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*All that glitters...: the Byzantine gold solidus, c. 300-1092\****Introduction**

'All that glitters' is a collaborative project using x-ray fluorescence (XRF) facilities at the University of Birmingham Department of Chemistry to examine Byzantine gold coins from the Barber Institute of Fine Arts (Birmingham, UK). Its primary aims are to establish whether and to what extent current XRF technology is suitable for obtaining consistent or accurate results from analysis of high-purity gold, with respect to major and minor elements. This paper considers the scholarly background to the study, its aims, recent developments in XRF technology, and methods.

**1. Background**

As a technique for analysing coins XRF was pioneered in Paris in the 1970s and 1980s, partially as a component of a landmark study of the metallic composition of Roman and Byzantine gold coins.<sup>1</sup> XRF technology was then capable of yielding data concerning only the major elements in a sample (in gold coins, usually gold, silver and copper), and alongside proton activation analysis, contributed the bulk of new data to a study which also collated results from other techniques of analysis, including specific gravity, touchstone and fire assay.<sup>2</sup>

Thereafter, XRF took a back-burner, as did the metallurgic analysis of Byzantine coins at all, with new publications mainly presenting results obtained far

earlier.<sup>3</sup> In the last decade, however, XRF has become the focus of new studies, partly generated by collaborations between manufacturers of scientific equipment and scholars. The non-destructive and comparatively cost-effective nature of XRF has also made it popular with museums and archaeological services. The result has been publications and presentations of XRF analysis on gold, silver and copper coinage and small archaeological finds.<sup>4</sup> Simultaneously, manufacturers of XRF equipment have become increasingly confident in their claim that their machinery is capable of detecting and quantifying trace levels of elements in alloys.

**2. Aims**

This study emerged from a desire to test those claims, and establish how far (if at all) current XRF technology is effective as a tool for numismatic analysis beyond its capacities in the 1980s. The initial aim was, therefore, to select a sample of coins and a strategy of testing which might suggest the:

relative sensitivity to minor elements in coins of different XRF equipment;  
extent to which repeated testing of the same coin yielded consistent results;  
extent to which cleaning coins for testing by various methods affected the results observed;  
level of variation in observed results as a consequence of testing different areas of a coin  
level of variation in observed results as a consequence of running different length testing cycles on the available equipment.

XRF technology has recently been re-introduced to the numismatic environment as, potentially, a comparatively affordable, available, easy-to-use and low-risk method of conducting analysis. Above all, it has on the basis of these claims been aimed at and taken up by numismatic scholars and museum professionals, especially at museums with limited funding for elaborate artefact analysis. This study is not an attempt to replicate or replace major archaeometallurgic projects, and does not claim the expertise they rely upon, nor does it

\* Written and developed in collaboration with Robert Bracey (British Museum), Jonathan Jarrett (University of Leeds), Colin Slater (Bruker AXS GmbH) and Maria Vrij (University of Birmingham/Barber Institute of Fine Arts). With the kind assistance of Jackie Deans (University of Birmingham), Mike Dobby (Independent Consultant), Andrew Oddy (Independent Scholar), Adrian Wright (University of Birmingham). Additional thanks to Nicola Kalinsky, Director, Barber Institute of Fine Arts, and the Trustees of the Barber Collection, Ian Leins (Department of Coins and Medals, British Museum). The S8 TIGER used in this research was obtained through Birmingham Science City: Creating and Characterising Next Generation Advanced Materials (West Midlands Centre for Advanced Materials Project 1), with support from Advantage West Midlands (AWM) and part-funded by the European Regional Development Fund (ERDF). Financial support for its use was provided by the Roman and Byzantine Fund of the Royal Numismatic Society. I am also grateful for comments and questions received during presentations at the International Numismatic Congress and the UCL-British Museum Joint Archaeology Seminar.

<sup>1</sup> Morrisson *et al.* 1985.

<sup>2</sup> Morrisson *et al.* 1985, pp. 17-38.

<sup>3</sup> For example: Morrisson *et al.* 1988; Morrisson *et al.* 1998; Bartlett *et al.* 2011.

