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Summary

Conservation scientists and conservators have used a variety of scientific instruments to examine, diagnose, and treat their museum's collections. One analytical method widely used in the museum laboratory is x-ray fluorescence spectrometry (XRF). No other technique gives the immediate ability to survey virtually all the elements on the periodic table -- potassium and higher for air-path instruments -- without having to remove a sample from the artwork. Its versatility alone makes it indispensable in a modern museum laboratory. It has been 50 years since XRF was introduced into the museum field, when Dr. E.T. Hall, an archaeologist and art historian, had the ingenious idea to develop XRF as a non-destructive analysis method, and subsequently used the technique to discredit the Piltdown Man as an elaborate hoax. His analysis results showed the presence of potassium and chromium in the bones suggesting the use of potassium dichromate in the staining process. His success prompted Oxford University to establish its Research Laboratory for Archaeology and the History of Art, which he led until his retirement in 1989. Dr. E.T. Hall is quoted as saying "these analyses were probably the very first practical use of XRF for either academic or commercial purposes" [1]. However, it wasn't until the 1970's when semi-conductor detectors and modern computers became available, which made it possible to quickly perform the tedious calibrations and complex mathematical computations and decreased the expense of the system, that XRF became accessible to museum laboratories. Innovators in the field such as Cesareo, Hansen, Frankel, and Hall began to extend the application of XRF analysis beyond archaeological objects to fine art objects [2,3,4,5].

With the emergence of the relatively inexpensive portable hand-held XRF spectrometers and portable laptop computers more museum laboratories have access to this analytical tool than ever before. These small hand-held systems can be operated with relative ease by scientists and conservators alike. XRF is increasingly being used to examine a wide range of artworks. However, conservators and curators should not expect too much from the technique, as many questions can only be partially answered or not be answered at all. There is a growing need to inform museum professionals who use the results of XRF analyses, about the limitation of the technique to ensure that misinterpretations and unrealistic expectations do not occur. This thesis is the culmination of

fifteen years of XRF analyses performed at the National Gallery of Art in Washington, D.C. It is hoped that the experience and expertise gained from these analyses will lead to a better understanding of the uses and limitation of XRF in the museum field.

Chapter 1 furnishes the museum professional with a better understanding of the principles of XRF, both theoretical and practical, to aid them when making decisions regarding the study, preservation and exhibition of the museum's collections. An overview of x-ray fluorescence theory and instrumentation is presented. The scope of x-ray fluorescence in the museum laboratory is demonstrated by discussing specific examples from the National Gallery of Art's collections of easel paintings, works on paper, photographic prints, sculpture and decorative arts. This chapter provides a protocol to use when analyzing artwork. Subsequent chapters present more in depth case studies while developing appropriate protocols for analyzing various classes of artworks with XRF.

The complex chemical nature and variety of physical appearances of platinum and palladium photographs are discussed in **Chapter 2**. The difficulty of analyzing these photographs with XRF is discussed. A set of facsimile photographs of known composition are produced and analyzed by XRF and the detection of known image materials is optimized. A protocol is developed that uses the facsimiles produced by known chemical processes as analytical standards. These standards are then compared and analyzed using XRF with several photographs in the National Gallery of Art.

Chapter 3 investigates the uses of XRF to answer questions of authenticity for a group of Renaissance bronze sculptures. Seven small busts of Pope Paul III Farnese attributed to Guglielmo della Porta are examined visually to determine whether their method of manufacture is consistent with sixteenth-century casting practices. They are then analyzed with XRF to determine whether the composition of the metal is in accordance with that of other Renaissance bronzes. Renaissance metallurgical practices are discussed and compared with modern refining and art foundry practices.

XRF analyses of over two hundred Italian Renaissance portrait medals in the collection of the National Gallery of Art, Washington are examined in **Chapter 4**. This chapter discusses how statistics are used to aid in the investigation of such a large quantity of data. A statistical model is developed for allocation of these medals into meaningful assemblages and an expanded nomenclature is formulated for the numerous alloys detected.

Chapter 5 investigates the unusual compositional nature of a series of portrait medals made by or attributed to Matteo de'Pasti. These medals were classified in **Chapter 4** as leaded bronzes containing 10-60 percent more antimony and arsenic than is common in Renaissance portrait medals. More than half the medals in this group are attributed to Matteo de' Pasti. This is the

only group of medals to exhibit such an unusual composition. The possibility that the artist has used a specific alloy composition led to an in-depth study of these medals. This study provides a possible link between the high levels of antimony and arsenic occurring in these medals and specific Renaissance ores.

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1 Hall, E.T. 'Riddle of the tenth man' in *Nature*, June 1996.

2 Cesareo, R., Gigante, G.E., Canegallo, P. Castellano, A., Iwanczyk and Dabrowski, A., "Non-Destructive Analysis of Chemical Elements in Paintings and Enamels: in *Archaeometry*, 14 (1972) 65-78.

3 Hansen, V., "Qualitative Elemental Analysis of Art Objects by Energy – Dispersive X-Ray Fluorescence Spectroscopy", *Applied Spectroscopy*, 27 (1973) 309-334.

4 Frankel, R.S., "Detection of Art Forgeries by X-Ray Fluorescence Spectroscopy" *Isotopes Radiation and Technology*, 8 (1970) 63.

5 Hall, E.T., Schweizer, F. and Toller, P.A., "X-ray Fluorescence Analysis of Museum Objects: A New Instrument, in *Archaeometry*, 15, 1973, 53-78.