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# THE USE OF NON-DESTRUCTIVE INSTRUMENTAL METHODS IN THE DETERMINATION OF METAL OBJECTS FROM THE ASIAN COLLECTION OF THE NÁPRSTEK MUSEUM[1]

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ABSTRACT: The article presents a methodical survey of standard non-destructive analytical methods applied recently to metal objects in the museum. These methods have helped to classify and describe particular pieces in the museum's collection of metal objects in a more complex ethnological, historical and museological context.

KEY WORDS: Non-destructive instrumental methods – XRF method – metal ware – Náprstek Museum, Prague – Middle East – India

The National Museum – Náprstek Museum of Asian, African and American Cultures holds an extensive collection of approximately two thousand metal items from the region of the Middle East, Central Asia, India and Indonesia. The collection features a whole range of objects – everyday vessels used in the kitchen and elsewhere, such as pots for cooking and carrying water, bottles, ewers, jugs, cups, caskets, betel sets, cosmetic boxes and flacons, and also ritual items such as various vessels and lamps for use both in the temple and at home. We have also included tools such as scissors, teaspoons and areca nut cutters.

The aim of measuring with the aid of physical methods is to support and render more precise some of the conclusions and assumptions on which we base our work when classifying museum objects, whether we are classifying them in terms of territory, time or material, with the aim of arriving at a typological breakdown of the collection, or a redesignation or more precise designation of specific objects. We may be describing and classifying the objects from a purely ethnological and art historical point of view, but we are doing so in combination with results of non-destructive instrumental

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methods. We achieve a certain added value in the form of quantification of the data received, which after evaluation may confirm or overturn a number of our assumptions.

In the case of vessels from various Asian countries we find many fixed opinions and hypotheses regarding the composition of the metals used. Most frequently, brass (or bell metal) in the case of cast vessels is mistaken for bronze. In the case of vessels with gilded, silvered or tinned surfaces, there may be uncertainty regarding the composition of the core.

## Methodology

To determine the material composition of metal items we used the non-destructive XRF method. The principle of the method consists in irradiating the material using high-energy radiation (usually X-rays are used in laboratory instruments or gamma radiation in portable instruments). These rays are partially absorbed by the atoms of the material being tested, and re-emitted as secondary radiation with lower energy (a phenomenon called fluorescence). Each element has its typical secondary radiation, which allows it to be clearly determined (Potts: 2008 56–82; Janssens 2004). The spectra of the individual elements generally do not overlap, and so there is less risk that they will be confused. This is a big advantage when analysing mixtures and alloys.

The measurement was carried out with the use of a mobile μXRF spectrometer, the Bruker ARTAX 400 (measuring parameters: a collimator with a diameter of 1.5 mm, voltage of 30 kV, current of 1.3 mA, measuring time 30 s, without the use of filters and protective atmosphere, the instrument is equipped with an X-ray using a molybdenum anode and a beryllium window).

