Proceeding for

Seminar on Application of Nuclear Science and Technology in characterization and conservation of Artefacts

Nuklear Malaysia and Department of Museum Malaysia

6-7.AUGUST.2019

Published by :

Malaysian Nuclear Agency (Nuclear Malaysia)
Bangi, 43000 Kajang, Selangor Darul Ehsan, MALAYSIA.
Phone : 03-8911 2000
URL : https://www.nuclearmalaysia.gov.my

First print : 2022

Perpustakaan Negara Malaysia Cataloguing-in-Publication Data

Seminar on Application of Nuclear Science and Technology in characterization and conservation of Artefacts (2019 : Kajang)
Nuclear Application in Cultural Heritage Artefact Characterisation : Proceeding for Seminar on Application of Nuclear Science and Technology in characterization and conservation of Artefacts, Nuklear Malaysia and Department of Museum Malaysia, (6-7.AUGUST.2019).
Mode of access: Internet
eISBN 978-967-2706-08-3
1. Nuclear engineering–Congresses.
2. Cultural property–Congresses.
3. Antiquities–Congresses.
4. Government publications–Malaysia.
5. Electronic books.
I. Title.
621.48

e ISBN 978-967-2706-08-3

9 789672 706083

Nuclear Application in Cultural Heritage Artefact Characterisation

ISSN: 978-967-2706-08-3

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FORWARD

Utilization of nuclear technique in cultural heritage investigation is an important in order to meet national needs as well as to assimilate new developments for improving cultural heritages process, safety, security, development, characterization and efficiency. These include preservation and conservation of objects significant to the archaeology, architecture, science and technology of a specific culture. This publications have a broad readership and are aimed at the interested scientists, conservative, researchers, curators, teachers and students, laboratory professionals and instructors. Cultural heritage is the legacy of physical artefacts and intangible attributes of a group or society that are inherited from past generations, maintained in the present and restored for the benefit of future generations includes buildings, monuments and artefacts.
As cultural heritage objects are frequently unique and non-replaceable, non-destructive techniques are mandatory and, hence, nuclear techniques have a high potential to be applied in investigation of artefacts. Nuclear techniques, such as neutron activation analysis (NAA), X-ray fluorescence (XRF) analysis, scanning electron microscopy (SEM) and neutron radiography have widely used and reliable investigation of precious materials, such as ceramics, stone, pigment and metal. Such information can help to repair damaged objects adequately, distinguish fraudulent artefacts from real artefacts and assist archaeologists in the appropriate categorization of historical artefacts. The Malaysian Nuclear Agency (Nuklear Malaysia) and Malaysian Department of Museum (JMM) as a leading supporter of the benefit and beauty use of nuclear technology to apply and develop nuclear methods for cultural heritage research for the benefit of socioeconomic development in emerging economies. Nuklear Malaysia and JMM wishes to thank all contributors to this publication for their valuable contributions for compiling and reviewing the articles. The encouragement by Director General of the Nuklear Malaysia and Department of Museum to pursue this publication is highly aprreciated.

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e ISBN: 978-967-2706-08-3

NUCLEAR AND SCIENTIFIC APPROACH IN CHARACTERIZATION AND CONSERVATION OF CULTURAL HERITAGE

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ABSTRACT

Preservation and conservation of cultural heritage artifact can be done once required characteristic of artifact are obtained. There are many analytical method could be used in the characterisation of artifact. Among others, nuclear technique is one non-destructive method widely used in investigation of artifact condition. Nuclear technique is classified by the utilisation of X-ray, gamma radiation, neutrons and also radioisotopes in the analysis. Several nuclear techniques used for analysis and investigation of artifact from cultural heritage object are discussed in this document.

Keywords: Cultural Heritage, Artifact, Preservation, Conservation, Nuclear

INTRODUCTION

Malaysian Nuclear Agency (Nuklear Malaysia) is a national research institute whose core activities are based on nuclear science and technology and other related technologies. Both are supported by professionals and supporting staffs, trained in their own respective areas. As a premier research and development organization, Nuklear Malaysia continues to play an active role to support and promotes the usage of science and technology (ST) to the public and other government agencies to ensure it remains a relevant public research institute for the country.

Scientific and nuclear approaches can be adapt to collect and preserve the artefacts including objects for conservation as to retain its cultural significance. Our greatest efforts should be put in to preserve and to maintain cultural heritage and Nuklear Malaysia believe that scientific and nuclear approaches is worthy of such task. Harnessing science and technology for preservation and conservation of cultural heritage in Malaysia is the challenging because this area still new in conservation practice. It includes identification, maintenance, preservation, restoration, reconstruction adaptation and interpretation of artefacts. It involves researches, historians, conservators as well as scientists. (Ion et al., 2008)(Pendlebury et al., 2004)

Over the past decades, radiation processing has been used in many sectors of country development. For example, sterilization, polymer cross-linking such as tapes, tubes, cables, tyre belt vulcanization and the irradian of certain food items for hygienization, are well established technologies (Chmielewsk, 2004b), (Chmielewsk, 2004a) and (Mehta and Haji-Saeid, 2008). Either gamma radiation from isotopic sources or high energy electrons from accelerators are being applied in these processes. One of the important area is to characterization and preservation of cultural heritage through the application of nuclear techniques with special emphasis on gamma irradiation treatment, making use of techniques including insect eradication and disinfection in various cultural heritage materials and consolidation of degraded materials with radiation-curing resins. Characterization and analysis of artefacts has been utilised the radiography using X-rays, gamma, neutrons or beta particles, X-ray fluorescence analysis, neutron activation neutron prompt gamma analysis, ion beam analysis like PIXE (particle induced X-ray emission) and synchrotron radiation technique. Many of these techniques are routinely operated, all around the world, in public cultural heritage institutions, universities, museums, libraries, archives institutions, restoration workshops (Havermans and Sabharwal, 2017).

Currently, Nuklear Malaysia has form an understanding with the Department of Museums Malaysia in which several joint projects have been discussed and would be put into action. Teamwork that comprised of both organizations would work together in which the co-existing of scientific and historical approach would be expected to provide excellence result in conservation and preservation of cultural heritage in Malaysia. The projects cover from conservation of artefacts, analysis of chemical composition of samples, radiocarbon dating and study the environment particle pollution. The Department of Museum Malaysia holds the responsibilities to preserve and disseminate knowledge on towards conserving, preserving and historical, cultural and natural heritage in its effort to instill awareness among the public on richness of the country's historical, cultural and natural heritage. These efforts will assist to create a harmonious society with high morality and also helps the government to promote and develop the tourism industry.

NUCLEAR AND SCIENTIFIC APPROACH

Scientific approaches in conservation using chemical and mineral analysis are applied in archaeological artefacts. Aimed to investigate the original sources, structures, and temperatures, the tools used are X-Ray Fluorescence Spectroscopy (XRF), X-Ray Diffraction (XRD), Atomic Absorption Spectroscopy (AAS), Inductive Coupled Plasma - Atomic Emission Spectroscopy (ICP-AAS), Quantitative Colour Difference Analysis (UV/VIS), and Scanning Electron Microscopy (SEM). Some equipment mentioned have been used for example on pottery sherds in Gua Angin, Jerantut, Pahang. Compositional and morphological analysis showed the same development in pottery technology over several thousand years in Gua Angin. Local pottery shows similarities with foreign pottery in some technology for example the firing method, thickness and porosity (Ramli et al., 2001). Other analyses could be investigated including the depth of monument structure as well detecting other sources or possible existence underneath. Magnetic detection method is effective in detecting artefacts containing a high level of magnetic reaction like metals or those artefacts made from bronze. Nevertheless, its effectiveness depends on the size, depth and strength of the artefacts.

Examination of artefacts study can be potentially using the following instruments;

1. X-Rays Diffractometer (XRD) in determination of compounds and phase analysis (Figure 2).

2. Fourier Transform Infrared spectroscopy (FTIR) for polymer identification and structural analysis.

3. X-Ray Fluorescence spectroscopy (XRF) for metal and alloy identification and elemental analysis (Figure 3).

4. X-Radiography and Neutron Radiography for internal structure examination of artefact.

ISSN: 978-967-2706-08-3

5. Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscopy (FESEM) for microstructure and morphology analysis (Figure 4).

6. UV-Vis Spectroscopy for optical characterization, color determination and reflectance measurement (Figure 1).

7. Arc-Spark Optical Emission Spectroscopy for metal, Al-base and Fe-base materials analysis (Figure 6).

8. Small Angle Neutron Scattering (SANS) for correlation to alteration of physical, chemical and mechanical , properties of crystallites and lattice of material (Figure 8).

9. Corrosion Analyzer for analyzing corrosion behavior and corrosion rate study.

Figure 1: UV-Vis Spec; Optical characterization color determination and reflectance measurement

Another nuclear technique used in conservation of artefacts is high intensity gamma radiation (mainly from cobalt-60 sealed sources) which has been used for many years for the disinfection or sterilization of collections of cultural artefacts made of wood or other organic materials. It has appeared necessary to establish an assessment of the state of the art of the applications of this technique to wooden artefacts (furniture, statues, archaeological objects, and ethnographic collections artefacts), basketwork, leather, paper and many more. Irradiation technique have been used from the early 70's as treatment to preserve cultural heritage artefacts. Based on the biocide effect of ionizing radiation, the technique was at the beginning developed mostly in Czech Republic and in France, with some resounding success such as the disinfection of the Ramses II mummy (Havermans and Sabharwal, 2017). In time ionising radiation proved to have other abilities useful for cultural heritage reservation. By initiating polymerisation crosslinking, radiation may be the clue in consolidation of destructured porous materials. A treatment

Figure 2: XRD; Phase Analysis

Figure 3: XRF; Determine C to Americium (Am) Qualitative determination.

is an intervention method applied in order to stop, or at least to reduce the rate of deterioration of an object. As such, it differs definitively from characterization techniques for which the aim is only to collect information, whatever this information could directly help to preserve the object or is only of documental interest. As for any other techniques used in the cultural heritage conservation restoration context, it has to respect ethical principle in order to keep the artefact “as close to its original condition as possible and for as long as possible”. Regarding to requirements of effectiveness within ethical

ISSN: 978-967-2706-08-3

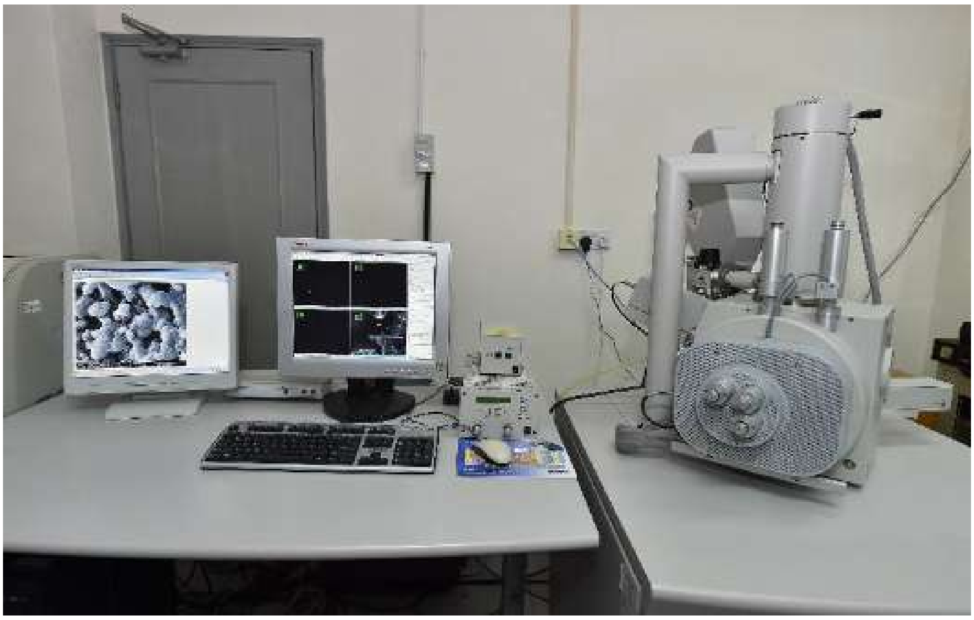

Figure 4: SEM; Microstructure and elemental analysis.

Figure 5: Field Emission Scanning Electron Microscope microstructural and elemental analysis.

guidelines such as minimal intervention, non-contact irradiation techniques is very attractive. Besides, it is enhanced by the penetration power of gamma rays that provides an interesting way to reach the inside of 3-dimension items (Havermans and Sabharwal, 2017).

Underwater conservation of artefacts which remain undisturbed on the seabed for centuries provide vital information about the past. However, once an underwater artefact is taken out from its original residence, it would be weak against the temperature and its level of exposure to rapid decay or deterioration is very high. They suffered from salt efflorescence causing loss of surface detail in the object itself. This phenomena is well known and a plethora of data exists will describe it as nature,

ISSN: 978-967-2706-08-3

Figure 6: Arc-Spark Optical Emission Spectroscopy; Metal, Al-base and Fe-base materials analysis.

Figure 7: Small Angle Neutron Scattering (SANS); In-homogeneity study Correlation to alteration of physical, chemical and mechanical properties of crystallites and lattice of material.

composition and cure. The challenge of scientific approach to be to understand the past by studying material traces without making any further deterioration on the objects. Research on conservation of marine artefacts is important to investigate the suitable methods in stabilization and reintegration of deteriorated underwater artefacts as well providing a good environmental condition for those artefacts. These activities involve the corrosion mechanisms and the processes of controlling the degradation of artefacts. Specific equipment are possible for the investigation includes; scanning electron microscope, radiography, X-ray fluorescence, scanning vibrating probe, portable corrosion measurement system and corrosion analyser.

ISSN: 978-967-2706-08-3

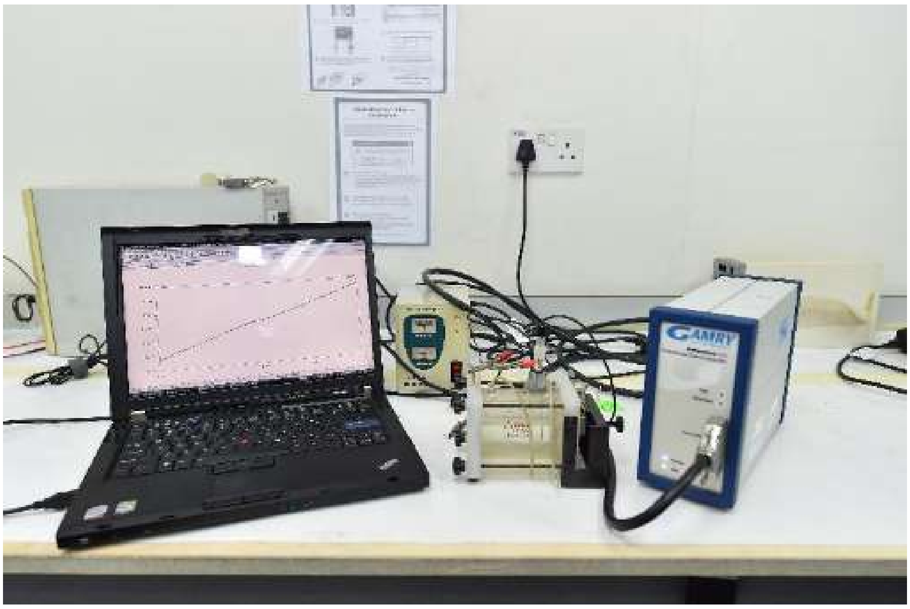

Figure 8: Corrosion Analyzer; Corrosion behaviour and corrosion rate study.

