Emerging nuclear methods for historical painting authentication: AMS-^{14}C dating, MeV-SIMS and O-PTIR imaging, Global IBA, Differential-PIXE and Full-field PIXE mapping

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Abstract

There is a considerable interest in developing new analytical tools to fight the illicit trafficking of heritage goods and particularly of easel paintings, whose high market values attract an ever-increasing volume of criminal activities. The objective is to combat the illicit traffic of smuggled or forged paintworks and to prevent the acquisition of fakes or looted artefacts in public collections. Authentication can be addressed using various investigation techniques, such as absolute dating, materials characterization, alteration phenomena, etc.; for paintings this remains a challenging task due to the complexity of the materials (paint layers, ground, varnish, canvas, etc.) and preferable use of non-destructive methods.

This paper outlines results from concerted action on detecting forged works of art within the framework of a Coordinated Research Project of the International Atomic Energy Agency (IAEA) called *Enhancing Nuclear Analytical Techniques to Meet the Needs of Forensic Sciences**. One of the main objectives is to foster the use of emerging Nuclear Analytical Techniques (NAT) using particle accelerators for authentication of paintings, with potential application to other forensics domains, by highlighting their ability to determine painting authenticity and to track restorations or anachronistic clues.

The various materials comprising a test painting were investigated using an array of NAT. Binder, canvas and support were directly dated by ^{14}C using Accelerator Mass Spectrometry (^{14}C-AMS);

binder and pigments' molecular composition was determined using Secondary Ion Mass Spectrometry with MeV ions (MeV-SIMS); paint layer composition and stratigraphy were accurately determined using Ion Beam Analysis (IBA) and differential Particle-Induced X-ray Emission (PIXE); and pigment spatial distributions were mapped using full-field PIXE. High resolution Optical Photothermal Infrared Spectroscopy (O-PTIR) molecular imaging was also exploited. Obtained results are presented and discussed. It is shown that the combination of the above-mentioned techniques allowed reconstructing the history of the test painting.

* https://www.iaea.org/projects/crp/f11021

1. Introduction

The vast pallet of Nuclear Analytical Techniques (NAT) is of potential interest in forensics science methodologies. Their acknowledged analytical merits, notably their ability to measure a wide range of chemical elements, isotopes and molecules with high sensitivity and accuracy, combined with their non-destructive character (with no or minimal sampling), make them highly suited to carry forensics scientific investigations while preserving the body of evidence.

There is a considerable interest in developing new analytical methods to fight the illicit traffic of heritage goods and particularly of easel paintings, whose very high market values attract an ever-increasing volume of criminal activities. Forensics study of paintings is crucial to combat the illicit traffic of smuggled or forged works and to prevent the acquisition of fakes or looted artefacts by public collections (museums). It should be noted, that the aim of forensics study of heritage artefacts is generally to detect forgeries, but it can sometimes be the opposite, i.e., to prove their authenticity. Indeed, an approach often used by the criminals or clients of stolen or smuggled paintworks is to claim the objects are fakes or modern copies, in order to hide the importance of the paintworks and its origin.

Among heritage objects, paintings stand out by their peculiar complex composition and layered structure, which deserve a short description. On top of the support, generally a linen canvas or a wood panel, a ground layer is applied to equalize its surface and favour adhesion of the paint composition. A preparation layer with a finer granularity, like a gesso, is then applied on this substrate to provide a smooth and coloured surface suitable for the application of the painted composition. The successive paint layers applied consist of pigments in the form of microscopic grains of natural or synthesized minerals dispersed in an organic binder, containing lipids (oil painting) or proteins (a tempera painting). Paint layer thicknesses vary from a few to several tens of micrometres. A varnish layer is eventually applied on top of the painting for protection and to improve its contrast. The study such a complex and layered structure is a challenging task requiring analytical methods capable of identifying organic and inorganic components, determining the layer stratigraphy and thickness, and possibly, the dating of the constituents.

As in other forensic science application fields, the authentication of paintworks relies on the extensive investigation of the composition materials by various experts from the field. The tasks cover the identification of the materials, their origin, and dating, and the way they were integrated in the composition, all of which provide complementary authentication clues [1]. The first authenticity criterion is the date. Organic constituents such as wood, textile, or binders can be directly dated by means of ^{14}C dating. Inorganic pigments can be indirectly dated through their composition, as various pigments appeared throughout history, notably in the 18th-19th centuries with the rise of the chemistry and its industrialisation [2]. This chronology is commonly used to tell whether the pigments present are coherent with the alleged date of the painting. Other indirect dating clues are ageing features such as a network of craquelures or the presence of organic compounds developing within or between the paint layer constituents, resulting from slow kinetics chemical reactions.

In routine operation, paintings are investigated using examination and analytical methods common to other forensic science fields [3]. First, extensive imaging combining visible, UV, and IR photography with X-ray radiography allows to screen the painting for significant and hidden clues. These non-contact examinations are generally supplemented with non-destructive analyses at selected locations, for instance by X-ray Fluorescence (XRF). The point analyses are complemented by the detailed study of a few millimetre-sized samples taken at strategic locations using optical and electron microscopies (SEM-EDX) to identify mineral pigments and molecular methods like chromatography (HPLC, GC-MS) or infrared spectroscopy (FTIR) to identify organic constituents. Sampling required for routine analytical work must be kept as limited as possible. Indeed, both the potential preciousness and uniqueness of the investigated works and its ownership, when unclear, favour the use of harmless/non-destructive, or at least techniques the least damaging as possible.

Herein we describe novel NATs using particle accelerators that either avoid sampling or limit sample size to a minimum and often preserve such important evidence. Four classes are considered:

- Direct ^{14}C AMS dating of organic components from microscopic samples: binder, canvas and support
- Secondary Ion Mass Spectrometry (MeV-SIMS) of binder and pigments using MeV ions
- Global IBA analysis of paint composition, including pigment/binder
- Differential PIXE determination of layer sequence
- Full-field PIXE mapping of pigments on the entire surface of the painting

Although not a nuclear method, the Optical Photothermal Infrared Spectroscopy (O-PTIR) imaging was included in this study because of its unique sub-micron imaging capability of organic constituents.

NATs were applied to a presumably old test painting especially acquired for this program. The objective was to evaluate their ability to determine the painting authenticity and to pin-point possible restorations or anachronic features, as would be the case in a real forensic case study. The results obtained by the different NATs are discussed and compared to state-of-the art methods to highlight specific advantages.