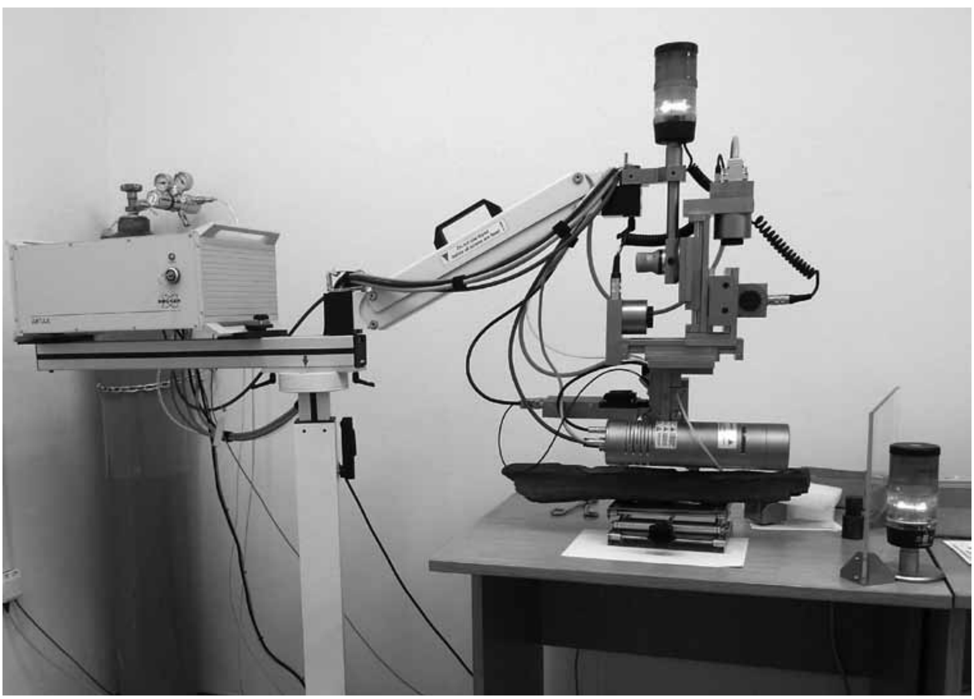

Fig. 1 Artax 400 x-ray spectrometer (photo by Michael Kotyk)

Among the main advantages of this instrument is the fact that it can be used to carry out non-destructive analysis (without the need to take a sample), while the adjustable arm allows objects of any size to be measured. The only limitation comes from the dimensions of the measuring head – it is not possible to measure places that are in hollows and dips, such as inside vessels. The measuring process is fast, does not require any sort of complicated preparation, and after calibration to known standards provides precise results.

Fig. 2 Measuring a brass vessel using an ARTAX 400 instrument (photo by Michael Kotyk)

Among the disadvantages are that it is not sufficiently sensitive to light elements (sodium, magnesium, aluminium) for which quantitative analysis is problematic. Elements lighter than sodium (such as hydrogen, carbon, nitrogen, oxygen) are not captured by the instrument at all, making it unsuitable for analysing organic materials and for determining the carbon content of steel. The results are also influenced by the calibration of the instrument – for precise analysis it is necessary to have standards available that are of a known composition and are similar to the material being measured. The Artax 400 instrument used in the National Museum has standards of several compounds – bronze, steel, some precious metals and glasses. The composition of other materials can only be assessed approximately – it is possible to determine what elements the materials contain, but not to establish their concentrations.

It should also be borne in mind that the analysis gives the best results on straight and smooth surface. If the surface of the object is uneven or dirty, as is often the case with archaeological material, results are less precise. Results may also be distorted by irregularities in the composition of the material (Padfield 1972: 220–236).

We used the Artax 400 not just to determine the composition of metal alloys, but also for the identification of pigments in their surface decoration. The substances most often used as pigments were crushed minerals and other anorganic materials. These can be identified by their elemental composition (Mantler 2000: 3–17). However, a clear identification is not always possible, since the same elemental composition may correspond to several kinds of pigment. Organic colorants, which are used to a lesser extent, cannot be determined using this method at all.

## Other methods

More detailed information about pigments in decorations may be gained using a combination of several instrumental methods. In such cases it is worth carrying out an analysis using other instruments, such as Raman and infrared spectroscopy, which are also suitable for the analysis of the organic binders of surface finishes. These methods make use of changes in the spectrum of visible and infrared light after interaction with the sample. The shape of the infrared spectrum depends not only on the elemental composition of the specimen, but also on the structures in which the atoms are arranged. The disadvantage is that the spectra gained are fairly complicated, and are difficult to evaluate when measuring mixtures of materials. It is usually also necessary to take a sample, although some machines also allow non-destructive measuring (Stuart 2007: 110–156).

For the analysis of the composition of surface finishes of metal vessels from the collection of the National Museum we used non-destructive measuring with a portable Raman spectrometer, the iRaman EX, and a table device, the DXR made by the Nicolet CZ company. Measuring enabled us to determine the type of pigments used in the surface finish of the vessel (vermilion and amorphous carbon). However, we did not manage to establish the nature of the binder of the finish using a Raman spectrometer.

Establishing the composition of organic binders is better done using infrared spectroscopy. With the aid of a Nicolet 6700 instrument at the University of Chemistry and Technology in Prague, it was possible to determine, for select vessels, the binders and some of the pigments of the surface finishes (such as shellac, rosin and drying oils). The composition of the pigments was further specified with the use of Raman spectroscopy.