Monuments and historical buildings are part of the precious national heritage. However, the historical building materials such as bricks and mortars experience to the process of decay. Inherent environment, nature of the ground, material structural defect, and physical, mechanical and chemical weathering as well bio deterioration are part and parcels of intrinsic causes leading to the deterioration of monument and historical building. Similarly, such degradation is also caused by an extrinsic causes, composing of man vandalism, natural catastrophe, climate and water pollution as well as biological growth. Neutron-induced prompt gamma-ray technique can be used for in-situ quantitative determination and analysis of industrial, environmental and archaeological materials as well as location of contaminants, particularly water and soluble salt in building materials. Compare to conventional methods, this new technique provides an accurate and reliable data as well as offers an excellence level of sensitivity. Hence, it is useful and suitable in providing solution for investigation of deterioration of monuments or historic buildings especially for investigating moisture and chloride problem (Watkinson et al., 2014).

NDT or Nondestructive testing has been developed and introduced in conservation and preservation of buildings materials. NDT is highly advanced and a variety of methods is available for metallic or composite materials. Regarding historical buildings in Malaysia, NDT focuses on the roots or sources of decay caused by age and environmental attacks. For instance, detection of corrosion holds the major priority in metal-based objects is one of NDT methods. Furthermore, NDT methods also involve ultrasonic, radar, thermography, visual experiment as well as radiography. Other than aiming for conservation and preservation purpose, NDT also provides several important information on historical objects such as structures, methodologies and quality of the object itself. Kota Cornwallis in Pulau Pinang is one of the good example of the implementation of scientific approach to conservation of historical buildings. Several methods are used comprising of sample matching, compressive test and microbiology studies and XRF (Taha, 2019). Remote Sensing technique has been applied at Tanjung Dawai aimed to detect the depth of the river in which alluvial soils and a theory of possible shipwrecks have been identified (Norman et al., 2012).

Scientific approach are going to be taken covering the identification of samples, a measurement standard, database and photographs. It involves aspects like material identification, diameters, wall thickness, and calculation of actual length and weight of sample as well as a case study that would confined to historical forts such as cannon at Kota Kuala Kedah (Taha, 2019). A research on fossil discovered in Gua Naga Mas is going to be taken using both historical and scientific approach. Type, age, preservation and conservation method of the fossil are the major interest of both parties. Radiography is one of the suggested technique but its actual implementation is still under careful observation and experimentation. Bricks industry has rooted in Malaysia since the sixth century. It disappeared in fourteenth century after the fall of Lembah Bujang but later, emerged again in eighteenth century. Therefore, it is suggested that a research on brick industry would be thoroughly and carefully planned on its origin, technology and porosity to seek information in order to fill in the gap between those phases.

Detection of Buried Objects by Ground Penetrating Radar (GPR) GPR or Ground Penetrating Radar is a broad band, impulse radar system that has been specifically designed to penetrate earthen materials. The radar transmits high frequency, short duration pulses of energy into the ground from a coupled antenna. Transient electromagnetic waves are reflected, refracted, and diffracted in the subsurface by changes in electrical conductivity and dielectric properties. Travel times of reflected, refracted and diffracted waves are analysed to give depths, geometry and material type information. The energy returning to the antenna is processed within the control unit and displayed on graphic paper.

Radiocarbon Dating has proven itself to be the most widely interesting of dating methods, notwithstanding that its time range of application is only 50,000 years or so. Carbon 14 or C14 establishes data on chronologies of glaciations and sedimentation, past sea levels and ancient climates. C14 also tells us about the sources and intensity of manmade pollution of the atmosphere, land, rivers, lakes and oceans, and the periodicity of earthquakes, floods and storminess. Previously, in order to determine the age of specific object, archaeological artefacts were sent abroad for radiocarbon dating. However, a development of radiocarbon dating in Malaysian Nuclear Agency make it possible for our archaeological artefacts being analysed locally. Prior to treatment, any artefact, particularly if encrusted with marine carbonates, must be critically evaluated in order to ascertain the possible presence and condition of metal, associated organic material or other material, such as ceramic and glass. Only after each artefact is evaluated and all options considered is a course of action decided upon. In archaeological conservation, various synthetic resins are used extensively, and they play an important role in the conservation of materials, especially organic and siliceous materials, from marine sites. It is, therefore, important that any conservator working on archaeological artefacts has not only a variety of resins at his or her disposal for use as glues and consolidates but also has a good understanding of their physical characteristics.

Challenges are inevitable especially due to lack of knowledge, experts, funds and awareness from the public. The climate change, vandalism, industrial development and the renewal urban activities combine with the shortage of funds, improper conservation techniques implemented, without proper documentation and lack of qualified personnel leading to less practical achievement then effected to quality of local conservation of cultural heritage. The proper documentation is essential to ensure a systematic arrangement of events, both historical and scientific. The Qualified Personnel and Officers in Charge Conservators must have aesthetic qualities and the technology of their production particularly in scientific approach.

CONCLUSION

Malaysia would strongly aims to retain and prolong the well-being of national cultural heritage by promoting the importance of conservation and preservation of cultural heritage through the application of scientific and nuclear techniques. The collaboration or join venture activity and expert among local agencies is important to increase the benefit and advantage of technology. The training and continuing professional development must continue throughout a conservator's career. The advanced instrumentation such as XRF, X-rays radiography, prompt gamma and SEM have been used for characterization and analysis of artefacts. Application of corrosion inhibitor onto ferrous materials are also important for conservation method. Determination and dedication, supplemented by sufficient knowledge would be a driving force in overcoming any challenge and threat in harnessing of science and nuclear technology for preservation and conservation of cultural heritage in Malaysia. Management, technical and investment supports must retained high for the sustainability of cultural heritage artefacts.

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e ISBN: 978-967-2706-08-3

SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE X-RAY ANALYSIS: APPLICATION IN ARTEFACTS CHARACTERIZATION

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ABSTRACT

Scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) is an essential equipment in studies of cultural heritage sites and material. SEM combine with EDX makes it possible for conservators to solve many history enigma by scientific approach. This paper review the studies that have been done for cultural heritage materials using SEM and EDX. The studies reviewed in this paper involving investigation and characterization of sudden deposit on artefact, old parchment, pigments, wood deformation and authenticity of the artefact. Studies conducted using these equipment shows how a conservator scientist can achieve better understanding of the artefact thus helping them to create a suitable environment for preservation and the best technique for conservation and consolidation of the artefact.

Keywords: Scanning Electron Microscope, Energy Dispersive X-Ray, Elemental Analysis, Artefacts Characterization, Cultural Heritage, Conservation Science.

INTRODUCTION

Today, arts and science walks together especially in the field of cultural heritage. One of cooperation between this two major fields can clearly be seen under the guidance of International Atomic Energy Agency (IAEA). This is by various research, training and meetings coordinated by IAEA. This is achieve through conducting of Technical Cooperation Program (TC Program), Coordinated Research Projects (CRP), Regional Training Course (RTC) and much more. IAEA, as a leading supporter of peaceful use of nuclear technology, has assisted laboratories in its member states to develop and apply nuclear methods in cultural heritage research. Ionizing radiation based techniques are now recognized as important tools for examination, investigation, characterization and analysis of art object or other cultural heritage artefact and their component material (J.B.G.A. et al., 2017).

It is time that Malaysia's conservator, archeologist and curator get involve and become familiar with such scientific facilities. It is also crucial for conservator, archeologist and curator to exchange and sharing of experience in handling cultural heritage artefact to the material scientist, physicist and chemist. Cultural heritage research is highly interdisciplinary and requires expertise in different fields. Therefore, collaborations are critical to success (Gates, 2014).

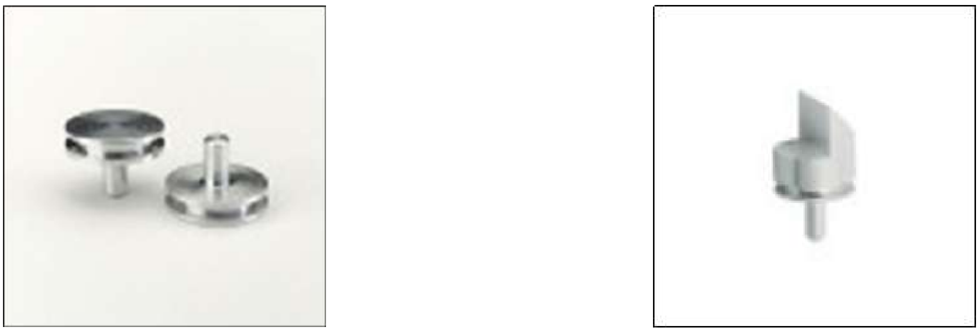
Cultural heritage research involves a wide range of materials that could include metal and corrosion product; textiles and dyes; mineral and organic pigments; gems, composite of biomaterials; fired ceramics and coatings and even polymers. The diversity of artefact materials, can be analyzed by variety of analytical methods (Schreiner and Grasserbauer, 1985). The determination of the chemical composition of material used, authenticity and origin of an artefact can be obtain by characterization and investigation using scientific analytical equipment. It will also help conservators to understand the degradation of artefact. The degradation of due to reaction of artifact in contact with soil, environment or ambient atmosphere can be study to confront deterioration and to conserve and preserve the artefact (Schreiner and Uhlir, 2006).

Due to these needs, this paper will give a brief introduction to scanning electron microscope (SEM) and energy dispersive x-ray (EDX). A simple overview on sample preparation for viewing and analyzing cultural heritage samples will be explain. This paper will also demonstrate a few cultural heritage studies that have been done using SEM combined with EDX for investigation and characterization of cultural heritage artefacts; conservation and consolidations materials.

SAMPLE PREPARATION, SEM AND EDX

Magnifying glass is the first equipment and the symbol use worldwide by detective to investigate any evidence and crime scene. To get a closer look is preliminary step to understand and evidence and this goes to investigation of cultural heritage artifact too. SEM enhances the viewing artefact to a greater magnification with added value of elemental mapping help to study any material to further depths. The reason SEM is used in cultural heritage studies, is in the sense that the SEM allows a sample to be examined at far higher magnification and resolution. Other advantage of using SEM is the huge range of contrast mechanism and the possibility of simultaneous imaging and localized elemental analysis (A. Adriaens, 2004).

Before using the SEM, the sample has to be prepared correctly, mounted on special sample holders and oriented properly. Metallic stubs show in Figure 1(a) is the usual sample holder used for common SEM while Figure 1(b) shows the special stub used for viewing cross-section of thin sample. The sample is stick to the stub using carbon tape in particular orientation so that the part of the sample that needs to be viewed will be in a particular orientation to the beam.



(a) (b)

Figure 1: (a) 12.5 mm diameter pin sturb, (b) 12.5 mm diameter crosssection stub

In a typical preparation of samples for SEM analysis, the sample has to be thoroughly cleaned using various method suitable to the sample. In cultural heritage samples, this is not necessarily done due to method of study that needs to be done on the sample. The oxide and carbonized layer of a typical scientific sample is always cleaned using plasma cleaner but this could not be done on cultural heritage sample to get the actual data that leads to history of the sample. Some of cultural heritage samples have deposits, corrosion products or even debris that need to be investigated. In this particular case, the sample should have minimal handling for sample preparation, taking care and having in mind that the information needed is on the surface of the sample and shouldn't be tampered.

For SEM analyzing, the sample should be dry and conductive. The sample can be dried using dryer if needed and then sputter coated with a conductive layer that usually is gold (Au), platinum (Pt) or carbon (C) to make the sample conductive. This conductive layer allows the electron a path to the local ground (Page, 2015). A non conductive area or sample will show up as whitish region with very less detail to be seen. Over the time, this whitish region will become brighter and losing even more details.

In studies of cultural heritage artefacts, some of the sample should have minimal contact and should be view as it is. The sample preparation for SEM may not be suitable for the sample. A new advancement in SEM is environmental scanning electron microscope (ESEM). By using ESEM, that sample can be analyze without coating and drying. The electron beam column of the ESEM requires a high vacuum, but the pressure in the sample chamber can be increased beyond 900 Pa (atmospheric pressure is -101,300 Pa). At these pressures, wet samples remain hydrated during examination and not damage due to drying or coating of the sample. As the electron react with the sample, they produce a few signals such as secondary electrons, backscattered electrons, characteristic x-rays which is pictured as Figure 2.

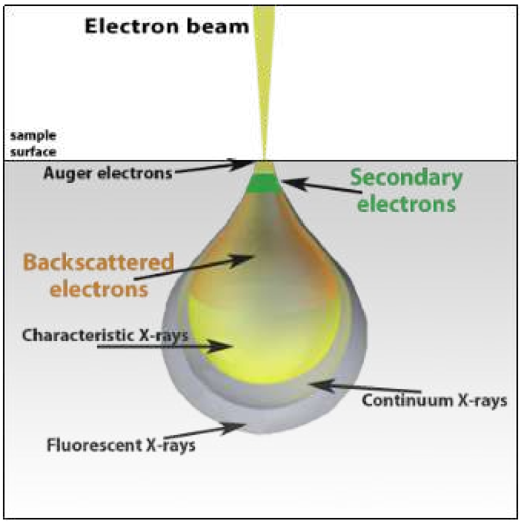


Figure 2: Electron beam-sample interaction

These signals are collected by one or more detectors to form images which are then displayed on the computer screen. When the electron beam hit the sample, it penetrates the sample to a depth of a few microns, depending on the accelerating voltage and density of the sample. When the image shows proper details and is magnified correctly, elemental analysis can be done by x-ray spectroscopy. Every material produces x-rays that have specific energy. So by detecting the energies of x-rays that emitted from the sample, it is possible to identify all the different elements that it contains. For samples where the corrosion product or the thin layer of coating is the aim of the investigation, a low accelerating voltage should be use. This is to ensure low beam penetration and the signal received represent only from surface of the sample.

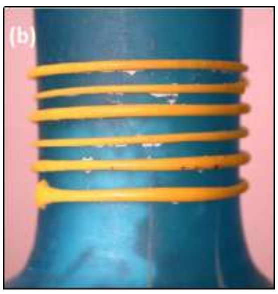
INVESTIGATION OF ARTEFACTS

Deterioration or artistic design

Determining if the appearance of an artwork results from product of decomposition or deterioration is not always as obvious. For example, conservators noticed the presence of a white crystalline material on the surface of the Venetian glass Ewer (Figure 3 (a) and (b)) while preparing it for exhibition. This artwork was created in the late 19th or early 20th century with the intention of appearing ancient or antique, the question arose whether the accretion indicated an unstable glass composition or if it was evidence of the“antiquing” process used by the creator and, therefore, should be preserved as part of the object’s history. However, the question remained whether the object itself was decomposing.

