Characterization of the pigments of Siceliot pottery decoration: the case of Centuripe ceramics

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Abstract

Two Centuripean vases dated back to the 2th century B.C were analyzed using complementary non-invasive and non-destructive portable XRF and Total Reflectance FTIR spectroscopies. The vases are of great importance since they represent a rare expression of the Hellenistic period. The two vases, a "Pyxis" and a "Lebes Gamikos" decorated with figures of different typology, are exhibited in Salinas archaeological museum in Palermo-Italy. The Pyxis vase consists of three parts: the body, a removable lid and a decoration egg. The Lebes Gamikos vase consists of the body and a non-removable lid. The body and the lid of Pyxis vase as well as the body of Lebes Gamikos vase are decorated with different painting scenes. The state of conservation of the paintings is very poor for both vases.

The aim of the investigation was to identify the used pigments for the decorations and the painting technique, to recognize the retouched areas and, eventually, to acknowledge the authenticity of these vases. XRF and IR analysis were performed on selected points representative of different colored areas. The analyzed points were selected from original and restored areas whose identification was performed with the aid of a restorer.

The decoration resulted by the superimposition of three layers. The inner one is a white layer composed mainly by calcium carbonate and calcium sulfate. The middle layer, red colored, contains iron oxides. The outer layer is patterned with pigments that are common in the Hellenistic period. In some areas, modern pigments were also identified. The decorations were made using a tempera technique, as inferred by the identification of proteins residues by reflectance IR spectroscopy.

One of the most interesting results concerns the identification of two calcium sulfate phases: the gypsum and the bassanite that undergo phase equilibrium promoted by temperature and humidity. The two phases are located only in some areas of the surface while in other only gypsum was identified.

Additional investigations are necessary in order to verify if the presence of gypsum or gypsum and bassanite could constitute a criterion to discriminate original areas from later restoration or falsification.

PART I-ARCHAEOLOGICAL BACKGROUND

CHAPTER I – The polychromatic ceramic of Centuripe

I.1 Typological features

The polychromatic Centuripean vessels which have been uncovered in the Centuripe Region-Sicily-Italy, are well-decorated vessels characterized by a local clay **[1]**, and above all by their unique shapes, outstanding relief ornaments and figure scenes applied in tempera colors on a black or pink background **[2]**.

Deussen has studied in his doctoral dissertation **[3]** the whole corpus of Centuripean ceramics and has made a classification of the polychromatic vessels according to their typological features since they are characterized as mentioned above by their shape, plastic decoration and painting scenes.

Starting from the classification by **shape**, four groups are distinguished:

- The Lekanis

It is the most common shape among Centuripean vessels and was preferred by most of the Sicilian painters **[4]**. The Lekanis shape is a luxury shape inspired by its direct red-figured ancestors, among which the production of the Lekanis continued to the end of the 4th century. The Lekanis shape is characterized by its conical cup on a relatively high foot, covered by a conical lid with two attached handles emerging from the body of the vase creating an angle. The finials of the lid of the Lekanis are decorated in different shapes and models such as tubular extension with painted decoration, or accented with plastic foliage, and knob-like final **(appendix 1, plate I fig.1)**. Because the conical shape of the base of the Lekanis, the painted scene is limited only on the lid. According to Deussen, all the Centuripean vessels were progressively developed, in terms of shape, from the functional shape that was utilized for daily use into the more monumental final appearance and were made through several phases:

- Early shape: primitive shape, based on red figures type with solid appearance.
- Transitional shape: more elongated and less rounded vase body, the handles have grown in size.
- Early developed shape: the walls go straight from the foot vertically; the lip is wide to receive the cover. The handles are attached indirectly; the lid is conical; symmetrical design.

- Fully developed shape: the plastic frieze only occupies about one third of the height of the cup and some plastic decoration on the cup's walls.
- The late developed shape: canonical shape, with slightly concave walls, long and thin vessels, with plastic adornment, with no handles indicating monumental function.

Based on these gradual developed shapes, the manufacture of Lekanis vessels was assigned into four different workshops (1,2,3, and unidentified workshop) by three different potters (Tendril and Medusa Master, Gorgon Master, and Imitation coroplast) respectively classified by Deussen[1]. Subsequent bibliography doubted the validity of such very precise classification, though agreeing about the trends of development detected by P. Deussen. The attributions to workshops- painters made by Deussen require stronger arguments and proofs, both of technical, stylistic and scientific nature.

- The Lebes Gamikos

It is a widely spread shape in Centuripean vessels in the Hellenistic Period **[3]**. Lebetes Gamikoi, have like-crater shape, they were used as marriage vessels. Lebes Gamikos vessels have long foot and short-lived shape. This kind of vessels appeared in the Attic pottery in the 6th century. The decoration of this group of vessels is a plastic decoration without vegetation such as (lion head spout, Aphrodita, Satyr masks, erotes) applied to the front and back of the objects **(appendix 1 plate I fig.2)** The lids of Lebetes Gamikoi are flat in one piece with the body and an opening in the center. With handles from the up and has non-functional uses.

- Pyxis

It is similar to a Greek bell-crater in appearance, but really this large vessel is based on the Sicilian red- figured skyphoid pyxis **[5]**. The lid of Pyxis is in a domed shape where always removable.

The Lebes (Pyxis) feet are relatively long and are similar to Lekanis feet. Some Lebetes are in handle-less (Lebes with attached lids) and other with handles. The vase is equipped with a two-pieced foot, with a tubular extension between the foot and the base of the vessel. The finals of the Lebes lid usually are in different shape and decoration such as knob-like, small Lebes Gamikos finial, and egg final **(appendix 1 plate I fig. 3)** The entire Lebes could reach the height between 70-80 cm and the diameter is about 30 cm.

1: see Deussen dissertation [3], Ch 1, P.28-29 shows the workshops of the lekanis shape.

Lebes vessels have been endured to various developed phases in order to get their monumental final appearance, as the Lekanis vessels:

- Early Shape: larger handles, domed lid and added foot, in addition to decorate with plastic decoration around the base and lip.
- Transitional shape: increases in vase's body size, hemispherical dome lid, the foot is higher and thinner.
- Early developed: soft and more cordial outline, proportionally good distribution of painted and relief- decorated space, sensitive and delicate articulation of the walls.
- Fully developed: absence of the handles and increasing in the size and weight, the lid became more rounded and higher dome, consequently lose the function.
- Late developed: is the final evolutionary stage, greater height in appearance and more decorated by plastic appliques, specifically on the lid.

Five different workshops with four painters were involved to produce the Lebes vessels according to the classification by Deussen[2]. As a matter of fact, he groups together two different shapes, the Pyxis and the Lebes Gamikos, so the correspondence between painters-workshops-shapes is more complex than in Deussen's analysis.

- The painted shield-clipeus

Deussen named "portrait" shields and "portrait" plates a type of clipeus-shield painted in tempera technique. They are non-functional, wheel made objects. The plate has a shape with large disk and high rim with one or two holes for the suspension of the object. The shields and plates were either attached to the wall or leaning on a table. The shields are disks which display the painted decoration on the convex outside.

- Other shapes

Other shapes are produced based on red-figure background. They were classified among Centuripe vessels groups. They are either of open shape such as bowls **(appendix 1 plate I fig.4)** or closed shape (aryballoi, squat lekythoi, bottles and alabastra).

➢ Plastic decoration

The Centuripe vessels are characterized by an outstanding plastic decoration that aims at imitating the vessels with precious metals. The painted decoration of the Centuripe vessels is a reflection of Hellenistic frescoes **[6]**.

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[2]: see Deussen dissertation [3], Ch 1, P.39-42 shows the workshops of the lebes shape.

Classification of the plastic decoration according to the shape of the vessels was made by Deussen as follows:

- Lekanis

The plastic decoration of the Lekanis vessels adopts popular motifs in the Hellenistic art. It probably symbolizes both nuptial and funerary significance **[3]**. Basically the plastic decoration on Lekanis is a vegetation decoration inspired by the decoration on contemporary vessels of precious metal. The floral and scroll motifs, such as vines and sprout leaves, buds or blossoms, tendrils with little winged erotes, acanthus or laurel leaves are observed on the different parts of the vessel. Busts (either Satyr and Maenad group, or Io-Isis, or Medusa and Aphrodite heads) also are placed with a blossoming ground paint **(appendix 1 plate I fig.1)**. The decorations are partly hand, partly mold-made and attached to the unfired vessel. Golden decoration is shown on the precious vessels which was common in Greek world.

- Lebes

The decoration of the Lebes are indirectly inspired from the buildings therefore many of the architectural, doric and corinthian friezes are evident in the Lebes vessels. Besides the application of blossom-rosettes is found on large Lebetes **[3]**. Egg and dart molding or simple bead- and reel molding decorated many different Lebes vessels carrying triglyphs and erotes (either striding, dancing, or crouching) that symbolize the fortune and happiness in the afterlife **[7]**. The finial part decorations of the Centuripean lebetes are divided in many different types either egg- finial surrounded by a ring of acanthus leaves, or a small Lebes Gamikos or tubular or T-shaped, or knob shaped **(appendix 1 plate II fig. 5)**.

- Pyxis

Plastic marine scene (dolphin, hippocamp) decorated the lids of the pyxides that point to hymeneal symbolism.

There is no observable decoration on the shields and plates. Concerning the decoration of other shapes of vessels, only plastic decoration without vegetation is recognized in this group applied to the front and back of the objects.

- **Painted scenes (iconography)**

The subject and the clues of the painting scenes on Centuripe vessels were for a long time discussed and studied by many scholars. Painted scenes are observed on the Lebes' or Pyxis' body and on the lid of the Lekanis vessels. The iconographies in the Centuripe vessels are considered to represent beliefs concerning the sex, life, death and marriage differences of ritual, burial arrangements and aspects of music and dance. The painting scenes are restricted only in the front body of the vessel that confirm a direct link between the scene that display on the vessels and the use of the vessels, since they were being put against the wall **[3]**. E.C. Portale, the archaeologist in Palermo university, suggests that the Centuripe vessels have a funeral significance since they have been found in the necropolises which personalize the idea of life and death **[8]** and certainly are not wedding gifts to a living woman, but 'monuments', prepared for a single frontal view, fragile and difficult to handle, the colors and plastic decorations brilliant, made just to impress the observers during the short duration of the funeral ceremonies, and come with the deceased buried **[9].**

The strange phenomena that couldn’t be interpreted and obstruct the full understanding and the meaning of the iconography is the presence of music instrument that probably could be interpreted for the festival of the marriage or the death **[8]**.

