The Role of Physical Science in the Study of Cultural Heritage

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We review the recent development of the use of scientific methods in the study of cultural heritage, in particular archeology and art. The strength and limitation of the scientific approach to problems in cultural heritage are described. Examples that illustrate successful application of physical science methods to the fields of archeology and art are presented. Finally, we draw on our experience in dating and authentication of Chinese ceramics to show that even the counterfeiters are going high-tech and our counter-measures.

1. CULTURAL HERITAGE PROBLEMS ADDRESSED BY PHYSICAL SCIENCE METHODS

For thousands of years practitioners of arts and crafts in every part of the world have gone about their trades using sensory organs. In the same vein, students of cultural heritage pursued their study by sights and touch. This humanistic approach is changing as technology in current physics research have been finding their way into the traditional humanity stronghold of archeology and art. Carbon 14 dating of carbon-containing man-made artifacts is probably the most well known example of the use of scientific technique in archeology [1]. Similarly art objects such as Roman paintings have been analyzed by Raman spectroscopy to reveal the organic composition of the pigments [2]. Radiocarbon dating and Raman spectroscopy allow us to probe physical parameters undetectable by human sensory organs. The purpose of radiocarbon dating is to discover the time of manufacture of the artifacts that are often preceded or unaccompanied by written record. Information about organic content of the pigments helps the restoration and protection of the paintings much ravaged by old age. Evidence gathered by scientific measurements augments and verifies written historical record. These are extra dimensions afforded by modern technology.

The advantage of scientific methods is of course the quantitative nature of the information rendered by scientific measurements that are untainted by human meddling. Beyond academic interests, the art market is also finding scientific methods valuable in the dealing of art objects, by virtue of the scientific objectivity. Some financial analysts have ranked art objects above stock and real estate as the best yielding investment. The authenticity of the art object must however be assured for the investment to have any chance of return. The counterfeiters have been very shrew in taking advantage of the inclination of the art dealers to rely solely on sensations evoked by an art object’s form, color and touch. Hence there has been no shortage of look-alike fakes in the art market. The objectivity of scientific authentication surely provides the much-needed peace of mind to the dealers and buyers. Both scientific dating and elemental/composition analysis have been applied to the authenticity determination. We will review the strength and weaknesses of the techniques.

2. ELEMENTAL/COMPOSITION ANALYSIS OF ANCIENT ARTIFACTS

In the past decades, increasingly advanced hardware in physics research such as synchrotron and inductively coupled plasma mass spectrometer (ICP-MS) has been put into service for dating or authenticating ancient artifacts. This trend reflects the advance and demand of science in heritage
In employing scientific techniques to tackle problems in art objects, it has been found that the correct use of tools formerly available only to physical science may provide definitive answers to questions of provenance and authenticity of arqueological finds. For arqueological finds, one is interested to know: How old is artifact? Where is it made? Was it made locally or was it imported? What are materials and technology used in making it? For works of art, one is likely to ask: Is the art object authentic? Which part of the object is authentic or which part is restored? Who executed the art object? With the art object authentic? Which part of the object is authentic or used in making it? For works of art, one is likely to ask: Is the artifact? Where is it made? Was it made in the 1930s? European Museums were declared authentic. Obviously the practitioners of PIXE and XRF in this case were not heeding the warning of Harbottle caution. For someone who is worried about very minute damage to the artifacts, surface techniques such as X-ray fluorescence (XRF) or particle-induced X-ray emission may be the choice. Either technique leaves no visual damage except for the X-ray irradiation. If one is to avoid the surface heterogeneity caused by corrosion, bulk analytical techniques such as laser-ablated ICP-MS in fact afford highly reliable data. Either a material sample must be removed from the artifact or the artifact must be small enough to be fit inside the sample holder. In the later case, only a crater a few tens of microns in depth remains after the application of laser ablation. The technique of elemental analysis has had success in well-recorded arqueological finds. An example is the painted sarcophagus found in Crete, of late Minoan period. Information obtained from elemental analysis sheds light on the pigments used in the frescoes and the degree of technological know-how of the ancient Minoans. Elemental analysis has been less successful in authenticity study however. A well-known case is the pair of blue and white vases purportedly of Yuan Dynasty. Based on the similarity of impurity patterns obtained from elemental analysis using PIXE and XRF techniques, the pair of vases was declared authentic. Obviously the practitioners of PIXE and XRF in this case were not heeding the warning of Harbottle who professed that unequivocal sourcing based on impurity pattern is impossible [4]. The authenticity of the pair of vases was refuted later by thermoluminescence dating and by historical arguments [5]. Therefore one must view authenticity study of artifacts based on elemental analysis data with great caution.