Extracting a small sample that included the glass and the accretion for SEM and EDX analysis showed with certainty that the white material had been applied, because fluorine was detected only in the accretion, not in the underlying glass substrate (Figure 3(c) and (d)). In this case, material analysis informed the proper conservation of the object. The accretion was evidence of the maker’s antiquing technique, thus it was preserved (Elliott and Giaccai, 2013).

(a)



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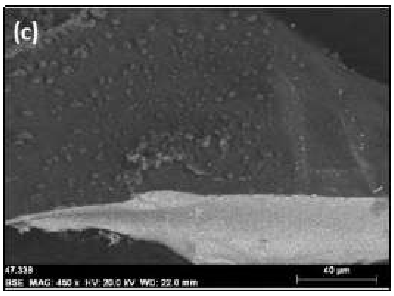
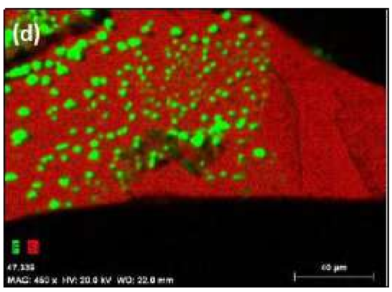


(c)



(d)

Figure 3: (a) Italian glass Ewer produced in the late 19th or early 20th century to mimic the style and appearance of ancient glass, (b) Detail of flakey white material on the ewer (c) SEM micrograph of the sample surface (d) EDX mapping of fluorine (green) and silicon (red) shows fluorine located in the encrustation but not in the underlying glass. (Elliott and Giaccai, 2013).

Ancient manuscript analysis and authentication of origin

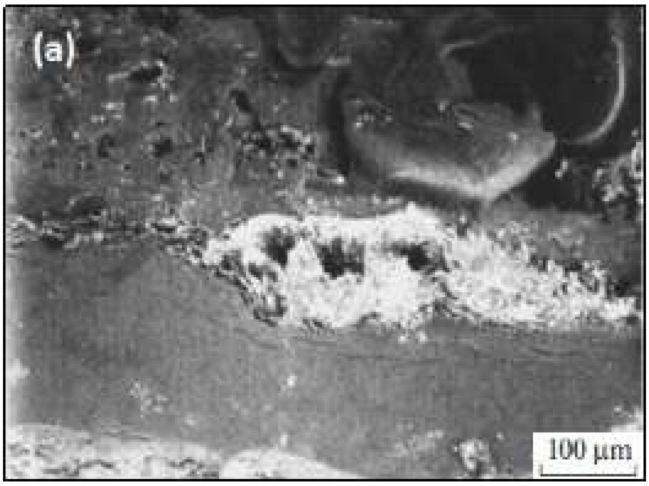
Al-Quran fragments dated to the 10th–11th centuries AD, parchment, and ink were investigated by the SEM–EDX methods (Vasiliev, 2016). A microanalysis of the parchment revealed carbon and oxygen in its composition (and thus confirmed the organic nature of this object of study), as well as Si, Na, K, Ca, Mg, Cl, and S. The presence of some elements may be related to the parchment processing aimed at imparting it with a certain hue. The manuscript text was written in inks of black, red, and green (Figure 4). An analysis showed that part of the red ink contains mercury and that it was made based on vermilion or cinnabar(HgS). Possible cinnabar sources are the river rock near the town of Takab (western Iran) or the mines near Fergana (Vasiliev, 2016) . At the same time, a number of red paint samples exhibited the presence of iron and oxygen, which was made based on ochre (a mixture of iron oxide with clay). Another component of red ink was based on an organic pigment. Green ink contained copper salts and black ink contained mainly carbon, with a small amount of iron impurity. Based on the EDX data and the established composition of the pigments, one can formulate suggestions about the sources of their origin.

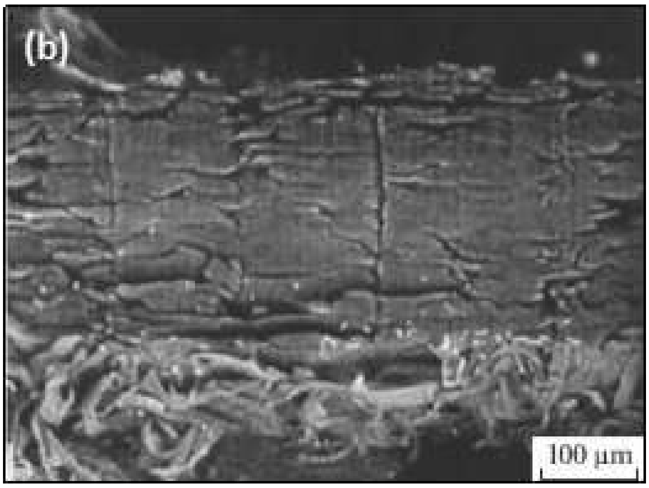
Figure 4: Al-Quran fragment with black, green and red ink (Vasiliev, 2016)

Degradation process investigation for storage of ancient documents

The degradation processes affecting collagen in parchment were studied in order to determine the optimum conditions for long-term storage of ancient documentsand manuscripts, such as the Dead Sea Scrolls. If stored in a relatively highhumidity environment, the collagen in parchment may gradually denature and form gelatin. Under such conditions, the parchment loses its fibrous structure and becomes soft and gummy. Also, at high relative humidity microorganisms may grow and attack on the parchment At low relative humidity, ancient parchment shrinks, deforms and becomes extremely fragile and brittle. Determining the appropriate conditions of compromise for storage between these two humidity conditions is a difficult task. Part of this process included the analysis of small fragments from the Dead Sea Scrolls in order to assess their condition and look for clues to their remarkable preservation. In this application, small fragments of the Dead Sea Scrolls were examined non-destructively (undried and uncoated) using the ESEM. The resulting SEM micrographs (Figure 5 (a) and (b)) show no image distortion due to surface charging.

The relatively high partial pressure of water vapor (-100 Pa) in the microscope's sample chamber provided long-term dimensional stability throughout the examination. Figure 5 (a) shows a cross-section of a fragment from the Dead Sea Scrolls. Layered fibrous structures are clearly visible (collagen) as well as an almost structure-less layer of material above and beneath the fibrous layer (gelatin). EDX analysis were also performed on several Dead Sea Scroll fragments revealed the presence of soluble salts in some ofthe scroll samples. Bromide and potassium chloride salts were detected in the parchment samples as well as soil and calcite deposits. When the humidity fluctuates the salts dissolve and recrystallize, producing stresses which may result in the delamination of the parchment. The delamination seen in some scroll samples was found to originate between the papillary upper layer of the parchment and the fibrous dermis under-layer. The salts probably come from the original processing of the animal skins into parchment using water from the Dead Sea (which contains high levels of bromine) since fresh water was scarce. Some of the scroll fragments were written on imported Egyptian papyrus that was processed with fresh water. Bromine salts were not detected in these samples. The salts in the Dead Sea Scroll parchment probably contributed to its not being consumed by microorganisms over the millennia (Doehne, 2003).





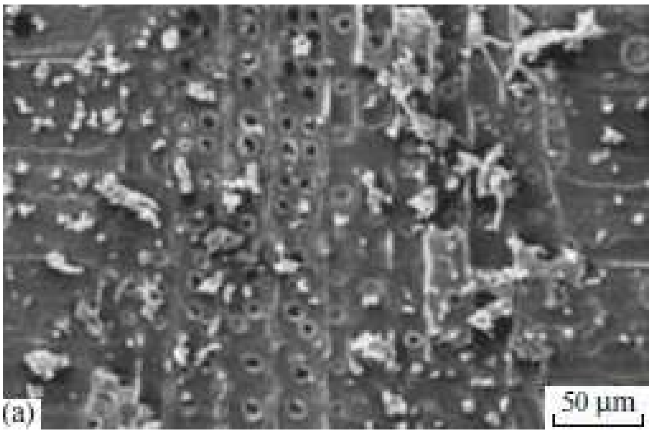
(a) (b)

Figure 5: (a) cross section cut from the Dead Sea Scrolls. b) Cross section of modem parchment showing well developed layered fibrous structure. (Doehne, 2003)

Degradation of wood

Another example of applying SEM in cultural heritage is the study of changes occurring in wooden articles (Vasiliev, 2016). The results of analyzing the changes occurring in wood cells and damage of cellular membrane were possible factors leading to material degradation were described. The degradation can be caused by different factors: physicochemical, mechanical, and biological. The physicochemical effects include heating; UV irradiation; and contact with chemical agents, such as metal oxides, chlorides, and potassium carbonate (potash). It was found that a thermal treatment at temperatures in the range of 190–240°C may cause formation of micro-crack sand structural decomposition, which manifests itself in a separation of lamellae. An increase in temperature in the presence of moisture and under pressure leads to the softening of lignin. This process may be accompanied by changes in cellular membranes and the formation of holes in pine wood (Figure 6(a)) (Vasiliev, 2016).

UV irradiation leads to the degradationof the wood surface via the destruction of wood cells and



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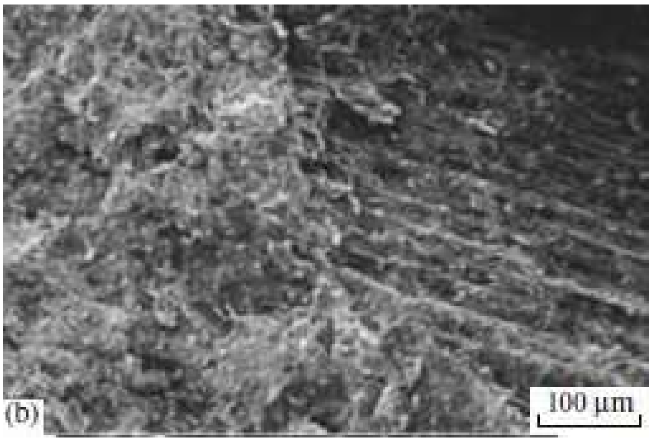

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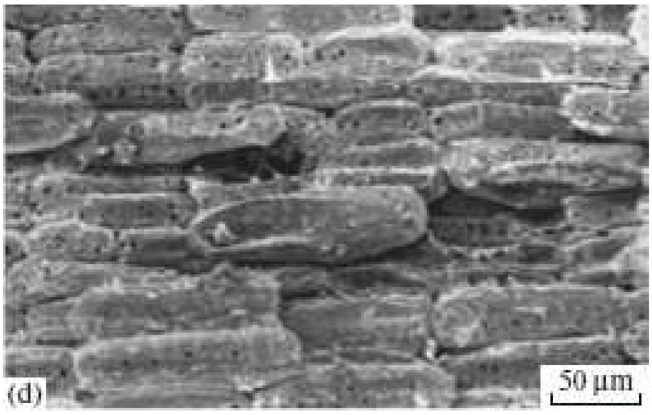

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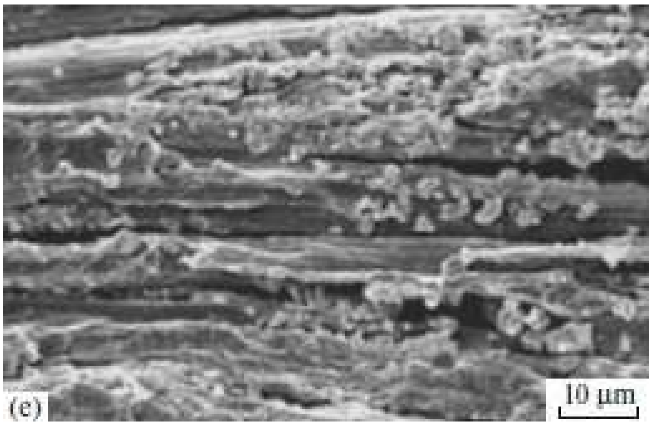


(e)

Figure 6: SEM micrograph of wood exposed to different impacts: (a) heating and moistening, (b) formation of a corrosion iron oxide film from the surrounding metal parts of the artifact, (c) mechanical stress, (d) fungal infection, and (e) covering by preserving agent with dust. (Vasiliev, 2016)

cellular membranes. However, according to the SEM micrograph of (Vasiliev, 2016), this destruction occurs very slowly and affects only the near-surface layer (2–3 mm thick). The metal corrosion products from the metal environment of an artifact, particularly iron ions, are catalysts for cellular-wall decomposition reactions. Metal ions can be accumulated in the inter-cellular space to form a replica of the original wood structurein the course of time (Figure 6(b)).

The study of mechanical effects was done and proven to cause wood destruction (Vasiliev, 2016). The defect which begins in the direction parallel to fibers, at the boundaries between cells, independent of the load direction. This is clearly shown in Figure 6(c).

The most hazardous and destructive damage of wooden articlesis caused by fungi (Figure 6(d)) (Vasiliev, 2016). Fungous enzymes decompose wood and initiate decay processes in it.There are several fungus species that destroy wood with decomposing both lignin and cellulose. It was noted that the decomposition rate depends on the fungus species and the state of wood. Traces of fungus infection can be found after several days. Fungi, which grow in cracks and holes, may lead to a significant damage after several months. They cause significant damages not only in wooden artifacts, but also in marble ones; these damages were also studied by SEM (Vasiliev, 2016).

In addition, the treatment procedures used in conservation (Figure 6(e)) and cleaning or gluing may also lead to the degradation of archaeological wooden objects (Vasiliev, 2016). Thus, gaining insight into the wood degradation processes helps one develop a protocol for reconstructing and preserving wooden artifacts.

Authenticity and Fake Detection

Identification, authentication and fake detection are about making judgments about identity and age, and involve looking at an item from many perspectives.The perspectives include knowledge and study of the history of the area and objects, stylistic analysis and connoisseurship, hands on experience with the objects, physical examination of the objects and performing scientific tests. Aging can be faked or caused by other reasons, such as poor storage conditions and handling. Being able to identify and understand materials is an essential part of identification. Because specific materials were often used during a specific period and certain artefacts are known to be made with specific materials. Fakes and forgeries are regularly identified because the material is inconsistent compared with the genuine item.

Being able to identify and understand the processes used to make items is also essential to authentication and fake detection of items. Authentic items must be made with processes consistent with the genuine item. Many fakes and reproductions are identified because they were made with incorrect processes, including processes introduced after the genuine item would have been made. There are a wide variety of scientific tests and methods used to examine objects and provide information about authenticity.

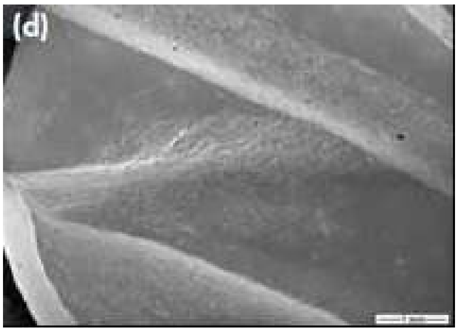
During a recent study of a jade artifact (Figure 7 (a),(b) and (c)), surface tool marks and silicone molds of the surface were inspected using stereomicroscopy and SEM. This study confirmed authenticity of the artifact. Tool marks from abrasives on carved jade, provide evidence that helps distinguish between ancient and modern techniques and can inform questions of authenticity. SEM micrograph shown in Figure 7 (d) clearly shows a surface prepared using loose abrasives. Ancient American societies carved jade extensively using loose abrasives that created irregularly and variably sized marks. Modern cottage industries also supply collectors with carved jade objects that imitate ancient production, although these techniques make use of fixed abrasives that leave marks appearing as fine, regularly spaced parallel lines.