The significance of the music aspects is observed in painted scenes of some of the Centuripe ciborium that demonstrated by some musical motifs **(appendix 1 plate II fig 6)** that show the musical significance by small music instrument carried by the central figure in the scene adorned and labeled "academy Music" the tambourines, in fact, apply to evoke all that sphere of ritual activities marking the preparation and the passage from childhood to adult role **[8].**

J.R. Green in his study of the iconography of the Raleigh Vase located in North Carolina Museum of Art presented in a Bulletin **[7]** suggests that both the marriage and death were significant since some features of wedding/funeral iconography are observed: Nikai which is considered to be gifts to the bride bringing the blessing of the spirits of the underworld, Erotes that symbolize for a good fortune and happiness and blessed destine in the afterlife. Apprehension attitude of the bride and the protectiveness of her friends is manifested clearly from the face of the central figure. The passage from an old life to a new life in both (marriage or/ and death) are represented from the stretching of the hand of one figure to lead the bride. The existence of a girl with the tambourine is assumed to be from the retinue of Dionysos and the blessed leading the bride on her way to the other world **(appendix 1 plate II fig 7. a,b,c)**

The mystic rite scene is quite popular in Centuripe vessels and was suggested by Richter in her study on the polychromatic Centuripean vessel in the Metropolitan Museum of Art in New York**[10]**.The scene exhibits four figures (women) standing by each other, each of the woman has three- quarter view and dressed colored chiton, one of the figures is seated in three quarters view holding a tambourine, the other one is with hands outstretched over a stand which is apparently an altar, the fourth figure standing watching the proceeding. The subject of this scene is quite popular on Centuripe vases.

However, when the mystic rite is the significance of the vessels may have played a part in Orphic or Dionysiac ceremonies such as the scenes on the vases in Museum of fine Arts in Boston (no. 151, 152) **[11]** or used as funerary offerings **[10]**.

Number of different vessels represent the Dionysos subject as the clue of their painting scenes such as the other vessel which is presented in the Metropolitan Museum of Art in New York and studied by Richter **[12]**.

According to the investigation that was done by Deussen **[3]**, the significance of painted scenes is related to wedding rituals whether represent a sacrifice, procession, the bestowal of gifts to the bride, and a Dionysiac scene. Therefore, the painted scenes on Centruipean vessels fall into four groups corresponding to the shape and plastic decoration.

The sacrificial scenes are illustrated mainly in the Lekanis lid that was occupied by some features such as the altar, burning fire and several figures that record the dedication and sacrifice with some personal issues as a custom usually done before the wedding ceremony in purpose of protection: the purpose of the sacrifice was originally supplicatory in question for protection, the desire for fertility or the gratefulness of preservation of purity.

Numerous of the Lebes vessels are characterized by processional scenes representing the bride and her maids on the way to the house of the groom, also music instruments as the tympanum and other participants like a marshal, boys and friends and relatives.

The act of giving gifts to the bride is also one of the scenes that demonstrate the activity that took place in the day after the wedding day by giving the bride different kind of gifts such as soaps, chests, perfumes. Normally the bride is shown as a seated figure.

The Dionysiac scene is shown in some Pyxis vessels and were served in the nuptial and funerary ceremonies. they illustrate the god´s of Ariadne. Dionysos seated on throne are observed.

I.2 History of studies and research

Only some important decorated vases have been survived and yielded from the excavation works that were not so many in Centuripe archaeological site.

The excavations are divided in two categories, irregular and regular, the so-called irregular excavations were being done widely secretively and without recording the archaeological finds therefore they were insignificant. P. Orsi, the late 19^{th}-early 20^{th} cent. famous archaeologist, tried to collect the polychromatic vases by buying them for the interest of the Archaeological Regional Museum in Syracuse.

The first regular excavation was taken place by P. Orsi himself in 1906 and other campaigns were carried by him later on in the year 1911, 1918 and 1932, but did not yield polychrome vases, beside one exception; then the excavations by L. Bernabò-Brea and A. Giucastro followed in 1942, 1950/51 in Contrada Casino necropolis and in monte Porcello necropolis, which were published by G. Libertini **[3]**.

Few overall studies have been done with the aim of identifying the chronology, the purpose, the decoration and the shapes of the vessels that have been survived from the Centuripe excavations.

G. Libertini, P. Orsi, and B. Pace have been discussing and collecting all the extant pieces in the first half of 20^{th} century. Sir John Beazley in 1943 studied the western Greek figured pottery **[5]**. A. D. Trendall provided the frame of references for the start of a production of red-figured vases in the Etna region around late 4^{th} century **[4]**. A scheme for the vases and the identification of a fresco painting technique and the investigations on the plastic decorations, manufacture techniques, and a date of the late 3^{rd} century for the vessels firstly were proposed by Biagio Pace **[6,13,14,15]**.

Studies had been carried out by G. Libertini, who proposed a date of 3^{rd} and 2^{nd} century B.C., and investigated the Hellenistic shapes influenced by local tastes and Hellenistic-Roman paintings from Egypt and Thessaly (Hadra, Pagasae and Fayoum), and suggested the funeral purposes for the vases and a Dionysiac interpretation. He also differentiated the plastic decoration between the floral and architectural ones. His studies were published in 1926 and 1932 **[1,16]**.

Mrs Richter made few investigations specifically on the painting technique and the pigments used and the relation with the Hellenistic painting on vases acquired by the Metropolitan Museum in New York **[10,12]**. These were for a long the only scientific researches on the technique and pigments, followed early in Seventies by the study by the German scholar Rieder **[17]** on some pieces on the antiquarian market in Germany, using the emission spectrum of the X-ray fine structure analysis and polarizing microscope, which was published as an appendix of the most comprehensive study and catalogue of the Centuripe vases made by Ulrike Wintermeyer, edited in 1975 **[18]**.

Few years earlier the PhD thesis of P.W. Deussen had treated in depth all the questions concerning Centuripe ceramics, but this study had a more restricted spread among scholars; more influent a paper published by Deussen himself was, concerning the nuptial significance of the imagery of Centuripe vases **[3]**. In 1980 a critical review of the previous bibliography was made by E. Joly.

In the last decades of past century and at the beginning of our century, several pieces were published, mainly in European and American museums collections, adding interesting observations and remarks such as the Raleigh Vase that is in the North Carolina Museum of Art **[7]**.

In 2011 an overall overview of the contexts, chronological questions, problems of iconography and meaning of such vases was made by E.C. Portale **[9]** followed by another paper (2014) concerning the musical imagery inherently connected to the Centuripan imagery **[8]**, completed with the terracotta figurines associated in funerary contexts in contrada Casino necropolis, published in the meantime by A. Musumeci (2010) **[19]**.

Finally, recently (end of 2015) the researchers of CNR-IBAM and University of Catania made research on the characterization of the pigments on the vases from Libertini collection in the Museum of Catania, of which an extensive catalogue was made for the first time **[20]**.

I.3 Historical Outlines-Places of discovery

The Centuripe vessels are called after the origin source of their manufacture in the small hill town of Centuripe, about twenty miles southwest of Mount Etna in eastern Sicily **(fig 1)**. It was Sikel native city increasingly influenced since the Archaic period by Greek culture. The city retained its independency in 339 B.C. and then had to submitted to Rome in 263 B.C. After proclaiming it as a free and immune city, and owing to this privileged condition in the Roman province, it came into light as one of wealthiest cities in Sicily between the third century and early imperial period. In particular, it had at disposal the rich agricultural lands lying in the plain of Catania and near the Etna volcano **[3,12]**. The significant position of the

Centuripe city has been extensively exposed when the archaeological excavations started to take place in its necropolises which revealed a series of highly interesting decorated, and polychromatic vases. Only few of them have been survived.

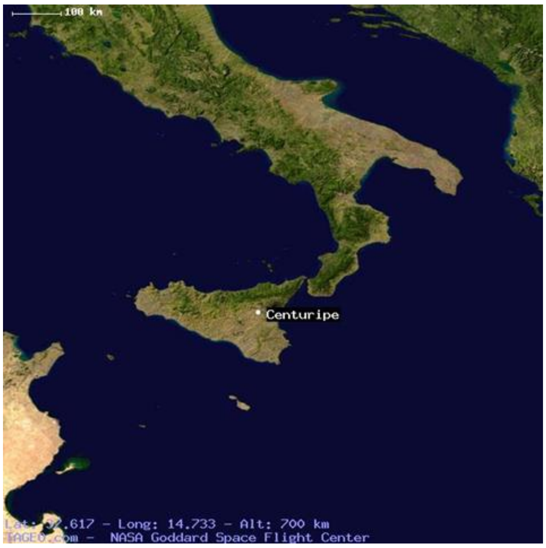


Fig.1: The location of Centuripe town in Sicily -Italy. The photo retrieved from http://www.tageo.com/index-e-it-v-15-d-m177866.htm.

Essentially the Centuripean vessels are yielded from Contrada-Casino necropolises that are located at the east of Centuripe at a distance of ca. 1.5 km. Two types of tombs were observed: the simple tomb with rectangle shape, the long sides of which were lined with polygonal walls and unpaved ground, and the second type of tomb which seems to be for successive burials of roman date with a larger chamber and paved floor and painted wall. The excavation works of the necropolis have been made mainly in 1912, 1918 and 1932 by P. Orsi but the contents have been published just recently by A. Musumeci, for the tombs with terracotta figurines. Previously, G. Libertini had published the vases which had been excavated by G. D'Amico.

Coins and other artifacts such as unguentaria and terra-cotta statuettes have been yielded as a context with the vessels and give the necropolises chronology of the Hellenistic period of around the third to the first century B.C **[3]**.

