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International Centre for Theoretical Physics*



SMR/1843-7

X-Ray Emission Techniques for Forensic Applications

28 May - 1 June, 2007

Case studies on “authentic fakes” and illicit trade of antiquities

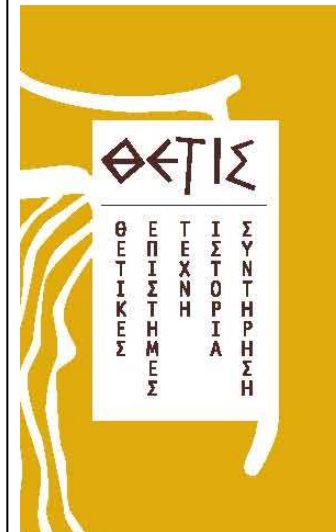
Eleni Aloupi
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www.thetis.gr

Case studies on “authentic fakes” and illicit trade of antiquities



ΘΕΤΙΣ

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Forensic applications

Real forensic applications of X-ray Emission techniques are still rather rare due to

- the reluctance of police departments to rely on other peoples' expertise
- lack of forensic laboratories in many countries
- forensic laboratories are not well equipped / lack of specialised personnel
- lack of communication between the criminologists' and physical science community

There some very closed, highly specialised societies of forensic scientists



Archaeological applications

The situation is similar to what was happening with the applications on archaeological materials and works of art 50 years ago

- development of a new field

Archaeometry / Archaeological Sciences / Archaeological Materials Science

- after 25 years of Archaeometry in Greece, the first (2) “archaeometrists” were appointed by the Hellenic Ministry of Culture this month
- portable XRF instruments are in fashion and readily available in many archaeological Museums
- the field of Archaeological/Historical Materials Science can serve the role of an interface between Forensic science and X-ray Emission applications, especially in view of the increasing need to control archaeological crime (illicit trade of antiquities and works of art)





ΘΕΤΙΣ

ΣΥΝΤΗΡΗΣΗ
ΙΣΤΟΡΙΑ
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www.archaeometry.gr

newsletter of the H.S.A.
Hellenic Society for Archaeometry

conferences . workshops
job vacancies . fellowships
announcements, new publications

THETIS . Science and Techniques for Art-History-Conservation



❖ Products

"Technologically authentic"
reproduction of ancient
ceramic artefacts destined for
Museum shops, special
exhibitions, private
collections and educational
projects...



❖ Thetis 4 Kids +

THETIS is involved in various
educational activities
organized in collaboration
with museums, schools and
universities...



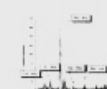
❖ Services

Our services include expert
opinion and consultancy with
respect to authenticity tests,
provenance and technology
studies and the investigation of
manufacturing processes through
laboratory experiments...



❖ R&D Projects

Thetis is also active in the
field of research focusing on
the use and development of
non-destructive analytical
techniques for the analysis of museum
artefacts...





Our **services** include expert opinion and consultancy with respect to

- authenticity tests
- characterisation of materials
- provenance and technology studies
- study of manufacturing processes through laboratory experiments
- preventive conservation, new techniques for damage assessment
- archaeological crime, elemental tagging techniques

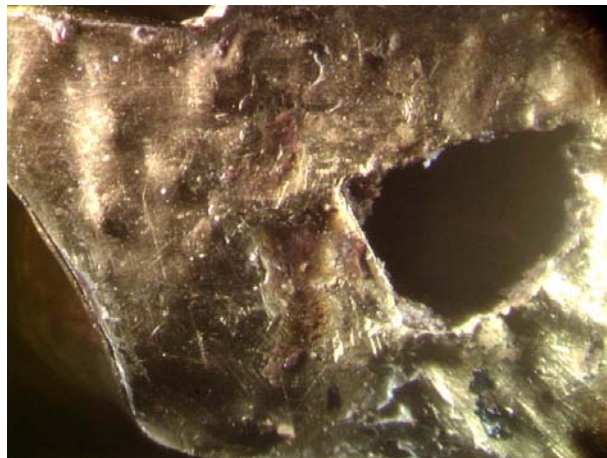
Attic marble grave stele, second half 4th cent.

- a real forensic case that can be addressed by XRF& nIR techniques
- December 2006-



Authenticity test
Benaki Museum Collection,
December 2000

- Hellenistic figurine of Venus, 1st c. BC or recent ?
- TL dating of the clay core
- XRF analysis of the gold
- Simple Microscopic analysis



Aloupi et al. 2000, *Benaki 1*

Authenticity test
Benaki Museum Collection
December 2000

White Ground Lekythos, 5th c. BC,
authentic vase with uncertain
decorative scene

- nd XRF analysis (1)
- UV-Vis-IR imaging
- nd XRF analysis (2)



Authenticity test Benaki Museum Collection



White Ground Lekythos, 5th c. BC,
genuine vase with faked decoration

- UV-Vis-IR imaging revealed the fingerprints of the painter



Vravrona Museum :

