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FEASIBILITY STUDY FOR DETECTING THE LOST LEONARDO MURAL BY PROMPT GAMMA NEUTRON ACTIVATION

The lost Leonardo mural refers to the »Battle of Anghiari« (BoA) by Leonardo da Vinci in the Palazzo Vecchio in Florence, Italy. This mural was commissioned by the Signoria (executive council) of Florence for a wall of the Salone Cinquecento (Chamber of the 500) in 1503. Leonardo was assigned the subject of the Battle of Anghiari. He produced a full-scale design drawing (*cartone*) for the mural which was put on display for public viewing. Leonardo also left Florence in 1505, going to Milan under the patronage of the King of France. He seems to have been discouraged by technical problems with his mural painting technique, and did no further work on the mural (Hatfield 2007).

There is some evidence that Leonardo prepared the wall for painting and transferred onto it at least one section of the *cartone*, the capture of the Standard (**fig. 1**; Hatfield 2007). However, it is not clear whether this was the actual painting or just the drawing. Whatever was there – was subsequently hidden behind another wall and mural by Vasari in 1564 during the remodeling of the Salone into a Ducal throne room (Hatfield 2007). Since then there has been continuing speculation about the existence of this lost Leonardo.

Several non-destructive test methods have been tried to detect it including ultrasound (Asmus 2003), thermography (Donadio 2011) and radar (Pieraccini 2005). Collectively these have shown a narrow air space between the inner and outer wall, but they have not been able to prove the existence or absence of the mural.

In 2007, DuVarney proposed the application of a neutron-based elemental analysis technique, prompt gamma neutron activation analysis

Fig. 1 Capture of the Standard, part of the *cartone* of the »Battle of Anghiari«, copy made by Peter Paul Rubens (1603). – (www.nationalgeographic.com/explorers/projects/lost-da-vinci/battle-of-anghiari-gallery/).

(PGNAA), to find the BoA by detecting elements characteristic of the pigments that Leonardo may have used (Clark 2008). The method is shown in **figure 2a**. Neutrons are generated by a portable neutron source, which can be either the radioisotope ^{252}Cf or a neutron generator, which uses the D-T fusion reaction. Some of the neutrons could penetrate through the intervening Vasari counter wall and then be captured by nuclei of the elements in the pigments of the Leonardo mural. These captures produce gamma rays with characteristic energies some of which travel back through the Vasari wall and are then detected by the High Purity Germanium (HPGe) detector.

The governing equation for gamma-ray emission from neutron capture at a point within a material is given by Lindstrom and Paul (2000):

pigment	color	formula	elements
sinope	red	Fe_2O_3	Fe [a]
sienna	yellow	FeOOH	Fe [a]
umber	brown	FeOOH	Fe [a]
ultramarine	blue	$(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)$	Na [a], Ca [a], Al [a], Si [a], S [a]
cinnabar	red	HgS	Hg, S [a]
lead white	white	$2\,PbCO_3 \cdot Pb(OH)_2$	Pb
charcoal	black	C	C
minium	red	Pb_3O_4	Pb
giallolino	yellow	Pb_2SnO_4	Pb, Sn
azurite	blue	$2\,CuCO_3 \cdot Cu(OH)_2$	Cu
verdigris	green	$Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2\,H_2O$	Cu

Tab. 1 Leonardo's palette used in »The Last Supper«. – (After Barcilon/Marani 2001). – [a] Also found in brick, mortar or gypsum plaster.

$$\gamma_i = n\,\sigma_a^i f^i \gamma_k^i \Phi_{th} \qquad \textbf{Eq. 1}$$

where: γ_k^i = gamma ray production rate (k^{th} gamma ray for i^{th} isotope), photons/s; n = number density of atoms of element in beam; σ_a^i = neutron capture cross-section of the i^{th} isotope; f^i = abundance of the i^{th} isotope, γ_k^i = yield of the k^{th} gamma ray for i^{th} isotope, and $_{th}$ = thermal neutron flux, $cm^{-2}\,s^{-1}$. The total gamma ray flux at the detector is the integral of this function over all points in the sample volume.

In theory, PGNAA would be capable of detecting the BoA given a suitable element among the pigments. However, to determine the feasibility of this method for finding the lost mural, a preliminary estimate must be made of the expected gamma-ray signal strength produced by the selected element.