For the analysis of the binders it was necessary to take samples from the surface of the vessels, since non-destructive measuring was impossible because of the dimensions of the vessels. From selected vessels we took microsamples of around 0.5mm on average, from places where the surface finish had been damaged. Taking such small samples in a careful way is practically possible only with the use of a stereomicroscope, which allows sufficient magnification and, thanks to the spatial depiction, enables the sample to be handled. When taking the sample we used a Leica MZ 16FA stereomicroscope, which allows enlargement of 0.32–230× with stereoscopic vision, great depth of field, and also a sufficiently large working distance (i.e. the distance of the lense from the object), which is necessary to handle the sample. We also used the attached CCD camera with a resolution of 8 Mpix to document the places from which the samples were taken.

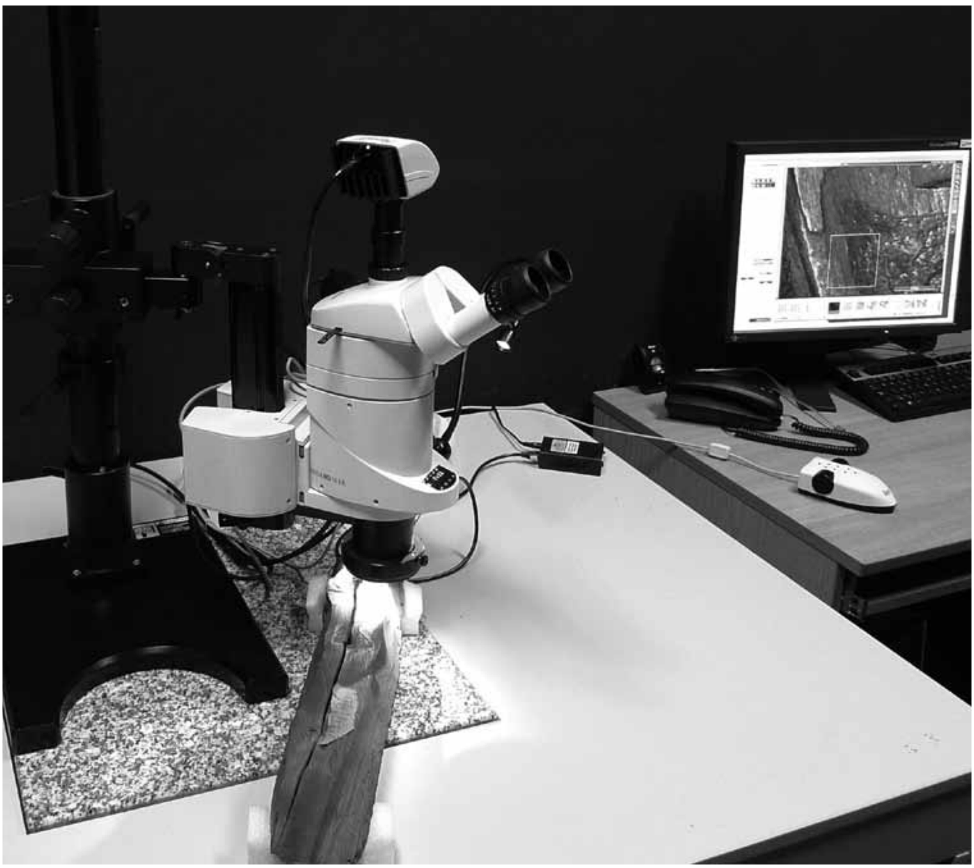

Fig. 3 Stereomicroscope LEICA MZ 16FA (photo by Michael Kotyk)

Optical examination of objects under a microscope is a basic analytical technique that in the study of metal vessels can also be used to ascertain: 1. the state of the object – corrosion, cracks, repairs, 2. the structure of the surface – engraving, stamping, 3. decoration – the smearing of the background of the decoration, colouring, inlay, 4. manufacturing processes (such as hammer blows, etc.).