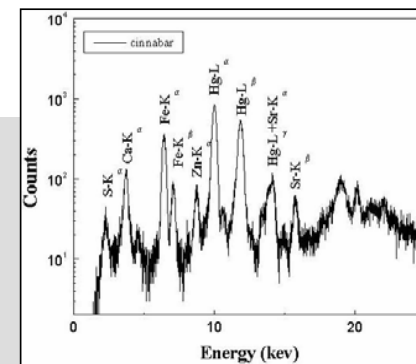
Polychrome lekythos from Merenta east Attica, excavated in July 2002

November 2002 - March 2003



ΕΤΙΣ

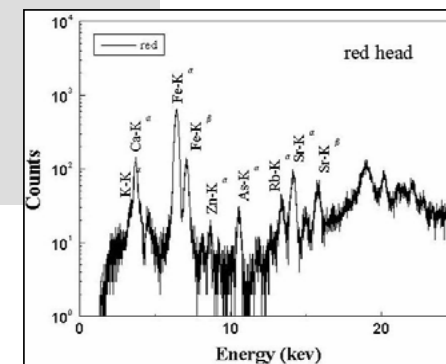
XRF and IR- ANALYSIS of a polychrome white ground Atticlekythos (5th cent. BC) bearing pre-firing (glossy black, white slip, hematite red) and post firing (mat black and cinnabar red) decoration. The analysis revealed an ancient restoration that explains the post firing retouching. March 2003



