THE APPLICATION OF SCANNING X-RAY FLUORESCENCE MICROANALYSIS IN THE EXAMINATION OF CULTURAL MATERIALS*

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The use of a new analytical technique for the elemental characterization of artefacts is described. The new equipment is capable of X-ray fluorescence analysis in conventional mode as well as for elemental scanning of small objects, fragments or microsamples. The Omicron, manufactured by Kevex Instruments Inc., is equipped with a microfocused X-ray tube, which can be collimated to a 50 μm beam and used to scan objects over a maximum range of 256 × 256 pixels. False-colour elemental distribution maps allow the user to image small features, differently pigmented areas, or whole objects in the machine completely non-destructively. Analyses can be carried out in air, under helium or in vacuum. Two examples of the application of the new technique are described: first, to the surface decoration on a Greek Attic white ground lekythos; and, second, to the pigments used on a small painting, a 'Pittura', on copper by the Dutch artist, Frans van Mieris (1635–81) in the collections of the J. Paul Getty Museum.

KEYWORDS: SCANNING X-RAY FLUORESCENCE ANALYSIS, ELEMENTAL MAPPING, INORGANIC ANALYSIS, PIGMENTS, NON-DESTRUCTIVE ANALYSIS, OMICRON

INTRODUCTION

The application of X-ray fluorescence analysis to the elemental characterization of works of art is well-known and has been, for the past 30 years, one of the most powerful tools for the non-destructive investigation of cultural materials. From studies of 17th-century dance costumes (Dalrymple *c*. 1984) to platinum and palladium photographic prints (McCabe and Glinsman 1996), from arsenic and lead in violin varnishes (Bohlen and Meyer 1996) to the development of Chinese overglaze enamels (Scott *et al*. 1995), the uses of X-ray fluorescence analysis range over a remarkably wide territory that encompasses both objects made primarily from inorganic materials and those where the inorganic components are less obvious, such as costumes for the dance—and in many of these varied materials, no samples whatever can be removed for analysis. Most of our own X-ray fluorescence analyses of works of art have been carried out in the past using a Kevex 0750A spectrometer, operating in a large lead-lined room, which enables objects of practically any size to be examined. This is by far the most generally useful instrumentation for museum application. This equipment is unfortunately, no longer manufactured by Kevex, and there is no really satisfactory replacement on the market, despite the ingenuity of Italian scientists who have created a workstation that allows X-ray fluorescence analysis, infrared reflectography, radiography and digital processing of images of works of art to be carried out simultaneously (Alessandro *et al*. 1994). Just recently, new XRF machines are now becoming available that are excellent for museum use. The advantages of the Kevex

0750A instrument are that it can be operated in air or helium, employing secondary targets (STXRF), which can be selected specifically for certain kinds of analytical investigations, and which provide optimum detection limits for the elements under study. For metals, we often use a barium/strontium secondary target. Other common choices are molybdenum (with barium/strontium, very useful for paintings), sulphur (for phosphorus in bone black), germanium or zirconium (for old photographs).

The present paper describes another very useful addition to the commercially available X-ray fluorescence analytical systems that operate in an enclosed chamber, of which there are many, the difference being that the Kevex Omicron instrument, described here, allows scanning X-ray elemental images of the object to be acquired from powders, fragments or solid artefacts that are small enough to be placed directly into the machine.

<div align="center">THE EQUIPMENT</div>

The idea for scanning acquisition of X-ray fluorescence elemental images began to become feasible little more than a decade ago. Schreiner and Wachter (1994) described a system that was developed at the Technical University of Vienna. This system, rather like a flat-bed scanner, is equipped with a Si(Li) detector and a spectroscopic X-ray tube with a maximum power of 2800 watts. The primary beam is collimated to a diameter of l.2 mm and d.c. motors are used to move the support for detector and X-ray tube in horizontal and vertical directions, parallel to the object and above it. The selected pixels for analysis can be spread over an area of up to $1000\,mm \times 800\,mm$. However, the equipment is rather expensive: a price of \$250 000 was quoted in 1996, which is about \$100 000 more than the Kevex equipment at that time.