<sup>4</sup> For example: Broodbank *et al.* 2007; Constantinescu *et al.* 2009; Gitler and Ponting 2003; Lal *et al.* 2011; Kantarelou *et al.* 2011; Le Niece and Cowell 2008; McArthur 2011; Parreira *et al.* 2009.

aim to re-write XRF theory. It is an effort to evaluate as practitioners the utility of current technology for precisely those smaller-scale inquiries which cannot afford (in terms of time, money, expertise or research priorities) to be the subject of lengthy, specialist laboratory testing, or for those collections which because of budget or security and preservation policies, cannot be subjected to destructive or invasive metallurgic analysis. Is modern XRF equipment, as manufacturers claim, a suitable tool in these circumstances?<sup>5</sup>

### 3. Developments in XRF technology

Although the constraints of XRF for the analysis of coins have been written about before, various recent technological developments have possible implications for analysis of coins by XRF.<sup>6</sup> The first is the development, and increasing availability, of Wavelength Dispersive (WD) as opposed to traditional Energy Dispersive (ED) XRF. XRF analysis can be described by three processes: excitation, dispersion and detection. In modern WD and ED spectrometers, excitation (the process of producing fluorescent x-ray photons from the sample being analysed) is achieved in the same way. However, in an ED spectrometer the detector handles both dispersion (determination of the energy of the incoming x-ray photon) and detection (counting how many photons of this particular energy are being produced). In a WD spectrometer, dispersion of incoming x-ray photons is achieved by an array of analyser crystals, which, when oriented at the correct angle according to Bragg's Law, diffract only photons of a particular energy, permitting x-ray photons from single elements to reach the detector rather than from multiple elements simultaneously. This allows WD spectrometers to perform elemental analysis with much higher resolution than ED spectrometers. Modern WD spectrometers are also generally much higher-powered than ED spectrometers, increasing the intensity of the observed signal for a given sample. Higher power and more complex construction, however, also make WD instruments usually larger (and less portable) than ED equipment, and more expensive to buy.

Second, there has been significant development in software used to compute concentrations from observed signal intensities. There is theoretically a linear relationship between the concentration of an element in a sample and the intensity of an observed signal for a given element. Usually, however, deviations from this linear relationship arise. These most commonly result from inter-element effects (also known as 'matrix' effects) within the sample itself but may also, for example, be the consequence of spectral artefacts, such

as signals from excitation of the components of the spectrometer itself.

A third development, connected with the second, has been the development of standardless quantification. For traditional standards-based XRF analysis, a series of samples of known composition, of the same material type as the sample are measured and the observed intensities correlated to the known concentrations for each element in the sample. This approach takes into account the majority of inter-element effects but relies on the analyst knowing which elements are likely to be observed and having standards for these elements available. The need for analysis of completely unknown samples has led to the development of modern standardless analysis packages (often termed 'Fundamental Parameters' packages) which calculate the concentration of each elemental component in the sample mathematically. This is potentially valuable for analysis of pre-modern numismatic material as it does not impose assumptions about what is likely to be found in alloys, or bias analysis towards combinations of elements typical of modern alloy (and therefore standard) production.

Fourth, the development of sample chambers which allow analysis to be carried out under either high vacuum or under a helium atmosphere has led to modern spectrometers offering greater sensitivity for light elements.

Finally, it is now possible on modern WD XRF spectrometers to select an appropriate counting time for the measurement. Detection limits, repeatability and precision in XRF are related to the ratio between the intensity of the signal used for quantification and the intensity of the background of the spectrum within that particular region (signal to noise ratio). Since intensities reported are an average of the count rates, integrated over the measurement time, longer counting times mean that these averages more closely reflect the intensity that correlates to the concentration of the element in the sample. As components present in trace levels will only produce very low intensity peaks, longer counting times also have the effect of 'flattening' the background of the spectrum making smaller peaks, with much lower signal to noise ratios, more visible. For numismatic analysis the potential of these developments for more accurate results and compositional analysis without the necessity to estimate likely components in advance is potentially valuable.

### 4. Methods

The project began with a pilot conducted in the Barber Institute of Fine Arts, using handheld and desktop ED XRF equipment. This demonstrated that while the ED XRF equipment read high gold levels in the coins tested - broadly comparable with the results of all testing methods collated by the Paris study - it offered little detection of minor elements: usually no more than silver and, sometimes, copper. It was therefore determined

<sup>5</sup> For example <http://www.geotek.co.uk/products/xrf> and <http://www.horiba.com/uk/scientific/products/x-ray-fluorescence-analysis/> (both consulted 29/02/2016).

<sup>6</sup> Beckhoff *et al.* (eds) 2006, especially chapters 1-4 and 7.8 (Engelhardt, 700-712).

that, while portable ED XRF might be a suitable tool for tracking major debasement cycles, involving large changes in the quantity of the major precious metal component of coins, the particular instruments that were used were not suitable for our study. Byzantine gold coinage for most of the period c. 300-1092 was famed for its high purity and stability, and the Paris studies of the 1970s and 1980s had demonstrated this to be broadly observable from metallurgic analysis. We therefore determined to continue our study using WD XRF technology, specifically a Bruker S8 TIGER, which conducts testing in a vacuum, and is regularly maintained and provided with software updates by Bruker AXS GmbH. The standardless analysis package included with this instrument offers a 2-, 8-, and 18-minute measurement method, thereby offering an opportunity to evaluate the major technological developments in recent XRF analysis. At these initial stages we also had use of a gold calibration standard loaned by the British Museum to use alongside the standardless analysis package.