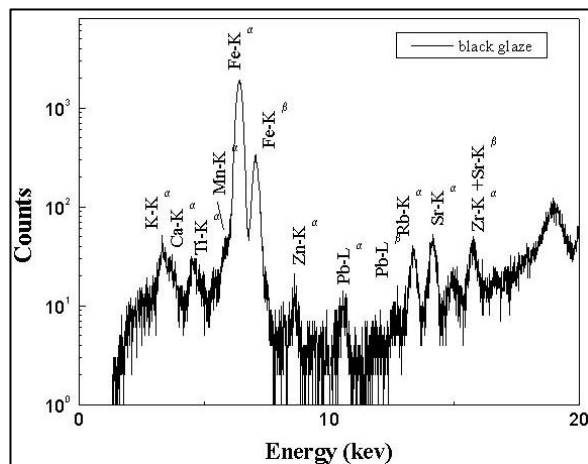
Hematite



Cinnabar HgS



**Vravrona Museum : Polychrome lekythos from Merenta,
XRF analysis INP NCSR Demokritos, November 2002**

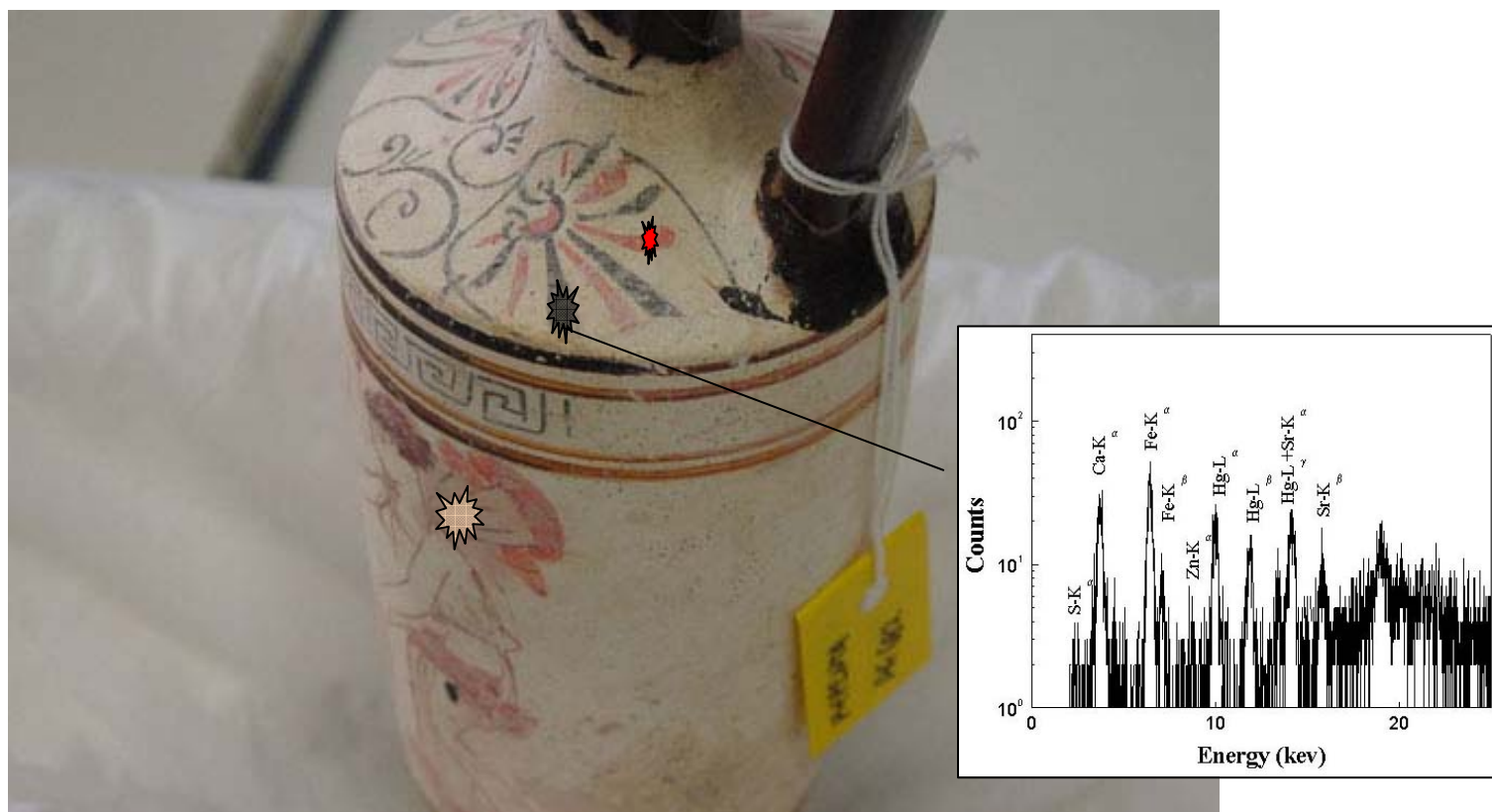


Clay slip → black glaze



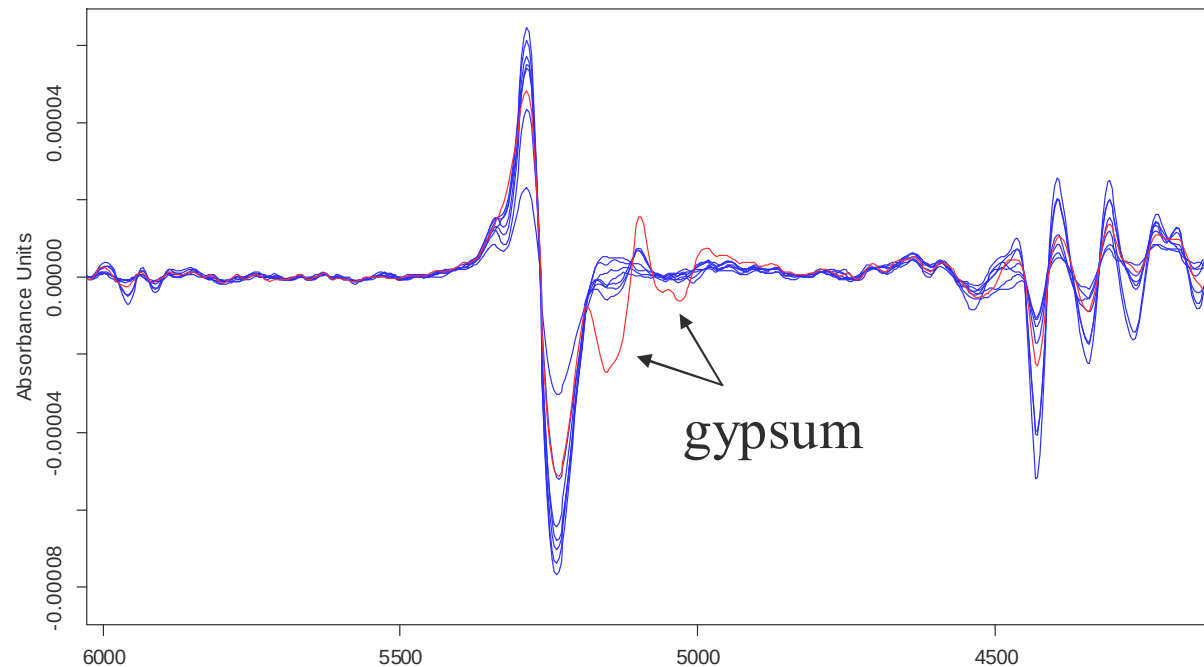
Kaoline
increased K, S
allunite ?

**Vravrona Museum : Polychrome lekythos from Merenta,
XRF analysis – INP, NCSR Demokritos, November 2002**



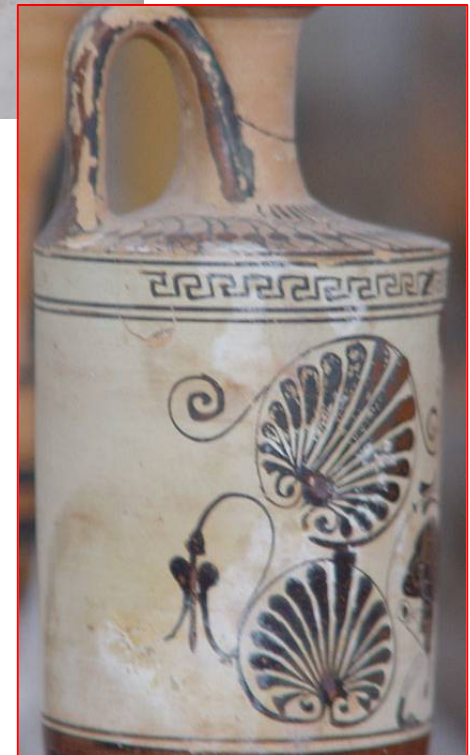
-  Cinnabar, HgS
-  Carbon shoot, C
-  Organic pigment?