ISSN: 978-967-2706-08-3

(a)

(b)

(c)



(d)

Figure 7: (a) Jade Crocodile Effigy Pendant (15.7 cm high) carved in Atlantic Watershed-style and attributed to ancient Costa Rica; (b) Toolmarks are difficult to discern on Crocodile's surface in this 10-mmlong photomicrograph. (c) Reflectance Transformation Imaging (RTI) micrograph (d) SEM micrograph of silicone impression from Jade Crocodile Effigy Pendant at 40x.

CONCLUSION

SEM combine with EDX microanalysis, has contributed extensively to the analysis of objects of cultural heritage and furthermore has been an indispensable tool to study the degradation processes of ancient as well as modern materials in art and archaeology. Additionally, ESEM allows the investigation of a much broader range of materials, as the electrical conductivity and the resistance towards high-vacuum conditions of samples are no longer pre-conditions. However, the results presented could demonstrate that scientific investigations should be carried out by a combination of several analytical techniques. Additionally, it should always be kept in mind that the so called non-destructive or non-invasive methods should be employed to minimize the amount of sample material that has to be taken from an object. Finally, it should be mentioned that the objectives should always be defined in an interdisciplinary discussion between the scientist and the art historian, archaeologist or conservator prior to the analytical procedure. Also the evaluation and interpretation of the results should be carried out as an interdisciplinary co-operation.

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Nuclear Technique Applications in Cultural Heritage Object Investigation, 2022: 21–31
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INTRODUCTION TO X-RAY DIFFRACTION (XRD) TECHNIQUE AND X-RAY FLUORESCENCE (XRF): APPLICATION IN ARTIFACT CHARACTERIZATION

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ABSTRACT

Non invasive analysis is needed to study cultural heritage without damaging the artifact itself. In order to do that, X-ray fluorescence (XRF) and X-ray Diffraction (XRD) are amongst the best solution. The chemical composition of ancient artifacts and pigments decorating them from different archaeological sites have been analyzed quantitatively by XRF and XRD technique and they are discussed in this article. From XRF analysis, the spectrum finger print could locate the originality or sources of the artifacts. Also, some coloring agent can be distinguished such as red pigments (hematite or ocher), manganese oxides (brown pigments), and magnetite or carbon of vegetable origin (black-pigmented layers). On the other hands, XRD could identified the compound in the artifacts. Therefore some case studies also included in this article in order to gain more insight regarding artifacts using XRF and XRD techniques.

Keywords: Artifact, X-Ray, XRD, XRF, Non-invasive

INTRODUCTION

X-Rays

X-rays are electromagnetic waves with high frequencies related to long waves or fluorescent photons with associated energy. The wavelength and energy ranges for X-rays are from 0.01 nm to 100 nm as shown in Figure 1. X-rays are produced in two ways; firstly during electrons deceleration and secondly by electrons transition within an atom. Both X-rays are produced upon the impacted when the target collided with charged particles and electrons are suddenly decelerated. The rays emitted are called bremsstrahlung radiation. Whereas, when electrons make transitions in the atom of heavy elements, generally between lower energy levels, then X-Rays are produced. X-rays emitted in this way have definite energy values which is determined by the atomic energy levels. These are called characteristic X-rays.

An ejected electron from the inner shell of the atom in the metal target,leave a vacancy which to be filled by an electron dropping down from higher energy level. The Bremsstrahlung process do not depend on the target material. It depends only on the accelerating voltage. Where as the characteristic X-ray process do depend on the target material. Every spectrum of X-Rays that stem from an element is characteristic of the element, because each element has its proper and unique set of atomic energy levels. The material to produce characteristic X-Rays spectra are essentially the from the heavy elements and within their inner shells. This is related with the energy levels about 100 to 1000 eV, rather than the light elements or the outer electrons in heavy elements that involve few eV and responsible for optical or visible spectra as Balmer's series or the others in hydrogen atom.

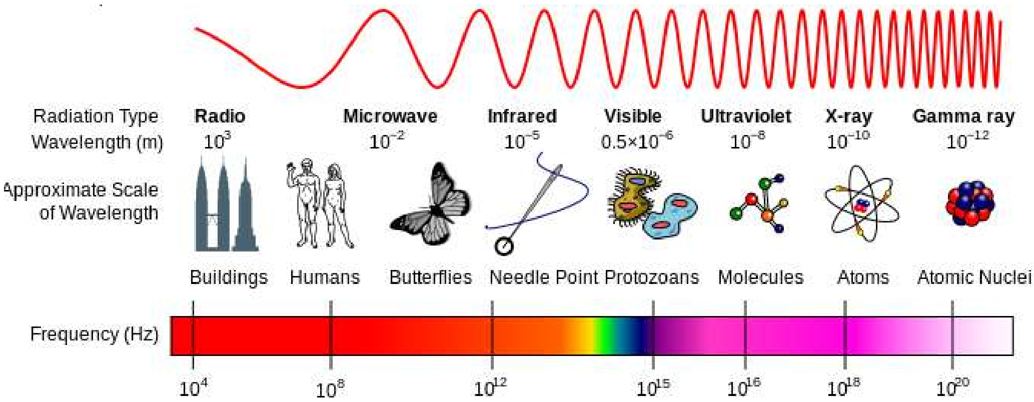


Figure 1: Electromagnetic waves.

The spectrum of X-ray contains two parts: The Bremsstrahlung part which is depending on the accelerating voltage; and the characteristic part is depending on the target element. Continuous spectrum or Bremsstrahlung is generated when the electron breaks the nucleus. Example in Figure 2 shows the intensity of the emitted X-ray versus its wavelength for the molybdenum element target.

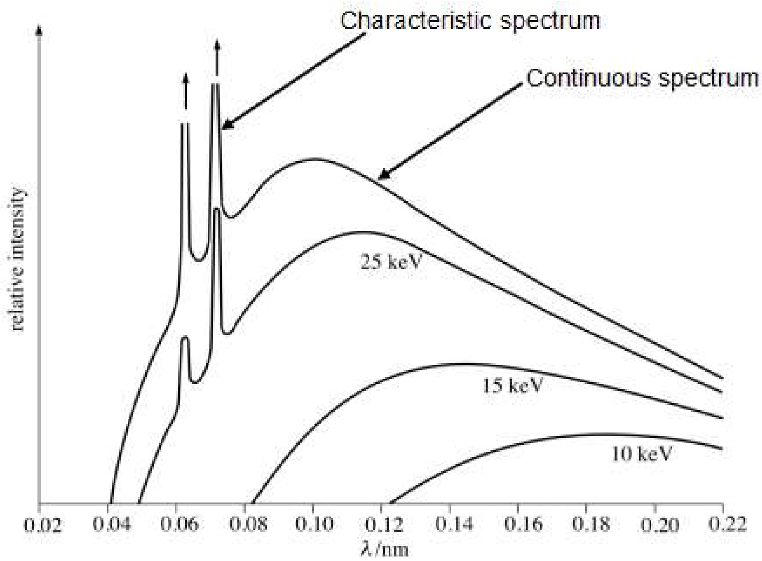


Figure 2: Line spectrum for X-rays.

While working with X-rays, some precaution such as biological protection shall be made as X-rays are ionization radiation. It can travels through the air and most of the media. It also can penetrate tissue and causes danger on the external body.

X-Ray Fluorescence (XRF)

When an element is placed in a beam of x-rays, the x-rays are absorbed. The absorbing atoms become ionized due to the x-ray beam ejects the electron in the inner shell. An electron from higher energy shell (e.g., the L shell) then fall into the position vacated by dislodged inner electron and emit x-rays or characteristic wavelength. This is called X-Ray Fluorescence process. This process is illustrated in Figure 3.

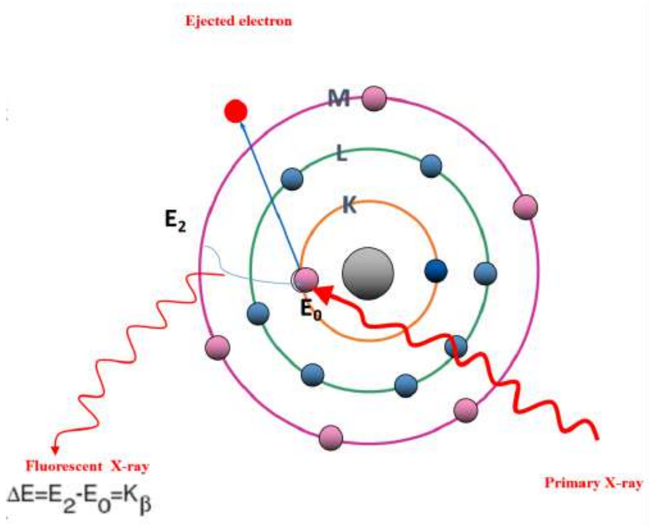


Figure 3: Line's Producing XRF

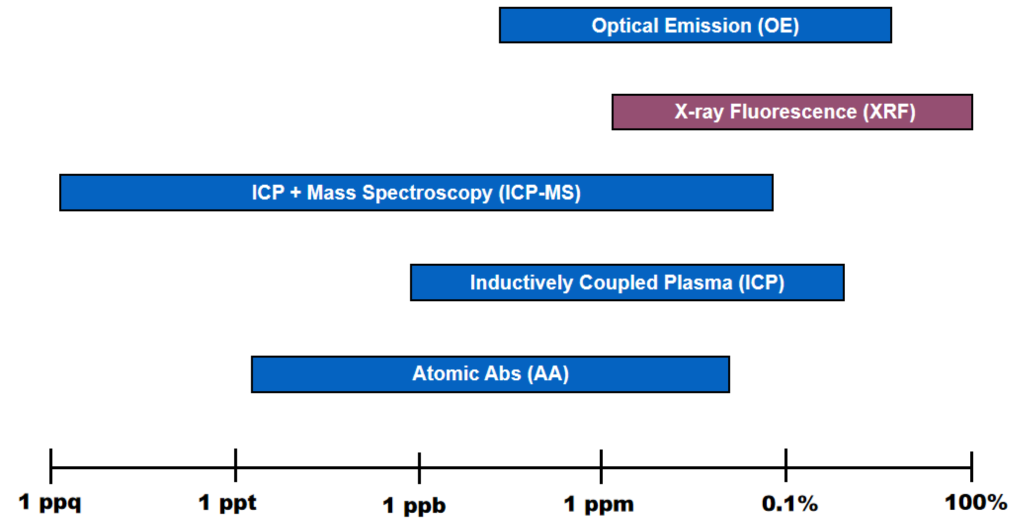


Figure 4: Concentration range for different analytical equipment.

XRF is an analytical method for determining the chemical composition of a substance. It is sometimes used to determine the concentration and thickness. XRF is the characterization of each excited element, the XRF wavelength calculation can be used to identify the elements. The intensity of the spectrum depends on the quantity of the element. Therefore, the calculation of the spectrum intensity allows quantitative element determination. Figure 4 shows the concentration ranges for different analytical equipment.

XRF analysis usually be chosen because it is non-destructive tests, it's easier to operate, can analyze different sample sizes, good resolution with improved detection limit, direct analysis of solid, powder and liquid samples, time saving as compared to conventional equipment, quick, accurate and simple sample preparation.

X-Ray Diffraction (XRD)

X-ray Powder Diffraction is used to determine the crystalline phases present in a sample object. As each phase has a unique powder diffraction pattern, it is possible to distinguish between compounds as the diffraction method is sensitive to crystal structure and not just composition (M.Loubser and S.Verryn, 2008). XRD technique is versatile, non-destructive testing to identify and do quantitative analysis, determination of various forms of crystals known as the phase for compounds either in the powder form or solid sample. Identification of a sample was achieved with comparison of XRD pattern known as' diffractogram' as illustraed in Figure 6a. The data obtained from unknown samples compared is compared with the internationally recognized database.

When monochromatic X-ray beam falls onto a crystal lattice which is arranged in a regular periodic manners of atoms, a diffracted beam will only result in certain directions. It is necessary that the waves diffracted by the individual atoms are in phase with each other in the direction of observation. Figure 5 illustrates this for a row of atoms separated by a distance, d. Usually a crystal lattice is drawn as a set of parallel lines at a distance d where all atoms are situated in these planes.

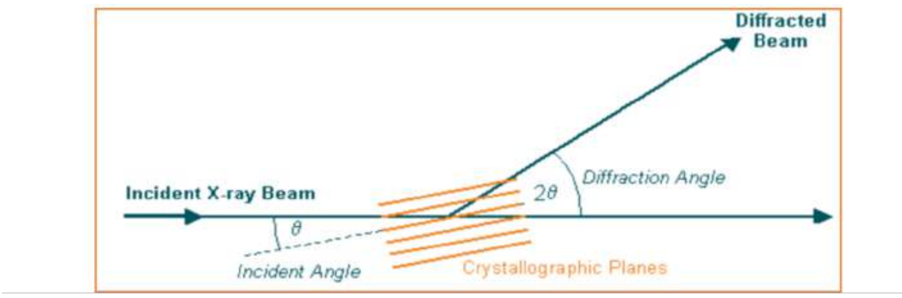
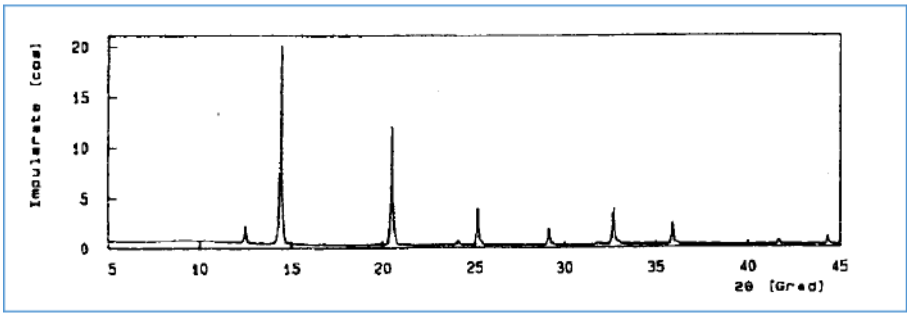
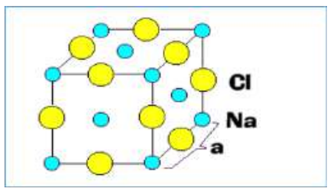


Figure 5: XRD phenomena.





(b)

(a)

Figure 6: Examples of (a) XRD pattern and (b) crystall structure of NaCl.

The distance, d, of the lattice plane depends on the size of the cell and determines the peak position on the diffraction pattern. On the other hand, the intensity of each peak is due to the crystal structure, the position of the atom in the basic cell and its own vibration. Whereas, the width and height of the peaks can determine the current state of the sample such as particle size. Figure 6 shows the examples of XRD pattern and its crystal structure.

