Fig. 21). Moreover, several diffraction peaks in the pattern cannot be identified definitely by normal XRD due to low content and inadequate resolution as well.

As for the serpentine sample, Fe and Ni were regarded as the primary elements, while Cr was present as a trace element according to the XRF spectrum (see Fig. 22a). Similar to the analysis processes described above, Fe was solely selected first at the XRD search match surface, which led to 978 possible phases. When the “Fe + O” case was considered, 860 possible phases remained; when the “Fe + Si” strategy was tried, 258 possible phases were recognised; when Fe, O and Si were all input, the number

Fig. 21 Normal XRD pattern of the nephrite sample

further decreased to 254. By comparing the measured pattern with the 254 candidates, the most likely phase was determined, as Lizardite-6T1 (ICDD 09-0444) (see Fig. 22b), which has a theoretical chemistry as $\text{Mg}_3[(\text{Si}, \text{Fe})_2\text{O}_5](\text{OH})_4$ according to the built-in database. On the other hand, when Ni was regarded as the only element present at the XRD search match surface, 171 possible phases were found. When the “Ni + O” strategy was tried, the number decreased to 164; when the “Ni + Si” combination was considered, 102 possible phases were listed; when Ni, O and Si were all selected, the number was still 102. Among these possible phases, Nepouite-1T (ICDD 15-0580), as theoretically written as $(\text{Ni}, \text{Mg})\text{Si}_2\text{O}_5(\text{OH})_4$, fitted the measured pattern best (see Fig. 22b). Moreover, when Fe and Ni were selected simultaneously without considering O and Si, 90 possible phases were found, but actually they did not coincide with the measured pattern, implying that Fe and Ni are located in different phases.

The normal XRD result indicates that the serpentine sample may be composed of three major phases, as Lizardite-1T (ICDD 02-0361), Lizardite-6T1 (ICDD 09-0444) and Nepouite-1T (ICDD 15-0580) (see Fig. 23).

Fig. 20 Patterns of the nephrite sample. **a** XRF spectrum. **b** XRD pattern

Fig. 22 Patterns of the serpentine sample. **a** XRF spectrum. **b** XRD pattern

Fig. 23 Normal XRD pattern of the serpentine sample

Since the chemistry of Lizardite-1T (ICDD 02-0361) is $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ according to the built-in database, it is clear why this phase was not considered above. By accessing to the XRD search match surface again and inputting Mg, O and Si, 249 possible phases were listed, among which Lizardite-1T (ICDD 02-0361) fitted the measured pattern very well indeed (see Fig. 22b). It can be found in this case that when the sample is a member of the Chinese jade family, the sample is probably composed of some light elements which cannot be adequately detected by the XRF, leading to the missing of the relevant phases. Furthermore, several uncertain diffraction peaks were also observed by the normal XRD, indicating that the serpentine sample may be much more complicated than divided into three isolated phases.

These three cases indicate that the nondestructive XRF–XRD system can be applied to identifying translucent samples, such as different members of the generalised jade family. In fact, although nephrite, serpentine and chrysoprase are all regarded as jades in Chinese culture, their actual values differ a lot. Therefore, the practicability of the system is of significant meaning. Compared with the

cases of the opaque samples, two more cases were found here. One is that the only metallic element present in the XRF result may “disappear” in the phase identification, and the other is that the undetected elements may form the major phases in fact. Both cases are caused by the coexistence and “absence” of O and Si, which is especially common in identifying jade samples. Moreover, compared with identifying samples composed of only a single phase, it is undoubtedly more difficult to identify multi-phase samples, especially those containing elements O and Si like jades, due to inadequacy of pattern resolution, missing of characteristic lines and more time spent on removing unlikely phases.

3.5 Analysis of the artificial emerald and YAG samples

The artificial emerald and the YAG samples were both man-made and fully transparent single-crystals in theory. According to the XRD theory and the references [37, 67–69], the identification of single-crystals is usually achieved by the X-ray single-crystal diffractometer through complicated data analysis processes, which is actually undesirable for preliminary identification of gem species. In this case study, the portable system, as a kind of powder XRD apparatus, was applied to this field to see if enough information about single-crystal gems’ elemental and phase composition can be obtained by the commoner XRD.