n-IR spectrometry revealed an ancient restoration



near-IR analysis, P1-NHRF, March 2003

- ★ Identification of an organic material (i.e. primal) used during a recent conservation to fix the kaolinitic white slip
- ★ Identification of Gypsum used during an ancient restoration. The crack on the shoulder of the vase was filled with gypsum after firing and the anthemion was painted by using cinnabar and



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-

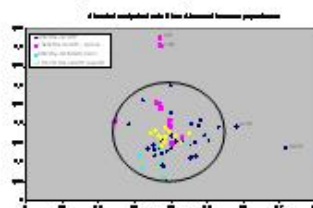


RECOVERY

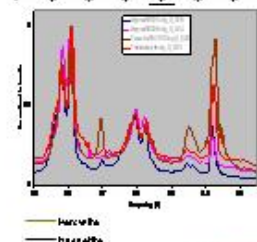
Recovery and Validation

Following the procedure developed in THETIS' Laboratory during the period 1999-2002, a number of clay suspensions based on three clay materials without the use of commercial deflocculants were analyzed chemically and mineralogically. A set of the produced black glosses was analyzed for comparison with the ancient sherds.

The validation of the particular clay slip formulation involved the preparation and firing of laboratory specimens followed by a detailed comparison with the surface properties of ancient sherds. The results verify the successful replication of the attic black gloss technique.



K/Si ratios vs Fe/Si for the classical Attic black gloss and the laboratory specimens



micro-XRD data from ancient BG sherds from the Athens Agora (2), Taranto (Sicily) and a modern reproduction. The modern BG is similar to the Athenian sherds.

The nature of the ATTIC BG: Several authors in the 70's argued that the Attic black paint is not a real glaze because it is not totally vitrified. They suggested the use of term "gloss". Our work in the past has shown that it consists of an amorphous phase rich in polycrystalline magnetite particles with sizes $<200\text{nm}$. It can thus be described as an **opaque alkali-aluminosilicate glass which is coloured by fine magnetite crystals**



Description of the iron reduction technique

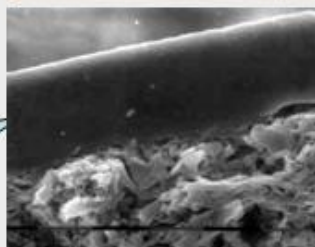


The material used for the decoration of the clay body is the finest fraction of an illitic clay rich in iron oxides with low CaO content, which when concentrated with boiling produces a thick "paint". The paint is applied on the unfired clay body and the vases are fired in a complex firing cycle up to 950°C involving three stages:

(a) one oxidising, during which both the paint layer and the body become red due to the formation of hematite Fe_2O_3 .



(b) one reducing stage at which the body and paint layer become black as the red hematite (Fe_2O_3) transforms to the black magnetite (Fe_3O_4) (i.e. partial reduction of $\text{Fe}^{III} \rightarrow \text{Fe}^{II}$)



At this stage the paint layer vitrifies (due to its fine particle size, the lack of CaO, and the higher alkali K_2O content, see the table below) while the moderately calcareous body becomes porous (see SEM micrograph, $2000\times$, $1\text{ bar} = 10\mu\text{m}$).

(c) in a third oxidizing stage the porous body reoxidizes to brick red ($\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3$), but the vitrified paint layer remains black).

Full-scale reproduction

Collaboration with traditional potters, vase painters and other artists or artisans (ceramists) in order to establish a pool of skills for later full scale ceramic reproduction. The work involved trial reproduction experiments of full scale artifacts using the documentation of the most common ceramic types of classical vases based on photographs, line drawings, measurements of dimensions, weight, volume etc. The full-scale reproduction process presented technical difficulties to the traditional potters due to the complexity of certain ancient shapes. Other problems encountered concerned vase painting details (i.e. failure to reproduce the so called relief line of Attic vases).



People involved

Researchers E. Aloupi, A. Karydas, Ch. Zarkadas

Students I. Aslani, A. Chaviara

Technical: Iph. Nalbani, Chr. Pantelidou
Various artisans (i.e. potters and vase painters)

Authentic fakes.....

Food for thought.....

- A well-documented problem, especially in the Mediterranean, is the illegal trade in archaeological value objects. The contemporary production of Museum quality, technologically authentic, and archaeologically documented ceramic artefacts may well mitigate the demand for the originals, while at the same time allowing access to a wider clientele.
- This policy has been adopted few years ago by the Peruvian government, which set up outlets for high quality 'certified' artefacts in order to reduce the illegal export of pre Columbian antiquities.
- One aim of the CERAMED project was the promotion of similar policies by the countries involved (Greece, Turkey, Spain, Morocco and Jordan).
- The Hellenic Ministry of Culture has already adopted such a policy by commissioning "museum quality" reproductions for sale at the major museum shops.
- Another measure adopted by the HMC is the creation of exhibitions promoting local history based on high quality reproductions of archaeological finds (Athens Metro stations, Corinth Suburban rail terminal).