Identification of characteristic pigment gamma ray

There is no complete record of the pigments that Leonardo used in painting the BoA. The closest approximation is the palette of pigments determined by technical examination of the Last Supper (Barcilon/Marani 2001). These are listed in **table 1** along with their elemental compositions. However, some of the more prominent elements are also found in the Palazzo Vecchio's construction materials – brick, mortar and gypsum –, which would generate a gamma-ray background that would overwhelm any signal from the small amount of mass in the paint layer. Thus, they cannot be used to detect the mural. After screening these out, **table 1** indicates that the only usable pigment elements are Cu, Sn, Hg and Pb. **Equation 1** shows that the gamma-ray signal is directly proportional to the thermal neutron capture cross-section, σ_a. A comparison among these four elements shows that Hg, a constituent of the red pigment cinnabar, is the most favorable with a value of σ_a at least 100 times greater than the others.

There are seven stable isotopes of mercury, but the only one that produces significant gamma rays is ^{199}Hg with $\sigma_a^i = 2.15 \times 10^{-20}\,cm^2$ and $f^i = 16.87\,\%$ (IAEA 2007). This isotope generates over 50 distinct gamma rays. The one with the highest yield, $\gamma_k^i = 69\,\%$ is produced at the energy of 0.367 MeV. However, in passing through Vasari's counter wall, this would be attenuated significantly as a consequence of its relatively low energy. Based on the chemical composition of a typical Renaissance Italian brick (Moioli et al. 1988), the attenuation factor at this energy is $0.20\,cm^{-1}$. The estimated thickness of the Vasari counter wall is 18 cm. Consequently, the 0.367 MeV gamma-ray intensity would be reduced to 2.9 % of its original value.

The next highest yield is for the 5.967 MeV gamma ray with a yield of $\gamma_k^i = 17.23\,\%$. Due to its high energy, these gammas would be attenuated much less to 37 % the original in passing through the counter wall. Also its position in the gamma-ray spectrum is in a region that is clear of interferences

pigment	weight Fl. lb[a]	cost[b]	
		lire	soldi
German blue	20	80	0
white	60	15	0
?	1.5	6	0
cinnabar(red)	2	1	16
green	6	3	12
yellow	4	2	8
minium (red)	1	0	8
?	4	0	8
ochre (red)	6	0	6
black	20	2	0
totals	124.5	109	58

Tab. 2 Leonardo's pigment purchases for the »Battle of Anghiari«. – (After Richter 1970). – [a] 1 Florentine pound = 2.94 kg; [b] 1 lira = 20 soldi ~ $28.67 (Cipolla 1989).

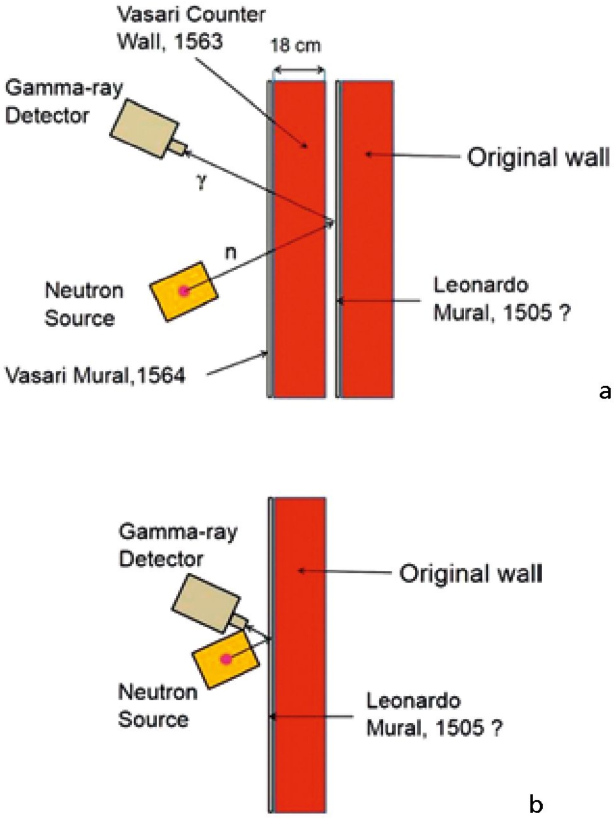

Fig. 2 **a** schematic of PGNAA configuration as proposed by DuVarney (after Clark 2008). – **b** schematic of ideal PGNAA configuration.

and has a relatively low background. Consequently, it is the one selected as the gamma ray that could be characteristic of Leonardo's pigment cinnabar.

