ABSTRACT

An overview of the techniques used in art and archaeology is presented and the applicability of X-ray radiography, X-ray fluorescence (XRF) and X-ray diffraction analysis (XRD) as a tool for non-destructive investigations of objects of art and archaeology is discussed. X-ray radiography e.g. is a standard technique widely used and accepted by art historians, archaeologists, curators and conservators as this method enables information about the manufacturing process and the condition of an object without “touching” the artifact. XRF and XRD enable a non-destructive determination of the material composition of artifacts and the determination of the crystalline structure of the components too. Air path systems and instruments with the micro-beam of X-ray and synchrotron radiation were applied for the analysis of easel paintings, pigments in paint layers, glass artifacts and coins.

Introduction

The application of analytical techniques, initially developed in the field of materials science, for objects of art and archaeology gives the art historians and archaeologists the possibility to gain information about the material composition of such objects and prepares answers to the questions of where, when or by whom such an artifact was made. Additionally, such investigations can help to understand the way of manufacturing artifacts and hence the way of life of the cultures studied. Scientific investigations are also valuable and in some cases indispensable for conservation projects in order to differentiate the original parts of an object from later additions, former restoration works, falsifications or even fakes. Furthermore, our cultural heritage is doomed to disappear because of ageing and deleterious effects of the environmental pollution. The degradation of monuments or outdoor bronzes is well known, but all artifacts, even in exhibitions or well conditioned museums, libraries, or archives are subjects of deterioration. These phenomena
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must be studied extensively in order to understand the kinetics of decay and to develop treatments and ways for preventing or slowing down these processes [1 - 5].

For the systematic investigations of the material composition two complementary sources of information are available. The holistic approach makes use of radiation from gamma-rays to infrared to generate an image of the object as a whole visible to the naked eye. These methods are in a strict sense non-destructive, which means that neither samples have to be gained from an object nor the material of an artifact is changed during the investigations. This accords well with the way an art historian, archaeologist or conservator would like to deal with works of art and, e.g. X-ray radiography or computer tomography are standard techniques widely used and accepted. These methods enable information about the manufacturing process and the condition of an object without “touching” the artifact [6, 7].

For the second source of information, where the material composition of small areas is determined, mainly chemical methods of analysis were available until World War II. Since the 1940s many techniques based on physics have been developed and used extensively for the elemental analysis. In some cases even spectacular results such as the redevelopment of lead-tin yellow could be achieved by e.g. optical emission spectroscopy. In the yellow parts of Dutch paintings of the 14th – 17th centuries Jacobi [8] determined the elements Pb and Sn. Systematic investigations at the Doerner Institute in Munich yielded the composition of Pb₂SnO₄, a yellow pigment, which was used by the Dutch painters and replaced by Neaples yellow [Pb(SbO₃)₂ or Pb₃(SbO₄)₂] in European easel paintings after approximately 1750. However, as the chemical and many instrumental analytical techniques are destructive and require small samples to be taken from an object, the application of these methods to objects of art and archaeology are severely limited nowadays. X-ray fluorescence (XRF) as well as X-ray diffraction analysis (XRD) have gained growing interest in the last decades [9, 10], as both methods have been proved to be sufficiently non-destructive, if used with care and respect to possible damages due to extensive radiation doses.

It is the purpose of this contribution to present an overview of the application of X-ray radiography, XRD and XRF to objects of art and archaeology and to present recent developments using a micro-beam for non-destructive determination of the elemental composition of painting materials as well as the crystalline structure of pigments, silver coins and glass of the Art Nouveau manufactured by Tiffany/USA and Loetz/Austria at the end of the 19th and beginning of the 20th centuries. On the other hand, this contribution should stimulate scientists working in the fields of XRD and XRF to co-operate with scientists in the field of art and archaeology in order to develop further methods and instrumentation for non-destructive analysis gaining more knowledge about past cultures, our cultural heritage, and for conservation and preservation of the materials used for artifacts.
X-ray Radiography