'Technologically authentic' reproduction of ancient ceramic artefacts for Museum shops, Public exhibitions, Private collections, Education



Meeting at the ancient Agora

March 2007, www.fhw.gr





ΘΕΤΙΣ

ΣΥΝΤΗΡΗΣΗ
ΙΣΤΟΡΙΑ
ΤΕΧΝΗ
ΕΠΙΣΤΗΜΕΣ
ΘΕΤΙΚΕΣ

Αρχαία Κεραμική Τεχνολογία από τη θεωρία στην πράξη

Ancient Ceramic Technology from theory to practice



Authentic fakes 2

- There is of course an intrinsic danger that the high quality reproductions might be artificially aged in order to enter the market as originals. As a safeguard against this eventuality and in compliance with the ICOM Code of Ethics for Museums that states

*.....If replicas, reproductions or copies of items in a museum's collection are made, for whatever purpose, they must **respect the integrity of the original** and **be permanently marked as facsimiles**. All items offered for sale should comply with relevant national and local legislation....*

- a “Museum Quality” label or elemental tag is stamped or inserted in the ceramic body and the production is documented and communicated to the Antique Market and major Auction Houses.



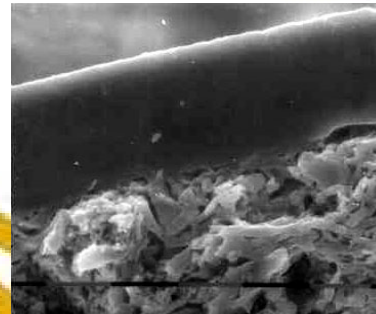
A collection of
artificially aged
ceramics made
for a private
collector,

April 2007

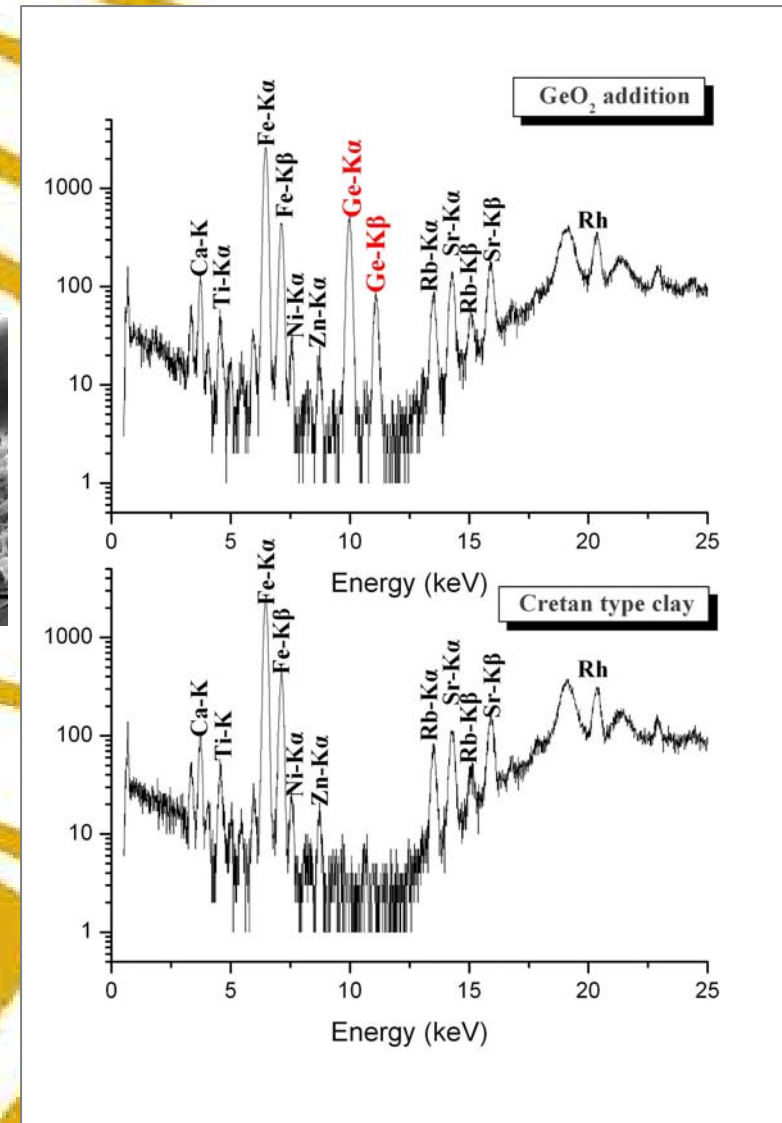


ΔΕΤΙΣ

Embodied Elemental Tagging



The material used for the decoration of the clay body is the finest fraction of an illitic clay rich in iron oxides with low CaO content, which when concentrated with boiling produces a thick "paint". The paint is applied on the unfired clay body and the vases are fired in a complex firing cycle up to 950oC involving three stages:





The ceramics production process has benefited from results obtained in the course of the CERAMED research project (www.cera-med.net), funded by the EU, and aiming at the recovery of ancient ceramic manufacturing techniques of the Mediterranean. 2003-2006.