As shown in Fig. 24a, Fe was regarded as the predominant element in the artificial emerald sample by XRF, and other elements detected included Cr, Ni and Ca. However, only an intense diffraction peak was observed in Fig. 24b, while other peaks can be ignored compared with that, which is probably caused by the preferential orientation, an effect indicating that the crystalline grain array is highly ordered in a specific direction. This effect is commonly observed when single-crystal gems are measured

Fig. 24 Patterns of the artificial emerald sample. **a** XRF spectrum. **b** XRD pattern

Fig. 25 Normal XRD pattern of the artificial emerald sample

using powder XRD, causing the enhancement of certain peaks' intensity and the reduction of the others' [70]. Consequently, the pattern cannot be directly used for phase identification.

Although there are one intense and several less intense peaks shown in the normal XRD pattern (see Fig. 25), the

whole pattern cannot be recognised by the Jade software automatically, which may be associated with the generally low signal–noise ratio of the pattern caused by the X-ray fluorescence interference.

As for the YAG sample, Zn and Ca were regarded as the primary elements by XRF, and Fe and Y were detected as well (see Fig. 26a). However, the signal–noise ratio of the XRD pattern was not quite satisfactory, and the platforms were also observed (see Fig. 26b), which indicate that the pattern's quality is not high enough to perform the phase identification accurately. Unlike the artificial emerald sample, the YAG sample assumed a multi-peak XRD pattern, which implies that the sample cannot be composed of a single phase in fact.

The low signal–noise ratio was found in the normal XRD pattern as well (see Fig. 27), which made it difficult to perform the identification. Similar to the case of the artificial emerald sample, the phenomenon may be caused by the X-ray fluorescence interference effect.

In a word, when the system is applied to identifying single-crystal gems, although the elemental information can be obtained by XRF, the preferential orientation leads to a significant variance among different XRD peaks' intensities,

Fig. 26 Patterns of the YAG sample. **a** XRF spectrum. **b** XRD pattern

Fig. 27 Normal XRD pattern of the YAG sample

which makes certain peaks look like missing, causing difficulty in phase identification. On the other hand, the system can be employed to judge if a stone is a single-crystal or not, which is useful for quick and preliminary judgment of the authenticity of some transparent stones. In this case, the low signal–noise ratio can also be observed in the XRD patterns, which typically assumes a kind of even diffraction pattern without very intense peaks and makes it difficult to conduct the identification as well.

3.6 Advantages, disadvantages and applicable range of the system

Based on the above discussion, the author believes that the element analysis and the phase identification of some gemstones can be achieved by the portable XRF–XRD system quite well. Compared with employing multiple methods or devices to obtain the same information, applying the XRF–XRD coupled method saves time and manpower. Meanwhile, the micro-area measurement feature is a favourable advantage compared with normal IR and XRD methods.

On the other hand, the author also noticed the disadvantages of the hardware system:

- (i) As the tube current is lower than those of normal X-ray diffractometers by 3 orders of magnitude (while the voltage can be set as the same level), the signal–noise ratio inevitably cannot reach the level by normal X-ray diffractometers, which causes the missing of details in many cases. Nevertheless, since the system is designed for portable use and detecting cultural heritages, safety of both operators and objects is of the primary consideration. Thus, the inadequacy of the signal–noise ratio or the power can be acceptable.

- (ii) The working distance from the laser interferometer to the sample surface is 94.85 ± 0.20 mm, which is designed primarily for the safety of cultural heritage samples, but it increases the interference from air on the other hand.
- (iii) The continuous mode of XRD is not available, while performing the step mode costs about 100 min (step angle = 0.1° , 2θ), which is much longer than that spent on a normal XRD apparatus.
- (iv) The apparatus is not equipped with vacuum devices, which makes the XRF detector not quite sensitive to the elements from atomic number 11 to 18.
- (v) Since the working distance is not fixed absolutely but controlled by the tripod, the accuracy of it is highly dependent on the stability of the tripod and the calm of ground, which means the vibration of ground may lead to momentary sharp variation of the working distance and the angle if the apparatus is not equipped with a shockproof cushion.