The present work was developed in the framework of the IAEA Coordinated Research Project F11021 entitled 'Enhancing Nuclear Analytical Techniques to Meet the Needs of Forensic Sciences'. It was conducted by 18 researchers from 11 institutions using 6 accelerator facilities available in the working group, where NATs in the cultural heritage domain are applied.

2. Test painting

To assess the capabilities of the array of new NATs for painting authentication, a supposedly old paintwork was acquired at an auction in Paris, France. The painting is an anonymous and untitled composition on canvas measuring 32 cm x 23 cm and given an identifier as Cobaye_one (Fig 1). This painting represents a natural landscape at sunset featuring a lake, a cliff with trees, a few houses in the background, and two small characters in the foreground. According to a painting expert from the National Centre for Research and Restoration in French Museums (C2RMF, France), such a style might correspond to a French school composition from the 17th-18th centuries. Several features such as the painting technique and the network of craquelures indicate that it could be authentic. Examination of the rear and the sides shows that the entire composition has been glued onto a new canvas at an unknown period, which is a common restoration procedure called lining. Whether the wood frame is authentic was an open question.

A series of 15 coupons measuring 2 cm x 1 cm were sampled in the sky, on the right border of the composition. This destructive protocol may appear surprising, considering the non-destructive character of the evaluated methods; however, the initial plan to circulate the painting between laboratories was found too time-consuming for the exercise. Hence, for the sake of efficiency, the sample coupons containing the entire stratigraphy (varnish to canvas) were distributed to the participants to assess the capabilities of the NATs methods.

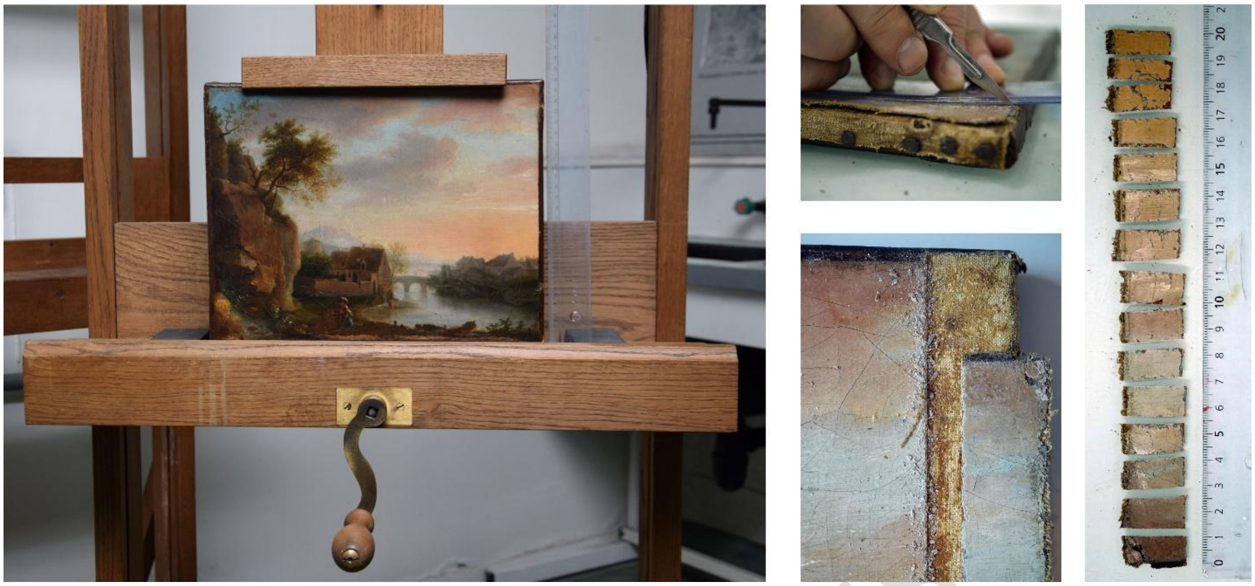

Fig 1. Test painting: Left, untitled and anonymous composition on canvas 32 cm x 23 cm. Right, sampling of painting coupons for distribution to participants.

3. Emerging Nuclear Analytical Techniques

3.1 Direct ^{14}C-AMS dating

^{14}C dating using accelerator mass spectrometry is a well-recognized method to authenticate paintings [4]. The accuracy of the method has constantly been improving by applying quality procedures and its applicability, particularly to cultural heritage and forensic science, benefitted from a dramatic downsizing of the required sample size, from grams to milligrams. Nowadays the minimal painting sample volume required for ^{14}C-AMS dating is comparable to that required for preparing a cross-section for microscopy (< 1 mm^3). In addition, improvements in the chemical sample preparation and direct injection of carbon dioxide in the accelerator mass spectrometer allows separation and dating of individual painting components: support, pigments, and binder.

Different materials present in the Cobaye_one samples were dated using two ^{14}C-AMS facilities operating at different energies: the tandem accelerator of the Helsinki University, operating at 12 MeV [5], using a dedicated sample preparation line [6] and the MICADAS (Mini Carbon Dating System) compact ^{14}C-AMS system of the Laboratory of Ion beam Physics at ETH Zürich operating at 0.2 MeV [7]. A radiocarbon age of 253 BP +/- 26 BP (BP = before present, defined as year 1950) was obtained in Helsinki for a paint layer sample of 57 mg and an original canvas sample of 131 mg (Fig 2).