The elemental tagging of THETIS products forms part of the GSRT Research Program - Operational Program Attica Region, co-funded by EU / European Regional Development Fund / Embodied Elemental Tagging Technologies and non-destructive techniques for authentication and identity verification of archaeological artefacts, works of art and Museum quality technologically authentic copies. 2006-2008





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Overview

Using XRF -- A Cost Effective Solution to Expensive Problems

In today's competitive, market-driven world, a company succeeds by providing the best products and services. KeyMaster's mission is to help your company succeed by providing unique solutions that improve your products and reduce your costs.

A technology leader for more than 20 years, KTI is celebrating the launch of its latest breakthrough first announced in NASA's May 11 press release: a handheld alloy analyzer, which can now accurately examine even aluminum and titanium alloys. The vacuum x-ray fluorescence (XRF) analyzer was jointly developed by scientists from NASA and KeyMaster Technologies. KeyMaster will manufacture and further develop the new instrument in partnership with Metorex, an instrumentation company based in Ewing, New Jersey and Helsinki, Finland.

NASA engineers at Marshall Space Flight Center in Huntsville, Alabama teamed with KeyMaster Technologies and Metorex to develop an Aluminum/Titanium analyzer that weighs 4 pounds and is capable of accurate analysis of light elements, even under field conditions. This capability promises to be a boon to the aerospace and aviation community because of unique requirements to analyze materials that have traditionally been undetectable with portable x-ray fluorescence- for instance, the need to analyze Space Shuttle propulsion systems on the launch pad. ([See full press release on KTI's "News" page.](#))

Exciting News!! Keymaster acquired by Bruker

PDF's on this page:

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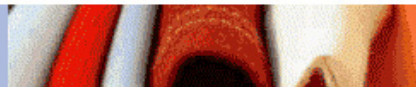
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Symposium S

Science & technology of cultural heritage materials: art conservation and restoration

28 May 2007 29 May 2007 **30 May 2007** 31 May 2007 01 June 2007

start at		Subject
GLASS 1	14:00	Glass of the Past: Characterisation of Artefacts and their Surfaces by Micro- and Nano-Techniques (view full abstract)
GLASS 2	14:30	Rediscovering ancient opaque glass technologies through crystals examination (view full abstract)
GLASS 3	14:50	Non invasive XRD investigation on fine Renaissance manufactures of Museo degli Argenti di Palazzo Pitti in Florence (view full abstract)
CONSERVATION 1	15:10	The Nanoscience Contribution to Conservation of Cultural Heritage (view full abstract)

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Authors : Luca Gregoratti and Matteo Dalmiglio Sincrotrone Trieste SCpA SS14-Km163.5 in Area Science Park 34012 Trieste Italy

CONSERVATION 3 16:30 **Synthesis of colloidal systems of $\text{Sr}(\text{OH})_2$ nanoparticles in homogeneous phase at low temperature**
(view full abstract)

CONSERVATION 4 17:10 **A new technology for anticounterfeiting of art works**
(view full abstract)

CONSERVATION 5 17:30 **DESERT VARNISH: CULTURAL HERITAGE AND CLIMATIC CHANGES**
(view full abstract)