At about the same time as the system in Vienna was being built, engineers at Kevex Corporation began to work on a concept designed to enable wafers for the electronic industry to be mapped for elemental distribution by X-ray microfluorescence analysis, employing a fine-focused X-ray tube capable of delivering enough flux to perform a satisfactory analysis over diameters as small as $10\text{--}50\,\mu m$. This instrument is the Kevex Omicron X-ray microfluorescence spectrometer (Kevex Corporation 1996).

The X-ray unit is self-contained and can be operated in air, under helium or in vacuum. The maximum size of objects that can be placed in the chamber is 240 mm long $\times$ 230 mm wide $\times$ 110 mm in height. For scanning, the objects must be held or placed in a holding device, which limits the useable size to about 220 mm $\times$ 190 mm $\times$ 100 mm, about the size of a large cigar box. The X-ray tube uses a molybdenum target, operating at 50 kV and l mA, and the X-ray beam can be collimated to diameters from $50\,\mu m$ to $500\,\mu m$. We generally use a $100\,\mu m$ beam size. Counts per second from a solid metallic matrix under these conditions may, for example, reach $2400\,c\,s^{-1}$, while painting cross-sections and small particles may provide $300\text{--}700\,c\,s^{-1}$. This is not a secondary target XRF system and, if desired, filters can be inserted into the primary beam to adjust the excitation conditions. We usually use the instrument without any filters, and in point analysis mode, acquire the spectrum for 200 s (excluding dead-time).

Powders or fragments can be held in polyethylene cups with Mylar[TM] film stretched across the bottom into which the powder or microsample can be placed. This has proved to be very useful with small flakes of paint, particles or fragments, enabling them to be analysed without mounting or coating. Polished cross-sections can also be examined in the instrument. Painting cross-sections can sometimes be rather too small to get really satisfactory information on different layers if these are only a few microns thick, but an overall view of elemental composition is still possible. An image of the object surface can be viewed in colour at all times on the video

monitor attached to the machine, since a miniature video camera is focused at the same area on the object as the X-ray beam and detector. While observing the object on the monitor, a joystick can be used to move the stage remotely, allowing any area of the object to be selected and brought into view.

Three different angles of lighting of the object are available, which correspond roughly to bright-field, dark-field and oblique illumination. Usually, one of these is satisfactory for optimal viewing of the sample while the spot analysis or X-ray scan is being performed. In order to preserve these optical components, the video camera shuts down automatically after 5 min; this is very useful if scanning an object for many hours. If the video image should be required once more, the button can simply be toggled on again and the same area examined. It is also possible to capture the video image of the area analysed using programs such as Snappy$^©$, which can then be printed out with the X-ray maps.

After setting regions of interest (ROI) for the scanning function, under Xmap/Chemimage$^©$, a number of variables concerning the scanning regime can be selected; for example, map size, number of frames, motor speed in steps per second and dwell time variation (time per pixel). The maximum map size is 256×256 pixels. Stage co-ordinates can be precisely set with a joystick, with a precision of $2\,\mu m$, and mapping can then commence. The X-ray source is stationary, while the stage can be moved in any direction over the X-ray beam. It should be borne in mind, however, that if any of the element ROI ranges overlap, then counts will be displayed for both elements, even if only one were actually present. For example, if lead and arsenic are both to be scanned in the same sample, then the ROIs for lead and arsenic must be specified as the Lb and Kb peaks, respectively, rather than left as La and Ka. This is a well-known feature of X-ray analysis: these overlaps can easily be seen visually on the spectrum, but cannot be seen in a mapping mode. The energy range for each element can also be adjusted to try to minimize overlap.

Depending on the motor speed and map size, the acquisition time may vary from some minutes to several hours. Longer scans can be set up to run overnight, which frees up the instrument during the day. Scans or simple X-ray fluorescence spot analysis of an object can be run at any time in air, under helium or under vacuum.