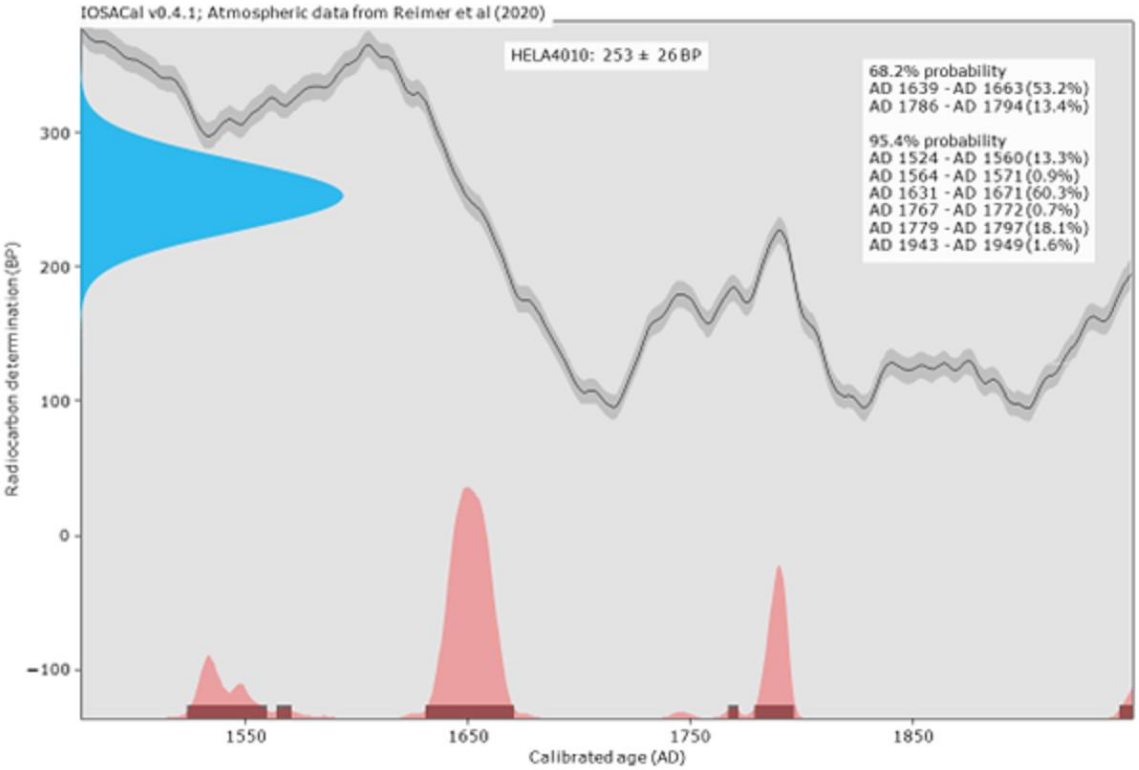

Fig 2. ^{14}C dating of a paint layer using the 12 MeV AMS facility in Helsinki. The shape of the calibration curve (in grey) converts the measured radiocarbon age (gaussian distribution in blue) in three date ranges (in pink).

Similar radiocarbon ages of 220 BP were found using the MICADAS system for the binder, the wood, and the pigments (Fig 3). Samples of 1 milligram were obtained by specific extraction procedures. The radiocarbon age of the restoration canvas appeared younger, about 180 BP. The main consideration with ^{14}C dating is the shape of the calibration curve used to convert radiocarbon age into actual dates. In the time range covering the production of historical paintings (from the 14th century to present), the curve presents large oscillations due to variation of concentration of ^{14}C in the atmosphere. The measured radiocarbon ages of the samples thus correspond to three possible date periods: ca. 1550, ca. 1660, and ca. 1790. The binder appears older than the support; however, there is still possibility of contamination with varnish on the surface of the paint. For the restoration canvas, an additional date range around 1920 has been considered. No abnormally high content of ^{14}C was measured that would be indicative of modern organic materials (> 1950, “post-bomb”).

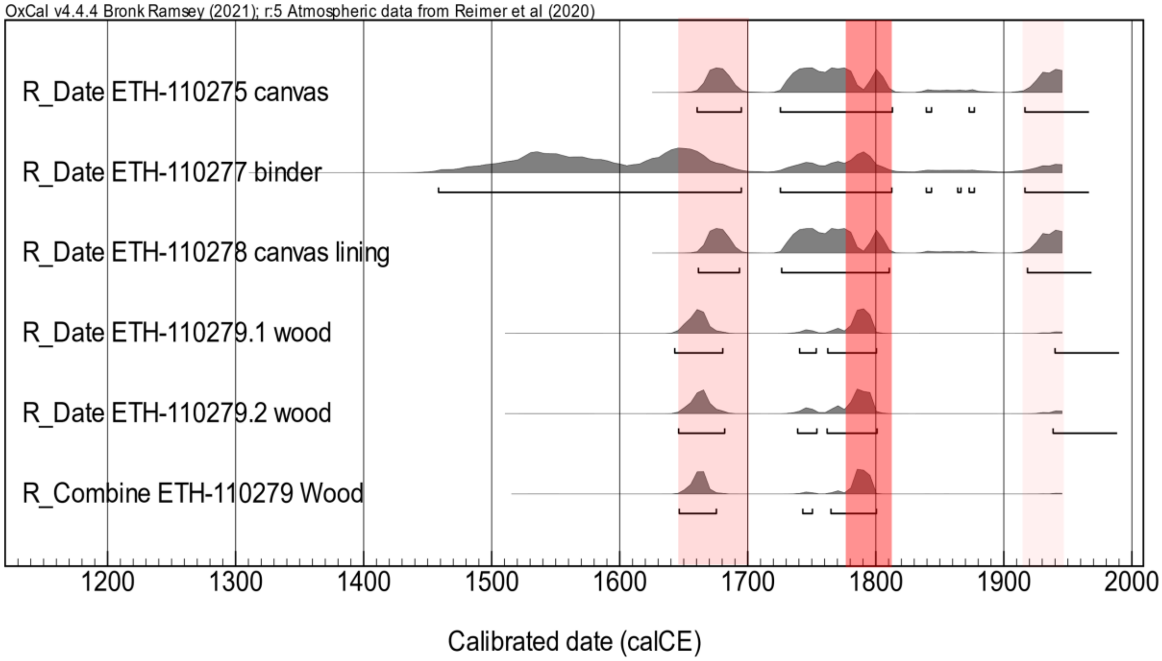

Fig 3. ^{14}C-AMS dating of the wood, canvas and binder using MICADAS facility. The dates ranges are 1630–1700 and 1720–1810, plus 1920–1940 for the restoration canvas. The vertical color bars highlight the date range that are in common for painting constituents.

Due to the high accuracy of the radiocarbon dating, the possible time periods are well defined and separated. Complementary measurements presented below allow to eliminate some possible time periods so that ^{14}C-AMS dating of the painting can be obtained with an accuracy of 50 years.

3.2 Mass spectrometry using MeV-SIMS

Characterisation of organic molecules in the paint layers is of high importance for authentication studies. Such compounds are routinely characterised by applying molecular techniques widespread in forensic sciences, such as conventional FTIR, HP-LC or GC-MS on micro-samples that are consumed, providing useful signatures. Imaging using a FTIR microscope allows mapping vibrational bands on mm² areas.