The contents from seven tombs in contrada- Casino containing polychromatic vessels have been studied by Deussen **[3]** (tomb VII, tomb 18bis, tomb 25, tomb 31, tomb 33, tomb 40bis, and tomb I Monte Porcello). Within some polychromatic vessels in different shapes were besides other artifacts including coins in some tombs. All the contents were yielded due to the excavation in 1942 and published by Libertini. All the vessels from those tombs are displayed currently in Syracuse museum. Additional Centuripe vessels particularly in lebes and pyxis shape were yielded in three tombs of which the (illicit) excavations are unrecorded. Some of the vessels are presented in Salinas Archaeological Museum in Palermo and the other are distributed among Rome, Paris and the Metropolitan Museum in New York.

I.4 Places of conservation: musea and collections

All the Centuripe vessels, whether yielded from regular excavations or from antiquarian markets or from private collection, are predominated mainly in Syracuse and Palermo museums, some of them with no available recorded information about the circumstances of finding **[3]**. Few isolated pieces are in Paris, London, Berlin, Karlsruhe, Princeton, Boston, and the Metropolitan Museum in New York which already possess five; most of them are in a rather bad state of preservation **[2,12]**.

Catania museum contains the private collection of G.Libertini, the scholar who for many years guided excavations mainly in Centuripe **[20]**.

I.5 Problems of interpretation

Many discussions and controversies have been raised among the scholars about the authenticity of the Centuripe vessels due to many reasons that could be classified as the following:

1) Due to the shortage of scientific excavations at Centuripe, that were carrying out without stratigraphical record of the context, and the secret digging which were taking place by popular in the purpose of looting and thieves, the associated findings were insignificant. Consequently, many of the vessels found their way to the antiquarian market then ended in public museums with no significant contextual information. One good example is the splendid ciborium which is presented in the Metropolitan Museum in New York, it was in the antiquarian market and the results of the investigation that have been done on it revealed that it comes certainly from Centuripe **[12,20]**.

2) The bad preservation state that resulted in missing most the important parts and colored scenes that have been applied with no fire. All of that lead to unclear or false chronology **[3]**.

3) Incompetent restoration by unskilled hands or repainting by unauthorized painter, aiming to increase the value of the vessels, that obstruct the interpretation of the scene. The ciborium with scene of epaulia (n. 211) that was introduced in the exhibition held in Syracuse in 2012, demonstrates the repainting and retouching of the vases aiming to increase the value of the piece in order to appear in a good condition: comparing it with old photos reveals many retouched and intervention works which have been conducted to this piece in many areas on the painting scene **[20]**.

Two different hands, which according to Deussen, were involved in the production of the pyxis vase no 152 in the Museum of Fine Arts in Boston **[11]** give a clear example using different hands and different techniques at the same vase.

4) The production of vases of somewhat similar shape, scenes, added colors by other workshops not using the local matrix (raw materials). For example, the Lipari group consists mainly of Skyphoid Pyxides, Lekanides, and Lebetes Gamikoi in red figured technique with richness of added colors produced by the same workshop and the same painter of Lipari and have the same general symbolism of the painting scenes (marriage) as the Centuripe vessels **[2]**.
5) The most important problem for the Centuripe vessels, that was discussed greatly in the recent study of Catania collection **[20]**, is the widespread of some well-organized workshops of counterfeiters (especially at Centuripe) creating modern replicas of the original vessels that being hardly recognizable from the original vessels since that the same shape and the same colors were imitated by skilled forgers for trade purposes in the black markets. One of the skilled forgers who has workshop particularly producing Centuripe false vessels is Antonino Biondi, who was with other painters, imitating and creating the same shape and sometimes using the same raw materials and making the same decoration and appearance in order to attract the public to buy and own it.

However, the main activity of counterfeiters of Centuripe is limited to the period of the formation of the Libertini Collection and some decades on, Antonio Biondi was continuing in the imitation until the second half of the twentieth century when the affirmation of thermoluminescence in archaeology was confirmed.

The vessels in the Libertini collection in Catania museum are either copied of forgeries bought from the black market or retouched. The ciborium vessel (no 203) **(appendix 1 plate II fig 8)** from Libertini collection illustrates that it is original comparing to an old one in spite of the incorrect repainting that has been made by unskilled people which was revealed by the study and the investigation of the color. Simultaneously another ciborium with the same shape and same decoration was found in antiquarian market **[20]**.

Also another example is illustrated in Portale study **[8],** the case of a Pyxis in Bern of which Jost was able to reconstruct the original scene with the infrared technique. It is existed already on the antiquities market of Monaco **(appendix 1 plate III fig 9)**.

CHAPTER II Ceramic of Centuripe in the Archaeological Museum of Palermo

II.1 Genesis of the collections

The polychromatic vessels in Salinas Museum are primarily produced from the illicit excavation that have been done in Centuripan necropolis and were published then by Libertini in 1926. Some of the vessels in Salinas museum are yielded particularly from a context which was unified by Deussen as "tomb 8" **[3]**.

The archaeological finds that have been found in the so-called tomb 8 are distributed among Salinas museum – one Pyxis and one Lebes (no. 71, 81)-, while one Pyxis (no. 34) and one finial of a Lebes (no. 69) are in the New York Metropolitan Museum. All the four pieces from this group belong to different workshop and consequently different painters. All the pieces are dated back by Deussen to the period 280-270 B.C. that reflect the possibility of utilization as presents at a single occasion; this chronology, however, has been disputed by subsequent bibliography, supporting a later date (end of the 3rd century- beginning of the 2nd century).

According to Deussen **[3]** and depending on the variety of the plastic decoration, classification of the manufacture of different shapes of Centuripe vessels is made into five workshops (1, 2, 3, 4 and unidentified workshop) with four different painters (Tendril-Altar Master, Medusa D-Veil Master, Gorgon-portrait master, and Dionysos painter).

Based on this criteria, classification of the collection in Salinas museum is divided as the following:

a) workshop 1 by Tendril-Altar Master:

- lebes no. 71 from the so-called tomb 8, fully developed shape 4 ca. (280-263 B.C.) ht. 51 (with foot 74), dia. 31
- lekanis no. 100 late developed shape 5; ca. (263-230 B.C.) (case no. 3003/96), ht. 61, dia. 42

b) workshop 1 by the Medusa D-Veil Master:

- lekanis no. 57, ht. 43 (incl. foot), dia. 60 (incl. handles), lid belongs to lekanis no.100 (supra, P.280) fully developed shape 4 ca: 280-263 B.C.

c) Workshop 2 by the Gorgon-portrait master:

- lebes early developed shape 3; ca. 289-280 B.C. lebes no 26 Palermo, private collection, Pisani, now lost ht. ca. 50, dia. ca. 42

d) Workshop 4 by the Dolphin coroplast:

- Lebes pyxis fully developed shape 4; ca. 280-263 B.C., lebes no. 81 from tomb 8, ht. 53, dia. 36

e) Unidentified workshop (s):

- finial nos (154, 155, 156)
- lebes foot no. 160

II.2 Typological classification of the artifacts

Currently in Salinas Archaeological Museum there are four Centuripean vessels **(appendix 1 plate III fig. 10)**

- Pyxis: no. 81 as Deussen record **[3]**, K57 in Wintermeyer **[18]**, NI#2237 in Salinas Arch Mus.
- Lebes Gamikos no. 71 as Deussen record **[3]**, K82 in Wintermeyer **[18]**, NI#2235 in Salinas Arch Mus.
- Lekanis without lid NI#2236
- Lekanis NI#2231 with lid NI#2236 erroneously put.

Two among the above mentioned vases were studied in this thesis (Pyxis no. 81 and Lebes Gamikos no. 71). Pyxis vessel is labeled as vessel (A) and Lebes Gamikos is labeled as vessel (B).

- ***Description the Pyxis vase (NI#2237 in museum, K57 in Wintermeyer's corpus, no. 81 in Deussen dissertation) (appendix 1 plate IV fig 11)***

Firstly, it is evident from the weight and volume of the two vessels that they have been fundamentally used as gifts or for funerary purposes **[3, 8, 9]**. They are the contents from the same tomb 8, as Deussen classified **[3]**, that means they have been for a single occasion and should be contemporary. Secondly, the decoration both painted and relief is confined to the front side of the vase, it must have been intended to stand against a wall.

Pyxis vessel is classified as the production of workshop 4 under the Dolphin coroplast. It is of fully developed shape **[3]** in which the vase losses its functionality and had become only for showplace. It is made in three parts: the finial egg, the lid, and the vase body. The Pyxis, derived from Sicilian Skyphoid Pyxis pot- shape **[3]**, is a common shape among the Centuripean vessel. It was probably found in tomb 8 in contrada Casino.

Shape: The body of the vase is standing on a relatively high foot and handle-less. The lid is in domed shape, removable and covered on the top by a removable finial egg shaped with an inventory number NI≠2232 **(appendix 1 plate IV fig. 12, 13)**

Painted scene: The painted scene is restricted only on the front view of the body; it is slightly being recognizable due to the bad preservation state **(appendix 1 plate IV fig. 14)**. On the body we can distinguish a painted scene, represented by two figures (they seem to be two women), one figure in yellow dress and the other in white dress looking at the same direction but one is sitting and the other is standing near her stretching her hand probably either carrying a musical instrument or handing her something as a gift. This scene corresponds both processional and epaulia scenes as Deussen proposed **[3]**. The Pyxis is about 73 cm high.

The painting on the lid is also limited in the front of the lid. Only two figures could be distinguished, a blue with greenish shade sinuous animal in an anguiform shape and a seated white marine horse (might be only horse with green tail).

Decoration: architectural decoration is observed around the rim of the body. The body is decorated from the bottom above the foot surrounding in a bead and reel design then with a plastic vegetative foliage decoration (acanthus and blossoms leaves put alternately), while the upper of the body vase around the rim bears a plastic architectural decoration in the lowermost, a molding of leaf and tongue design, the cornice frieze directly above the lowermost decorated with lion-head spouts and rosettes, the cornice is crowned by a molding of bead and reel design around the lip of the vase. The lid is decorated with a cornice decoration in the surrounding lower part and at the top end of the lid, surrounded with plastic friezes in the lower part showing marine motif such as golden dolphins, hippocamp. The final egg is embedded in a ring of acanthus leaves.