Also, considering the software, the author thinks there are some points needing promotion:

- (i) The automatic phase identification is not quite smart so that it may provide users with hundreds of possible phases. Thus, the correct screening of phases is strongly dependent on users' experience.
- (ii) In some cases the characteristic lines are not shown in the XRD fitting results, which may cause users to regard a single phase as multiple phases.
- (iii) The built-in editing function is not developed enough to undertake the data processing and conversion tasks.

Users need to take themselves a consistent part in the improvement process of the system, such as providing more valuable cases, trying more efficient searching strategies and summarising the relevant experiences, as well as communicating with the manufacturer to make their demands clearer to the developers.

In a word, the author generalises the essential conditions for the system to perform well on testing gemstone samples:

- (i) Samples must have at least one surface to receive the whole laser spot for the measurement of the working distance. Thus, the surface must have an area not smaller than $2\text{ mm} \times 2\text{ mm}$.
- (ii) Polycrystalline stones are preferred in the XRD measurements owing to the fact that their characteristic peaks are detected more completely than those of the single-crystal gems by the powder XRD instrument.

- (iii) For XRD measurements, samples must have at least one flat surface to receive the X-ray beams at desired angles. Thus, gems with facets are preferred, while samples with only curved surfaces may not be measured very well.

4 Conclusions

The portable XRF–XRD system, in particular cases, can be applied to qualitatively analysing the elemental composition and the phase of some gemstones without any destructive sample preparation processes. The demands of gem samples include having at least one flat surface not smaller than 2 mm × 2 mm to receive the whole laser spot and the X-ray beams at desired angles (for performing XRF measurements only, surfaces with lower flatness are also acceptable), as well as possessing the polycrystalline characteristic. The optimal experimental parameters for XRD are as follows: working voltage: 50 kV; tube current: 75 μ A; step angle: 0.1°; working distance: 94.85 ± 0.05 mm. Although the resolution of the XRD patterns does not reach the level by normal XRD apparatuses, with the elemental measurement results obtained by XRF and proper elemental combination strategies, the XRD patterns can be analysed effectively and the quantity of the most likely phases can be refined to an acceptable range. Considering the elemental combination modes properly, such as judging the location of elements (coexisted in a single phase or located in different phases), focusing on the primary elements and ignoring the trace elements when necessary, or considering the coexistence possibility of O and Si when too many possible phases are found by the system automatically, is significant to the correct and efficient identification. The whole test process including preparation, measurement and data analysis, can be finished in 3 h, which is very efficient compared with conducting a series of experiments by various methods. In general, the portable XRF–XRD system is a promising tool to play a greater role in the nondestructive identification of gems. Meanwhile, it still remains great potentials for further improving the hardware and software functions, such as further developing optional accessories to adapt better to real demands of cultural heritage examination, and updating the software constantly to eliminate bugs and improve user experience. Users also need to take themselves a consistent part in this improvement process.

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Compliance with ethical standards

Conflict of interest The author declares that there is no conflict of interest.