The MeV-SIMS technique we used permits direct identification of varnish, binder, pigments, and possible degradation products. Although sampling is necessary and the sample needs to be placed in a vacuum chamber, only a very small amount of sample is sufficient for the analysis. Furthermore, usually not the whole sample is used for the MeV-SIMS measurement, hence it can be used for subsequent complementary analyses. The MeV-SIMS method applies MeV heavy ions to desorb secondary molecular ions from the sample surface [8]. Desorbed molecules were detected using linear TOF spectrometer attached to the heavy ion nuclear microprobe at the accelerator facility in Zagreb, Croatia [9]. Compared to MALDI, another widespread molecular technique, the advantage of MeV-SIMS is that it doesn't need a matrix and don't destroy the sample with laser beam. Further, it can focus ions down to several microns, while MALDI doesn't feature such a high lateral resolution for imaging; its resolution is around 100 microns x 100 microns. MeV-SIMS can measure up to 2 kDa while MALDI detects heavier molecules up to 10 kDa.

Small fragments were cut from the painting coupon and pressed with a flat and clean aluminium plate into an indium substrate for measurement (99.99% in tear drops). The beam focused to 10 µm x 10 µm was scanned over an area measuring 1 x 1 mm², which allows selecting different areas in the analysed paint coupons, in our case the varnish, the paint layer and the preparation layers. In addition, MeV-SIMS can be conveniently combined with other Ion Beam Analysis (IBA) techniques, such as PIXE analysis of the same area to combine molecular with elemental information about the pigments. The MeV-SIMS method has already been successfully applied to study modern paint materials [10] and inks [11].

A high yield of secondary molecular ions with *m/z* up to 1200 were collected in a positive-ion mode. A series of lead ions and lead oxide/hydroxide species were identified in the mass range between *m/z* 200 and 900 and can be assigned to lead white pigment. Fatty acid fragments (linoleic and stearic acid) were detected in the lower mass region, composing an oil binder (Fig 4). In addition, degradation markers were observed, likely resulting from the reaction of the binder with lead white (lead soaps) and the decay of triacylglycerols of the oil (TAG), possibly due to light exposure. No phospholipids could be identified, including in the negative ion mode mass spectra, that would indicate presence of an egg-based binder.

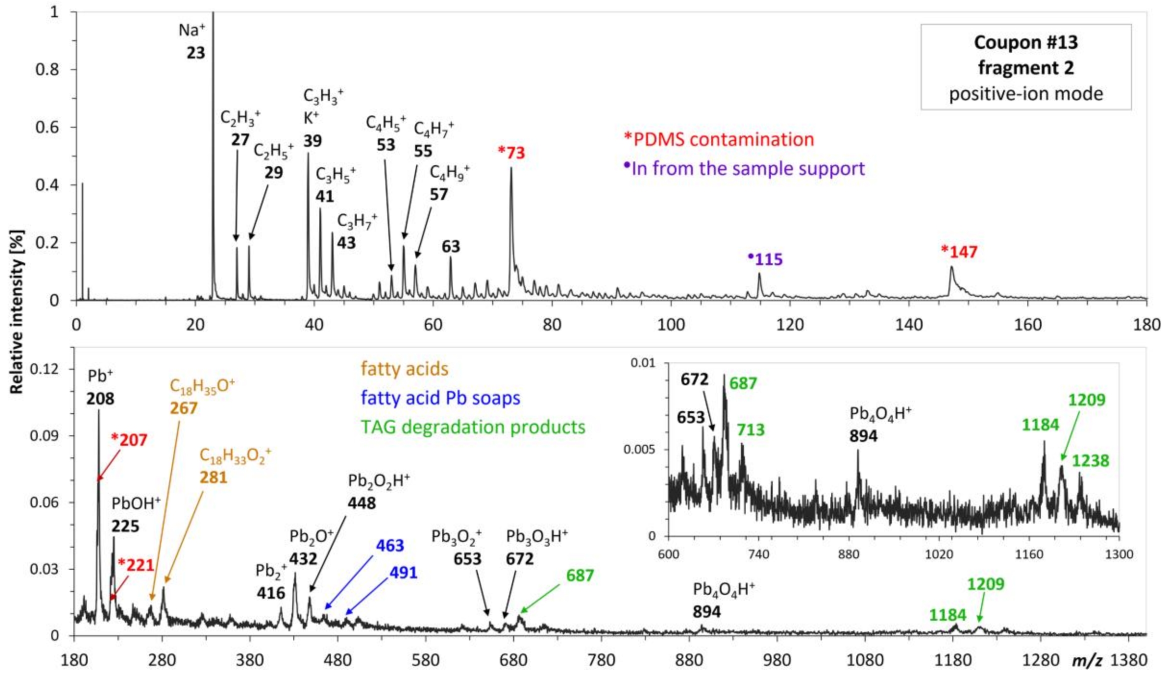

Fig 4. Positive-ion mode MeV-SIMS spectrum of the paint coupon fragment. An insert for the spectrum region between m/z 600 and 1300 is displayed bottom right.

Since only the species that are characteristic of aged oil paints were identified, such as fatty acids, fatty acid lead soaps, and TAG degradation products, we may presume that the investigated painting is oil-based and that egg yolk can be excluded as the binding material. All these results are consistent with an old painting made with oil binder.

3.3 Mapping molecular bands using O-PTIR

Optical Photothermal Infrared Spectroscopy enables non-contact, submicron IR hyperspectral imaging in reflection mode. It is a new analytical method to analyse polymers, life science samples, and painting fragments, to name a few. During experiments conducted at the Singapore University, a tuneable pulsed mid–IR Quantum Cascade Laser (QCL) illuminated the sample, causing small photothermal responses (rapid conversion of photon energy into heat occurring within a few picoseconds). This effect was detected as modified scattering intensity of a continuous visible green laser (532 nm) co-located with the IR light. Under certain conditions, the photothermal effect is proportional to the IR absorption, thus collected spectra can be directly compared with classic FTIR spectroscopy results [12]. The spatial resolution in O-PTIR is essentially defined by the spot size of the short wavelength green laser and not the diffraction limit of the long wavelength IR source. The QCL was operated in pulsed mode, with 500 ns pulses at a repetition rate of up to 100 kHz, corresponding to a maximum duty cycle of 5%.

The focused spot size of the probe green laser was about 500 nm to deliver submicron spatial resolution. Spectra were collected within the region of 1800 – 800 cm^{-1}; the number of co-added scans per spectrum was optimized during the study to 32. The laser powers of the IR and probe were each set to approximately 1–5 mW per spectrum.