- ***State of conservation of Pyxis vase***

The vase is partly preserved. It seems that has been subjected to prior restoration and previous intervention due to the clear colored filled incision that are evident to the naked eye. Some of the decoration in the lid and the rim of the body vase are missed in addition to the absence of part of the painted scene and the colors in both the body and the lid possibly due to possibly bad preservation state.

- ✓ The lid

As seen from the **(Fig. 2 a, b)**, the lid is covered with a white layer, particularly the colored areas in the rear side are completely covered, that make it quite difficult to distinguish the different color areas. The decoration is very abraded. Parts of the yellow and golden decoration (dolphins) have been missed or removed and some appear to have been reattached. Due to some distinctive small fractures that existed in the lid, one can discern that the background of the original pottery is red tending to brick color.

a)

b)

Fig. 2: (a) shows the rear side and (b) shows the front side of the lid of Pyxis vessel A in Salinas Museum in Palermo

The painting scene of the lid is painted against dark red background and it is partly damaged and not well preserved. The central part of the lid is tinted with a reddish pigment on which have been designed, for overlapping backgrounds of some figures. The images have the blacks contours or in some cases the same gnawed background. The embossed details are covered with gilding that have a yellow ocher layer preparation at several points still very compact. This layer in some areas is of brown color, probably due to a form of alteration. The lid has undergone a restoration as it is possible to observe from the stucco that affect the gaps and incision. These were filled with a "mortar" pigmented in a slight reddish hue that takes the color of the clay. On the inside of the lid it is not possible to observe these incisions because the lid has been entirely covered with an orange substance **(fig. 3 a-d)**.

a)

b)

c)

d)

Fig. 3: different profiles show the bad preservation state of the lid

✓ The body

The vase body is completely covered by a thin white layer. The central part of the body of the vase has the same reddish (pink) pigment present on the lid. It is noted that the figures that are represented in this area are obtained fairly savings, taking advantage of the bottom of the white color, and the details and the contours are made with a delimiting black pigment.

Fig. 4: the outside and inside view of the body of vase A.

It seems from the gradual hue of the red color that there are two different red hues, the light red hue which is the background which is most used and the darker in many places such as on a detail of a figure, under the band with relief decoration, the neck of the vase, and in some places on the leaves that decorate the front part.

On the rim of the top of the body of the vase A, the blue pigment is altered by taking a darker color. The surface is abraded and very dusty. The vase seems to have undergone a previous restoration, there are several gaps in an orange color in light hue. The foot of the vase has undergone numerous additions and was subjected to the body of the vase through a thick grout that can be observed even from the inside **(fig. 4)**

- ***Description of the Lebes Gamikos vase (NI#2235, K82, no. 71) (appendix 1 plate IV fig 15)***

Shape and decoration: It is classified as the production of workshop 1 under the Tendril-Altar Master. It is of fully developed shape 4. It is made in two parts, the lid and the vase body. It is reputed by Deussen to come from the findings in the so-called tomb 8.

The vase stands on a modeled tall foot and stem. Between the foot and stem and the body sits a disc support. At the bottom of the body, immediately above the disc, there is a molding decorated with a leaf- and dart pattern. Above the molding is a ring of foliage comprising a combination of acanthus leaves alternating with long lotus petals in well-developed form, and in between, small buds and rosette flowers. All the foliage in the ring was made separately and applied on the surface of the vessel. The acanthus leaves and probably the lotus were painted pink and some gold, the rosettes are yellow- gold.

The decoration on the top of the body is characterized by the Doric frieze. A line of astragal, or bead-and-reel, the metopes containing little erotes are placed surrounding the rim of the vessel applied against the dark blue background of the metopes, the astragal, the triglyphs, and the figures are picked out in gold. The metopes are made from the same series of molds and attached against a blue background. Among the erotes, some seem to run and others to fly. Above the frieze, and slightly raised above the background surface, is a flat zone painted in red color as well lion heads are alternating above the frieze. Those objects are gold against a dark blue background which seems to have had pink applied over. The lid has domed shape with a hole in the center. There is no decoration or painted scenes on the lid, therefore, it represented only the ceramic composition.

Painted scene: basically the Lebetes of workshop 1 display processional scenes **[3]**. The scene on the body dominated the front view of the body. The whole is painted against a pink background. Much of the lower part of the scene has suffered damage. The composition is made up of two figures (women). the first figure on the left is wrapped in a pale yellow himation. Her face turns toward the center. The second woman with a red himation and brown tied hair turns her face toward the first woman, stretching her right hand in the opposite side **(appendix 1 plate IV fig. 16)**

- ***State of conservation of Lebes Gamikos vase***

There is no decoration or any other distinguishable colors on the lid of the vessel (B). In the upper edge of the vase, the plating is covered by a brown layer very compact. At the top rim of the body vase both the blue pigment and the gilding of the relief decorations are well preserved.

Also in this case the figures are formed in savings from reddish pigment bottom. There are two red colors used here, the light red of the background and the dark one used for the mantle of the central figure.

Compared with the vessel (A) the pictorial decoration is less dusty and shinier and smooth. This may be given either by a better state of preservation or due to a protective applied during the restoration. There are stucco traces and the foot of the vase has undergone many reinstatements.

Objective of the study

The authentication and the verification of the antiquity of an object is a great challenge in archaeology and in the world of art. Even if the visible part of an object of culture heritage is the most attractive aspect for admirers of arts, the full knowledge of it from the manufacturing to its usage and history constitutes the main focus for archaeologists and historians. The first question that keeps asking is that "are we looking to an authentic objects or to a reproduction?" **[21]**. Therefore, the authenticity is becoming one of the most crucial issues that should examine when the object is a rare relic. The authentication can be determined by the characterization of the materials such as pigments since their historical use is well documented **[22]**. Moreover, the characterization of the pigments would be greatly help in recognizing the original layers with respect to the later retouches or repainting.

The authenticity of the Centuripean painted vessels has been the object of vivacious argument and a challenging issue that has to be justified since the Centuripe vessels are considered a rare testimony of the ancient Greek-Hellenistic tempera painting **[3]**. The Centuripe vases are abundant on the antiquarian market without any documents asserting their originality. This situation raised the question about the range of credibility and reliability as to the authenticity, knowing that the false are very similar to the original vases whether in the form, iconography and paint used. Not so many surveys have been performed regarding their authenticity. The main problem is that the imitation and the fake of Centuripe vases are widely prevailing.

More and further investigations need to be performed; particularly for the inventoried vessels whether they are from excavation works or from antiquaries.

The main objective of this study is to judge the authenticity, distinguish any restoration treatments that have been applied onto the vessels through identifying the pigments and the preparatory layers, without forgetting that they could be retouched using the latest and modern pigments **[23]**. This provided, in addition, the opportunity to evaluate and verify the painting technique that was used.

This goal was achieved through the use of non-invasive and in-situ investigations on the painted surface of two Centuripean vases (Pyxis and Lebes Gamikos) in Salinas archaeological museum, Palermo-Italy.

Centuripe vases are considered as fabricated by five different workshops with four painters **[3]**. Therefore, they can be considered to be heterogeneous vases and may have undergone different evolutions and modification according to local manufacturing conditions.

Since we are aimed to characterize the pigment used and to find hint or any information that might give an indication about the painting technique a complementary combination of two techniques, Portable X-Ray Fluorescence (PXRF) and reflectance Fourier Transformed InfraRed (FTIR) spectroscopy, was used.

The results of this study lead to increased value of previous results and improve the archaeological knowledge. In addition, the results would be extremely useful to art historians and conservators to understand the evolution of painting techniques and interventions that have taken place over time; they will be also useful for further investigations or to plan proper restoration interventions. Simultaneously the results could enhance the virtual access to collections and inventories of the museum, to assess the state of the items gathered for conservation planning and management of cultural heritage.

PART II – ARCHAEOMETRY

1. Investigation strategy

From a methodological point of view the scientific community has reached a common proposal that can be defined as a Standard Operating Procedure (SOP) for the application of portable non-invasive techniques for in-situ analyses.

In the SOP it is suggested not to simply apply the techniques one after the other but it is suggested that to enhance the result of a single technique it is necessary to relate the results of each technique to the preceding ones and to the subsequent ones thus producing an organic set of self-explanatory data **[24]**.

In-situ and ex-situ analyses are the two basic strategies for investigating painted layers **[25]**. In situ analysis is performed directly on the artifact by using portable non-invasive techniques. These allowed a spread "sampling" of the surface layers to a certain depth thus making available results, that even if at a lower resolution as compared to those available with laboratory techniques, allowed a fully characterization of the artifact. Only in cases of no clear conclusion it is necessary to proceed with a micro sampling on which ex-situ analyses can be applied.

Another of the advantages of using portable non-invasive techniques lies on the possibility to perform analyses even if the object is a part of an exhibit in a museum. In fact, in this case the sampling is forbidden and the transport poses serious problems regarding the integrity, preservation and security of an art object.

Many studies concerning the identification of the chemical elements characteristic of the pigments have been based on the use of XRF spectroscopy. Among them, XRF has been applied on investigating the traditional mural painting of 18th century in Korea **[26]**; on miniatures of the Italian miniaturist Napolene Verga **[27]**. Szokefalvi et al show the powerful application of XRF spectroscopy to find out the fake in the painting in Hungarian National Gallery **[28]**. Ferrero et al. **[29]** demonstrates the application of portable XRF in quick detection of the inorganic elements that compose the yellow pigments in altarpieces at Museo de Bellas Artes of Valencia-Spain.

Numerous studies have been conducted by using FTIR in reflectance mode in the culture heritage field and have been mainly focused in the identification of pigments. C. Ricci et al.

[30] by using a fiber optic mid- FTIR reflectance have identified the materials in two Italian marble work of art from Parma and Firenze. M. Bacci et al. **[31]** illustrates the powerful of reflectance IR in identification of both painted layers with different binding media and the identification of varnish layer in prepared layered samples. D. Buti et al. **[32]** have performed reflectance IR in mid and near regions to invasively characterize the green pigments in different types of artwork.