APPLICATION OF XRF AND XRD IN ARTIFACT CHARACTERIZATION

Case Study 1 - Ancient pottery analysis

Multivariate statistical analysis of XRF data points to four composition groups, in fair agreement with archaeological classification shown in Table 1. Each group is mainly composed of pots intended for different use and group separation is related to the choice of specific production practices. In particular, based on XRD analysis (Figure 7) pots used for cooking were non-calcareous and abundant in quartz inclusions; storage and transport pots were tempered with calcite and fired at low temperatures; various types of tableware were calcite-tempered and well fired.

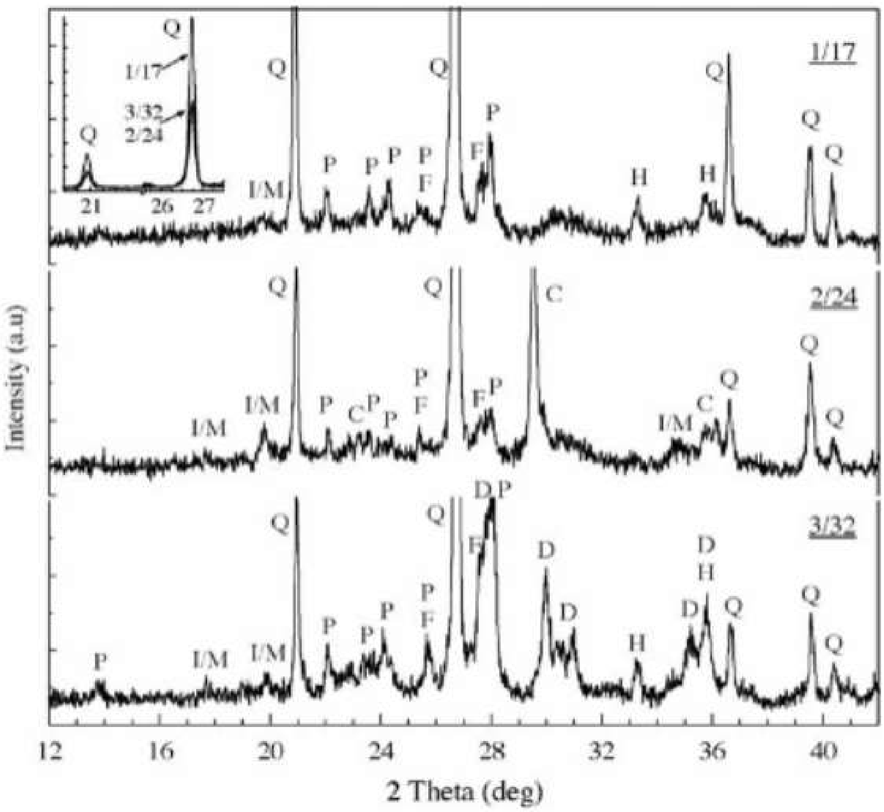


Figure 7: XRD diagrams of samples allocated to clusters ORR-A (1/17), ORR-B1(2/24) and ORR-B2 (3/32). The indicated mineral phases are illite/muscovite(I/M), quartz (Q), plagioclase (P), K-feldspar (F), calcite (C), diopside (D) and hematite (H).

Apart from significant differences in calcium levels, the main body of shards showed a quite uniform chemical profile, implying that all relevant pots were produced locally (C.Papachristodoulou et al., 2006). The analysis of the elements contained in the clay could determine where the pottery came from because the composition of clay varies geographically (E.Frahm and Tryon, 2018).

Case Study 2 - Obsidian stone analysis

Obsidian was prized by ancient people for making stone tools. Obsidian stone also easy to shape and the edges can be made extremely sharp. Obsidian is created during volcanic eruptions. Although the stone is primarily made by silica, other elements are also present. The combination and ratio of these

Table 1: Elemental composition of the four pottery groups identified by XRF.

	ORR-A		ORR-B1		ORR-B2		ORR-C		ρ
	M	ρ	M	ρ	M	ρ	M	ρ	
K	0.94	28.10	1.39	20.80	1.22	21.00	1.22	23.80	26.80
Ca	1.01	30.10	7.38	27.60	4.94	32.90	3.99	39.40	61.30
Ti	0.72	17.90	0.59	20.50	0.70	17.40	0.76	19.00	20.50
Cr	535.00	32.80	366.00	21.30	377.00	25.10	377.00	37.80	32.10
Mn	0.24	43.50	0.15	26.00	0.17	25.30	0.17	38.60	39.90
Fe	7.64	17.00	6.85	17.80	7.85	15.10	7.16	15.80	16.80
Ni	253.00	28.80	216.00	20.90	245.00	19.90	107.00	65.10	29.80
Cu	51.10	48.50	41.20	33.60	46.90	37.50	33.20	29.60	39.70
Zn	178.00	35.30	134.00	30.10	150.00	38.20	153.00	20.20	35.00
Pb	45.30	30.40	34.40	36.70	27.20	29.10	52.20	23.10	40.20
Rb	97.60	30.00	98.70	26.20	69.50	34.20	127.00	11.50	34.10
Sr	162.00	19.50	298.00	20.60	215.00	27.40	218.00	30.10	39.90
Y	46.60	26.20	25.30	25.10	26.80	17.60	32.20	19.30	36.40
Zr	340.00	22.90	210.00	13.70	185.00	11.20	356.00	13.80	33.90
Nb	30.30	24.40	16.90	29.40	21.90	37.40	32.70	23.50	38.30

The average concentrations M are given in $^{-1}$ (ppm), unless otherwise indicated, and the spreads ρ (standard deviation) in % of M. The spread ρ_{mean}(%) in elemental concentrations throughout the whole data set is given in the last column.

elements act almost like a fingerprint, and archaeologists can use this information to figure out where the obsidian used to make a tool came from. Obsidian tools are found all over the world, and knowing where the stone originated from provides important insight into ancient trade networks and economies (Figure 8) (E.Frahm et al., 2014). Figure 9 shown the 'spectral fingerprint' for different obsidian stone sources.

Figure 8: Examples of obsidian stones from Armenia

Case study 3 - Artifact analysis for ancient Egypt

In this work, XRF technique was used to analyze some artifacts from the Egyptian Collection of the National Museum (Rio de Janeiro, Brazil), which is probably the oldest in the Americas (C.Calza et al.,

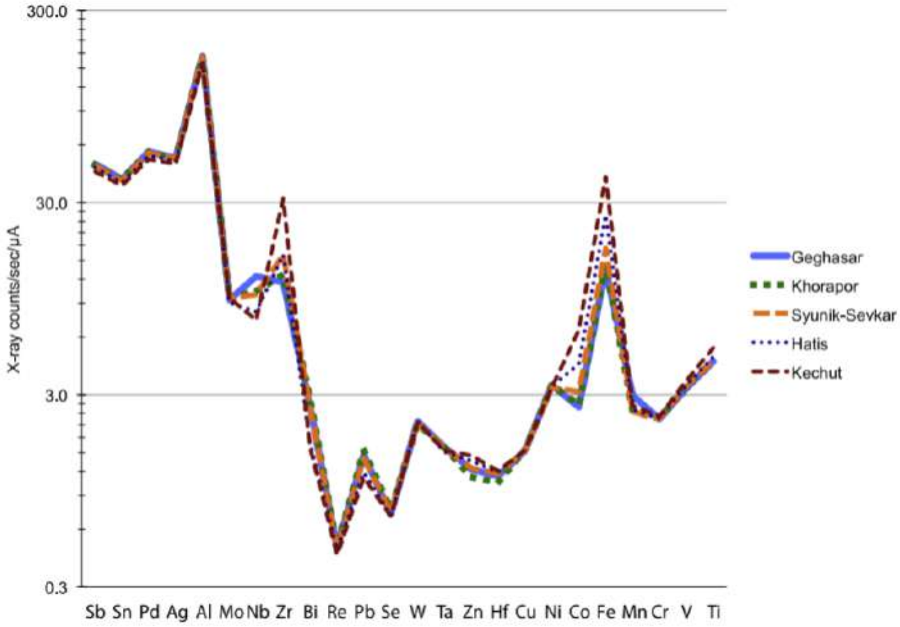


Figure 9: Comparison of "spectral fingerprints" for different obsidian sources. Only five are shown here for clarity. The vertical axis is the X-ray intensity for each element, measured in X-ray counts per second per microAmp of X-ray tube current and plotted on a logarithmic scale.

2011). In the red line at the pectoral adornment of the lady, the presence of sulfur(S) and arsenic(As) indicates the use of realgar (αAs_4S_4). There are some regions of orange color in this red line that presented the same elements in the XRF analysis. This result revealed an example of the photochemical degradation of this pigment, which changes into the orange pararealgar (γAs_4S_4). Figure 10 shows a characteristic XRF spectrum of the orange region.

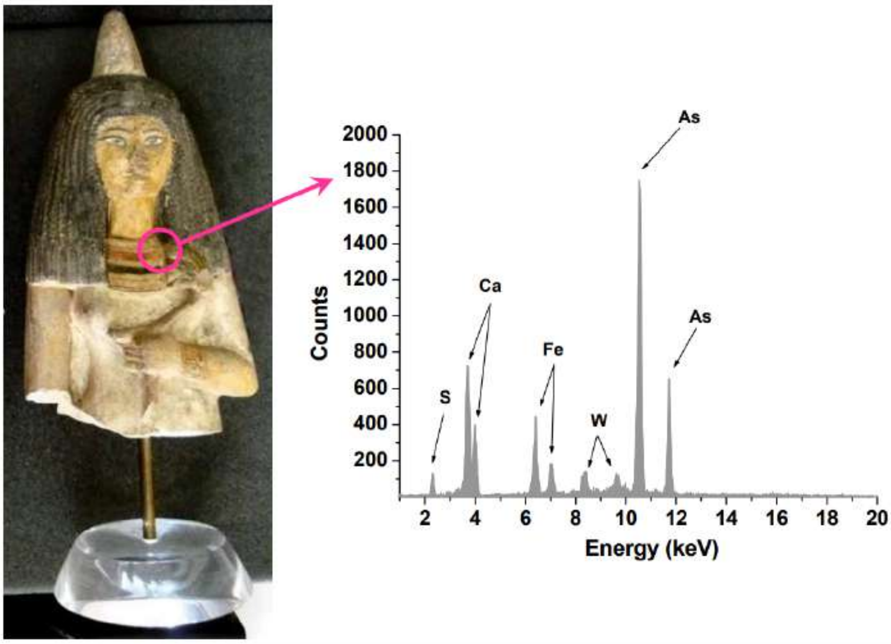


Figure 10: Characteristic XRF spectrum of the orange color.

The identification of pigments and techniques used by the Egyptian craftsmen during antiquity will provide an important aid to the researchers about this period and, also, to the evaluation of conservation and restoration procedures. This data were shown in Table 2.

Table 2: Pigments identified by XRF, key elements, characteristic color, chemical composition and period of use.

ELEMENTS	PIGMENTS	CHEMICAL COMPOSITION	PERIOD OF USE
Ca,Cu	Egyptian blue	$CaO.CuO.4SiO_2$	3000 BC - VII century
Cu	Malachite	$CuCO_3.Cu(OH)_2$	Antiquity - XVI century
S,As	Realgar	αAS_4S_4	1500 BC -XIX century
S,As	Pararealgar	γAS_4S_4	1500 BC -XIX century
Fe	Yellow ochre	$Fe_2O_3.H_2O$	Prehistory - still in use
Ca	Calcite	$CaCo_3$	Antiquity - still in use
Fe	Black Iron oxide	Fe_3O_4	Prehistory - still in use height

Case study 4 - artifacts analyzed at Malaysian Nuclear Agency.

Arabic Coin

Figure 11 shows ancient Arabic coins send by local client. Table 3 shows the result for elemental analysis of the coin using XRF technique.

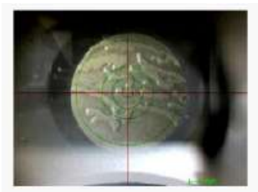


Figure 11: Ancient Arabic coin.

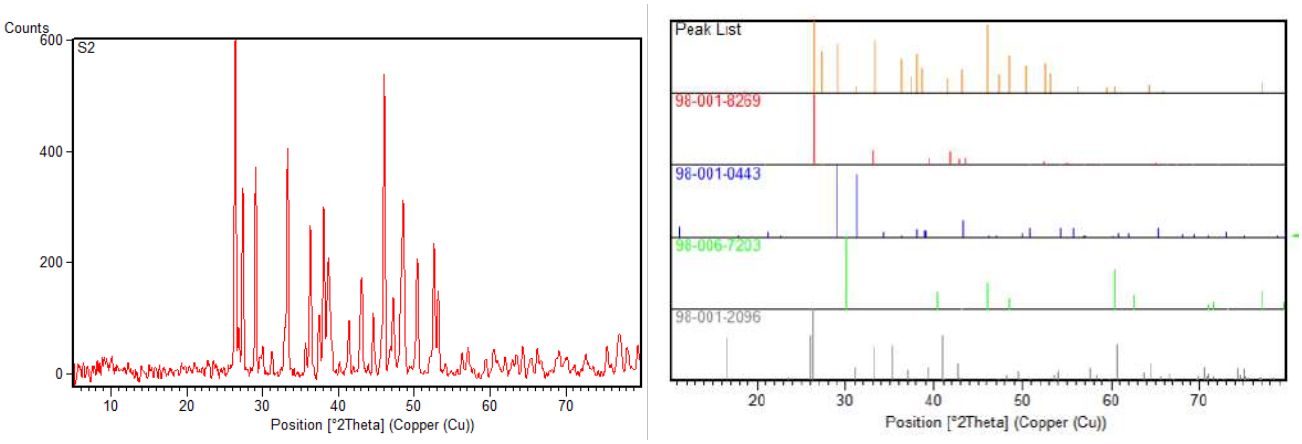
Table 3: Elemental analysis of ancient Arabic coins.

Element	Result(%)	3ρ
Cu	58.103	0.079
Zn	36.410	0.056
Pb	1.838	0.025
Sn	1.134	0.030
Si	0.984	0.203
Fe	0.556	0.005
Ni	0.370	0.004
I	0.258	0.043
Tb	0.165	0.028
Ca	0.158	0.016
Mn	0.024	0.004

ISSN: 978-967-2706-08-3

Pottery

Table 4 shows the list of elements of pottery sample based on XRF technique with major component is silica and calcium. In order to distinguish the compound in the pottery, further analysis by XRD technique has been done and the diffraction pattern is shown in Figure 12a. The XRD pattern is compared with The International Centre for Diffraction Data (ICDD) as shown in Figure 12b. From the XRD analysis, ratio of compound in the pottery was identified and shown in Figure 13.



(a) (b)

Figure 12: (a) XRD pattern for pottery sample and (b) ICDD data as references.