The application of O-PTIR to the paint cross section yielded a detailed hyperspectral IR image (Figure 5, lower left). Of the recorded data, several vibrational bands could be mapped, notably those connected to lead white, varnish and preparation layer. The 1490 cm^{-1} band was ascribed to the lead white pigment [$\nu_{as}(CO_3^{2-})$ of carbonates] and the 1520 cm^{-1} band to its degradation [$\nu_{as}(COO^{-})$ of carboxylates]. The 1660 cm^{-1} band [ν(C=O amide I)] present in the thin (3 µm) varnish layer corresponds to proteins, possibly egg white. The OPTIR images appear highly resolved and enable distinguishing fine features within the paint layers (Fig 5). O-PTIR spectroscopy is a very recent technique [13,14], commercialized just a few years ago. Considering that spectra collected during non-contact mode experiments have very high signal to noise ratio and offer sub-micron resolution, this technique appears promising for analysis of historical paintings, as well as other cultural heritage objects. Its potential has not yet been fully evaluated, however.

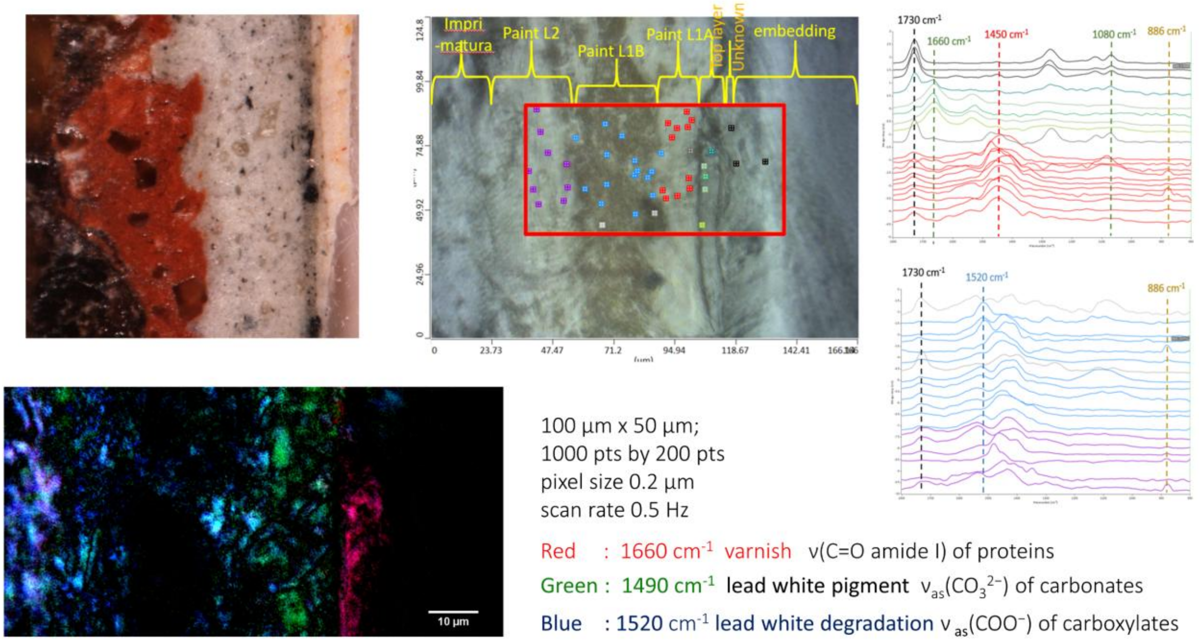

Fig 5. O-PTIR mapping of organic molecular bands in a cross-section of a coupon from the Cobaye_one painting. Upper left, painting cross-section photographic image. Center, close-up of the studied area. Paint layers are indicated in yellow, the rectangular scanned area in red, and the colored dots correspond to specific points. Upper right, spectra recorded at specific spots (color of spectra correspond to the dots). Lower left, RGB image of the area, combining the intensity of vibrational bands ascribed to the varnish (red), lead white (green) and its degradation products (blue).

3.4 Global IBA

The complete sample composition was determined in a single experiment with the simultaneous application of several IBA techniques, in the spirit of the "Total IBA" approach [15,16]: PIXE, Elastic Backscattering Spectrometry (EBS) and Particle-Induced Gamma-ray Emission (PIGE). Elements heavier than sodium can be measured by PIXE, lighter elements such as C, N and O by EBS, and Li, B, F or Na by PIGE. As a result, the composition of the pigment can be determined, as well as that of the organic binder, including their relative ratios. The reliability of IBA quantitative analyses derives from the high quality of fundamental data (cross-sections, attenuation coefficients, etc.), the tightly controlled experimental conditions, and the availability of advanced programs for data analysis and simulation, such as SIMNRA for the EBS spectra [17] and GUPIXWIN for PIXE [18].

Global IBA was applied on the first layer of the painting using the external beam produced by the 3 MV tandem accelerator of the LABEC in Florence, Italy [19] in a beam line designed for cultural heritage samples [20]. Four proton beam energies (4.97, 3.95, 2.93, 1.91 MeV) were used with a beam intensity in the range of several tens of pA. No light elements (Na, F, B or Li) could be detected by PIGE. From the analysis of EBS spectra, in particular using 2.93 MeV protons (Fig. 6), it was possible to determine the presence of a varnish layer and its thickness was estimated to be 15 µm. It was possible, as well, to determine the sample matrix composition (H 13%, C 13%, O 54%, Pb 20% in atom), which is in good agreement with the theoretical composition of a lead white paint layer $(PbCO_3)_2 \cdot Pb(OH)_2$). The hydrogen concentration was estimated from the mass deficit of the elements determined by EBS. All these data were further applied in the processing of PIXE spectra collected at the four different energies for Differential PIXE.