EXAMPLES OF APPLICATIONS

There is an exciting range of possible applications of the scanning capability of the system, as long as the object or sample can be accommodated in the machine. One of the largest objects we have so far examined is a Greek Attic white ground lekythos with figure decoration, in the Getty Museum collections, number B3.AE.4l, shown in Figure 1. The part of the line drawing of the figure that was examined is shown in the rectangle over the enlarged view of the surface, also shown in Figure 1, and this corresponds to the elemental maps for calcium, iron, titanium, mercury and manganese which accompany this illustration, prepared by the Getty postgraduate intern for 1998, Yoko Taniguichi. The vase was scanned over an area of $4\,mm \times 6\,mm$ for $8\,h$ in air. Higher colour saturation towards the red, orange and yellow regions of the spectrum represents higher counts for the associated elemental regions of interest (ROI). For example, in our scan, calcium is depleted in the regions of the drawing relative to the background levels of calcium in the ceramic fabric, while the concentrations of titanium and manganese do not reveal any discernible difference. The concentration of iron is clearly greater in the line drawings, and a subtle increase can also be seen for mercury, corresponding to one thicker line, which has presumably been infilled in cinnabar. The use of cinnabar to provide subtle contrast of shading to the iron-rich line drawing would have been particularly difficult to confirm here, due to the fine
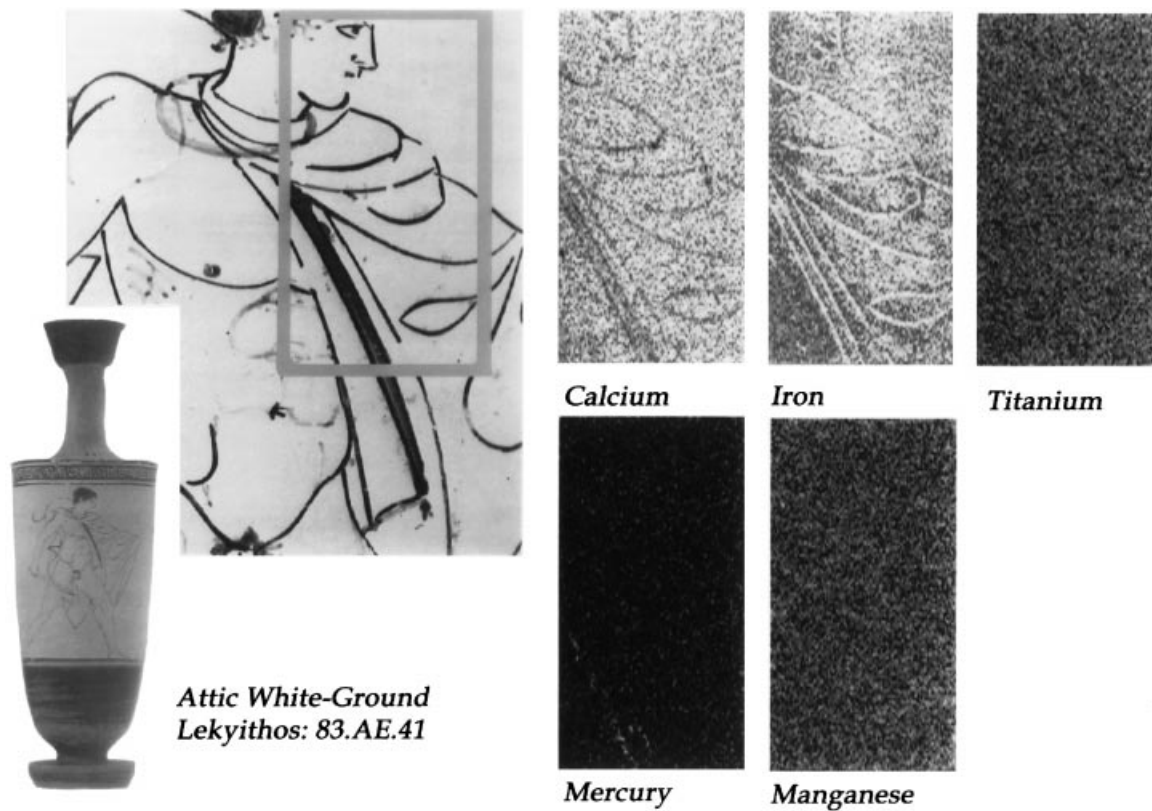
Figure 1   *The Greek Attic white ground lekythos, showing part of the line drawing. The area scanned is shown in the rectangle. The use of cinnabar for shading over iron oxide red can be inferred from the mercury detected here.*