Figure 1 depicts the structure of an easel painting with the support and the different paint layers, which are characteristic for the artist’s creative process of a painting. That structure can partly be studied by technical means of X-ray radiography, where due to the varying absorption of X-ray radiation, e.g. by the pigments used, a visualization of the material distribution can be achieved. Usually, details and also changes in the design of an object – so-called pentimenti – can be shown. The instrumentation for such investigations is very simple and a scheme is given in Figure 2. Beside the X-ray source, the object and an X-ray sensitive material for the detection of the transmitted radiation, e.g. film is required.

The paintings collection of the Academy of Fine Arts in Vienna contains several paintings on canvas with veduta of Venice (veduta = city views) painted by the famous Venetian painter Francesco Guardi (1712 – 1793). He was the younger son of Paolo Guardi, who was a famous painter too, as well as his elder brother. The painting shown in Figure 3 is called the Orologio (the clock tower on the San Marco place in Venice). Figure 4 depicts the X-ray radiograph of the upper right corner of the painting. In this radiograph clearly the clock plate can be recognized, as it was painted by using lead white \([\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb(OH)}_2]\). Additionally, the head of a woman with a veil (St. Mary) can be seen holding a nappy in her hands, where a small baby lies. On the right side of the painting the head of an ox, in the centre of the X-ray radiograph the head of a donkey with his two long ears, and in the upper right corner the face of a man with his bald head and an aureole (St. Joseph) can be recognized.

The interpretation of these results by the art historians is that Francesco Guardi used an ecclesiastical painting of the Christmas gospel and over-painted it with the representation of the Orologio. However, it is rather impossible to draw any conclusion from these results, whether the painting underneath the clock tower of Venice was painted by himself, his father, his brother, or by another painter. Also no information about the materials used in the painting underneath as well as in the presentation seen by the naked eye can be gained from such radiographs. However, such investigations should be obligatory and precede the use of the second source of information, where the material composition of a small area is determined by analytical methods.
Structure of an Easel Painting

Figure 1: Structure of an easel painting.

Figure 2: Scheme of the instrumentation for X-ray radiography.
Figure 3: The easel painting “The Marcus Place in Venice with the Orologio” (the clock tower) by Francesco Guardi (1712 – 1793), oil on canvas, 62.5 x 89.5 cm², Gallery of the Academy of Fine Arts Vienna, No. 502.

Figure 4: X-ray radiograph of the upper right corner of the painting of F. Guardi, shown in Figure 3.
Identification of Pigments in Paint Layers by Micro-XRD

The most common way for studying the stratigraphy of paint layers, as shown in Figure 1, has been to take a small specimen containing all layers, to embed the splinter, e.g. in epoxy resin, and to perform a cross-section. The examination of the cross-section by light microscopy and UV-fluorescence microscopy provides sufficient information about the structure of the paint layers, grain size and grain size distribution of the various pigments as well as varnish layers or organic binding media [11]. However, for the identification of individual pigments additional investigations are necessary, where scanning electron microscopy (SEM) in combination with energy dispersive X-ray microanalysis (EDX) has been used widely [11, 12]. In such cases mainly the elemental distribution (X-ray mapping) yields to the most significant elements present in the pigments and their distributions in the paint layers. As many inorganic materials and some of the most interesting pigments can occur in different crystalline structures, XRD has been proved to be a valuable tool for the clear identification of pigments. With common XRD it is rather difficult to achieve such results, as the thickness of the paint layers is in the range of several tens microns or even below.