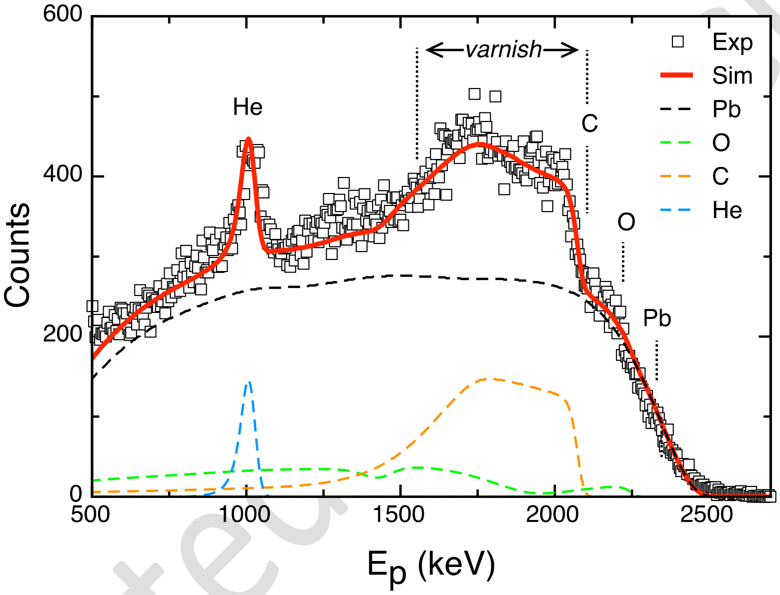

Fig 6. EBS spectrum of the fragment of the painting obtained with 2.93 MeV proton together with the SIMNRA simulation. The contribution of the different elements to the simulation is also shown. He is not present in the sample itself but is a "parasitic" element, common to EBS spectra when measurements are performed in an external beam set-up under helium flow.

3.5 Differential PIXE

In differential PIXE the elemental depth profile of a sample is determined without contact by recording PIXE spectra at a series of proton energies (e.g., 1, 2, 3, 4, and 5 MeV). This method exploits the fact that the probed depth varies with incident proton energy. When protons of increasing energy impinge on the painting stratigraphy, they interact with increasingly deeper layers in the painting. The coupled processing of the spectra (comparison of PIXE spectra at different energies, hence the name of differential PIXE) yields a chemical depth profile at a number of depth-points equal to the number of incident proton energies (Fig 7). In this study, two approaches were applied. The direct processing of PIXE spectra recorded at seven protons energies (0.66, 1.15, 1.48, 1.77, 2.03, 2.50 and 2.99 MeV) was carried out with the external beam of the accelerator facility at the JSI in Ljubljana, Slovenia using energy degraders. In the first case, depth profiles were derived processing the characteristic peak areas using a specifically developed algorithm [21]. In the other approach applied at the LABEC facility in Florence, four proton energies (4.97, 3.95, 2.93, 1.91 MeV) were produced by changing the energy of the accelerator. the layer sequence was determined by processing of spectra with a widespread program, namely GUPIX [13], and considering the departure of the calculated results from those of a homogeneous sample. The measured variation in element ratio with increasing proton energy (depth) allowed to determine the layer sequence (Fig 8). The decrease of Hg/Pb and Zn/Hg ratios led to the following sequence:|Zn|Hg|Pb|, while the simultaneous increase of Fe/Pb, Ca/Pb and K/Fe ratios led to |Pb|Fe|K|.

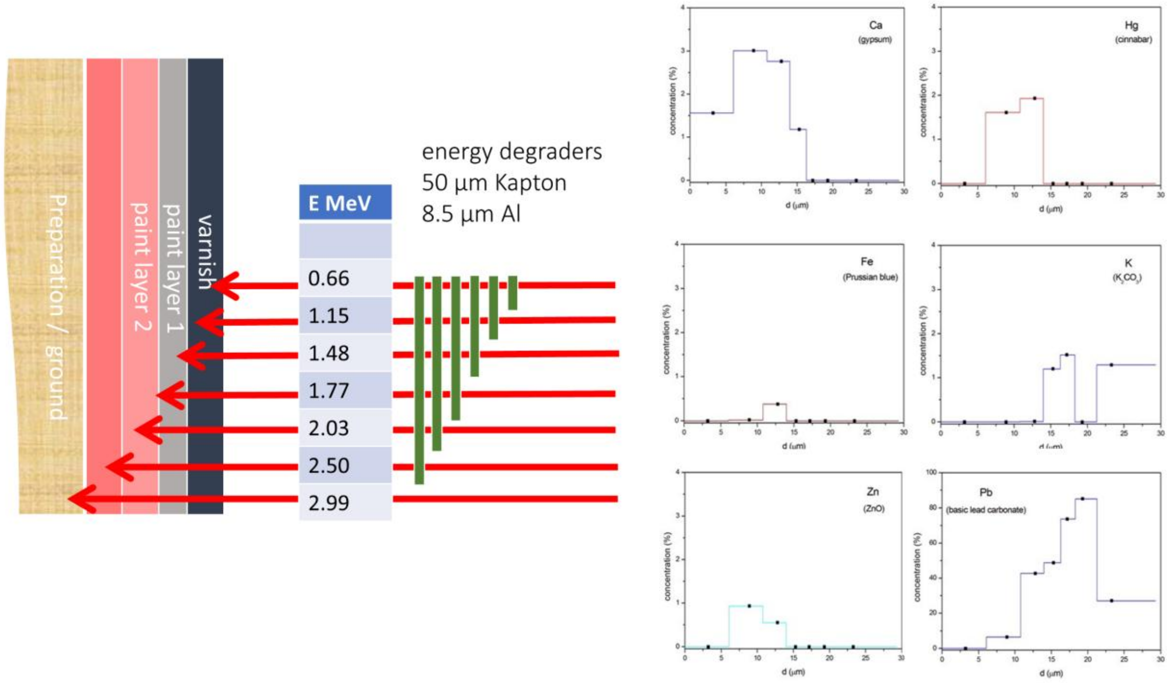

Fig 7. Left, differential PIXE principle and implementation using energy degraders. Right, element depth profiles derived from the coupled processing of the spectra.

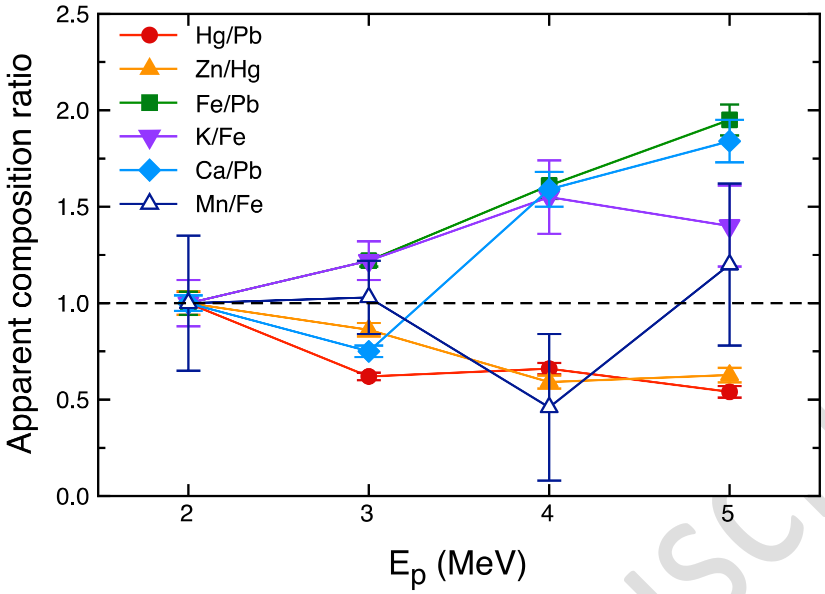

Fig 8. Apparent composition ratios of the main elements as a function of the different initial proton beam energies as obtained by differential PIXE analysis.