scale of the drawing, the delicacy of the applied red areas and the impossibility of removing any sample for study. Since cinnabar sublimes at a temperature of 580 °C, its presence on white-slipped ground as decorative paint is indicative of post-firing application, especially since most estimates of firing temperature for this kind of ceramic range from 800 °C to 1000 °C (Maniatis and Tite 1981). Examples of the use of cinnabar as post-fired red decoration are rare according to Jones (1986), although this apparent rarity may be related to the analytical techniques used in previous investigations.

Although the iron concentration is higher in the lines than the body, it is not possible to deduce the composition of the black line decoration from this scan, but we know that it is probably not simply, or even, a carbon black, and since manganese is not present at elevated concentrations, pyrolusite, MnO_2, can also be eliminated as a possibility. The paint used here is almost certainly an iron-rich clay, a coloured earth containing an iron ochre, or a combination of the two, which, on firing in the final, oxidizing environment, tends to produce a glossy black or very dark brown colour. The presence of umber can also be ruled out, since there is no elevation of manganese associated with the iron-rich line decoration.

A second example of the use of the instrument is in the examination of a small oil painting on a copper support, by the Dutch artist, Frans van Mieris (1635–81) in the collections of the J. Paul Getty Museum. In this painting, 'An Allegory of Painting', a 'Pittura', a woman is shown holding a palette with seven different colours, as shown in Figure 2. The painting is signed to the right of the woman's shoulder, 'F. v. Mieris/Ao 1661'. To protect the surface from any abrasion in the carrier frame, felt strips were laid down over the metal rails to provide a suitable support during the analysis, work which was carried out by our postgraduate intern for 1996, Joris Dik.

We scanned three different areas of the painting. The upper two images, shown in Figure 2, for the elements copper and lead, reveal part of the copper panel and the lead white ground preparation layer. The higher concentration of lead in a series of horizontal and vertical lines reveals where the copper panel has been scored to improve the adhesion of the ground to the copper. The area of the palette was scanned over an area of 4l mm × 52 mm, for 466 min, taking seven frames at a speed of 110 steps per second. For greater sensitivity, the speed of the scanning process can, if desired, be reduced to levels of about 30 steps per second, although the scan time then becomes greatly increased.

The elemental distribution maps for calcium, iron, mercury and tin are illustrated in Figure 2. The calcium content of the black pigment is strongly indicative for ivory or bone black, which originally contains calcium hydroxyapatite, $Ca_5(OH)(PO_4)_3$. According to Mayer (1970), bone black comprises roughly 15–20% carbon, 60% calcium phosphate, $CaPO_4$, and 20% calcium sulphate, $CaSO_4.2H_2O$. Phosphorus is not as readily detected as calcium in these applications.

The presence in many areas of both iron and a small amount of manganese attests to the presence of umbers in the painting. Since the only common red pigment containing mercury is cinnabar, we may infer the presence of that pigment from the elemental maps shown here. Not only do these maps illustrate the presence of quite clearly different pigment areas, but they also reveal the subtle shift in the painted outline of the palette, indicated by arrows on the elemental scans, which are especially visible in the maps for iron and mercury. This is good evidence for an original pentimenti by van Meiris in shifting slightly the position of the painted palette. The discovery of this pentimenti by means of scanning X-ray fluorescence is a good indication of the potential of the technique: it was later confirmed by infrared examination, which is beyond the scope of this note.