Fig. 4 Optical examination of objects under a microscope (photo by Michael Kotyk)

Table Measurement no. 1592

| No. | Element | Line | Energy [keV] | Cycl. | Net | Backgr. | Sigma | Chi | Conc. [%] | Sigma C [%] | LLD [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 | Fe | K12 | 6,405 | 16 | 3645 | 2 001 | 87 | 2,96 | 0,042 | 0,001 | 0,002 |
| 14 | Co | K12 | 6,931 | 16 | 181 | 2 433 | 71 | 2,54 | 0,003 | 0,001 | 0,002 |
| 15 | Ni | K12 | 7,480 | 16 | 1 468 | 4 234 | 100 | 4,68 | 0,041 | 0,003 | 0,005 |
| 16 | Cu | K12 | 8,046 | 16 | 367 402 | 6 280 | 616 | 141,44 | 11,968 | 0,020 | 0,008 |
| 17 | Zn | K12 | 8,637 | 16 | 198 378 | 5 674 | 458 | 80,14 | 5,671 | 0,013 | 0,006 |
| 20 | Se | K12 | 11,224 | 16 | 577 | 2 874 | 80 | 1,19 | 0,014 | 0,002 | 0,004 |
| 22 | Ag | K12 | 22,163 | 16 | 37 776 | 958 | 199 | 22,50 | 71,884 | 0,379 | 0,177 |
| 24 | Cd | K12 | 23,173 | 16 | 1 | 576 | 34 | 1,13 | 0,001 | 0,029 | 0,064 |
| 29 | Sb | L1 | 3,604 | 16 | 1 | 2 230 | 67 | 4,54 | 0,001 | 0,055 | 0,102 |
| 33 | Ba | L1 | 4,466 | 16 | 107 | 731 | 40 | 0,46 | 0,069 | 0,026 | 0,053 |
| 34 | Au | L1 | 9,713 | 16 | 64 | 2 282 | 68 | 6,48 | 0,014 | 0,015 | 0,031 |
| 36 | Hg | L1 | 9,989 | 16 | 1 817 | 2 499 | 83 | 20,16 | 0,386 | 0,018 | 0,032 |
| 38 | Pb | L1 | 10,551 | 16 | 1 027 | 2 680 | 80 | 3,02 | 0,216 | 0,017 | 0,033 |

## Results

During 2014-2015 a total of 3806 measurements of metal composition were carried out on objects from the Asian collection of the Náprstek Museum.

We present an example of one measurement as follows. It is a lamp from Syria or Egypt, 19th century, made of brass, copper and silver. The dimensions are: h. 44.5 cm, diam. 45.7 cm. Inv. No. A2809. The lamp is in the shape of a bulbous vessel, with eight round holes around a larger hole in the centre of the top lid, with all-over engraved, openwork and inlaid geometric and plant decoration with calligraphic inscriptions. The decoration is inlaid with silver and copper.

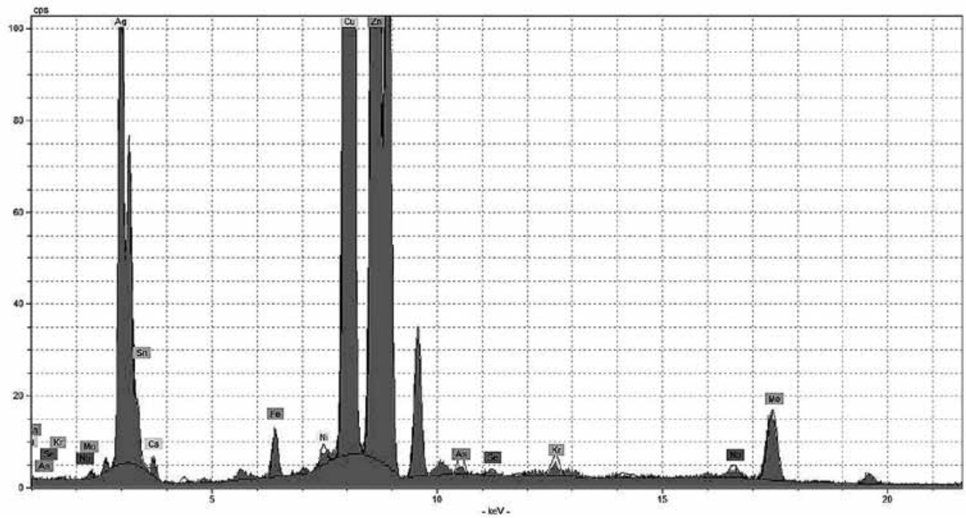


Fig. 5 Measured spectrum no. 1592

For clearer documentation of the place of measurement, together with the results we have included a macrophotograph from the camera of the instrument and a photograph of the object during measuring.