References

- Vertriest W, Detroyat S, Sangsawong S, Raynaud V, Pardieu V (2015) Grandidierite from madagascar. *Gems Gemol* 51:449–450
- Moore PB, Araki T (1976) Painite, $\text{CaZrB}[\text{Al}_3\text{O}_{18}]$; its crystal structure and relation to jeremejevite, $\text{B}_5[\text{Al}_6(\text{OH})_3\text{O}_{15}]$, and fluoborite, $\text{B}_3[\text{Mg}_9(\text{F},\text{OH})_9\text{O}_9]$. *Am Mineral* 61:88–94
- Armbruster T (2002) Revised nomenclature of högbomite, nigerite, and taaffeite minerals. *Eur J Mineral* 14:389–395. <https://doi.org/10.1127/0935-1221/2002/0014-0389>
- Verlet P (1978) Sancy diamond returns to louvre. *Gazette des Beaux-Arts* 92:165–168
- Edwards O (2005) Romance and the stone: a rare Burmese ruby memorializes a philanthropic woman. *Smithsonian* 35:40
- Sucher SD, Attaway SW, Attaway NL, Post JE (2010) Possible “sister” stones of the hope diamond. *Gems Gemol* 46:28–35. <https://doi.org/10.5741/GEMS.46.1.28>
- Li Y, Xue Q, Li L, Chen M, Yin Z (2011) Gemmology tutorial. China University of Geosciences Press, Wuhan (in Chinese)
- Guo L, Han J, Luo H (2006) The Infrared reflectance spectra and the identification system of gems. *Acta Petrol Mineral* 25:349–356 (in Chinese)
- Li J, Tian L, Cheng Y, Chen Z, Meng L (2008) Routine application of infrared spectrometer in gem identification: comparison with KBr pellet. *Infrared* 29:28–36 (in Chinese)
- Schmetzer K, Kiefert L (1990) Water in beryl: a contribution to the separability of natural and synthetic emeralds by infrared spectroscopy. *J Gemmol* 22:215–223. <https://doi.org/10.15506/JoG.1990.22.4.215>
- Kiefert L, Hänni HA, Chalain JP, Weber W (1999) Identification of filler substances in emeralds by infrared and Raman spectroscopy. *J Gemmol* 26:501–520. <https://doi.org/10.15506/JoG.1999.26.8.501>
- Peretti A, Schmetzer K, Bernhardt HJ, Mouawad F (1995) Rubies from Mong Hsu. *Gems Gemol* 31:2–26. <https://doi.org/10.5741/GEMS.31.1.2>
- Martin F, Mèrigoux H, Zecchini P (1989) Reflectance infrared spectroscopy in gemology. *Gems Gemol* 25:226–231. <https://doi.org/10.5741/GEMS.25.4.226>
- Meng L, Gong S, He Y (2009) Organic spectral analysis. Wuhan University Press, Wuhan (in Chinese)
- Bersani D, Lottici PP (2010) Applications of Raman spectroscopy to gemology. *Anal Bioanal Chem* 397:2631–2646. <https://doi.org/10.1007/s00216-010-3700-1>
- Kuebler KE, Jolliff BL, Wang A, Haskin LA (2006) Extracting olivine (Fo–Fa) compositions from Raman spectral peak positions. *Geochim Cosmochim Acta* 70:6201–6222. <https://doi.org/10.1016/j.gca.2006.07.035>
- Bersani D, Andò S, Vignola P, Moltifiori G, Marino IG, Lottici PP, Diella V (2009) Micro-Raman spectroscopy as a routine tool for garnet analysis. *Spectrochim Acta A* 73:484–491. <https://doi.org/10.1016/j.saa.2008.11.033>
- Dele ML, Dhamelincoirt P, Poirot JP, Dereppe JM, Moreaux C (1997) Use of spectroscopic techniques for the study of natural and synthetic gems: application to rubies. *J Raman Spectrosc* 28:673–676. [https://doi.org/10.1002/\(SICI\)1097-4555\(199709\)28:93.0.CO;2-H](https://doi.org/10.1002/(SICI)1097-4555(199709)28:93.0.CO;2-H)