Estimation of mercury-number density

To estimate the mercury-number density, n_{Hg}, it is necessary to make some assumptions about Leonardo's use of cinnabar. Obviously, he would not cover the entire surface with a uniform layer, but rather he would apply it in localized patches for features such as articles of clothing. Thus, the surface coverage would be significantly less than 100 %. It is also necessary to consider the color saturation, which is the fraction of the pure pigment in the paint layer at a given point. According to Leonardo's own writings on painting, a pigment would rarely be used in its pure form (Kemp 1989). Instead, it would be mixed with neutral white or black pigments, or other colored pigments, to provide visual effects such as perspective, highlights or shadows. The coverage and saturation of cinnabar in the BoA are unknown, but it is possible to make an indirect estimate of their product. Among Leonardo's records, there is a note on the purchase of pigments for the mural, which is given in **table 2** (Richter 1970; King 2012). This list has an item for two Florentine pounds of cinnabar, thereby validating the assumption that the mercury-bearing pigment could actually be present in the mural. Also, the total mass of pigments in the list is 124.5 pounds. Thus on the average, cinnabar would make up 1.61 % of the paint layer by weight. The density of cinnabar is 8.18 g/cm^3, its molecular weight is 232.65 g/mol, and the mercury molfraction in it is 0.86. Thus, the n_{Hg} in pure cinnabar is 1.82×10^{22} Hg atoms/cm^3. Finally, the estimated n_{Hg} in the paint layer is 1.6 % of this value, or 2.93×10^{20} Hg atoms/cm^3.

Gamma-ray signal strength calculations

At this point, values have been determined for all the factors in **equation 1** except for the thermal neutron flux, Φ_{th}. A commercially available portable neutron generator emits about 10^8 n/s fast neutrons isotropically into the complete 4p steradians of solid angle. For PGNAA, these neutrons have to be slowed down to thermal energies in the moderator surrounding the generator, and in the process, many of them will be absorbed in the moderator. Numerical simulations of the neutron transport indicate that the therma l neutron flux actually reaching Leonardo's mural would be limited to about $5 \times 10^3\,cm^{-2} \cdot s^{-1}$. A higher flux is ruled out primarily because of radiation safety considerations rather than technological constraints. The resulting calculation using **equation 1** then gives a gamma-ray production rate of 916 photons/$cm^3 \cdot s$. This is at a point on the surface of the inner wall. To reach the detector, the gamma rays must travel through the counter wall, which involves attenuation and geometrical divergence. However, an analytical solution of these transport factors is extremely difficult, and consequently numerical simulations using Monte Carlo codes would be necessary. As a first approximation, these transport calculations can be avoided by simply assuming the neutron source and detector are located next to the inner wall as shown in **figure 2b**. This assumption is justified by the fact that this configuration would yield the maximum gamma-ray count rate. The effect of including the transport factors would be to reduce this rate.

The total gamma-ray signal strength at the detector is the integral of the point production rate over the volume of detection in the target. In the case of a cylindrical detector next to paint layer, this would be a thin disk with a depth set by the layer thickness and a radius equal to that of the end face of the detector. Based on Leonardo's »Last Supper«, the paint layer thickness is estimated to be 100 µm (Barcilon/Marani 2001). With a detector radius of 3.75 cm, this defines a volume of 0.44 cm^3, and hence a total emission rate of $916 \times 0.44 = 405$ photons/s. This has to be reduced by a factor of 0.5 to correct for the photons traveling away from the direction of the detector, so that the actual number reaching the detector is 202 photons/s.

Finally, the efficiency of a typical HPGe detector for a 5.967 MeV photon is 1.5×10^{-4} (Saleh/Livingston 2000). Consequently, the count rate of gamma rays actually detected would be 3.04×10^{-2} counts per second (cps), which is two orders of magnitude below a practical count rate of 1 cps.

Signal to background ratio

To put the calculated gamma-ray strength in perspective, it is necessary to know the background radiation level. The background around 5.967 MeV is due mainly to cosmic rays (Knoll 2000). This is relatively constant around the Earth for a given latitude. Consequently, it is possible to estimate the background in Florence from PGNAA measurements made in Colonial Williamsburg/Virginia, on an 18th century brick wall. This investigation found a background level around 6 MeV on the order of 0.1 cps (Livingston/Taylor 1991). This would give a signal to background ratio (S/B) for the Hg in the BoA of 0.304.

This is the best possible S/B ratio because it assumes that the detector is right next to the surface of Leonardo's mural. Taking into account the presence of the Vasari counter wall introduces two additional factors that would reduce this ratio. One is the 18 cm separation between the source of the gamma rays and the detector. The signal intensity falls off as the square of the distance. This separation would reduce the signal by factor 0.022. In addition, as discussed above, attenuation of the 5.967 MeV gamma ray in the brick would cause another loss factor of 0.37. Thus, the overall S/B ratio would be 0.0027, which implies that detection of the mural would not be feasible.