Most of research on painting techniques and characterization of pigments are non-invasively conducted by coupling several techniques. As an example, Miliani C. et al. **[33]** performed an investigation and exploited the potential benefits of the use of multi technique (XRF and IR in different modes) on the Pierre-August Renoir painting "Woman at her toilet." The combination of XRF and FTIR coupled with principal component analysis (PCA) **[34]** confirms the powerfulness of using this multi technique approach to identify the pigments and the fillers used in two paints of Paul Cézanne.

2. Analytical protocol

Two Centuripean vessels (Pyxis and Lebes Gamikos) in Salinas Archaeological Museum in Palermo-Italy were analyzed in this study.

Once supposed, on the basis of archaeological information, that their decorations have been realized by tempera technique, complementary techniques must be utilized in order to have a fully identification of the organic binding media and of the inorganic pigments.

The combination of Portable X-ray fluorescence and total reflectance FT-IR techniques are a powerful tool for the complementary analysis of organic and inorganic components in the painting layers. The following analytical protocol was employed in the investigation of the pigments in Centuripe vases:

- Elemental analysis was carried out on selected points by applying P-XRF.
- Molecular identification was carried out on selected points by applying Total Reflectance FT-IR spectroscopy.

The procedure of in-situ measurements was applied by following the SOP:

- General visual observations on the vases were taken in collaboration with a restorer in order to clarify the present state of the vases and to identify the analysis points.
- Photos have been taken for each vase under study.

This allowed getting documentation on the actual state of the vases and taking trace of the analysis points.

- P-XRF measurements on some points from the different colored zones in Pyxis vase A (body, lid, and finial egg) (see appendix 4 fig.1(a) for the analyzed parts and appendix 4 fig. 2-6 for the analysis points).
- P-XRF measurements on some points from the different colored zones in the body of Lebes Gamikos B (see appendix 4 fig. 2 (b) for the analyzed parts and appendix 4 fig. 7 for the analysis points).
- TR FT-IR measurements on some points of Pyxis vase A (body, lid, and final egg) (see appendix 4 fig. 8-10 for the TR FT-IR analyzed points in vase A).

The results will, eventually, be used to plan further measurements devoted to find answers to unclear or new arising questions.

CHAPTER III - Physical chemical analytical methodologies

III.1 X-ray Fluorescence Spectroscopy (XRF)

X-Ray Fluorescence is a primary technique that applies widely in the field of culture heritage **[35]**. Numerous properties make XRF spectroscopy a popular and favorable technique for both the scientists and the archaeologists. The first and more important property is the availability of portable XRF instruments that can be easily used in museums for examination of the art works. Besides it is a combination of non-invasive and non-destructive analysis with no sample preparation involved. The data acquisition is fast and the detectors used have good resolution **[35]**. Additionally, it is a multi-element technique with the capability to identify a wide range of the periodic table elements with high sensitivity. XRF is a relatively inexpensive technique and could be applied for various types of samples.

However, the representation of the sample and its homogeneity is a critical parameter that affects the uncertainty of the total measurement besides the morphology, uniformity, moisture contents and surface conditions of the artifacts **[36]**. XRF spectroscopy is not a perfect tool for analyzing the light elements (lighter than Na with atomic number Z=11) due to the weak X-ray emitted by them that are absorbed by few centimeters in air and few micrometers in the sample bulk **[37]**. The measurements of the light elements must be carried out under vacuum **[35]**. XRF usually is used for qualitative elemental analysis. To perform quantitative and semi quantitative analysis is necessary to use laboratory instrumentation with the aid of standard samples. No indication or information about the form of molecules and crystals could be achieved **[37]**

Regarding the portable XRF, generally the P-XRF analysis is undertaken on a sample area of a few mm^2, depending on the beam spot size. The X-ray penetration depth depends on the compositional nature of the material of which is composed the object **[35]**. Therefore, the analysis is considered to be a surface analysis and mainly dependent on its conditions.

The basic physical principles are based on the excitation of the atom by irradiation with incident primary X-ray photon having enough energy to subtract an electron from the inner K or L shells of the atom. This event generates an excited ion that is stabilized by a process in which an electron from the upper shells (L or M….) falls to fill the hole in the lower shell by emitting the excess energy as a secondary X-ray photon whose energy, depending on the energy of the involved electronic levels, is characteristic of the element. This characteristic X-ray is evidenced as a peak in the XRF spectrum of intensity versus wavelengths or energy **[38]**. In order to identify the presence of an element all the characteristic lines of a series (i.e. K series, Kα and Kβ) must be present in the proper intensity ratio. The intensity of photons of a particular line, as well as their energy, depends on the probability of the corresponding transition involved. The probability of a transition, as well as the corresponding energy, increases with the atomic number. This implies that, on increasing the atomic number, a peak series is detected at higher energy with a higher intensity. Due to their electronic structure, only elements from the second period of the periodic table can undergo this fluorescence process. In detail, all elements of the second period show only the K series at low energy (lesser than 3 keV) and low intensity. The elements from the third period can display both K and L series or even M series.

However, the detection of a line series in a spectrum depends on the properties of the material under analysis and on the instrumental set up. Only X-rays generated within the critical penetration depth range **[35]** can be detected. Depending on the source properties and on the range of available energies, the K series or the L series or both are detected.

The experimental set up for the acquisition of P-XRF spectra consists of an X-ray source, a detector and a multichannel analyzer. In order to avoid the peaks overlaps and interferences that can be caused by either the source, the detector or the matrix effects, the detector is a silicon drift one allowing detection at high resolution and higher count rates **[39]**. The multichannel analyzer is coupled with the software for element identification, background subtraction, and peak evaluation.

III.2 Fourier Transformed Infra-Red Spectroscopy (FTIR)

The vibrational spectroscopies are used to identify molecules in organic materials and molecules as water [H_2O], bound atom clusters such as carbonate group [CO_3^{2-}], hydroxyl groups [OH^-], silicate groups [SiO_4^{4-}] and others, in inorganic materials. The IR wavenumber (20-14000 cm^{-1}) range is enough to cover energies that promote transitions between fundamental and excited vibrational modes from the vibrations involving heavy atoms up to the breathing modes in polymers. Therefore, IR spectroscopy is a powerful technique to examine the vibrational states of the molecules and to identify the compounds. A change in the electric dipole moment that accompanies the vibrations makes the molecules active in the IR range **[40]**.

The infrared spectral range is subdivided into three regions **[40]**:

- NIR: is the closest to visible radiation (λ = 750−2500 nm, n = 13300−4000 cm^{-1})
- MIR: with the wavenumber between (λ = 2.5−20 µm, n = 4000−500 cm^{-1})
- FIR: which is the closest to microwave radiation (λ = 20−1000 µm, n = 500−10 cm^{-1})

The NIR range is used to identify the organic bands based on the combination and overtones of the -OH, =CH- and =NH. The MIR is the region where the vibrational modes of functional groups of organic molecules and of molecular anions of inorganic compound can be identified. FIR is the region where the crystal lattice vibration and the vibrations of molecules containing heavy atoms are detected and is helpful for characterizing compounds containing halogen atoms, organometallic compounds and simple inorganic compounds that contain light atoms such as NaCl, KBr, ZnSe **[41, 42]**.

Depending on the purpose of the analysis and the type of the sample, basically two methods can be used for performing the IR measurements: transmission and reflection.

The IR spectrum in transmission mode is acquired by measuring the amount of IR photons absorbed or transmitted as a function of the frequency. This method is commonly used with liquid, solid and gaseous samples. It is applied widely for quantitative calculation depending on the Lambert Beer law **[40, 43]**.

The IR spectrum in reflection mode is acquired by measuring the amount of IR photons reflected by a surface. Reflection methods can be divided into two categories, internal reflectance or so-called attenuated total reflectance (ATR) and external reflectance. The reflection methods are usually widely used for studying the surface or the coating of samples **[44]**.

Internal reflectance (ATR-IR) is applied for thick-layered samples that can be examined directly in the solid or liquid state without further preparation. The internal light reflected by the layer of the sample can be reflected through a small ATR crystal in direct contact with the sample **[40]**.

External reflectance enables collecting the specular reflection from smooth surfaces directly (specular reflectance) and also enables collecting the reflection from a rough surface, even powdered sample, (diffuse reflectance, DRIFT) **[40,44]**. Specular reflectance occurs when the angle of the incident radiation is the same as the angle of reflected radiation. The yielded reflected light depends on many parameters: the angle of the incident radiation, the refractive index of the material, the surface roughness and the absorption properties of the sample. Since the reflected IR spectra appear composed by 'derivative-like' bands, in order to have a corrected spectrum that appears like the familiar transmission spectrum, the IR reflectance spectra is corrected by using a Kramers–Kronig transformation (K–K transformation) **[44]**.

The diffuse Reflectance (DRIFT) involves reflection, diffraction, scattering, absorbance and transmittance reflection that occurs when the radiation penetrates the surface of the sample and reflected in all direction. It is applied to the rough surfaces. The depth of the penetration depends upon the angle of the incidence, the roughness of the sample, the sample geometry and the sample absorptivity. Being unknown the path length, a quantitative calculation is difficult. It is particularly useful for powdered samples mixed with KBr. The main disadvantage of the reflectance technique is due to the low signal-noise ratio as a consequence of the difficulty to collect all the reflected light from the surface of the sample **[45]**. It is a nondestructive method with fast sample preparation.

The infrared spectroscopy is an easy, fast and relatively inexpensive method. Due to its sensitivity it is commonly used for studying many types of samples including solids, liquids, gases, polymers, organics, inorganics, biological materials, pure substances and mixtures. Moreover, only small amount of sample is requested to perform an analysis. The availability of extensive databases of reference IR spectra makes the interpretation of the IR spectra quite easy. The FT-IR technique can be applied only to "active" materials and this constitutes a limit of the technique. Another limit derives from the contamination by water and other contaminants as CO_2 that cause contributions to the spectra and can lead to confusion during interpretation **[46]**.