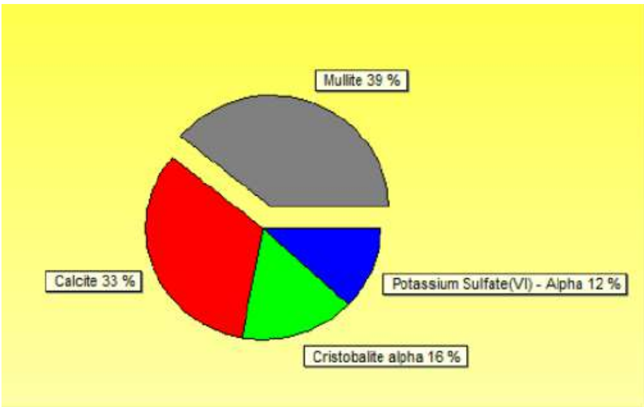


Figure 13: Different compound in the pottery sample.

Table 4: Elemental analysis of pottery sample from Jabatan Muzium Malaysia

Analyte	Calibration status	Compound formula	Measured (kcps)	Used (kcps)	Concentration (unit)	Calculation method
Na	Calibrated	Na_2O	0.176	0.212	0.195%	Calculate
Mg	Calibrated	MgO	1.418	1.710	0.426%	Calculate
Al	Calibrated	Al_2O_3	15.792	21.837	7.706%	Calculate
Si	Calibrated	SiO_2	89.870	124.979	42.035%	Calculate
P	Calibrated	P_2O_5	10.872	15.408	3.288%	Calculate
S	Calibrated	SO_3	3.021	3.962	1.045%	Calculate
Cl	Calibrated	Cl	1.438	1.331	0.302%	Calculate
K	Calibrated	K_2O	13.381	15.645	4.151%	Calculate
Ca	Calibrated	CaO	88.696	104.599	34.206%	Calculate
Ti	Calibrated	TiO_2	1.057	0.982	0.532%	Calculate
Cr	Calibrated	Cr_2O_3	0.190	0.079	502.5ppm	Calculate
Mn	Calibrated	MnO	0.401	0.261	0.115%	Calculate
Fe	Calibrated	Fe_2O_3	10.774	11.080	5.345%	Calculate
Ni	Calibrated	NiO	0.584	0.321	991.6ppm	Calculate
Cu	Calibrated	CuO	0.450	0.139	375.3ppm	Calculate
Zn	Calibrated	ZnO	1.047	0.915	0.117%	Calculate
Rb	Calibrated	Rb_2O	5.241	2.862	577.8ppm	Calculate
Sr	Calibrated	SrO	6.677	5.532	0.167%	Calculate
Y	Calibrated	Y_2O_3	2.709	0.889	246.7ppm	Calculate
Zr	Calibrated	ZrO_2	4.871	2.808	718.1ppm	Calculate
Pb	Calibrated	PbO	0.887	0.318	294.0ppm	Calculate

CONCLUSION

An overview of the method use in archeology and art is presented and application of XRF and XRD as a tool for non-destructive analysis of artifacts are discussed. The results revealed that the elemental composition of the material employed to make the artifacts and the original pigments used in the decoration of some artifacts suggested the origin of blue, malachite, realgar, red and yellow ochre and black iron oxide pigments. It is important for increasing the analysis efficiency and intensify overall understanding in order to preserve and decreasing the risk from damage of artifacts.

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Nuclear Technique Applications in Cultural Heritage Object Investigation, 2022: 32–39
e ISBN: 978-967-2706-08-3

APPLICATION OF NUCLEAR TECHNIQUES IN ARTIFACT'S DATING

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ABSTRACT

There are various methods could be used in dating of artifacts. Thermoluminescence dating and radiocarbon dating are two absolute techniques that provides quantitative information about the historical data of artifacts. Thermoluminesce dating is an electron trap method of dating suitable for ceramic base materials that contain compounds such as oxide, fluoride, sulphate, nitric and borate. This method of dating comprises of two common techniques, additive dose method and pre-dose method. Radiocarbon dating on the other hand is a form of radiometric dating that utilizes the naturally occurring radioisotope carbon-14 to estimate the age of organic materials. There are few common techniques used in radiocarbon dating such as benzene synthesis, Carbosorp and acceletor mass spectrometry (AMS). The technique under development in Malaysian Nuclear Agency is the most conventional method, benzene synthesis. There are few constraints and challenges that need to be overcome for both dating methods. For thermoluminescence dating, the lack of exposure database at different soil levels of archaelogical site and high doserate beta irradiator need to be overcome. As for radiocarbon dating, the inefficient facilities available needs to be upgraded.

Keywords: dating, radiocarbon, thermoluminescence,artifact, cultural heritage

INTRODUCTION

Dating of artifacts comprises of relative and absolute dating (K.Greene, 2002). Relative dating is a series of techniques that are used to compares artifacts to determine which is older. This method assigns a speculative date to an artifact based on many factors such as location, type, similarity, geology and association. Basically, relative dating give us no idea of the historical data of an artifact or site. Some example of relative dating techniques include the cation ratio, dendrocronology (Figure 1), cultural affiliation, fluorine dating, obsidian hydration, patination, pollen analysis, rate of accumulation, seriation and varve analysis.

The second technique that provides quantitative information about the historical data of artifact is the absolute dating. Among the known absolute dating techniques are archaeomagnetism, astronomical dating, dendrocronology, electron spin resonance, fission track, optically stimulated luminescence (OSL), oxidizable carbon ratio (OCR), potassium-argon dating, racemization, uranium-thorium dating, radiocarbon dating and thermoluminescence dating. Each dating techniques has it own characteristics that refers to the dating period ranging from a few hundred years to millions or billions years BP and chemical composition of the artifact. Currently, Malaysian Nuclear Agency is in the process of developing two most common dating techniques which are thermoluminescence dating and radiocarbon dating.

Thermoluminescence (TL) is an electron trap method of dating as opposed to radiometric technique

Figure 1: Dendochronology of tree ring method (Salisbury, 2008)

such as carbon dating. TL signal increases with time. It is suitable for ceramic base materials that contain compounds such as oxide, fluoride, sulphate, nitric and borate. The materials including rocks, minerals and potteries are among of them. This method dates items between the years 300 - 100,000 BP with better measurement accuracy as the sample gets older. The principle of TL-dating is based on the material that has been heated in the past which gives up all of its stored thermoluminescence, for example in the case of pottery the firing of the clay would form this function.

Thermoluminescence materials are based on the emission of TL on heating of previously exposed crystalline materials. The intensity of the emitted TL is a function of the dose deposited in the material, and can therefore be used for dating analysis. The basic process of the thermoluminescence is shown in Figure 2. In real situation, the production of TL in crystalline materials is a complex, multistage process involving the transfer of charge and energy between different defect states within the crystal (McKinlay, 1981). The final measured TL intensity is the net result of the reaction between photons or nuclear particles of the irradiation field, the type, number and distribution of the defects present within the crystal at the time of irradiation and heating, the nature of the irradiated crystal and on other factors such as the irradiation rate, temperature, and energy of the absorbed particles.

Radiocarbon dating on the other hand, is a form of radiometric dating that utilizes the naturally occurring radioisotope carbon-14 to estimate the age of organic materials. The method was developed by Willard Libby and his team at the University of Chicago in 1949. Dr. Libby was awarded the Nobel Prize in chemistry for his work on this technique. The development of 14C dating has become a crucial tool for archaeologists in that it can give accurate ages of organic (carbon-containing) materials that are up to 60,000 years old.

Radiocarbon dating is possible due to the production and radioactive decay of carbon-14, a process that takes place both in the atmosphere and on Earth's surface and occurred at equilibrium. Radioactive carbon dioxide ($^{14}CO_2$) like normal CO_2 is evenly distributed in the atmosphere and dissolved in the

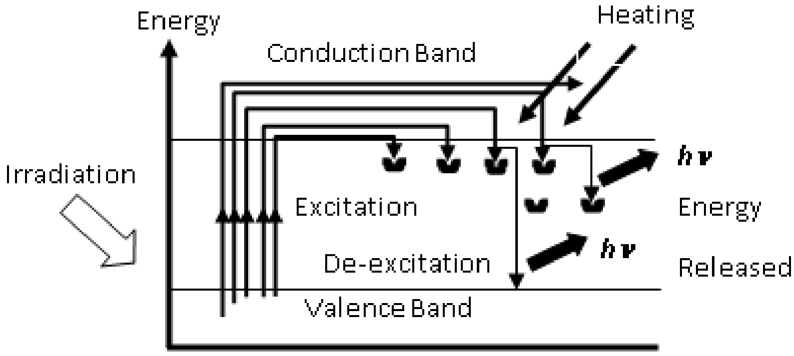

Figure 2: The thermoluminescence process.

oceans, becoming part of the global carbon cycle. Thus all living terrestrial creatures continuously replenish their ^{14}C content and keep the $^{14}C/^{12}C$ ratio constant.

However, at death of plants or animals, the ^{14}C intake stop, decreasing the $^{14}C/^{12}C$ ratio according to the radioactive decay half-life of ^{14}C. In order to estimate the age of the samples or the time elapse from its deposition, there are two matters that have to be considered:

(i) The present day $^{14}C/^{12}C$ ratio of the samples and,

(ii) Estimation on the original equilibrium $^{14}C/^{12}C$ ratio of the carbon reservoir that supplied the sample (K.G.Sushil and Henry, 1985).

Radiocarbon dating is essentially a method designed to measure residual radioactivity. By knowing how much carbon-14 is left in a sample, the age of the organism when it died can be known. It must be noted though that radiocarbon dating results indicate when the organism was alive but not when a material from that organism was used.

Aside from dating of archaeological artifacts, numerous studies have applied radiocarbon dating to establish chronologies of the timescale in hydrological systems. Carbon-14 of cosmogenic origin is incorporated in groundwater during recharge by interaction of infiltrating water with soil CO_2 from plant root respiration and microbial degradation of soil organic matter. Following recharge, dissolved inorganic carbon (DIC) becomes isolated from the modern ^{14}C plant–soil gas–air reservoir and decays with time. Many physical and chemical processes can affect the ^{14}C content of DIC in groundwater, other than of radioactive decay. This information can be used to estimate modern and palaeorecharge rates to aquifers, to recognize non-renewable palaeowaters, to extract palaeoclimatic information from the groundwater archive, to calibrate groundwater flow models, and to investigate the availability and sustainability of groundwater resources in areas of rapid population growth (P.K.Aggarwal, 2013).

METHODOLOGY

Thermoluminescence Dating

Thermoluminescence measurement comprises of two common techniques. However the more commonly used is an additive dose method, whereby radiation doses are added to the pre-existing natural thermoluminescence dose to obtain the glow curve of the TL signal versus radiation dose. An example of the measurement point of the glow curve is given as following:

Natural TL dose (kept without irradiation); NTL
Natural TL dose + beta dose : NTL + βGy
Natural TL dose + 2*beta dose: NTL + 2βGy
Natural TL dose + 3*beta dose: NTL + 3βGy

In another study, (J.Kusiak et al., 2002) et al. used Cobalt-60 gamma source for sample irradiation. Plot of the natural and induced glow curve is given in Figure 3(a). Figure 3(b) shows the beta emission growth curve of the sample.

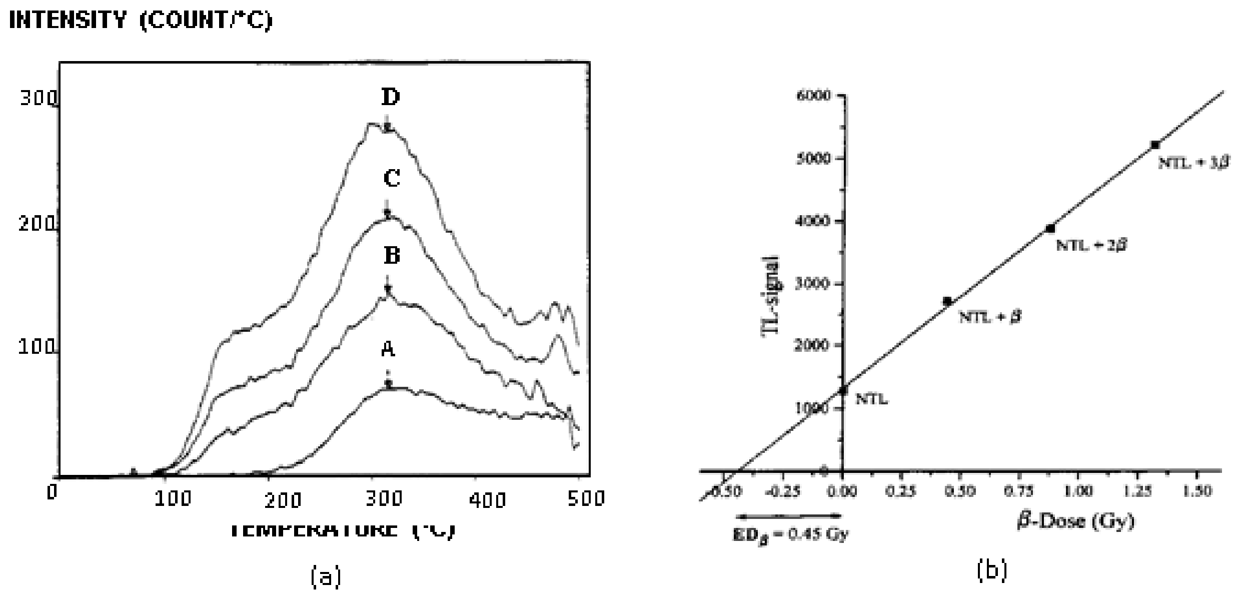

Figure 3: (a) Natural and induced glow curve and (b) is beta addition growth curve of ceramic sample (Corte, 1993)(Corte, Biennial Report).

Another technique is called pre-dose method which enhance of TL-sensitivity of sample low temperature (<160 °C), for example 125 °C TL peak of quartz to measure radiation dose. This method is more complicated and time consuming, but found considerable application in cases where the additive method is not feasible because of spurious signal or low signal in the high temperature range (300-500 °C), and also for recent object that contain quartz. This method seem to be suitable for certain difficult cases that exhibit poor TL characteristic

Radiocarbon Dating

Conversion of C to C_6H_6 is summarized in Figure 4.