Most of the objects analysed contained a metal core, most frequently a copper alloy. In the case of copper, bronze and brass objects, for which we have calibration standards, the analysis results in a complete breakdown of the alloy by element. Where the material contains elements that the instrument is unable to capture, such as carbon in steel, the results gained are incomplete. This represents a limitation when classifying objects from the countries of the Near East, where steel objects can be found, or objects commonly given as steel. In the case of these objects we then give just the content of iron and of metal admixtures. The carbon content could be established using metallographic analysis, but this is not non-destructive – it requires a sample to be taken.

It is difficult to interpret the results when measuring objects with thin layers of metal surface coverings, such as silvered and gilded copper. Given that the measuring captures the composition of material to a certain depth, which in the case of metals is up to 10 μm, depending on composition (Potts 2008, 56–82), it is not clear from the results whether the measured content corresponds to the content of copper in the silver,

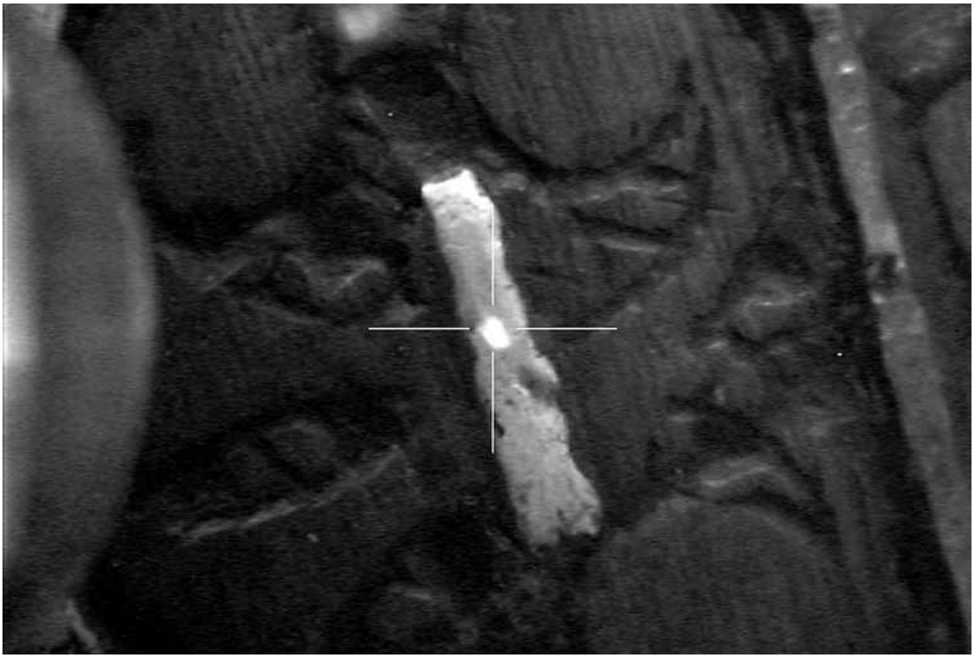

Fig. 6 Macrophotograph of the place of measurement no. 1592

or whether the copper core of the object makes itself felt in the results. Similarly, in the case of tinned copper objects we have to avoid wrongly classifying the object, because the results may appear, in the language of numbers, to indicate bronze. In the case of tinned copper or brass objects the amount of tin in the brass cannot be precisely determined and differentiated from the tin on the surface of the object. Sometimes it is possible to find an unmetalled area on the surface of the item and thus to ascertain the composition of the core. Where this is not possible, and if we wanted to measure the composition of the alloy of the vessel without the metal surface, we would have to use a destructive method and drill away a sample with no surface covering. This is not, however, for the most part possible. In these cases, measuring using the chosen method has to be understood as orientational, and we need to rely on visual clues or on art historical and museological comparative methods based on field research in the given areas and local workshops, plus the study of other museum collections and catalogues of domestic and foreign museums.

In India, the surfaces of objects made out of bronze or copper were decorated with coloured lacquers.  In these cases, too, we come up against limits in the use of the XRF method. All we have been able to do is to qualitatively establish the content of elements in anorganic pigments.