III.2.1 Infrared reflection Spectroscopy (Total reflection FTIR)

The MIR is almost the most used region in the IR spectroscopy since many molecules have strong absorbance in this region **[46]**. The mid reflection FTIR has been become a primary tool employed successfully for the identification of art and archaeological materials particularly in the identification of pigments and organic compounds used as pigment binders and in the identification of inorganic phases, minerals, and restoration materials **[40]**. The portability coupled with the low acquisition time and the non-invasive measurements allows the technique to be employed as in-situ technique.

Both specular (surface) and diffuse (volume) refection contributes to a reflection IR spectrum. These two contributions result in many odd and distortions of band shape, position and intensity that make the reflectance IR spectra difficult to interpret. In the specular reflection there are two types of spectral distortion that produce derivative-like features (organic compounds) and inverted or Restrahlen bands (inorganic compounds). In the diffuse refection some effects originate from the absorption process that give some differences of relative band intensities **[47]**.

Therefore, both the specular and diffuse reflections are affecting the total IR reflection spectral features and depend on the optical properties of the materials and the roughness of the surface. As a consequence, an optical flat surface will provide a greater amount of the specular light while rougher surfaces will generate mainly diffuse reflected radiation. As a result, the interpretation of the reflection spectra would be a quite complicated issue due to the coexistence of derivative shape bands, Reststrahlen effect, and intensity enhancement. This makes the application of Kramers-Kronig and Kubelka-Munk corrections impossible **[47]**.

III.2.2 Interpretation of mid-IR spectra

Several factors may complicate the interpretation of IR spectra and may lead to misinterpretation of bands **[48]**:

- Overtone and Combination Bands: Overtone bands in an infrared spectrum are multiples of the fundamental absorption frequency and usually the first overtone appear at twice the wavenumber of the fundamental. Combination bands arise when two fundamental bands absorbing at ν_1 and ν_2 absorb energy simultaneously. The resulting band will appear at ($\nu_1 + \nu_2$) wavenumbers.
- Fermi Resonance
- Coupling
- Vibration–Rotation Bands.

The Mid IR region is divided into four different frequency regions and each region has the specific bands that help to assign the unknown molecules:

- 4000-2500 cm^{-1} region for characterizing the X-H bands including =C-H-, =N-H and -O-H.

- 2500-200 cm^{-1} region for the triple bonds.
- 2000-1500 cm^{-1} region for the double bonds.
- 1500-400 cm^{-1} fingerprint region that mainly contains the characteristic bands for the functional groups of molecules.

The position, the shape and the frequency have to be taken into account in the interpretation of the spectra. In order to optimize and improve the identification of compounds in a complicated sample as painted ceramics, spectral subtraction can be followed. It consists in identifying one component then eliminating or excluding its characteristic bands from the next identification for the remaining of the unknown bands. Once identified the most significant compounds, the procedure can be stopped taking into account that it is not necessary to identify all the bands present in the spectra **[49]**.

CHAPTER IV - Experimental Investigation and Results

1. X-Ray Fluorescence Spectroscopy

1.1 Instrumentation.

Energy dispersive X-Ray fluorescence analysis was carried out using a portable spectrometer Tracer III SD Bruker AXS. The detector is a 10 mm^2 silicon drift X-Flash detector with Peltier cooling system and resolution of 145 eV at 100,000 cps. The source is a Rhodium Target X-Ray tube operating at 40 kV and 11 mA, with two different filters allowing a good sensitivity both at lower and higher energies (up to Ba K - lines). Each spectrum was acquired for 60 s and a window of 3-4 mm diameter determines the analyzed spot. No vacuum has been performed in the head of the instrument. Under these conditions the portable instrument allows the detection of elements with atomic number higher than Na ($Z > 11$). The window of the instrument is placed in contact with the sample surface. The S1PXRF® Software rules the data acquisition. The spectra interpretation has been performed using the X- ray software (ARTAX®).

1.2 Identifying of spectra.

XRF measurements have been undertaken on various points from the different colored zones in Pyxis (vase A body, lid, and finial egg) and on some points from the different colored zones in the body of Lebes Gamikos (vase B body). Due to the high number of analyzed points the following criterion has been established to univocally identify them.

The Pyxis, vase A, is composed of three parts that have been identified by a different symbol as follows: egg part symbolized as E, lid part symbolized as L and body part as B. The Lebes Gamikos, vase B, is composed by one part, the body symbolized as B. A progressive Arabic number identifies each analysed point. To take into account the spectroscopic techniques used, an initial capital letter has been used: X for P-XRF and R for FT-IR.

Each analyzed point, on the above basis, is identified by three capital letters: the first letter to identify the technique, the second the vase (A or B) and the third, separated by underscore from the previous, to identify the part of the vase. As an example, the XA_E2 identifies the point number 2 in the egg of vase A on which P-XRF measurement has been undertaken.

1.3 Results and data elaboration.

All P-XRF spectra are reported in appendix 3. As an example, a typical spectrum is shown in figure 5. In the same figure the attribution of line energy to a peculiar transition of an element is reported.

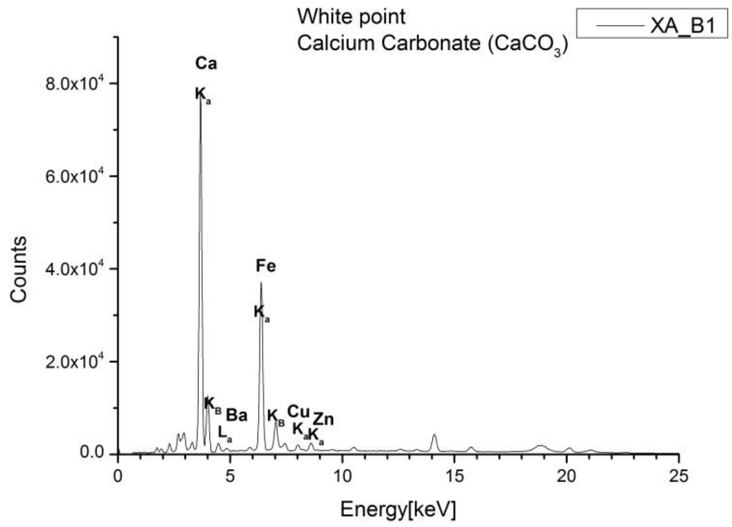


Fig. 5: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the white point (XA_B1) of the body of vase A. Attribution of some of the lines to the emitting elements is shown.

The element identification has been performed by using the ARTAX® software. The presence of Zr and Ar in some spectra arises from contribution from the inner walls of the instrument and from the environment, respectively. The presence of Rh, Rb and Pd are contribution from the source and the detector.

The area of the peaks was calculated by integration after background subtraction using the fitting procedure provided by the ARTAX® software.

Areas have been normalized after eliminating contributions from Zr, Ar, Rh, Rb and Pd. The normalized area is expressed as percent of the total net area.

The computed values are organized in tables. For comparison reasons, each table group results related to a color. The color of the area was decided after visual observation performed by the restorer. The major elements are those whose percent is bigger than 10%, the minor elements are those whose percent is lesser than 10%. As an examples in table 1 are shown the computed values for the points acquired on the egg of vase A.

Table. 1 PXRF results obtained from the egg points of vase A expressed as percentage of the net area.

Analyzed points	Area %														Ca/Fe
	Major elements		Minor elements												
	Fe	Ca	Sr	Ni	Ti	Si	K	Mn	Zn	Ba	S	Pb	Cu	Al	
XA_E24	55.09	30.80	4.03	1.42	1.81	1.70	2.76	0.80	0.56	0.20	0.21	0.05	0.25	0.12	0.56
XA_E25	49.04	38.60	4.27	1.28	1.40	1.38	1.80	0.66	0.25	0.24	0.43	0.10	0.19	0.14	0.79
XA_E26	56.60	28.13	5.53	1.70	1.89	1.76	1.36	0.75	0.36	0.45	0.69	0.07	0.27	0.25	0.50
XA_E27	56.13	30.41	4.57	1.42	1.76	1.31	1.81	0.62	0.39	0.33	0.64	0.10	0.23	0.09	0.54

All results are reported in tables 2, 4, 6, 8, 10, 12, 14, 16, 18 for vase A and tables 20, 22, 24, 26, 28, 30 for vase B, in appendix 2.

Semi quantitative analysis is limited by several considerations such as the uncertain thickness of the painting layer, the dilution of the pigments with the organic binding media that in turn influence the real concentration of the pigments and inhomogeneous distribution of the paintings. Notwithstanding, once known that the measured XRF radiation comes mostly from the surface painting layer and from the underlying layers depending on the thickness and the absorption properties of the materials **[50]** the following criteria were followed to suggest the presence of a pigment:

- the detection of a specific element that characterize the pigment.
- The presence of a certain group of elements that suggests the presence of a particular pigment.
- The presence of an element with relatively high intensity as compared with the same element detected in other analyzed points having the same color.

These criteria allowed identifying inorganic mineral or synthetic pigments, or even give a hint of the presence of organic pigments.

The results of this procedure are reported in tables 1, 3, 5, 7, 9, 11, 13, 15, 17 for vase A and tables 19, 21, 23, 25, 27, 29 for vase B, in appendix 2. In each table the analyzed point, a short description of the point, the color and the suggested pigment are reported. As an examples in table 2 are reported the results of the above procedure for the points acquired on the egg of vase A.

Table. 2 Analyzed points and their position, color of the investigated area and guessed pigment as inferred from PXRF results for Egg in the vase A.

Analyzed points	Position	Color	suggested pigments
XA_E24	Inside border edge under egg	White	No pigment
XA_E25	The rear side of egg	White	No pigment
XA_E26	The front side of egg	White	No pigment
XA_E27	Outside border edge egg	Gray	No pigment

However, the poor preservation state of the vases and the small quantity of the remaining pigments and in some points the limitations of the techniques in identify the light elements pose a barrier to identify the pigment used in all the selected analyzed points.

1.4.1 Vase A

a) Egg points

Four different selected points were analyzed in the egg parts. Three of them are considered to be white colored (XA_E24, XA_E25, XA_E26), the fourth point is considered as a gray point (XA_E27).