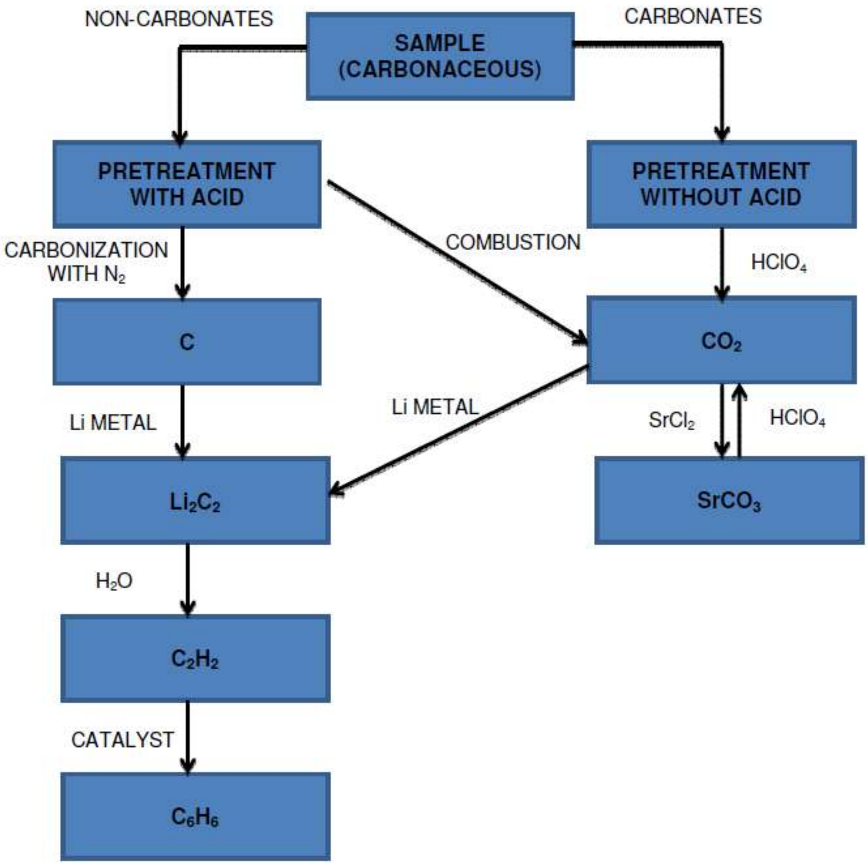

Figure 4: Benzene synthesis from carbonaceous sample.

(a) Physical pre-treatment
Any intrusive contaminants such as rootlets, clay, soil, sand and other obvious contaminants will be removed from the sample. The sample will be ground to desired particle size to increase the overall surface area in order to facilitate the production of CO_2 by combustion.

(b) Carbon dioxide preparation
The CO_2 is prepared either by carbonization or combustion method. The carbonization/combustion of organic matter in a stream of oxygen and the subsequent wet chemistry purification and recovery of CO_2 are carried out in a glass vacuum system. The chemical reactions involved are given as

$$O_2 + C \rightarrow CO_2$$

(c) Carbonization
Carbonization method is recommended for samples such as wood, cloth, clean plant and any material that contains >50 °C. Sample is placed in a quartz tube of diameter >4 inch and length

>10 inch with openings as inlet and outlet for N_2 gas flow. The quartz tube containing the sample is then placed inside furnace.

N_2 gas is allowed to flow continuously for at least 10 – 15 mins. Temperature of furnace is set to 300 °C. The temperature is then increased to 400 °C and finally 500°C. The sample is continuously heated for approximately 1 – 2 hours until the smoke completely dissipates. The brittle charcoal ash (containing C) obtained is left to cool in the furnace in the presence of N_2 gas until the temperature goes down to 80°C. The ash is weighed to determine the amount of pure C obtained.

The ash obtained is then mixed with Li metal in 1:3 ratios by weight in the carbide reactor. The mixture is then heated at 700 - 800°C for 30 minutes to produce Li_2C_2. The Li_2C_2 will be further subjected to hydrolysis reaction to produce C_2H_2.

(d) Combustion
About 8 – 14 g of moisture free powdered sample is weighed and placed onto a quartz glass boat. The glass boat is then inserted into the combustion tube. The combustion tube is closed and ensured that it is airtight. Heating of the combustion tube and application of vacuum to the line is done simultaneously.

(e) Carbide Reaction
Carbide reaction is given as follow:

$$2CO_2 + 10Li \rightarrow Li_2C_2 + 4Li_2O$$

Carbide reactor containing Li metal is heated to 600°C in vacuum. The temperature of furnace is set to 600°C. Vacuum is applied to the line by opening necessary valves. The required weight of Li metal is calculated with reference to amount of CO_2 produced in the previous step. At this temperature, Li melts and forms mirror like surface. CO_2 collected previously is then reacted with the Li metal. The appearance of green flame indicates fast reaction.

The CO_2 gas should be completely absorbed in less than 30 minutes. The temperature is then set to 700 – 800°C. The temperature is maintained for 30 minutes. After that, the furnace is then switched off and the reactor is left in the furnace for 1 hour before applying cold water to it.

(f) Acetylene Synthesis
The formation of C_2H_2 gas is accomplished by hydrolyzing Li_2C_2. The hydrolysis reaction is as follow:

$$Li_2C_2 + 2H_2O \rightarrow C_2H_2 + 2LiOH$$
$$2Li + 2H_2O \rightarrow 2LiOH + H_2$$

It is important to ensure that the carbide reactor remains cold throughout the reaction by placing it in ice water bath. Approximately 1 L of distilled water from a glass reservoir is allowed to drip steadily and slowly into the carbide reactor. Excess of water will produce H_2 gas which will be released out from the line.

(g) Benzene Synthesis
C_2H_2 is converted to C_6H_6 on a chromium coated silica-alumina catalyst.The trimerisation reaction can be written as:

$$3C_2H_2 \xrightarrow{\text{catalyst}} C_6H_6$$

The catalyst reaction chamber is earlier filled with catalyst beads. The catalyst is activated by heating it to 150°C (if it is moisture free) or 300°C (if it contains moisture). The heating is carried out under vacuum condition. Once the catalyst is activated, warm water is applied to gas trap to convert the frozen C_2H_2 to gas form. The C_2H_2 gas is passed through moisture trap. It is then transferred to the catalyst reaction chamber for approximately 40 minutes. The light yellow color catalyst changes to greygreen during the C_2H_2 conversion. At the time of transfer, the temperature of the catalyst should be maintained between 80°C to 90°C. C_6H_6 synthesized from the trimerisation reaction is then passed through moisture trap to eliminate any moisture that may be present. The C_6H_6 is finally recovered in a liquid N_2 cooled trap and is analyzed using liquid scintillation counter.

CONSTRAINTS AND CHALLENGES

The accuracy of TL dating of archeological ceramic based material are very much dependent on the measurement accuracy of the external and internal radiation doserate, measured from the sample and surrounding the samples. Monitoring of the external doserate from a known depth is necessary for dating analysis. The data can provide an idea about exposure and can be correlated to the age of the sample. Therefore exposure database at different soil levels of archeological site is necessary for future use and for quick estimation about the age of the sample without going to the site. Further collaboration with Jabatan Muzium Malaysia on the natural exposure dose mapping at different soil level of the archeological sites is needed to ensure this project can be executed.

The lack of high doserate beta irradiator facility at Nuclear Malaysia is another concern. As an alternative, the study on the conversion factor of TL sensitivity from gamma to beta irradiation of archeological sample is needed be further investigated.

Radiocarbon dating rises interests in many parties in Malaysia and can be However, the facilities available in Nuclear Malaysia is ineffecient with recurring gas leakage on the benzene synthesis line. A new line or a new technique is necessary to ensure that this laboratory can be the first radiometric laboratory in Malaysia. Aside from that, Malaysia also needed more expert in this field.

CONCLUSION

Nuclear techniques is important as one of the techniques in determination of an artifact's age since it is an absolute method which provide quantitative information on the historical data. This will also prevent any fraud activity in the antiquities trade. However, Nuclear Malaysia needs to improve more on the facilities so that this techniques can be widely offer to any interested parties.

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Nuclear Technique Applications in Cultural Heritage Object Investigation, 2022: 40–47
e ISBN: 978-967-2706-08-3

APPLICATIONS OF NEUTRONS FROM TRIGA PUSPATI REACTOR FOR INVESTIGATION OF CULTURAL HERITAGE OBJECTS

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ABSTRACT

Two crucial aspects when reveal the fact of cultural heritage object are, an information of internal configuration and type of materials with their compositions that formed the object. These informations determines the value of cultural heritage object. The internal structure tells the creation of object can be revealed by imaging technique by neutron radiography and tomography. The type of materials and their compositions are determined using neutron activation technique. These techniques are utilised the thermal neutron from nuclear reactor at TRIGA PUSPATI Reactor in Nuclear Malaysian Agency.Some analysis have been conducted on several cultural heritage object using neutron imaging and neutron activation techniques. The methodology, results and some comments about the technique are discussed. These works are presented in this article.

Keywords: Neutron, Imaging, Activation, TRIGA PUSPATI Reactor, Cultural Heritage

INTRODUCTION

The facts and figures of cultural heritage objects are crucial and valuable information but quite difficult to obtain. There is required historian expertise with some scientific tools that can assist to obtain characteristics and properties of the object. Cultural heritage object such as the ancient statue, ancient kitchen ceramics, textiles, weapons and etc are among the most attractive items to the collectors or muzium for exhibition. The characteristics and properties of the object furthermore will tells about the people, materials, technology and tools that had been using to make the ancient object. Authenticity and age of the cultural heritage object also can be determine by scientific tools. One of the unique characterization technique to analyse the cultural heritage object is by using thermal neutrons produced in nuclear reactor. These techniques are called neutron imaging and neutron activation. These techniques are among nuclear method that being used in the investigation of cultural heritage object as reported (IAEA, 2011). Furthermore, nuclear technology also utilized X-ray and gamma radiation or beta and alpha particle for the analysis of cultural objects non-destructively. Dating of ancient object also can be done by utilizing the half-life of C-14 radionuclide or thermaluminesen technique.

Nuclear techniques as reported in (IAEA, 2011) such as neutron activation analysis (NAA), X ray fluorescence (XRF) analysis or ion beam analysis (IBA), have a potential for non-destructive and reliable investigation of precious materials, such as ceramics, stone, metal or pigments from paintings. Such information can help to repair damaged objects adequately, distinguish fraudulent artefacts from real artefacts and assist archaeologists in the appropriate categorization of historical artefacts. Although the application of scientific methods to art and archaeological materials has a long tradition, it is due to the stimulation of institutions such as the United Nations Educational, Scientific and Cultural Organization (UNESCO), the United Nations Environment Programme (UNEP) and the IAEA that applications of natural science techniques are increasingly being accepted by museum curators and cultural heritage researchers.

Utilization of neutron imaging for the analysis of cultural heritage object in Malaysia has been conducted for Vishnu Deity statue as describes elsewhere (Muhammad et al., 2008). This worked was obtained from the collaboration of Muzium and Antiquity department of Malaysia. The modernization of neutron imaging facility and neutron activation analysis allows new collaboration with more work will be conducted (Zin et al., 2015). Therefore, this article describes the technique and some results from neutron imaging and neutron activation analysis utilising neutron from TRIGA PUSPATI Reactor to apply in cultural heritage research of ancient object.

METHODOLOGY

Nuclear technique discusses in the article are; firstly neutron imaging such as neutron radiography and neutron tomography and secondly neutron activation analysis. These techniques utilises thermal neutron produced from nuclear reactor core of TRIGA PUSPATI Reactor. Layout of this reactor shown in Figure 1 describes the reactor core consist of nuclear fuel element as well as neutron radiography and imaging (NURI) facility at horizontal channel and the vertical tube for neutron activation facility.

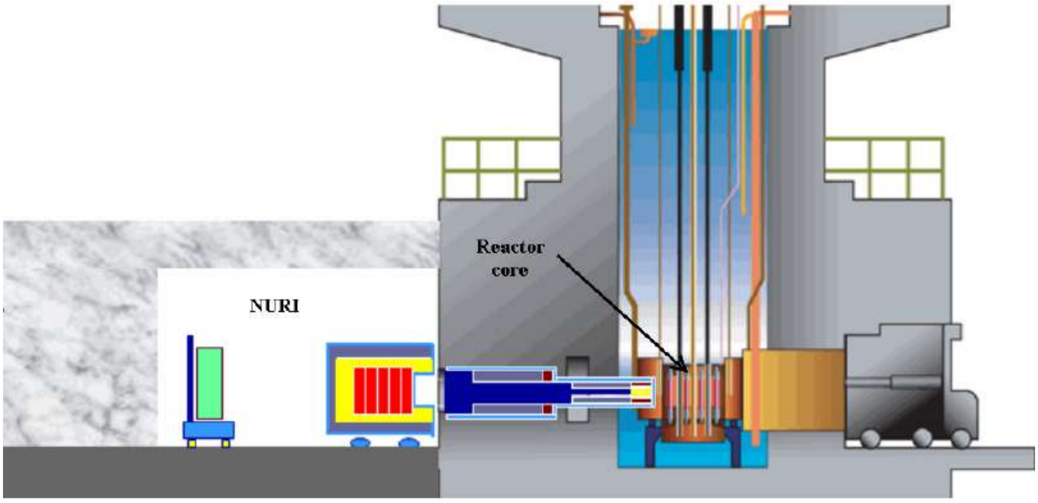

Figure 1: Vertical cross-section of TRIGA PUSPATI Reactor showing the Reactor Core where the thermal neutron is produced for application of neutron activation analysis and Neutron Radiography and Imaging (NURI) facility.

Neutron Imaging

Neutron Imaging technique is divided into radiography and tomography. Neutron radiography is used to reveal the distribution of neutron attenuation coefficient of object plane in the form of image contrast. Neutron tomography is the technique to reveal the distribution of neutron attenuation coefficient in the form of image contrast for slices from three dimensional image.Tomography images can be obtained from radiography images. One radiography image is equivalent with one projection in tomography technique, at least more than 180 projections are required to reconstruct one slice of tomography image. The principle of radiography technique is given in Figure 2.Source of neutron from the reactor core where white neutron spectrum is produced from fission process. Neutron from fission is comprised of a wide range of energy, from several eV up to 20 MeV. Thermal neutron with energy around 0.025 eV is utilised for neutron radiography facility. Detection system consists the materials which has high sensitivity with thermal neutron compared with other neutrons and gamma radiation.

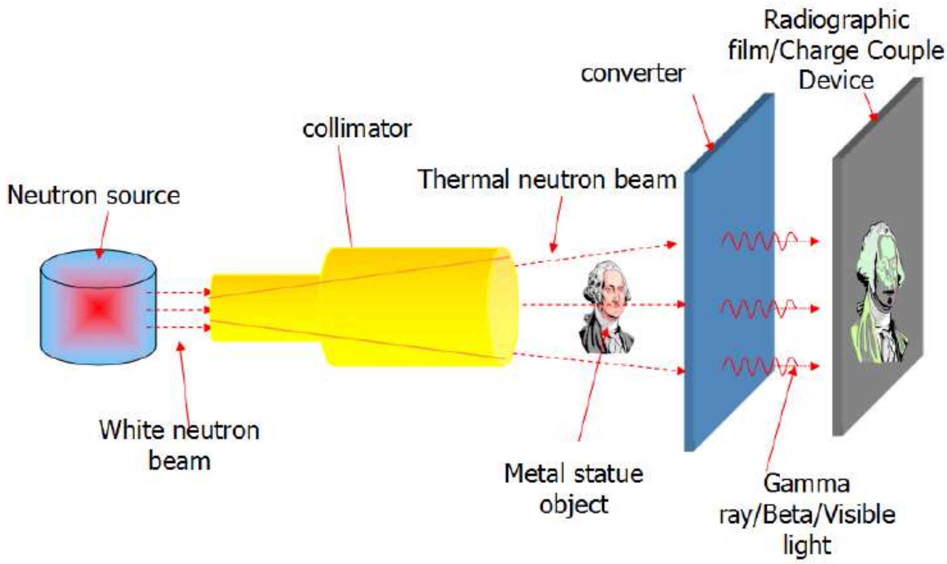

Figure 2: Layout of basic setup for neutron radiography principle where neutron source is PUSPATI TRIGA Reactor.