Elemental scans are also shown for the face, where iron, manganese, calcium and mercury are present in the painted image. For example, two small circular dots can be seen in the centre of the calcium map, corresponding to the bone black used for the pupils, and the higher concentration
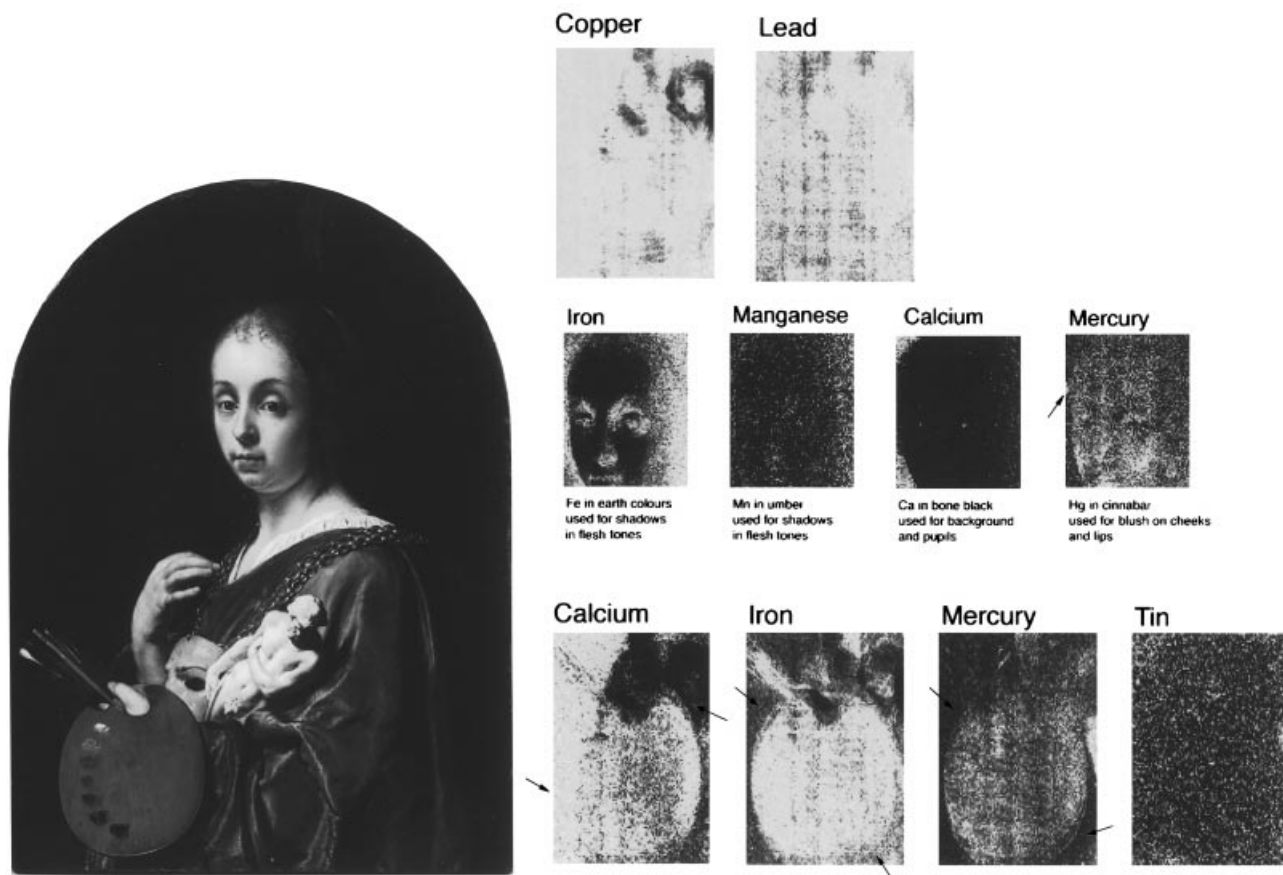
Figure 2   *A small painting on copper by Frans van Mieris, 'An Allegory of Painting', showing the results of elemental scanning for the elements Cu, Pb, Ca, Fe, Hg, Mn and Sn.*

to the left-hand side of the calcium map, showing that bone black was used for the background. The iron map shows that earth colours have been employed for the shadows in the flesh tones, and there is a faint echo of this pattern in the map for manganese, showing that some umber was used. The map for mercury shows a close relation to the red blush on cheeks and lips, which indicates that cinnabar was used for these parts of the face. The small area of tin just caught in the far right-hand side of the scan for the element shows that van Mieris probably made use of lead–tin yellow in the painting. He used this pigment in the golden chain, and also in the paint depicted on the hairs of the thick brush, which was determined by an XRF point analysis rather than a scan. Care must be taken in choosing the appropriate line for these elemental scans, particularly for the elements gold, mercury, lead, arsenic, platinum, bromine and sulphur. Careful selection of the appropriate Lb or Kb peaks for some of these elements, rather than La or Ka, will alleviate overlap, as with any energy-dispersive X-ray system.