19. Łodziński M, Sitarz M, Stec K, Kozanecki M, Fojud Z, Jurga S (2005) ICP, IR, Raman, NMR investigations of beryls from pegmatites of the Sudety Mts. *J Mol Struct* 744:1005–1015. <https://doi.org/10.1016/j.molstruc.2004.12.042>
20. Barron LM, Barron BJ, Mernagh TP, Birch WD (2008) Ultra-high pressure macro diamonds from Copeton (New South Wales, Australia), based on Raman spectroscopy of inclusions. *Ore Geol Rev* 34:76–86. <https://doi.org/10.1016/j.oregeorev.2007.07.003>
21. Melquiades FL, Appoloni CR (2004) Application of XRF and field portable XRF for environmental analysis. *J Radioanal Nucl Chem* 262:533–541. <https://doi.org/10.1023/B:JRNC.0000046792.52385.b2>
22. Potts PJ, Ellis AT, Kregsamer P, Strelci C, Vanhoof C, West M, Wobrauschek P (2005) Atomic spectrometry update. X-Ray fluorescence spectrometry. *J Anal At Spectrom* 20:1124–1154. <https://doi.org/10.1039/b511542f>
23. West M, Ellis AT, Potts PJ, Strelci C, Vanhoof C, Wobrauschek P (2014) Atomic spectrometry update: a review of advances in x-ray fluorescence spectrometry. *J Anal At Spectrom* 29:1516–1563. <https://doi.org/10.1039/c4ja90038c>
24. Vanhoof C, Bacon JR, Ellis AT, Vincze L, Wobrauschek P (2018) Atomic spectrometry update: a review of advances in x-ray fluorescence spectrometry and its special applications. *J Anal At Spectrom* 33:1413–1431. <https://doi.org/10.1039/c8ja90030b>
25. Liu B (1992) X-ray fluorescence spectrometric analysis of environmental samples. Xinjiang University Press, Urumqi (in Chinese)
26. Jin PJ, Ruan FH, Yang XG, Zou HX, Yi J, Zhang Y, Zhao Y (2017) Microstructural and componential characterization of the plating technology on Chinese Han Dynasty bronze fragments. *Archaeometry* 59:274–286. <https://doi.org/10.1111/arc.12246>
27. Bottaini CE, Brunetti A, Montero-Ruiz I, Valera A, Candeias A, Mirão J (2018) Use of Monte Carlo simulation as a tool for the nondestructive energy dispersive x-ray fluorescence (ED-XRF) spectroscopy analysis of archaeological copper-based artifacts from the Chalcolithic site of Perdigões, Southern Portugal. *Appl Spectrosc* 72:17–27. <https://doi.org/10.1177/0003702817721934>
28. Alfeld M, Mulliez M, Martinez P, Cain K, Jockey P, Walter P (2017) The eye of the Medusa: XRF imaging reveals unknown traces of antique polychromy. *Anal Chem* 89:1493–1500. <https://doi.org/10.1021/acs.analchem.6b03179>
29. Van der Snickt G, Dubois H, Sanyova J, Legrand S, Coudray A, Glaude C, Postec M, Van Espen P, Janssens K (2017) Large-area elemental imaging reveals Van Eyck's original paint layers on the Ghent Altarpiece (1432), rescoping its conservation treatment. *Angew Chem Int Ed* 56:4797–4801. <https://doi.org/10.1002/anie.201700707>
30. Tavares da Silva A, Legrand S, Van der Snickt G, Featherstone R, Janssens K, Bottinelli G (2017) MA-XRF imaging on René Magritte's *La condition humaine*: insights into the artist's palette and technique and the discovery of a third quarter of *La pose enchantée*. *Herit Sci* 5, #37. <https://doi.org/10.1186/s40494-017-0150-5>
31. Xiong Y, Gong Y, Xia J, Wu J (2010) The analysis of porcelains from Yue kiln by EDXRF. *Sci Conserv Archaeol* 22:28–34. <https://doi.org/10.16334/j.cnki.cn31-1652/k.2010.04.002> (in Chinese)
32. Wen R, Zhang Y, Wang D, Wang L (2017) The compositional characterization and painting technique of Chinese red and white porcelain by EDXRF and SR-μXRF mapping analysis. *Anal Methods* 9:4380–4386. <https://doi.org/10.1039/c7ay00860k>
33. Hou X, He Y, Jones BT (2004) Recent advances in portable X-ray fluorescence spectrometry. *Appl Spectrosc Rev* 39:1–25. <https://doi.org/10.1081/ASR-120028867>