At the University of Birmingham Department of Chemistry, we first tested coins uncleaned, in museum collection condition - i.e. kept in neutral and safe conditions, probably cleaned at some point historically and now subject to occasional handling. We then cleaned and re-tested the same samples, leaving one coin uncleaned as a control, using a soft toothbrush and acetone to remove grease and other surface accretions. Finally, we used cleaning methods developed on the Staffordshire Hoard Project to clean coins (including those previously cleaned lightly) using acetone and a *berberis* thorn to remove further surface contamination, and re-tested. In order to evaluate the effectiveness of different measurement times for providing consistent and accurate results, we tested the same set of coins on both 8- and 18-minute methods. For all stages of testing we have included previously-analysed coins alongside new samples in order to enlarge our total corpus while simultaneously testing for machine consistency. In order to test consistency further, we analysed one additional coin four times on each side, without removal from the sample holder, or any other modification of testing conditions. All coins were given unique running numbers, since Barber Institute collection numbers run chronologically and might have directed our interpretation.

The S8 TIGER requires samples to be loaded into sample cups, and is not suitable for testing on the edge of coins, or on pierced or cracked areas of coins. Instead, masks can be used to isolate a specific area of the coin surface. Most of our tests were performed using an 8 mm diameter testing area on each face of each coin. Each test was photographed so that the precise area tested could be identified subsequently. In order to investigate the issue of surface homogeneity, however, we ran a further round of tests (with new and repeated samples) using two 5 mm spots on each face of the selected coins, in order to admit variation between spots,

but also between the results of testing a large central area of a coin, and two smaller spots on the same coin. While our initial aims have been methodological, our selection of coins was made with the aim of allowing historical analysis, should the quality of results obtained make this viable. We situated our area of study in the context of the existing findings of Morrisson *et al.* in the 1980s. The Byzantine component of the Paris study focused mainly on gold coinage from the tenth century onwards. By choosing the period immediately prior to, during and after a known and dramatic debasement, discussed in contemporary sources and ultimately clearly visible by eye, Morrisson and her collaborators were able to provide new insights into the testimony of documentary sources, demonstrating that debasement had begun before the period at which it was condemned in textual sources.<sup>7</sup> 'All that glitters...' therefore decided to focus its attention on the earlier centuries of Byzantine coinage, during which consistency is the apparent hallmark, despite extended periods of political, economic and military volatility. Should results of our methodological tests permit it, our selection of coins is intended to allow examination of the parameters of that consistency, across time, space and gold denominations, and in particular, contribute to work, also emerging from the Paris studies, into the particular cases of the Syracuse and Carthage mints.<sup>8</sup>

So far tests have involved 86 Byzantine or contemporary coins:

- 79 Byzantine, attributed to the mints of Alexandria, Carthage, Constantinople, Ravenna, Syracuse and Thessaloniki, with one attributed either to Cyprus or Alexandria. They date from 491 to 842 and comprise 61 *solidi*, two *semisses* and 16 *tremisses*.
- 7 coins contemporary with the Byzantine coins being tested but from different regions, in particular, the Sasanian Empire and the Umayyad Caliphate, the province of Sind in the Indian subcontinent, an Ostrogothic Roman *solidus* in the name of Justinian I, and an imitation *solidus* of uncertain origin of Phokas (listed by its donor to the Barber as 'Avar').

Coins have been selected in pairs of the same emperor, mint, and where possible, workshop and type, as a precaution against single anomalous samples, and coins have been included from different discovery contexts, where these are known, including coins found in the sea. In total we have conducted 20 tests using the Bruker handheld, 92 tests using the tabletop ED XRF M10ra and 290 tests using the S8 TIGER, of which 224 were conducted on the 18 minute cycle.<sup>9</sup>

<sup>7</sup> Morrisson *et al.* 1985, pp. 114-18.

<sup>8</sup> Morrisson *et al.* 1983.

<sup>9</sup> These figures include tests conducted subsequent to the INC meeting in Taormina in September 2015, but prior to submission of this contribution in March 2016.

## Conclusion

The above is a summary of the background, aims and methods of our study. Testing is not yet concluded and full publication of results will follow, which will reflect on both methodological and, if viable, any historical conclusions suggested by our results.

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