3. RADIOCARBON AND THERMOLUMINESCENCE DATING

Compared to elemental/composition analysis, dating of arti-
facts by radiocarbon or thermoluminescence generate relatively simple data sets. There is no question of similarity and dissimilarity of the impurity patterns with the established groups. The time of decease (for radiocarbon) or the time of manufacture (thermoluminescence) of the artifact is arrived at by measuring the level of radioactivity in either case. Since the level of radioactivity of the artifact is relatively immune to external events (except for the case of intentional irradiation to produce fake; see the section to follow), the mode of manufacture, use and storage would not alter the dating result. For a carefully calibrated and well-executed measurement, scientific dating can provide an accuracy of ±10% of the actual time of manufacture. The sparseness of the dating data may not offer fertile evidence to the archeologist who wants to probe deep into the ancient world, but may prove succinct enough for authenticity determination, which is often decisive in any dealing of art objects.

4. THERMOLUMINESCENCE DATING OF CHINESE CERAMICS

We will draw on our experience on dating and authentication of ancient Chinese ceramics to illustrate the conflicting role of physical science in art dealing, in part because of the relative importance of Chinese ceramics in the antique market. Presently Chinese ceramics are estimated to take up more than 50% of the trading volume of all Chinese antiques. Antique Chinese ceramic is routinely sold for hundreds of thousands of US dollars. Such high price proves to be strong stimulus for fabricating fakes. Fortunately scientists and collectors alike are equally determined to devise counter measures to defeat the fakes by scientific authentication.

Since the first observation of luminescence emission from a ground-up pottery upon heating by Kennedy and Knopff in 1960 [6], thermoluminescence (TL) testing has found wide applications in the dating of pottery of archeological interest and the authentication of work of art [7]. Samples must be taken from the object to be tested. The required weight is as little as a few milligrams to preserve the physical integrity of the artifact. The sample is then processed into fine grains. Luminescence is emitted from the fine grain sample on a hot plate when temperature is raised from room temperature to about 500 °C. The plot of luminescence intensity versus temperature (in degree Celsius) is called a TL glow curve. In principle the last date of firing of the ceramics and hence the archeological age can be determined from the TL glow curve. However it was reported [8] that the TL glow curve could be faked by irradiating a copy with x-rays. In addition, the margin of error given by several TL service providers has been far too wide to be of value in determining the true archeological age (e.g. a pottery figurine was given an estimated age between 1,000 to 2,000 years before present by a TL service provider. The span of 1,000 years in fact covers more than 10 dynasties from Western Han to Northern Song in Chinese history.) We will give a brief review the principle of TL testing in art authentication. Later we will discuss methods to improve the accuracy and uncovering forgeries exposed to external radiation.

Estimate of the archeological age of the sample is obtained from the following formula

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\text{Age (years)} = \frac{D_{\text{accumulated}}}{D_{\text{annual}}}
\]

where \(D_{\text{accumulated}}\) is the radiation dosage absorbed by the sample over the years and \(D_{\text{annual}}\) is the annual absorbed dosage. The accumulated dosage is determined from the intensity of the luminescence emitted from the sample when heated (thermoluminescence). This is because the accumulated radiation is stored in the sample as trapped electrons that can be released as luminescence when activated by heat. Therefore there is a conversion of radiation into luminescence (\(x\) amount of radiation for \(y\) amount of luminescence). The ratio \(x/y\) is sometimes called the TL sensitivity and can be deduced from the TL response of the sample to a calibrated dose of radiation. Dividing the peak intensity by the TL sensitivity gives the accumulated dosage. Generally the accuracy of the measured accumulated dosage improves with higher sensitivity.