Methods allowing the determination of paint layer chemical composition sequence without sampling are few. One is confocal X-ray fluorescence, where the probed microvolume is defined by the focusing X-ray optics of the incident X-ray beam and of the fluorescence emission reaching the detector. The depth resolution is determined by the incident photon energy and the density of the sample, typically reaching 20 µm for laboratory set-ups [22]. Differential PIXE could provide depth profile information with a resolution down to 15 µm, finer than using laboratory-based confocal XRF (not considering large scale facilities such as synchrotron).

3.6 Full-field PIXE mapping

In full-field PIXE mapping, PIXE spectra are recorded from an array of points that span the entire surface of the painting. An external proton micro-beam is rapidly scanned across the paint surface and a PIXE spectrum is recorded in a few milliseconds at each point (Fig 9). The collected elemental maps correspond to pigment distribution, which usefully complements routine imaging. For instance, X-ray radiography reflects the distribution of the most strongly absorbing materials, which is dominated by lead, while optical imaging bears poor specific chemical information. Full-Field PIXE can be considered as a colour radiography as it can map a large area of elemental distributions as markers for a variety of pigments, including those hidden by overlaying layers. Full-field PIXE also allows extending the results obtained with point-methods like global IBA to the rest of the composition and screening for non-authentic features.

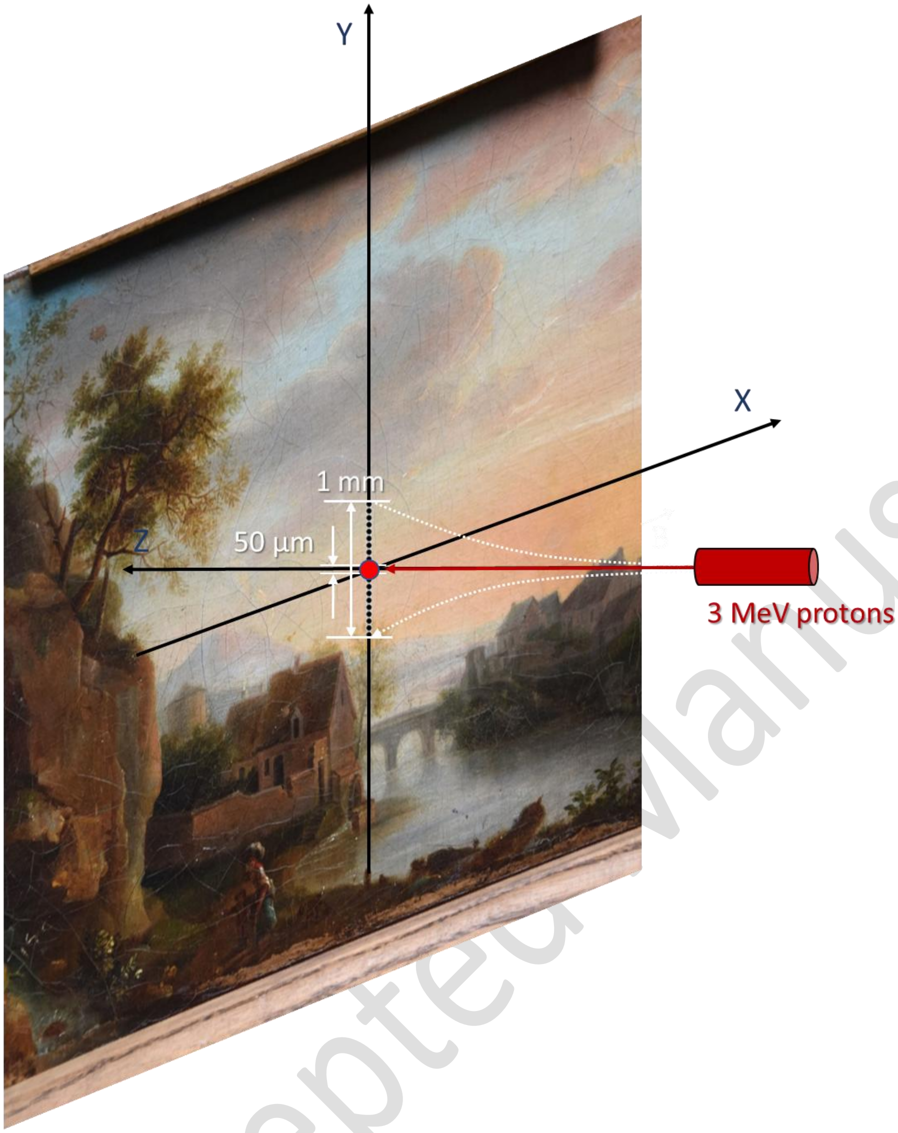

Fig 9. Principle of full-field PIXE scanning. The painting is mechanically raster-scanned under rapidly deflected beam to cover its entire surface. The push broom beam size is 1 mm by 50 µm and the painting moves at a speed of 4 mm/sec. The final resolution is 100 µm.

Full-field PIXE was carried out at the new AGLAE accelerator of the C2RMF in Paris, France [23]. An external beam of 3 MeV protons was scanned over an area measuring 240 x 230 mm (almost the entire painting) with a pixel size of 100 µm, resulting in elemental maps of 2396 x 2236 pixels. With a 0.006 sec dwell time, the scan took 15 hours. The beam intensity was 3.7 nA, corresponding to a fluence of 0.4 µC/cm², which is considered non-damaging conditions [24]. Three X-ray detectors with 125 µm Be absorbers were employed to collect X-rays at 10^5 counts/sec. Data were processed using specific programs for PIXE elemental imaging [25]. The derived elemental maps reveal that the main pigments contain lead (lead white pigment), iron (ochre, umbers, Prussian blue), and mercury (vermillion), which all are pigments available before the 19th c. A restoration *retouche* combining more recent pigments was evidenced in the maps of Cd (cadmium yellow > 1840), Cr (chrome yellow > 1820), Zn (zinc white > 1840), and Ti (titanium white, patented in 1921 in France). A small level of Zn was found to be almost evenly distributed over the original surface. It is therefore not connected to any other pigment but is rather associated to a surface treatment.