The collimator is installed in the beamport so that neutron from the reactor core can be extracted and filtered before penetrating the object. Gamma radiation from the reactor core is suppressed by bismuth rod placed in the collimator. Neutron beam from the collimator has large thermal neutron to gamma ratio. Collimated and filtered neutron beam from the collimator will shine the object and than transmitted neutron after passing the object will interact with a converter. The converter is made by high neutron cross section so that more interaction can be obtained.

Nuclear interaction happened between neutrons with nucleus in the atoms of converter material will result in emitting some secondary radiation of light, depending on the materials. Converter material utilised for NURI detection system is Li6F/ZnS:Ag with 0.4 mm thick and peak emission at 455 nm of blue light. The nuclear interaction between neutron with nucleus atom ^{6}Li produces energy 4.71 MeV with tritium and helium as describe in Equation 1. The intensity of blue light will be recorded by the camera which reflects the absorption of neutron by object. Converter materials determine the wavelength of light emitted during the interaction with neutrons.

$$^{6}Li + n \rightarrow {}^{3}H + {}^{4}He + 4.71MeV \tag{1}$$

Recorded of emitted light will gives radiograph of object under test. Object for radiography testing can be rotated into an interested angle. Radiograph recorded at each angle is called projection in tomography technique. Therefore, tomography image can be reconstructed from radiographs recorded in radiography technique. Tomography technique required at least 181 projection for image reconstruction. Tomograph gives picture of slice image of object.

Neutron Activation Analysis

Neutron radiography utilises collimated neutron beam emitted from the reactor core. But, neutron activation analysis utilises neutron in the reactor core. The sample is placed inside or close to the fuel element in the reactor core. The sample is irradiated with neutrons until it is activated. Gamma radiation is emitted from radionuclides in the activated object. The method is based on conversion of stable atomic nuclei into radioactive nuclei by irradiation with neutrons and subsequent detection of the radiation emitted by the radioactive nuclei and its identification. The interaction between neutron with atomic nuclie can be illustrated in Figure 3.

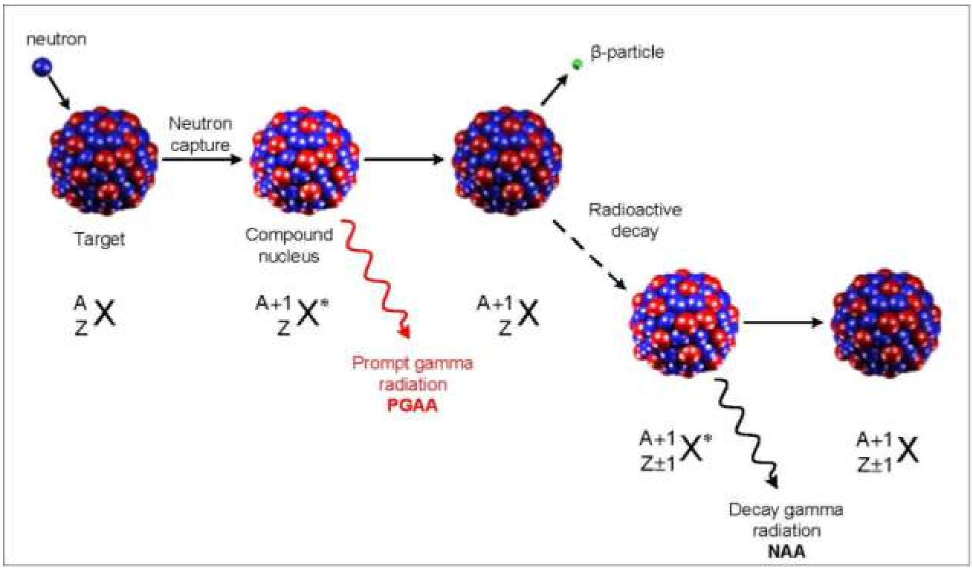

Figure 3: Illustration showing the interaction between neutron with atomic nuclei as a basic principle in neutron activation technique.(Hamidatou et al., 2013).

The (n, γ) reaction is the fundamental reaction for neutron activation analysis. For example, consider the irradiation of iron sample where the reaction is characterised in following Equation 2.

$$^{58}Fe + {}^{1}n \rightarrow {}^{59}Fe + \beta + \gamma \tag{2}$$

^{58}Fe is a stable isotope of iron while ^{59}Fe is a radioactive isotope. The gamma rays emitted during the decay of the ^{59}Fe nucleus have energies of 142.4 KeV, 1099.2 KeV, and 1291.6 KeV, and these gamma ray energies are characteristic for this nuclie. The spectrum of these energy is detected and recorded using gamma spectrometer system. Each radionuclie has unique decay energy therefore will gives different energy spectrum. Therefore, the element that form the object can be determined from the detected energy spectrum. There are two approach of neutron activation method, first is detection of prompt gamma, this is useful for detection of short live radionuclie and secondly detection of delay gamma, this is useful for detection of long live radionuclie. Details material composition of object can be determined with quite reasonable accuracy.

RESULTS AND DISCUSSION

The selected results of worked done in neutron imaging and neutron activation analysis of cultural heritage objects are presented in this article. The Vishnu deity statue as shown by the photo shown in

(a) (b) (c) (d)

Figure 4: (a) Photograph of the brass statue Vishnu deity 6th or 9th century, Lembah Bujang, Kota Kuala Muda Kedah.(b) Neutron radiograph of Vishnu deity statue (Azali Muhammad et al., 2008). (c) Photograph Tibetan brass statu depicting Buddha as a medical doctor in 18th century. (d) Vertical slices showing the hollow sculpture filled with sandy soil (Anheuser, 2015)
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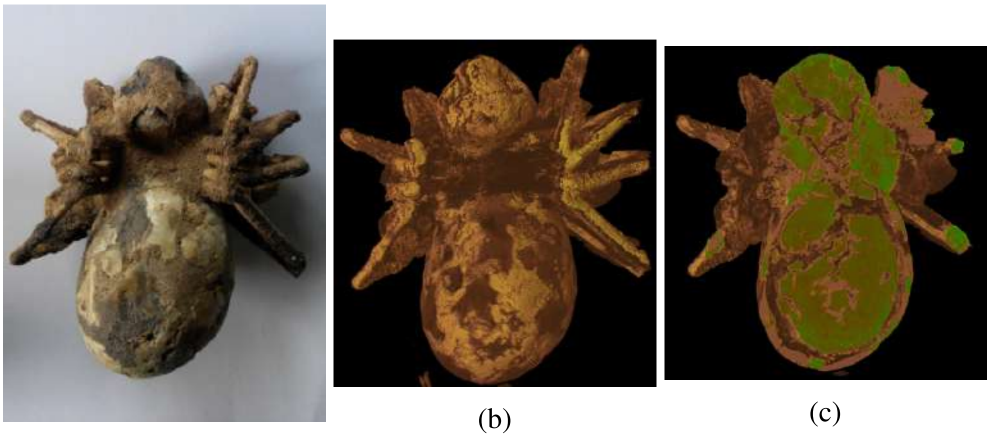
Figure 4(a) has been investigated using neutron radiography. Figure 4(b) shows the neutron radiography image of Vishnu deity statue. There is some place in the radiograph indicates that some material other than brass has been used in making this object. The Vishnu deity status was made by a solid brass. The value of statue sometime determined by weight, in this case the solid one will be more valueable compared with the hollow or empty statue. However, in order to make heavy, the empty statue made by a precious metal has been filled up with cheap material. Example for this case is for Tibetan statue as shown in Figure 4(c). Sandy soil was inserted in the statue to make it heavy and become solid. Evident for this case is revealed by neutron radiography image as given in Figure 4(d), there is clearly seen sandy-soil inside the statue and it is randomly distributed.

Neutron imaging also can be used to determine the authenticity of the object. This is important because there are many fake object claimed as valuable ancient object. In this case, analytical tools such imaging and dating are crucial tools. The example of imaging applied for investigation the authenticity of object is applied for analysis of claimed fossilised spider as shown by the photo in Figure 5(a). This sample is bought from collector shop in Bandar Baru Salak Tinggi Sepang, Selangor, Malaysia and be claimed as spider and being fossilised. It is difficult to decide the authenticity of this object by visual inspection event through fractured surface. There is no evident of skin structure on the fracture leg, but filled with silicon only. Further investigation has been done using neutron radiography and tomography, the 3D neutron tomography image is shown in Figure 5(b). The slice of 3D tomography image in Figure 5(c) showing the internal structure in the abdomen and head sections, it is seen that the leg and abdomen is made by same material. There is also the gap between the skin for abdomen and the inner part, which is not expected. The decision is made that the spider is fake and it is man-made, this is decided after details analysis of slices from 3D neutron tomography image.

Genuineness of gold-string object of several samples and origin has been analysed from delay gamma spectrum after being activated by neutron in the reactor core of TRIGA PUSPATI Reactor. The gamma



(a) (b) (c)

Figure 5: (a) Photograph of collector claimed fossilised ancient spider. (b) Three dimensional neutron tomography image obtained from neutron radiography image. (c) Horizontal cross-section of neutron tomography image shows the object internal structure. It is decided that the sample is a fake object (Muhammad Rawi Mohamed Zin et al., 2015)

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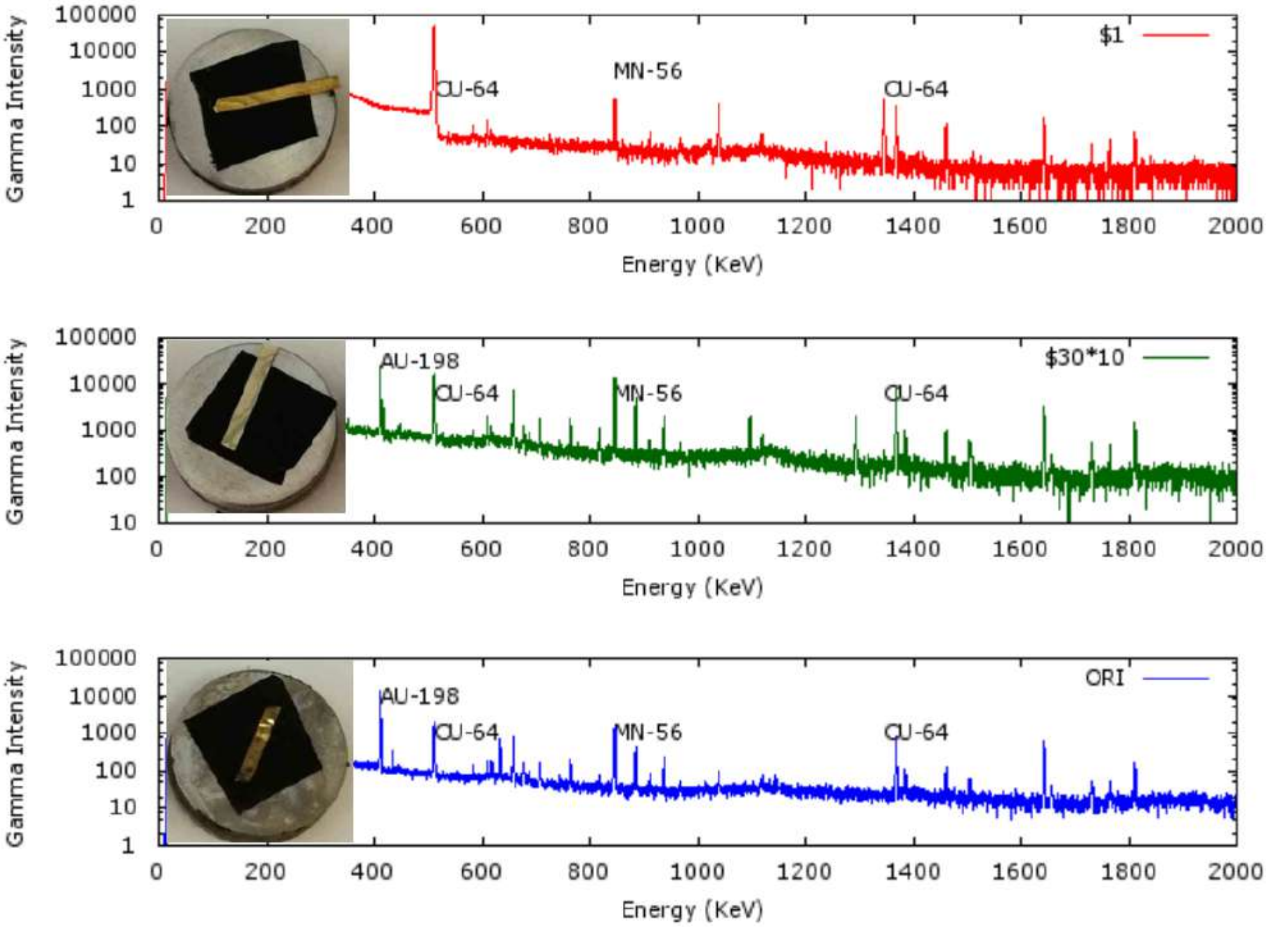

Figure 6: Insets are the photograph of the string sample \$1, \$30 and ORI tested. Gamma spectrum from Neutron Activation for string samples \$1, \$30 and ORI. Sample \$1 does not contain any gold (AU-198) while sample \$30 contains 10% less gold compared with sample ORI.

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spectrum for each gold-string sample is given in Figure 6. The gamma spectrum at the top and bottom are for samples $1 and ORI respectively, while the sample $30 is located in the middle. Photograph for each sample is place as inset in the associated gamma spectrum. There is clearly seen on the specturm for samples $30 and ORI consists gamma energy 411.80 keV, while does not available for sample $1 (Bode et al., 1990). This energy indicates that sample $30 and ORI is composed of gold(AU-198) and there is no gold in sample $1. Since the experiment and measurement were made at similar condition, it is decided that the amount of gold is ten(10) times higher compared with the gold contained in ORI sample. This is indicated from the peak height of sample $30, where it is multplied by factor of 10 in order to get similar gamma intensity. Furthermore, the peak-height of gamma spectrum shown in this figure is dominated at energy 511.00 keV for sample $1 which is for copper(CU-64). Therefore, sample $1 is made mainly by copper, where as sample $30 and ORI also contains copper but much less compared with sample $1. Manganese also the main component in making this gold-string for decoration of fabric.

CONCLUSIONS

This article indicates that the nuclear technique in general and neutron application in particular is quite important tools in the analysis of cultural heritage object. Neutron imaging is a complementary to other imaging anomaly applied in the internal structural analysis of cultural heritage item. On the other hand, neutron activation technique will provide tools for elemental analysis of cultural heritage objects. Information obtained from the analysis makes cultural heritage object be more valuable.

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e ISBN 978-967-2706-08-3

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