The annual absorbed dosage requires measurements separate from that of the accumulated dose. For ceramic artifacts in archeological sites, the contribution to the absorbed radiation derives from the environment and from the artifact itself (clay minerals that are weakly radioactive). For work of art, it is mainly the radioactive minerals in the ceramics artifacts that produce the radiation. Because of the short penetration depths and hence high-energy deposition of \(\alpha\) and \(\beta\) radiation (penetration depths of tens of microns for \(\alpha\) and about 1 mm for \(\beta\) in typical Chinese ceramics), these two types of radiation from the ceramic itself are responsible all the radiation absorbed by the sample. Determination of \(\beta\) radio-activity requires the measurement of \(\beta\)-active element (primarily potassium-40) in the ceramic sample, whilst \(\beta\) measurement needs a sensitive scintillation counter. Typically for Chinese ceramics, the \(\beta\) activity is weaker. Since the scintillator counter often registers less than 100 counts per day, accurate \(\beta\) counting requires several days. In general, both \(\alpha\) and \(\beta\) measurements are needed, but the TL sensitivity is different for either radiation. It is not unusual for a ceramic sample to respond to either \(\alpha\) or \(\beta\) radiation only.

We have tested thousands of ceramic samples of Chinese origin, provided by antique dealers, collectors in Hong Kong and from Far East and by research institutes in China. All samples show very weak \(\alpha\) and \(\beta\) activities as expected of
typical clay materials that contain trace amount of radioactive elements such as K-40, U-238, Th-232. For example the annual dose from Chinese blue and white porcelains of Ming and Qing Dynasties vary from 1 mGy to 7 mGy with a scattered distribution. That is to say: one blue and white shard can have an annual dose of 1 mGy and it is just as likely for another shard to have annual dose of 7 mGy. Our statistics does not indicate a higher probability for the mean dose at 3.6 mGy. The substitute use of actual radioactivity measurement by some so-called typical annual dose will lead to wide-error margin in the estimate of the archeological age. A case in point is the authentication of Ge ware with crackling glaze. Since its first appearance in Southern Song dynasty, copies of Ge ware were made for official or civilian use in Ming, Qing Dynasties. If one were to use the accumulated dose determined from the TL glow curve and some presumed typical annual dose without actually measuring the radio-activity, a copy in late Qing can be mistakenly determined to be that of Song dynasty or vice versa. Such authentication process would certainly leave the customer in distress.

5. HIGH TECH CHINESE CERAMICS FORGERY AND DETECTION

It was reported in Wall Street Journal in September 1, 2000 [8] that modern copies of expensive Chinese ceramics of Yuan or Ming dynasties were exposed to X-rays to simulate the TL results. We have in fact come across samples submitted for TL testing which have been exposed to external radiation intentionally or unintentionally. We will show three cases in the sections to follow. In each case, we have been able to reveal the true archeological age of the items by TL testing. Our TL results also yield conclusive evidence that the items have been subject to external radiation.

Case 1 is an under-glaze-red flask claimed to be of early Ming-dynasty [Fig. 1]. Similar flasks can fetch a price of US 1 million in an art auction. The TL glow curve shows a very complex structure of multiple peaks starting at temperature as low as 100 °C. For comparison, we used a blue and white lidded jar from Ming Dynasty during the reign of Hongzhi which is also in the earl-middle Ming era [Fig. 2]. Both the flask and the jar should have been made in Jingdezhen, the porcelain hub in Southern China. The difference becomes obvious when we compared the two glow curves. A single peak at 320 °C is observed in glow curve of the Hongzhi jar. From the annual dosage measurements, we then deduced that the flask has been subject to saturating radiation that could only be artificial in nature.