Conclusions

Based on the neutron capture cross-section, gamma ray energies and yields and lack of interferences from elements in the materials surrounding the mural, 5.967 MeV mercury gamma ray as the most favorable candidate for indicating the presence of a hidden BoA mural. The count rate was modeled using the operating specifications of existing PGAA systems, including thermal neutron flux and gamma ray detector efficiency. However, even under ideal conditions, i.e. no intervening brick wall, the ex pected count rate, 3 × 10-2 cps, would be too low to be practical. Taking into account the Vasari counter wall and a typical natural gamma-ray background gives a signal to background ratio of 0.0027, which implies that detection of the mural would not be feasible.

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Summary / Zusammenfassung

Feasibility Study for Detecting the Lost Leonardo Mural by Prompt Gamma Neutron Activation

There has been considerable interest in the application of non-destructive test methods for finding the lost mural of the »Battle of Anghiari« by Leonardo da Vinci in the Palazzo Vecchio in Florence, Italy. This mural was thought to have been painted in 1505, but it was subsequently covered over by another mural in 1560. Most recently, it has been proposed to use a neutron-based elemental analysis technique, prompt gamma neutron activation (PGNA), to detect elements characteristic of the pigments that Leonardo may have used. To determine the feasibility of this method for finding the lost mural, a preliminary analysis of the probability of detection (POD) has been made using the Curie Equation for estimating the minimum detectable limit for a given element. The first step was to determine the pigment most likely to be detected by PGNA. This involved identifying the palette that Leonardo may have used and then screening them for detectable elements by neutron capture cross-section, gamma-ray energies and yields. In addition, interferences from elements in the materials surrounding the mural had to be taken into account. Based on this analysis, mercury, an element in the red pigment vermilion, was the most favorable candidate. The next step was to estimate the total mass of mercury in the field of view based on vermilion layer thickness and surface distribution. Finally, the mercury count rate was modeled using the operating specifications of existing portable PGNA systems, including thermal neutron flux and gamma-ray detector efficiency. It was concluded that the count rate would be too low to be practical.

Machbarkeitsstudie zum Auffinden des verlorenen Leonardo-Wandgemäldes mithilfe von Prompt Gamma Neutronen-Aktivierung

Es besteht ein beträchtliches Interesse an der Anwendung von zerstörungsfreien Prüfmethoden, um das verlorene Wandgemälde der »Schlacht von Anghiari« von Leonardo da Vinci im Palazzo Vecchio in Florenz, Italien, zu finden. Es wird angenommen, dass dieses Wandgemälde 1505 gemalt, doch danach 1560 durch ein anderes Wandgemälde überdeckt wurde. Kürzlich kam der Vorschlag, eine neutronen-basierte Element-Analysetechnik, Prompt Gamma Neutronen-Aktivierung (PGNA), zu verwenden, um Elemente nachzuweisen, die für die Pigmente charakteristisch sind, die Leonardo verwendet haben dürfte. Um die Durchführbarkeit dieser Methode zur Auffindung des Wandgemäldes zu ermitteln, wurde eine vorläufige Wahrscheinlichkeitsanalyse für den Nachweis mithilfe der Curie-Gleichung erstellt, um die untere Nachweisgrenze für ein gegebenes Element zu bestimmen. Der erste Schritt war, das Pigment herauszufinden, das am wahrscheinlichsten mit PGNA nachgewiesen werden kann. Dies bedeutete, zunächst die Pigment-Palette zu bestimmen, die Leonardo verwendet haben dürfte, und sie anschließend nach Elementen zu durchsuchen, die nach Neutroneneinfangs-Wirkungsquerschnitt, Gamma-Energien und Ausbeute nachweisbar sind. Zusätzlich mussten Störungen von Elementen in den Materialien berücksichtigt werden, die das Wandgemälde umgeben. Basierend auf dieser Untersuchung war Quecksilber, ein Element im roten Pigment Zinnoberrot, der günstigste Kandidat. Der nächste Schritt bestand darin, die Gesamtmasse von Quecksilber im Sichtfeld zu bestimmen, basierend auf der Schichtdicke von Zinnoberrot und dessen Verteilung auf der Oberfläche. Schließlich wurde anhand der Betriebsdaten existierender tragbarer Prompt Gamma Neutronen-Aktivierungssystemen die Zählrate aus Quecksilber modelliert, einschließlich des thermischen Neutronenflusses und der Effizienz des Gamma-Detektors. Man kam zu dem Schluss, dass die Zählrate zu klein sein würde, um praktikabel zu sein.

Keywords

da Vinci / Anghiari mural / cinnabar / PGAA / neutron / mercury