CONCLUSIONS

The purpose of this note is to draw attention to the applications of scanning X-ray microfluor-escence analysis in art and archaeological contexts. The instrumentation is now readily available and has been shown to have useful strengths as an analytical tool for a wide variety of objects and samples, which can be introduced into the sample chamber without the need for any preparation. Materials can be studied visually, and at the same time point analyses can be made, in air, under helium or in vacuum. Selected areas of the object can be chosen for elemental mapping. The heterogeneity of many ancient materials in either sectional study or surface examination makes the technique a very useful addition to the methods available for characterizing ancient materials.

Note that the minimum hardware requirements to run Xmap are a 80486-based PC, Microsoft Windows 3.1 or later, a SVGA card/monitor, 8 Mb RAM, a hard disk with at least 4 Mb of free disk space, a 256 or more colour graphics card/monitor and a HP 1200 colour printer.

REFERENCES

Alessandro, C., Falcucci, C., and Rinaldi, S., 1994, IMAFLU: una stazione mobile di analisi non distruttive per la diagnostica e lo studio delle opere pittoriche, *Kermes*, **7**, 52–73.

Bohlen, A. von, and Meyer, F., 1996, Arsen und Blei im Geigenlack: zur Elementanalyse in kleisten Lackproben, *Restauro*, **102**, 472–8.

Dalrymple, H. E., n.d. (*c.* 1984) A seventeenth century dance costume: results of analysis, in *The laboratories of the National Museum of Antiquities of Scotland* (eds. T. Bryce and J. Tate), vol. 2, 111–17, National Museum of Antiquities of Scotland, Edinburgh.

Jones, R. E., 1986, *Greek and Cypriot pottery: a review of scientific studies*, Fitch Laboratory Occasional Papers No. 1, The British School of Archaeology at Athens, Athens.

Kevex Corporation, 1996, *Omicron spectrometer user's guide*, Fisons Instruments Manufacturing Inc., Valencia, California. (Note that the company merged with Rhone-Poulenc Inc., then with Fisons Instruments Manufacturing Inc., and then with Thermo Inc. as of 1997. It is no longer part of Fisons Instruments Manufacturing Inc.)

McCabe, C., and Glinsman, L. D., 1996, Understanding Alfred Stieglitz' platinum and paladium prints: examination by X-ray fluorescence spectrometry, in *Research techniques in photographic conservation: proceedings of the conference in Copenhagen*, 14–l9 May 1995, 31–40, Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen.

Maniatis, Y., and Tite, M. S., 1981, Technological examination of Neolithic – Bronze Age pottery from central and south-east Europe and from the Near East, *Journal of Archaeological Science*, **8**, 59–76.

Mayer, R., 1970, *The artist's handbook of materials and techniques*, 3rd edn, The Viking Press, New York.

Schreiner, M., and Wachter, O., 1994, in Ein erwitertes System der Rontgenfluoreszenzanlyse zur zerstorungsfreien Analse von Kunstwerken und Anwendung bei tintenfrassgeschadigten Papierobjekten (eds. M. Koller and R. Prandtstetten), *Zum Thema Papier und Graphik*, 43–56, Verlag Mayer & Co., Vienna.

Scott, R., Wood, N., and Kerr, R., 1995, The development of Chinese overglaze enamels: part 1, in *The ceramics cultural heritage: proceedings of the international symposium 'The Ceramics Heritage' of the 8th CIMTEC-World ceramics congress and Forum on new materials, Florence, Italy*, 28 June – 2 July 1994 (ed. P. Vincenzini), 153–60, TECHNA, Faenza.