Case 2 is a Longquan zong in celadon glaze purportedly of Southern Song Dynasty [Fig. 3]. The customer claimed that the item has been subject to examination by PIXE and XRF for trace elements analysis. The PIXE results indicated that the elemental patterns of the glaze and of the clay materials is consistent with that of genuine Longquan ware in Song dynasty. Small samples have been taken from the foot-rim for TL testing by a TL service provider [see the two circular cuts at the foot-rim in Fig. 3]. The TL provider claimed that the item might have had secondary heating, rendering the TL result inconclusive. This item was then submitted to us for further TL testing. A triangular cut was made at the foot-rim to extract some sample [see the triangular cut at the foot rim, Fig. 3]. Routine TL test using the pre-dose technique (a TL technique often used in testing stoneware or porcelain) produced inconclusive result as all curves coalesced. We how-
ever discovered that the item responded to $\beta$ and in particular $\alpha$ radiation. Careful measurement of the radio-activity and the TL response led us to conclude that the piece was in fact less than 100 years old.

Case 3 is a Ding Yao Meiping vase in brown glaze purportedly of Song dynasty [Fig. 4]. Routine TL testing by pre-dose technique was also inconclusive. The TL glow curve from 20 °C to 500 °C however showed a TL signature different from that induced by $\alpha$ or $\beta$ radiation. We then irradiated the sample by 100 keV x-rays for 60 minutes and was able to reproduce similar signature features in the TL glow curve. When we questioned the customer who submitted the item if it was ever exposed to external radiation, he admitted that the item has previously been examined by surface analytical techniques including x-ray fluorescence and cathodo-luminescence, thus the chance of exposure to external radiation.

Having examined many Chinese ceramics exposed to x-rays or other external radiation by the customers, we have also carefully simulated the x-ray effects on the TL characteristics of Lithium Fluoride (a crystal well known for its TL properties) and some Chinese ceramics in our lab. The TL glow curves induced by x-rays or by $\alpha$ and $\beta$ radiation show drastically different characteristics. One should be able to differentiate samples exposed to recent x-rays injection from those subject only to internal $\alpha$ and $\beta$ radiation. We also come to the conclusion that exposing the ceramics to saturating radiation (e.g. x-rays at 100 keV for 60 minutes) will cause the pre-dose technique to fail.

Tempted by the seemingly non-destructive nature, art collector and dealers have been drawn to use modern surface analytical techniques such as PIXE in attempt to authenticate ancient Chinese ceramics. Such attempt however may be futile. PIXE study provides only elemental/composition analysis (e.g. x percent of silicon, y percent of aluminum, z percent of iron etc.). Ceramics of similar composition were manufactured in China for at least 2000 years. The trace elemental patterns are also susceptible to materials exchange during manufacture and use. In the absence of other contextual evidence, data from elemental analysis tells of nothing about the time the ceramic was made. Furthermore subjecting Chinese ceramics to modern surface analysis such as PIXE etc. may have harmful side effects. X-rays or $\gamma$ radiation generated during neutral or charged particle bombardment of the surface of the ceramics could contaminate pristine TL signature. The true archeological age of the item cannot be deduced because measurement of the radioactivity of the sample could never reveal the amount of x-rays and $\gamma$ rays incurred during surface analysis.

6. NON-DESTRUCTIVE CO$_2$ LASER-HEATED THERMOLUMINESCENCE DATING

Finally, we would like to point out that the cut at the foot-rim that irks many customers during routine TL test might soon be a thing of the past. We have investigated and successfully demonstrated the feasibility of non-destructive TL testing of ceramics by CO$_2$ laser heating [9, 10]. This technique requires no cut on the ceramics. The heating is provided by the guided or unguided 10.6 $\mu$m infrared radiation from a remotely located CO$_2$ laser. The physical integrity of the ancient ceramic is preserved. The possibility of high-energy radiation induced damage on the artifact is also greatly reduced.

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7. REFERENCES