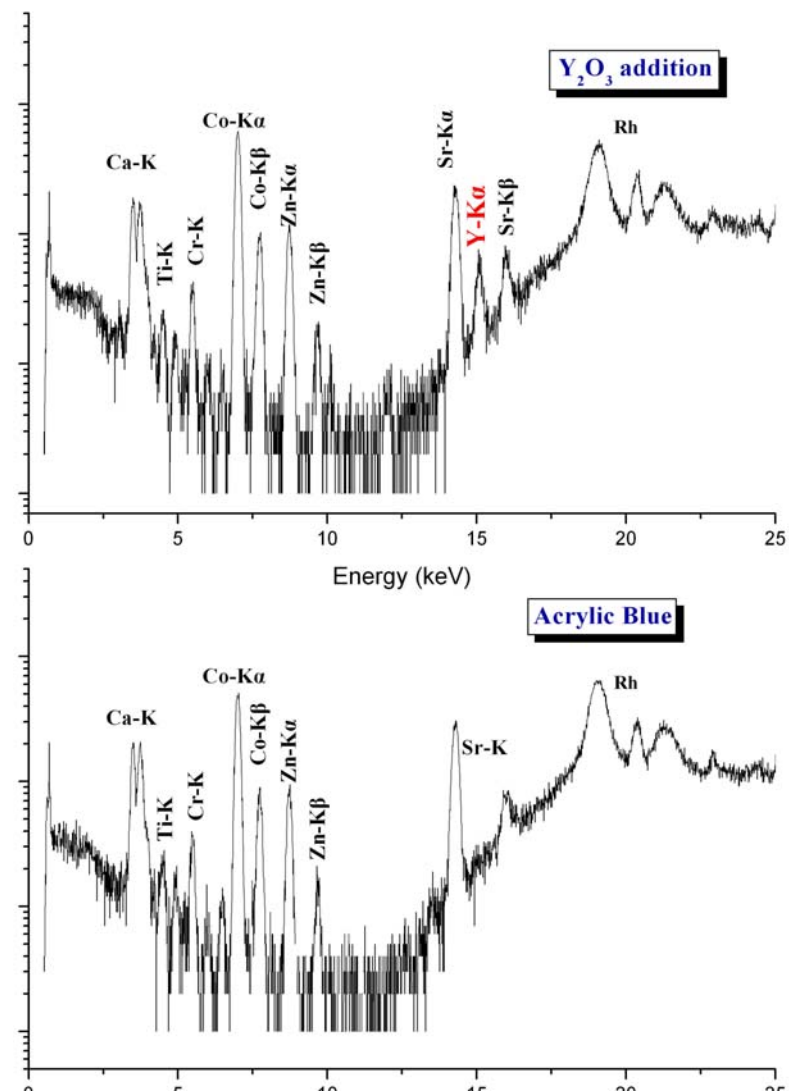
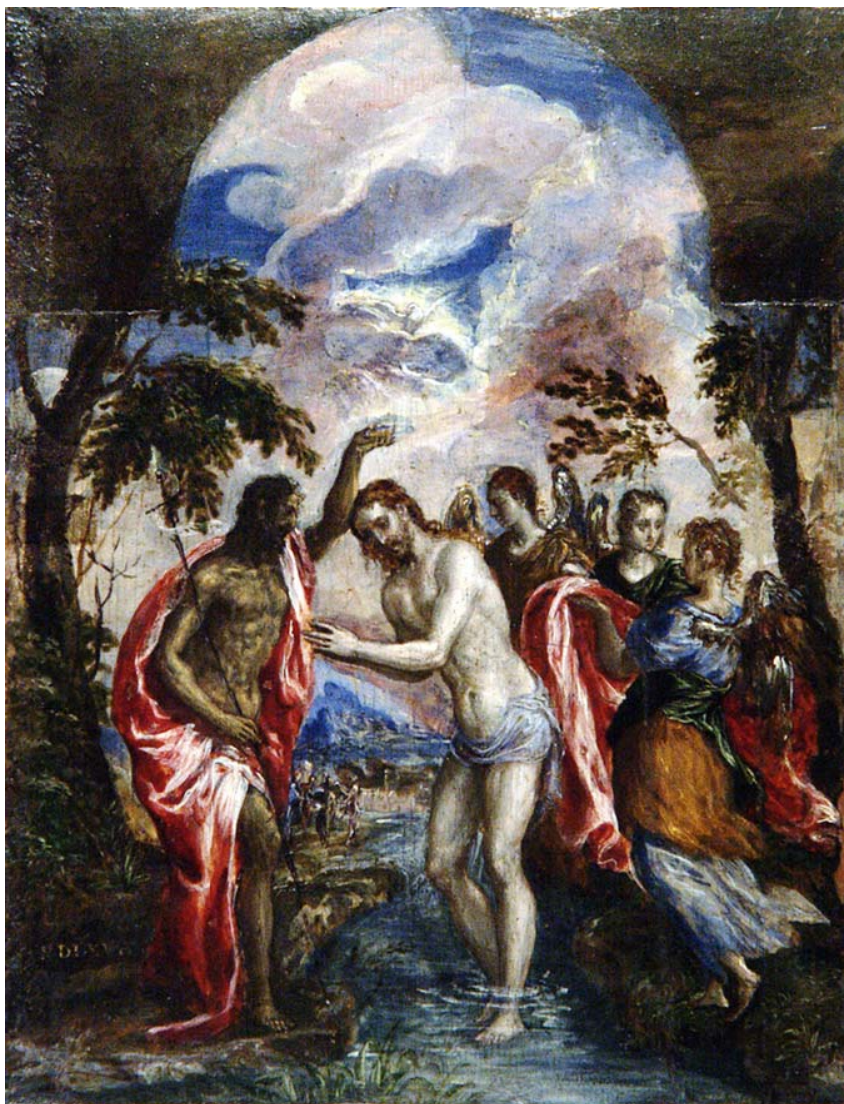
Authentic fakes 3....

This preoccupation with replicas possibly passing as originals is not universal. As one of the most respected archaeological materials scientists writes

".... Some people, especially Westerners, want every replica labelled on the bottom, denouncing unlabeled examples as attempts at deception, fakes, or forgeries; however, the Chinese want the possibility of personal interpretation as to whether a ceramic is "real." Such connoisseurship was part of the measure of a Mandarin scholar, and this cultural tradition is being preserved in the new China. The old technology is being kept alive and even improved upon, economic benefits and elevated social status accrue to artisans and factory owners, and tourism comes to cities where wonderful ceramics are produced. Respect for an ancient craft is generated, and artisans in other areas with similar raw materials try to emulate the "originals." Occasionally, they succeed so well that museum curators and scientists are fooled in the process of appraisal and acquisition, but this only adds to the game of having knowledge confer status....."