34. Szökefalvi-Nagy Z, Demeter I, Kocsanya A, Kovács I (2004) Non-destructive XRF analysis of paintings. *Nucl Instrum Methods B* 226:53–59. <https://doi.org/10.1016/j.nimb.2004.03.074>
35. Fang Q, Yu W (2002) Principles of crystallography. National Defense Industry Press, Beijing (in Chinese)
36. Nakai I, Abe Y (2012) Portable x-ray powder diffractometer for the analysis of art and archaeological materials. *Appl Phys A* 106:279–293. <https://doi.org/10.1007/s00339-011-6694-4>
37. Zhang N, Lin C (2016) Review on the application of x-ray diffraction in gem identification, synthesis and crystal structure research. *Rock Miner Anal* 35:217–228. <https://doi.org/10.15898/j.cnki.11-2131/td.2016.03.002> (in Chinese)
38. Yu JS, Lei XR, Zhang JH (2011) X-ray powder identification manual of minerals. Huazhong University of Science and Technology Press, Wuhan (in Chinese)
39. Scott DA (2002) Copper and bronze in art: corrosion, colorants, conservation. Getty Publications, Los Angeles
40. Wang YY, Gan FX, Zhao HX (2012) Nondestructive analysis of Lantian jade from Shaanxi Province, China. *Appl Clay Sci* 70:79–83. <https://doi.org/10.1016/j.clay.2012.09.012>
41. Kang B, Miao J, Qin D (2014) Raw materials for making glaze excavated in Ding Kilns site. *J Natl Mus China* 33:143–153 (in Chinese)
42. Huang X, Wang K, Guan L, Hu D (2018) Research on the inlaid ornamentation of hoof-shaped ingots excavated from the tomb of Marquis Haihun. *Sci Conserv Archaeol* 30:11–20. <https://doi.org/10.16334/j.cnki.cn31-1652/k.2018.04.002> (in Chinese)
43. He L, Wang N, Zhao X, Zhou T, Xia Y, Liang J, Rong B (2012) Polychromatic structures and pigments in Guangyuan Thousand-Buddha Grotto of the Tang Dynasty (China). *J Archaeol Sci* 39:1809–1820. <https://doi.org/10.1016/j.jas.2012.01.022>
44. Romano FP, Pappalardo L, Masini N, Pappalardo G, Rizzo F (2011) The compositional and mineralogical analysis of fired pigments in Nasca pottery from Cahuachi (Peru) by the combined use of the portable PIXE-alpha and portable XRD techniques. *Microchem J* 99:449–453. <https://doi.org/10.1016/j.microc.2011.06.020>
45. Padeletti G, Fermo P (2013) Significant findings concerning the production of Italian Renaissance lustred majolica. *Appl Phys A* 113:825–833. <https://doi.org/10.1007/s00339-013-7725-0>
46. Cotte M, Checrroun E, De Nolf W, Taniguchi Y, De Viguier L, Burghammer M, Walter P, Rivard C, Salomé M, Janssens K, Susini J (2017) Lead soaps in paintings: friends or foes? *Stud Conserv* 62:2–23. <https://doi.org/10.1080/00393630.2016.1232529>
47. Abe Y, Nakai I, Takahashi K, Kawai N, Yoshimura S (2009) On-site analysis of archaeological artifacts excavated from the site on the outcrop at Northwest Saqqara, Egypt, by using a newly developed portable fluorescence spectrometer and diffractometer. *Anal Bioanal Chem* 395:1987–1996. <https://doi.org/10.1007/s00216-009-3141-x>
48. Romano FP, Pappalardo G, Pappalardo L, Rizzo F (2006) The new version of the portable XRD system of the LANDIS laboratory and its application for the non-destructive characterisation of pigments in ancient Roman frescoes. *Nuovo Cimento B* 121:881–885. <https://doi.org/10.1393/ncb/i2007-10020-9>
49. Bish DL, Blake D, Sarrazin P, Treiman A, Hoehler T, Hausrath EM, Midtkandal I, Steele A (2007) Field XRD/XRF mineral analysis by the MSL ChemMin instrument. *Lunar Planet Sci* 38: Abstract #1163
50. Chiari G (2008) Saving art in situ. *Nature* 453:159. <https://doi.org/10.1038/453159a>
51. Gianoncelli A, Castaing J, Ortega L, Dooryhée E, Salomon J, Walter P, Hodeau JL, Bordet P (2008) A portable instrument for in situ determination of the chemical and phase compositions of cultural heritage objects. *X-ray Spectrom* 37:418–423. <https://doi.org/10.1002/xrs.1025>