Synchrotron X-ray micro-diffraction could be applied recently at the European Synchrotron Radiation Facility (ESRF) in Grenoble/France in order to identify the crystalline structure of the pigments in the cross-section of the paint layers in Figure 5. The experimental set-up for micro-diffraction at beam-line ID22 of ESRF as well as parts of the results have been published already elsewhere [13]. In conclusion it has to be mentioned that a thin section of approximately 300 μm has to be prepared from the cross-section in Figure 5 prior to analysis, as the micro-diffraction is carried out in transmission mode. As shown in Figure 6a, the complete micro-diffraction analysis was accomplished by step-wise moving the thin section in steps of 4 μm across the intensive X-ray beam focused by compound refractive X-ray lenses. After 160 steps the beam passed through all seven layers of the specimen. Hence 160 diffraction spectra were obtained (Figure 6b) representative for the crystalline compounds in the layers, which could be processed and evaluated by Bragg’s law. This procedure makes the data comparable to tabulated values of known compounds present e.g. in the collection of the International Centre for Diffraction Data (ICDD). Using the Powder Diffraction File (PDF 2000) identification of the crystalline phases, summarized in Table 1, could be achieved.
Figure 5: Cross-section of the specimen taken from a mural painting of the Baroque period with a thin layer of gold on the surface (layer 1).

Figure 6: Thin section of specimen in Figure 5 for micro-XRD measurements at beam-line ID22, ESRF in Grenoble/France. 160 steps over the thin section (a – left image) yielded 160 diffraction patterns (b – right image), which could be evaluated by using the Powder Diffraction File (PDF 2000).
Layer | Appearance of the layer in light microscopy | Elements determined by EDX analysis in the SEM | Phases determined by micro-XRD
--- | --- | --- | ---
1 | yellow | Au | gold (Au)
2 | red/orange | Ca, Ba, S and/or Pb | barytes (BaSO₄ - permanent white), calcite (CaCO₃ - chalk)
3 | transparent | C | ---
4 | yellow | C, Ca, S and/or Pb | cerussite (2 PbCO₃.Pb(OH)₂ - lead white), gypsum (CaSO₄.2H₂O)
5 | white | Ca, S and/or Pb | cerussite (2 PbCO₃.Pb(OH)₂ - lead white), gypsum (CaSO₄.2H₂O)
6 | white (yellowish) | Ca | gypsum (CaSO₄.2H₂O)
7 | white (gray) | Ca | calcite (CaCO₃ - chalk)

Table 1: Results of the elemental analysis in the SEM/EDX and µ-XRD obtained for the cross-sectioned paint layers in Figure 5 and Figure 6.

XRF and µ-XRF for the Analysis of Artifacts

X-ray fluorescence analysis (XRF) has been applied widely for material analysis as it is, in principle, applicable to all elements except the first two (H, He) of the periodic system. However, many light elements are quite difficult to be measured and require advanced instrumentation, which often limits practical work to atomic numbers above 11 (Na). Even in that case, the detection of the characteristic radiation of the elements with an atomic number between 11 and 16 (Na – S) is difficult due to the fact that most of the instruments used for non-destructive analysis of artifacts have to be air-path systems and the characteristic radiation of the elements Na – S is absorbed by the ambient atmosphere [14 - 16]. Additionally, traditional instruments are using an X-ray beam of several mm in diameter, which limits the application of XRF to specific problems such as the identification of pigments in miniature paintings or tiny decorations of objects made of glass, ceramics or metals.

The development of micro X-ray tubes used in combination with poly-capillary lenses for focusing the primary beam to less than 100 μm as well as highly sensitive detectors for the secondary X-ray radiation are an additional step forward to fulfill the requirements for non-destructive analysis of art objects. In a research project [17] supported by the European Union a
portable instrument could be built, where an X-ray tube of Oxford Instruments/USA (50 kV, 50 W), a poly-capillary of X-ray Optics Systems/USA for focusing the primary X-ray radiation and a silicon drift chamber detector of Röntec/Germany for energy dispersive X-ray analysis were employed to assemble a compact micro-XRF spectrometer [18]. A stage with a small table, which supports objects up to approximately 1 kg, is further used to move an artifact in three dimensions in order to select the point to be measured and to adjust the distance between the measuring system and the object. Additionally, a microscopic unit with a zoom optic enables to visualize and record the area to be analyzed. The purpose of such an instrument is to permit local, non-destructive analysis in the µm-range and to be transported into museums, libraries and archives in order to carry out the investigations on site.