From "Preserving Art through the Ages", Pamela B. Vandiver, Guest Editor, Materials Research Society Bulletin, January 2001 Issue.

Elemental tagging on conservation materials adopted by the Benaki Museum





CONSERVATION OF WORKS OF ART

The Conservation Department of the Benaki Museum was established in 1974 and currently consists of seven specialized laboratories engaged in the conservation of icons, easel paintings and woodwork, paper, textiles, metalwork, glass and bone artefacts, ceramics, wall-paintings, mosaics and photographs.

The main activities of the Department are the technical examination, the conservation and restoration of artefacts of the museum's collections, as well as the prevention of any further deterioration of their condition by ensuring that appropriate environmental conditions are maintained for exhibition and storage.

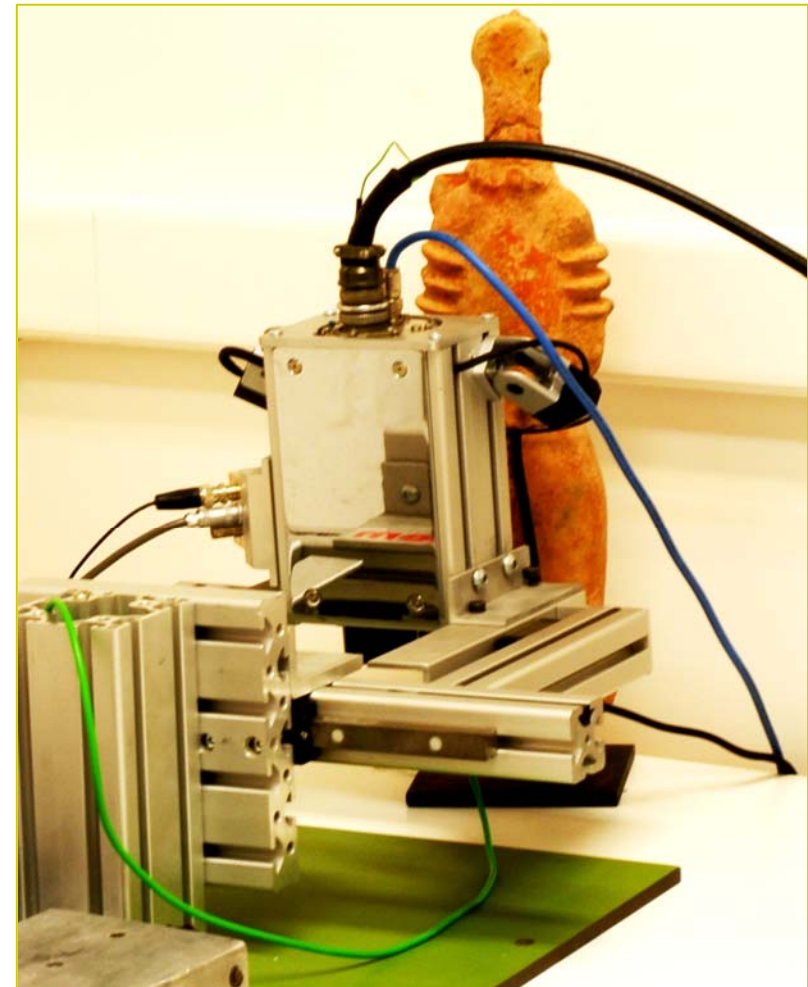
These activities aim at the conservation of the work meticulously in an aesthetically acceptable and apt manner and always in accordance with the intention of the artist, taking also into account the passing of time, any possible weathering caused by unfavourable conditions of preservation and other irreversible factors.

One of the department's most significant fields of endeavour is to conduct research into the artefacts investigating their structure, the materials from which they were made, as well as their state of preservation with the aid of sophisticated photographic methods including radiography, microscopy and other analytic techniques.

A relatively recent area of interest for the department is undertaking of conservation for other parties (i.e. museums, foundations, public or private organizations, churches, and monasteries) and individual collectors as well as the performance of environmental surveys and the study of suitable ways of exhibition, protection and storage of the artefacts they own.

- [Icon, Oil Paintings and Woodwork Conservation Laboratory](#)
- [Paper Conservation Laboratory](#)
- [Photographic Conservation Laboratory](#)
- [Textile Conservation Laboratory](#)
- [Ceramics Conservation Laboratory](#)
- [Metal, Glass and Bone Artefact Conservation Laboratory](#)

- Thetis Authentics Ltd:
E. Aloupi, I. Aslani, A. Chaviara, I. Nalbani
- Benaki Museum, Conservation Department:
S. Stassinopoulos, V. Paschalis, D. Kotzamani
- INP, NCSR Demokritos:
A. Karydas, Ch. Zarkadas
- ITPC, NHRF:
G. Chryssikos, V. Gionis



Benaki Museum: THETIS Analytical Laboratory / April 2007