52. Uda M, Sassa S, Yoshioka T, Taniguchi K, Nomura S, Yoshimura S, Kondo J, Nakamura M, Iskandar N, Zaghloul B (1999) X-ray analysis of pigments on ancient Egyptian monuments. *Int J PIXE* 9:441–451. <https://doi.org/10.1142/S0129083599000553>
53. Uda M, Sassa S, Taniguchi K, Nomura S, Yoshimura S, Kondo J, Iskander N, Zaghloul B (2000) Touch-free in situ investigation of ancient Egyptian pigments. *Naturwissenschaften* 87:260–263. <https://doi.org/10.1007/s001140050716>
54. Eveno M, Moignard B, Castaing J (2011) Portable apparatus for in situ x-ray diffraction and fluorescence analyses of artworks. *Microsc Microanal* 17:667–673. <https://doi.org/10.1017/S1431927611000201>
55. Duran A, Perez-Rodriguez JL, Espejo T, Franquelo ML, Castaing J, Walter P (2009) Characterization of illuminated manuscripts by laboratory-made portable XRD and micro-XRD systems. *Anal Bioanal Chem* 395:1997–2004. <https://doi.org/10.1007/s00216-009-2992-5>
56. Duran A, Castaing J, Walter P (2010) X-ray diffraction studies of Pompeian wall paintings using synchrotron radiation and dedicated laboratory made systems. *Appl Phys A* 99:333–340. <https://doi.org/10.1007/s00339-010-5625-0>
57. Eveno M, Duran A, Castaing J (2010) A portable x-ray diffraction apparatus for in situ analyses of masters' paintings. *Appl Phys A* 100:577–584. <https://doi.org/10.1007/s00339-010-5641-0>
58. Pifferi A, Campi G, Giacobbo C, Gobbi E (2009) A new portable XRD/XRF instrument for non-destructive analysis. *Croat Chem Acta* 82:449–454
59. Van de Voorde L, Van Pevenage J, De Langhe K, De Wolf R, Vekemans B, Vincze L, Vandenabeele P, Martens MPJ (2014) Non-destructive in situ study of "Mad Meg" by Pieter Bruegel the elder using mobile x-ray fluorescence, x-ray diffraction and Raman spectrometers. *Spectrochim Acta B* 97:1–6. <https://doi.org/10.1016/j.sab.2014.04.006>
60. Agresti J, Osticioli I, Guidotti MC, Kardjilov N, Siano S (2016) Non-invasive archaeometallurgical approach to the investigations of bronze figurines using neutron, laser, and x-ray techniques. *Microchem J* 124:765–774. <https://doi.org/10.1016/j.microc.2015.10.030>
61. Hatipoğlu M, Can N, Karali T (2010) Effects of heating on fire opal and diaspore from Turkey. *Phys B* 405:1729–1736. <https://doi.org/10.1016/j.physb.2009.12.078>
62. Hatipoğlu M, Başevirgen Y, Chamberlain SC (2012) Gem-quality Turkish purple jade: geological and mineralogical characteristics. *J Afr Earth Sci* 63:48–61. <https://doi.org/10.1016/j.jafrearsci.2011.11.004>
63. Patrizi G, Vagnini M, Vivani R, Fiorini L, Miliani C (2016) Archaeometric study of Etruscan scarab gemstones by non-destructive chemical and topographical analysis. *J Archaeol Sci Rep* 8:381–391. <https://doi.org/10.1016/j.jasrep.2016.06.039>
64. Chi G, Zhang Q, Zhao A, Zhong H, Hu J (2012) Experimental conditions of x-ray powder diffraction for sepiolite measurement. *Rock Mineral Anal* 31:282–286. <https://doi.org/10.15898/j.cnki.11-2131/td.2012.02.009> (in Chinese)
65. Suastika KG, Yuwana L, Hakim L, Darmaji Khusnul D (2017) Characterization of central Kalimantan's amethysts by using x-ray diffraction. *J Phys Conf Ser* 846, #012024. <https://doi.org/10.1088/1742-6596/846/1/012024>
66. Tomasini EP, Cárcamo J, Castellanos Rodríguez DM, Careaga V, Gutiérrez S, Rúa Landa C, Sepúlveda M, Guzman F, Pereira M, Siracusano G, Maier MS (2018) Characterization of pigments and binders in a mural painting from the Andean church of San Andrés de Pachama (northernmost of Chile). *Herit Sci* 6, #61. <https://doi.org/10.1186/s40494-018-0226-x>
67. Harris KDM, Tremayne M (1996) Crystal structure determination from powder diffraction data. *Chem Mater* 8:2554–2570. <https://doi.org/10.1021/cm960218d>
68. Fan K (2001) Spectroscopy introduction. Higher Education Press, Beijing (in Chinese)
69. Harris KDM (2011) Powder diffraction crystallography of molecular solids. In: Rissanen K (ed) *Advanced x-ray crystallography. Topics in current chemistry*, vol 315. Springer, Heidelberg, pp 133–177
70. Zhang G, Zhang Q (1992) Preliminary study of gems and jades identification with x-ray diffraction technique. *Hunan Geol* 11:315–317 (in Chinese)

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