The elemental composition of the egg points is similar to each other (Table 1). The major elements in the egg points are iron and calcium. Strontium, nickel, silicon, potassium and titanium are considered to be minor elements with percent between 1 and 10%, zinc, barium, sulfur, manganese, lead, copper and aluminum are considered as trace elements (percent lesser than 1%)

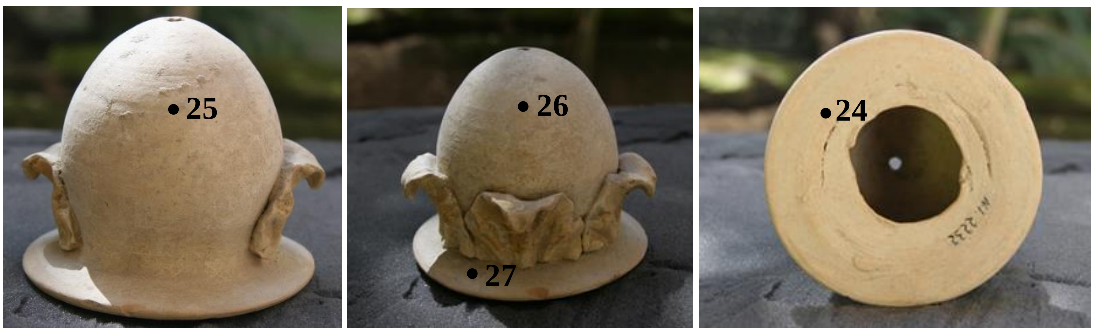


Fig. 6: XRF egg points in vase A

The high percentage of Fe followed by Ca suggests that these elements are the major components of the matrix compounds.

No element characteristic of a particular pigment has been detected (Table 2).

b) White points

Six points from various white areas in different hues in vase A (lid and body) were analyzed. Points XA_L6, XA_L7 were from the white part of the marine horse in the painting scene in the front side of the lid of vase A (appendix 4 fig. 3). Points XA_L17, XA_L19 were from the white area in the rear side of the lid (appendix 4 fig. 4). Point XA_L16 was from the border inside the lid (appendix 4 fig. 5). Point XA_B1 was from the body of the vase A (appendix 4 fig. 6).

The elemental composition of the white points is summarized in table 4 of appendix 2. The major elements in the white points are iron and calcium.

High contributions of Zn, Ba and S are observed in the points XA_L6 and XA_L7 thus suggesting the presence of lithopone ($ZnS+BaSO_4$) as the white pigment.

The higher intensity of calcium relatively to the intensity of iron in the points (XA_L17, XA_L16, XA_L19, XA_B1) suggests the presence of calcium based white pigments in those areas. Due to the sulfur presence, the use of calcium sulfate can be guessed in the points XA_L17, XA_L16.

Regarding the point XA_L16, lead has been detected as minority element. Its presence could be considered as a contamination from the orange neighbor area inside the lid.

Regarding the point XA_B1, copper has been detected as minority element. Its presence could be considered as a contamination from the black neighbor area, i.e. the black outline in the figure in the body of vase A. Also notable contributions for Zn and Ba could be explained as a presence of small quantity of $ZnS+BaSO_4$ (lithopone) as a white covered layer above or mixed with the $CaCO_3$ layer.

c) Red points

Six red points from the vase A were examined: two of them were from the body and four were from the lid. Points XA_L2, XA_L4, XA_L8 were located in the front side of the lid (appendix 4 fig. 3) and point XA_L18 was located in the pink area of the rear side of the lid (appendix 4 fig.4). Points XA_B2, XA_B6 (appendix 4 fig. 6) were located in the pink background and in the red top background of the decoration of the body, respectively.

The elemental composition is summarized in table 6 of appendix 2. The major elements are iron and calcium. The minor elements are Sr, Ni, Ti, Mn, Si, Zn, Ba, S and K. Traces elements are Cu and Pb.

The high percent of Fe relatively to Ca in the points XA_B6 and XA_L2 indicates the presence of red ochre as the red pigment.

The red ochre is applied as a red pigment in different hues in the front lid points XA_L4, XA_L8 and in the red point in the rear side of the lid, XA_L18. The different hues could be ascribed to the erosion of the red layer because of the bad preservation (appendix 4 fig. 3) or to a coverage of the rear side of the lid by a thin white layer (appendix 4 fig. 4).

d) Blue greenish points

Three points from blue greenish areas from the front of the lid, XA_L1, XA_L3 and XA_L21 (appendix 4 fig. 3) and two points from white greenish area in the rear side of the lid, XA_L22 and XA_L23 (appendix 4 fig. 4) were examined.

The elemental composition of the blue greenish points is summarized in table 8 of appendix 2. The major elements are iron and calcium even if in different ratios from point to point.

Considering only the most predominant elements, being the Fe is the most abundant element in the points XA_L21, XA_L22 and XA_L23, the greenish shade might be due to the contribution of green earth. As far as the points XA_L1 and XA_L3 are concerned, the high content of Cu detected is an indication of the presence of a Cu-based pigment. Probably, copper blue $Cu(CH_3CO_2)_2.2Cu(OH)_2$, Egyptian blue ($CaCuSi_4O_{10}$) or azurite ($2CuCO_3.Cu(OH)_2$) could be used. Moreover, the addition of lead oxide cannot be excluded based on the amount of Pb detected.

It has to be noticed that the points XA_L21, XA_L22 and XA_L23 are shaded by a white patina (appendix 4 fig. 3,4). By considering the high percentage of Ca, Zn and S that might allow suggesting the presence of zinc white (ZnO) and calcium sulfate in the patina.

e) Orange points

Four points from orange areas were examined. One from the front of the lid, point XA_L5 (appendix 4 fig. 3), one from the rear of the lid, point XA_L20 (appendix 4 fig. 4), and two from the inside the lid, points XA_L12, XA_L13 (appendix 4 fig.5).

The elemental composition of the orange points is summarized in table 10 of appendix 2. The major elements are iron and calcium. The minor element Mn, Si, Ni, Sr, S, Zn, Ba, Zn, K, Cu and Pb are present in appreciable different amounts in the points XA_L12, and XA_L13.

The high content of Pb detected in the points XA_L12 and XA_L13, indicate the presence of a lead based pigment, probably read lead, Pb_3O_4, that give the orange color.

By considering the most predominant elements detected in the points XA_L5 and XA_L20 we could suggest that the orange color in light hue is due to a mixture of iron oxide and calcite with small quantity of lithopone.

f) Gray points

Three gray points from the lid of vase A were analyzed. Point XA_L9 is from the top surface back of the lid (appendix 4 fig.3), the points XA_L14 and XA_L15 are on the border edge of the inside lid (appendix 4 fig. 5).

The elemental composition of the gray points is summarized in table 12 of appendix 2. The major elements are iron and calcium. The minor elements are Zn, Ba, S, Ni, Sr, Si, Mn and Ti and traces elements are Cu, Pb, and Al. The composition that can be inferred from the percentage of elements in these points is comparable with those of the bulk.

A notable intensity of Zn, Ba and S in the points XA_L9 and XA_L15 suggests the presence of small quantity of lithopone (white color) besides the iron oxide in those two points.

g) Yellow, golden points

Four yellow, golden points were analyzed. Two points were from the lid: the first one is the golden point XA_L10 and the second one is the yellow point XA_L11 from the decoration (appendix 4 fig.3). Two points were from the body: the golden point XA_B5 in the top decoration and the yellow point XA_B3 in the yellow dress of the figure (appendix 4 fig. 6).
The elemental composition of the yellow, golden points is summarized in table 14 of appendix 2. The major elements are iron, calcium, with a high intensity of iron as compared to calcium, and golden in the points XA_L10 and XA_B5.

The distinctive strong contribution from Au indicates the presence of golden leaves in the points XA_L10 and XA_B5. Moreover, from the high percent of iron with respect to calcium we could suggest the use of the red bole beneath the metallic layer and the preparation layer. The presences of traces of Ag suggest that the gold has been refined from alloys containing silver. The primary metal had undergone a refining process consisting of two stages: a first stage of separation of the precious metals from the base metals followed by parting the gold from silver. The refining process of the primary metal was a common practice over classic to Hellenistic and roman periods **[51]**.

The high percent of Fe relatively to Ca in the yellow points XA_L11 and XA_B3 indicate the presence of yellow ochre, natural limonitic $Fe_2O_3.H_2O$. Moreover, the contribution of Zn, Ba and S in the point XA_B3 indicate the presence of small quantity of lithopone mixed with yellow ochre.

h) Black point

Only one black point, XA_B4, was analyzed from the body of the vase A (appendix 4 fig. 6).

The elemental composition of this point, summarized in table 16 of appendix 2, illustrates the main contribution from Ca, Fe and Cu and trace of Pb besides the minor contribution from Sr, Ni, Zn, Ba, S, K and Mn. The copper presence suggests the use of copper oxide in drawing the outline of the figures of the painting scene even if the presence of charcoal or carbon should not be excluded.

i) Stuccatura point

The so-called Stuccatura point is referring to the suspected intervention area that the vases have been subjected to during possible previous restoration. The Stuccatura points were chosen with the help of the restorer during the preliminary inspection.

One Stuccatura point, XA_B7, that appeared orange colored in the top of the body vase A (appendix 4 fig. 6) was investigated. The elemental composition is summarized in table 18 of appendix 2. The main contribution come from Fe followed by Ca, the minor contributions were from Sr, Ni, Si, S, Ba and Zn, traces of Cu, Mn and Pb were also detected, the notable contribution of Zn, Ba and S besides the high intensity of Fe followed by Ca indicates the application of lithopone together with hematite mixed with calcite.

1.4.2 Vase B

a) White point

Only one point from the white area in the side view of the background in the body of vase B (XB_B7) was analyzed (fig. 7 in appendix 4). The elemental composition of this point is summarized in table 20 of appendix 2. Basically this point is composed of calcium followed by the iron and minor contributions from S, Sr, Ni, and K. Besides traces of Cu, Pb, Ba, Ti, Mn, Si, Al and Zn were detected.