A scheme of the COPRA-instrument and the assembly itself are presented in Figure 7. Figure 8 summarizes the results obtained on a glass fragment of an iridescent Art Nouveau artifact. As the decoration on the glass surface consists of tiny and fine lines the micro-beam facility seems to be appropriate. The line scan over such an area depicts the distribution of the elements Pb and Co, as lead oxide has been used to achieve the bright decoration in the blue bulk glass colored by additions of cobalt oxide.

Figure 7: The COPRA-instrument built within an EU-funded project [17].
Figure 8: Fragment of an iridescent glass (top) with the distribution of Pb (centre) and Co (bottom) along the line indicated.
Classification of Iridescent Glass Artifacts of the Art Nouveau by XRF

In a joint research project of the Museum of Applied Arts in Vienna/Austria, the Research Centre Seibersdorf/Austria and the Academy of Fine Arts in co-operation with the Historical Society in New York/USA a “recognition” procedure was developed, which enables a fast and reliable classification of the provenance of Art Nouveau iridescent glass objects [19]. The procedure is based on non-destructive analysis using XRF as well as Fourier transformed infrared spectroscopy (FTIR). The data obtained are processed and statistically evaluated in a self-written software package based on multivariate (cluster) analysis. Furthermore, a characterization of the manufacturing technology of the thin iridescent surface layer has to be carried out in the project in order to obtain the differences as well as the similarities between the two most important Art Nouveau glass companies, Tiffany in the USA and Loetz in Austria (Figure 9).

Figure 9: Art Nouveau glass artifact with iridescent surface of Loetz/Austria
Iridescence itself is an interference effect occurring, whenever bulk material is coated with a very thin layer with optical properties different from those of the bulk. Therefore, XRF measurements were carried out during the project on the iridescent and the non-iridescent side. Fragments of Tiffany and Loetz glasses as well as half products available in the Museum of Applied Arts and the Historical Society could be investigated. For comparison also fragments of Aurene Glass/USA and modern glass artists and manufacturers such as Jack Ink/Austria and Strini Art Glass/California were included. The intensities of the various elements determined by XRF were used as an input for the statistical pattern recognition. As can be seen in Figure 10, the results of the factor analysis show a clear differentiation between Tiffany and Loetz. Additionally, the products of Aurene, Jack Ink and Strini Art Glass form clusters too due to the chemical composition of the bulk glass as well as the elements present in the iridescent surface layer.

![Figure 10: Results of the factor analysis considering the elements Si, K, Zn, and Se in the bulk glass and Pb and Ag in the bulk and the iridescent surface layer.](image)

On the iridescent surface of most of the glass fragments also tin could be determined with XRF, but no further conclusion could be drawn from these investigations. Therefore, photoelectron spectroscopy (XPS) had to be used for the identification of the surface layer yielding the iridescent effects as the thicknesses of the layers are in the range of several ten nanometers. The set-up for these measurements contained a twin anode (Mg, Al) X-ray tube without monochromator and
a hemispherical analyzer as detector operating in fixed retarding ratio mode. Further details of the measurement conditions can be found in the literature [20]. As shown in Figure 11, the strongest lines of the glass fragments investigated (Tiffany T16 and Loetz L 294) correspond to the elements Sn, O and C. The signals of Si are rather weak and the elements Pb, Ag, K, and Ca, also determined by XRF, could not be detected by XPS. An atomic ratio of c(Sn):c(O) of 1:4 was found on the surface by applying a quantitative algorithm based on fundamental parameters. Taking into account that the glass samples could not be cleaned prior to the analysis, the C-lines and partly the high intensity as well as the broadening of the O 1s line may be caused by sample contamination. However, the high oxygen content indicates the presence of SnO$_2$ as the topmost layer causing the iridescence of such glass artifacts. This result is in accordance with one of the patents of Tiffany, where a treatment of the hot (approximately 500 °C) hollow glass with an alcoholic solution of SnCl$_2$ is described.