The data measured and their evaluation form part of the collection documentation and represent a valuable source of information for further work with the collection. The results gained were also published in the form of a DVD catalogue as an appendix to the book *Umění kovu v zemích Blízkého východu a Indie*.[3]

[3] POSPÍŠILOVÁ, Dagmar – MLEZIVA, Jindřich. *Umění kovu v zemích Blízkého východu a Indie*. Praha: Národní muzeum, 2015, 231 stran. ISBN 978-80-7036-456-7. DVD: The Art of Metalwork in the Countries of the Middle East and India. The collection of metal items in the Náprstek Museum and Museum of West Bohemia in Pilsen. ISBN 978-80-7036-473-4.

## Conclusion

The methods described above help us to assess the museum's collection of metals from several angles and to put it into a broader ethnological, historical and museological context. Measuring took place in the case of 1300 items – most of them vessels from the extensive territory of the Near East and India, mostly from the period of the 19th–20th century. A smaller number of the objects, around 20% of them, are of an older date. A typical object is a vessel of non-rare metals from the 19th century. This common Indian vessel is brass, maybe copper, in both cases possibly tinned. Indian brasses have a relatively high zinc content (around 35%), regardless of area. We may therefore talk about an India-wide trend in the use of this type of brass, unlike the countries of the Near East, where the zinc content is around 20%). This finding has enabled us to pre-designate several cups whose standard forms make it difficult to classify them geographically. A comparison of the result of measuring the elemental composition of brass items highlighted a group of objects that showed a different composition and that thus found themselves outside the group with similar composition all from one area. Tinned brass objects are found in northern India and have connections to objects from the Islamic countries of the Near East, where they are regularly used. Here the material composition does not help us determine their provenance. Instead, we have to use a comparative method on the basis of shape and decoration.

The metal plating of precious metals are more of a rarity in India, appearing mainly in production from the turn of the 19th and 20th century and aimed at European customers, especially in combination with enamels. However, we also know them from Turkey, where gilding was used on copper vessels (*tombak*). The inlaying of ordinary metals with precious ones was something commonly found in the countries of the Near East (see example above), but in India only in specific Indian objects known as *bidri*, which are cast from zinc and inlaid with silver, sometimes with brass or gold. It was interesting to discover that one of the objects is not inlaid with brass, but gold. Because gold was used for inlaying less often than bronze, with bronze predominating in the case of older objects in particular, the object is likely to be more recent than previously thought.

The results gained will be subjected to further research with the aim of further specifying the origin and age of the objects being measured, with an awareness of the advantages and limits of the methods chosen.

## Literature:


CRADDOCK, Paul. *Scientific investigation of copies, fakes and forgeries*. 2009. [Elsevier]

JANSSENS, Koen – VAN GRIEKEN, René (eds.). *Non-destructive micro analysis of cultural heritage materials.* 2004. [Elsevier]

MANTLER, Michael – SCHREINER, Manfred. X-ray fluorescence spectrometry in art and archaeology. In *X-ray Spectrometry*, 2000, pp. 3–17.

PADFIELD, Tim. Analysis of Byzantine copper coins by x-ray methods. In Hall, Edward Thomas – David Michael Metcalf (eds.). *Methods of chemical and metallurgical investigation of ancient coinage – a symposium held by the Royal Numismatic Society in London on 9–11 December 1970*, 1972, pp. 220–236.

POSPÍŠILOVÁ, Dagmar – MLEZIVA, Jindřich. *Umění kovu v zemích Blízkého východu a Indie.* 1. vyd. Praha: Národní muzeum, 2015.

MLEZIVA, Jindřich – POSPÍŠILOVÁ, Dagmar – STŘÍBRNÁ, Adriana – KOTYK, Michael – PECH, Michal. *The Art of Metalwork in the Countries of the Middle East and India. The collection of metal items in the Náprstek Museum and Museum of West Bohemia in Pilsen*. DVD, 1st ed. Praha: Národní Muzeum, 2015.

POTTS, Philip J. – WEST, Margaret (eds.). Portable X-ray fluorescence spectrometry: Capabilities for in situ analysis. In *Royal Society of Chemistry*, 2008, pp. 56–82.

REARDON, Arthur C. (ed.). *Metallurgy for the non-metallurgist*. USA, ASM International, 2012.

STUART, Barbara H. *Analytical techniques in materials conservation*. Chichester, 2007.