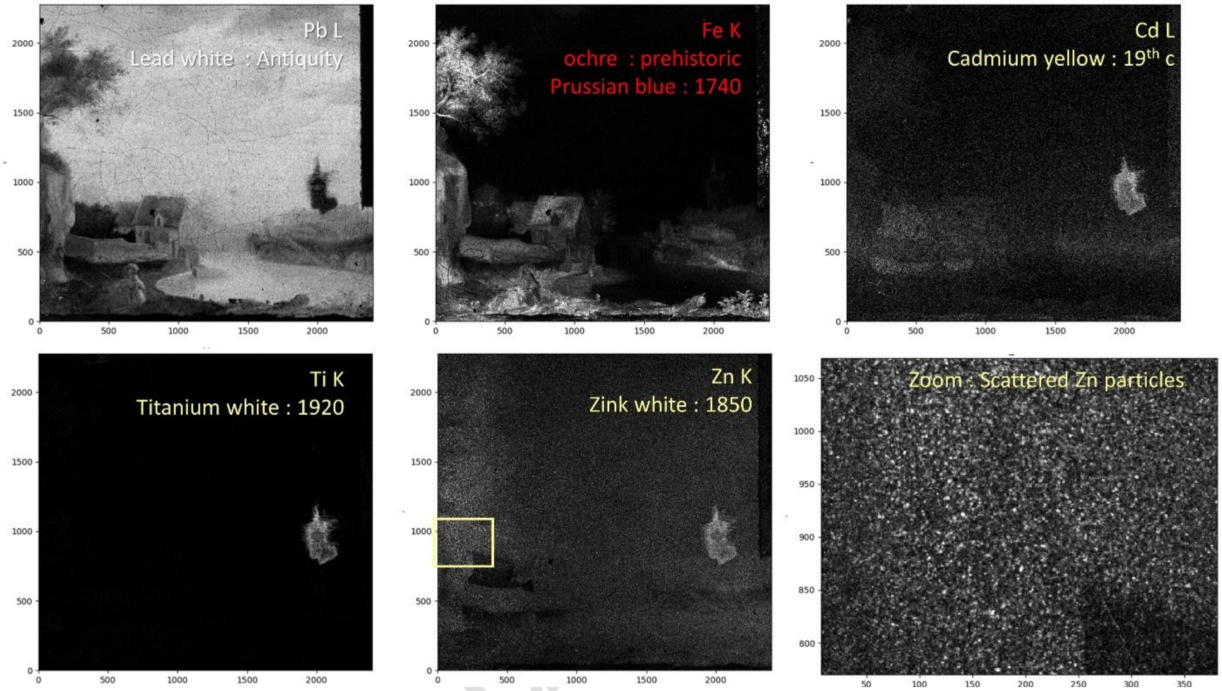

Fig 10. Elemental maps of the entire surface. Pb and Fe corresponds to old pigments: lead white, ochre, Prussian blue. Cadmium, Titanium and Zinc are anachronistic pigments present in a restored area. The entire painting is covered by a shallow layer of Zn-bearing grains, probably an insecticide in the varnish (non-original).

4. Results and discussion

The combination of the new NAT methods allowed tracing back the history of *Cobaye_one*. First, ^{14}C-AMS dating gave three possible date ranges for the paint composition and its wooden frame: ca. 1550, ca. 1660 and ca. 1790. The application of MeV-SIMS and O-PTIR evidenced ageing features in the paint layers (formation of lead soaps, degradation of oil binder), which are important clues in favour of such old dates. While the pigment palette determined by IBA on the coupons seems globally compatible with the ^{14}C-AMS dates (prior 19th century), presence of zinc casted doubts on those dates as it could correspond to zinc white, a pigment introduced later. Differential PIXE established that Zn is in a superficial layer and full-field PIXE imaging that it is uniformly distributed over the painting surface, without spatial correlation with the composition.

It might correspond to zinc sulphate, a siccative commonly employed in varnish. O-PTIR evidenced a thin proteinic layer in front of the varnish, likely corresponding to animal glue (gelatine or casein-based) applied in the facing procedure during the lining of the painting. Scientific imaging also revealed that the blue pigment employed in the sky is Prussian blue (ferric ferrocyanide) as it appears dark in the infrared false colour image. This was confirmed by the presence of its characteristic vibrational band at 2080 cm^{-1} using portable FTIR spectrometry (results not presented here). Considering that this Prussian blue was invented in 1709 and used until the end of the 19th c., the two oldest ^{14}C-AMS date ranges (ca. 1550 and ca. 1660) could be ruled out, leaving the 1790 range as the only possibility. Wide-field PIXE mapping also revealed a local restoration conducted in the 20th c. using anachronistic pigments (combination of titanium white synthesised in 1920, cadmium and chromium yellow in the 19th century).

Based on these results the test painting could be authenticated. *Cobaye_one* appears as a genuine work, probably painted at the turn of the 18th c. or in the first decades of the 19th c. The wood frame is the original one. The composition was lined (glued) onto a new canvas between WW1 and WW2, probably because the original canvas was too degraded, keeping its original wood frame. Traces of proteins and zinc in the varnish layer might result from the *facing* during the lining. A *retouche* was applied on a small area, possibly at the time of the lining. Its motivation remains unclear, whether for restoration of local damage or application of a palimpsest to hide the steeple of a church, we do not know.

5. Conclusion

The combination of the NATs techniques resulted in information of the test painting with identifier *Cobaye_one* comprehensive enough to draw conclusions on its authenticity which, if considered individually, could have led to misleading results. In addition, most NATs are non-destructive and when sampling is required, it is of microscopic size and can often be preserved after analysis. The wide range and high quality of these results and information content present attractive assets in Forensics Science applications, notably in the Heritage domain. The access of Forensics science community to NAT platforms should be considered through the development of strengthened cooperation between Forensic, Heritage, and Nuclear Science communities.

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