![Figure 11: Results obtained by XPS on the iridescent glass surface.](image-url)
Is it a Fake? – The Identification and Characterization of Coins

Objects of art and archaeology are mainly relicts of the past and their authenticity is primarily proved by stylistic considerations. The trained eye of an art historian or archaeologist can detect these with relatively little difficulty, although styles and objects were sometimes copied at locations and times different from those, for which they are most characteristic. However, forgeries offered on the world market are sometimes so well done and aged that they will deceive even the most expert opinion. Hence the large museums are restoring more and more to scientific examination in order to satisfy themselves.

The big demand of minted coins during various periods in the history and the possibility to raise money by relative simple methods has yielded to contemporary imitations as well as later copies of coins since the ancient periods up to now. A well known technique for manufacturing copies has been to form a chill mold and cast a counterfeit. However, minted and cast coins are characterized by their typical microstructure, as depicted in Figure 12. The minting process yields in most cases (in dependence of the pressure) to an orientation of the dark (copper rich) and the bright (silver rich) phases of a silver coin, whereas the microstructure of a cast coin shows a homogeneous distribution and statistic formation of the components.

Figure 12: Microstructure of a minted (left) and a cast (right) coin, seen with SEM.

As in many cases coins are rare, even unique and of high value, non-destructive analysis has to be carried out in order to determine the microstructure of an object. Additionally, it has to be kept in mind that most of the coins were buried in the ground and corrosion phenomena occur yielding the typical green patina on the surface of the silver/copper alloys. As a consequence of that corrosion process, silver is relatively enriched in the near surface domains, whereas copper is depleted, when the coins are cleaned. Analytical investigations by XRF would yield results, which are not
representative for the chemical composition of the bulk material and can’t be used for the determination of the provenance or authenticity of a silver coin.

A project has been started in co-operation with the Bonn University/Germany in order to investigate the potential of TOF (time of flight) neutron diffraction and texture analysis for the characterization of archaeological coins at the ROTAX neutron diffractometer installed at the spallation source ISIS of the Rutherford Appleton Laboratory in the United Kingdom. The experimental set-up and details of the measurements on the ROTAX instrument are already described in the literature [21, 22]. Cast and minted specimen of pure silver, Ag/Cu alloys as well as a selection of genuine and fake coins (Ferdinand-Taler, 16\textsuperscript{th} cent.) of the Kunsthistorisches Museum in Vienna were analyzed there. Each of the objects was wrapped in a protective aluminum foil and mounted

Figure 13: Experimental pole figures of the fcc reflections of silver and copper in genuine (left) and cast (right) silver coins made of Ag/Cu alloys. The results were obtained by TOF neutron diffraction carried out at the ROTAX instrument at the spallation source ISIS of the Rutherford Appleton Lab/GB.
on a texture goniometer in order to record data from 144 different coin orientations. In a first step, all the single patterns of a particular coin were summed up in order to obtain a “quasi”-texture-free average diffraction pattern that can be used for phase identification and for quantitative determination of the phase content. In a second step, the neutron intensity variations in the 144 single diffraction patterns were used to compile so-called pole figures that give information about the grain orientation distribution in a coin and that provide information on the manufacturing technique. Figure 13 shows pole figures of four coins, each of them represented by six pole figures. Two of the coins exhibit the hallmarks of minted coins produced by cold-rolling (Figure 13, maps on the left), whereas for two other coins irregular grain distributions are observed (Figure 13, maps on the right) which are typical for cast objects.

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