The composition indicates the presence of Ca-based pigment, probably calcium carbonate or calcium sulfate with the presence of iron oxide in small quantity that justify the pale white color.

b) Red points

Two red points were analyzed. The point XB_B1 is from the dark red dress of the figure and the point XB_B2 is from a pink area from the background of the painting scene (fig. 7 in appendix 4). The elemental composition is summarized in table 22 of appendix 2. The major elements were Ca, Fe and Hg (point XB_B1), minor contributions were from Sr, Ni, Mn, Zn, S and traces were from Cu, Pb, Al, K, Ti and Si.

The high percentage of Hg detected for the point XB_B1 indicates the presence of vermilion or cinnabar (HgS) as the red pigment.

No particular elements were detected from the pink point XB_B2 thus the color could be attributed to the mixing of the calcite with hematite.

c) Golden point

One point from the golden decoration, point XB_B6 was analyzed (fig. 7 in appendix 4). The elemental composition is summarized in table 24 of appendix 2. Iron, calcium and gold are the major elements with minor contribution from Sr, Ni, Zn and traces of Cu, Pb, K, S, Ba, Mn, Al and Si.

The distinctive high percent of gold indicates the applying of a golden leaf for the decoration. The percentage of Fe suggests the applying of the red bole beneath the metallic layer as a preparation layer. No traces of silver were found in this point.

d) Brown points

Two brown points were analyzed. The point XB_B3 is from the hair of the figure and the point XB_B5 is from the brown decoration in the top rim (fig. 7 in appendix 4).

The elemental composition is summarized in table 26 of appendix 2. Calcium and iron are the major elements, the Sr, Ni, Zn, K and S are the minor elements and Si, Ba, Ti, Pb, and Cu are traces elements.

By considering the contribution of Fe and the notable contribution of Mn in the point XB_B3 it is possible to suggest the use of the brown ocher ($Fe_2O_3.H_2O$) mixed with the manganese oxide (MnO_2) as the brown pigment.

As far as the point XB_B5 is concerned, no particular element is present. This could be consequence of the scraping of the pigment layer because of the bad preservation state of this vase.

j) Blue point

Only one point (XB_B4) was analyzed from the top background of the decoration (fig.7 in appendix 4).

The elemental composition is summarized in table 28 of appendix 2. The main contribution comes from Ca and Fe. Sr, Ni, Zn, Ba, Mn, Ti, Pb and Cu are present as minor elements, K, S, Si and Al are present as traces elements.

The high percent of both nickel and copper together with the high percent of Ca could allow suggesting the use of copper based pigment together with nickel oxide as the blue pigment. Moreover, the small amount of Pb could be assumed as an indication of the use of finely crushed copper blue glass in agreement with the indication of Deussen **[3]**.

k) Stuccatura point

The Stuccatura point (XB_B8) is considered to be the point of an intervention in the lower area of the base (fig. 7 in appendix 4).

The elemental composition is summarized in table 30 of appendix 2. The major element was Zn besides the strong contribution of Ba, Ca and Fe (percent more than 10%), and Sr, Ni, Pb and S as minor elements and traces of Cu, Mn and Si.

The distinctive contribution of zinc allows suggesting the use mainly of the zinc white in this intervention area together with a thin layer of lithopone. The contribution of the matrix (calcite and hematite) could justify the brick orange color. Probably, a small contribution of lead oxide in order to obtain the wanted hue has to be considered.

2. Experimental Reflectance-FTIR Spectroscopy

1.4 Instrumentation.

A portable Bruker ALPHA spectrometer was used to record the FTIR spectra. It is made up of a Globar IR radiation source, a Rocksolid® interferometer and a DTGS (Deuterated TriGlycine Sulfate) detector. The overall dimensions of the instrument are 30x12x20 cm^3. Spectra were acquired in the range 5900-360 cm^{-1} at a resolution of 4 cm^{-1}. The spectrometer allowed an excellent signal to noise ratio throughout the range used even for short acquisition time as long as 60 sec (the acquisition time used for data collection in the present work). The operations were performed using the software OPUS 7.5®.

The spot size on the investigated sample was of 1 cm^2 area. The instrument was kept perpendicular to the sample surface (normal geometry) using a Manfrotto tripod equipped with a special frame that support the instrument and avoid vibrations during measurements. The instrument is kept in contact with the point analyzed. The total reflectivity, R due to the combined diffuse and specular components, was collected using the spectrum from a golden mirror plate for background correction. Spectra were expressed as function of pseudo-absorbance A\` where A\`= log(1/R).

1.5 Results and data elaboration.

The IR measurements were performed only on the Pyxis vase A in the three parts (egg, lid, body) (fig. 1A in appendix 4) from several colored areas. The points analyzed in the egg, lid and body part is shown in figures 8-11 in appendix 4.

IR spectra have been numbered by following the criterion described in paragraph 1.2.

All IR spectra are reported in appendix 3. As an example, a typical spectrum is shown in figure 7. In the same figure is indicated the attribution of the peaks to the molecules that have been identified.

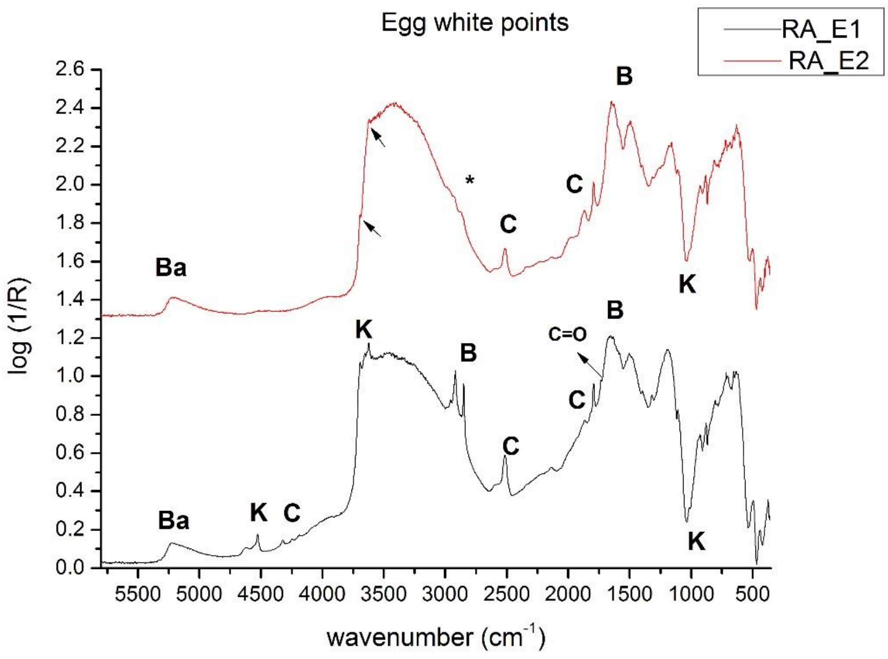


Fig. 7: reflection spectra of the egg points (RA_E1, RA_E2) in vase A characterized by k=kaolin, C=calcite, Ba=basanite, and B=organic binder

Since the mid infrared range covered in this study is between 6000 and 500cm^{-1}, in order to interpret the reflectance spectra, the experimental spectra were divided into three regions:

1) The finger print region between 2000–500 cm^{-1}.

2) Region between 3500 and 2800 cm^{-1} that includes C-H, N-H and O-H stretching modes as well as combination and overtone modes of some inorganic anions (carbonates and sulfates).

3) Region between 6000 and 3900 cm^{-1} mainly including combination and overtone bands **[52]**.

Due to the physical limits expressed in paragraph III.2.1, the analysis of IR spectra is complicate. As a consequence of the distortions induced in the shape, position and intensity of the band by the specular and diffuse reflectance contributions to the overall spectrum **[47]**, the first-order bands that usually are used for the identification of the vibration modes in the transmission spectra were not employed in the present work. The procedure followed to elaborate the spectra is as follows:

- the bands were identified by taking into account the presence of combination (sum or difference of fundamental bands) and overtones bands. This allowed identifying the inorganic materials such as silicate, carbonate and sulfate **[47]**.

- the combination and overtone bands of SO_4^{-2} ($\nu_1 + \nu_3$ SO_4, $2\nu_3$ SO_4; $\nu_2+\nu_L$ H_2O) in the range 2500-1900 cm^{-1} and the combination band of OH^- (ν_1/ν_3 OH+ν_2 OH) in the range 5000-5300 cm^{-1} were used to distinguish between the state of hydration of the sulfate minerals (bassanite and gypsum) **[53]**
- the kaolin was identified by comparison with the spectrum from IRUG database **[54]**
- once eliminated the contributions due to the identified compounds, the remaining bands were attributed
- shift between 10-15 cm^{-1} in the bands position were attributed to the mathematical correction applied during the evaluation of the spectra, as well as to the presence of reflection distortions, which shift the fundamental vibrations. Typically, for example, this phenomenon is common in reflectance spectra of sulfates **[47]**.

The band position, their attribution and the identified compound are enrolled in table 3. The identification of the organic binding media has been based on the results of Miliani et al **[47, 52, 55-57]**.

Table. 3 Band position, assignment to a vibration mode and identified compound.

Band position (cm^{-1})	Assignment	Compounds
1800 2512, 2594 sh 4264	• $\nu_1 + \nu_4$ (CO_3^{-2}) • $\nu_1 + \nu_3$ and/or $_2\nu_2 + \nu_4$ (CO_3^{-2}) • $_3\nu_3$ (CO_3^{-2}) and $\nu + \delta$ (OH)	Calcite ($CaCO_3$)
2010 2114, 2132 2230 5064, 5140	• $_2\nu_1$ SO_4 • $\nu_1 + \nu_3$ SO_4 • $_2\nu_3$ SO_4; $\nu_2 + \nu_L$ H2O • ν_1/ν_3 OH+ν_2 OH	Gypsum ($CaSO_4.2H_2O$)
2014 2093, 2134 2218 5212	• $_2\nu_1$ SO_4 • $\nu_1 + \nu_3$ SO_4 • $_2\nu_3$ SO_4; $\nu_2 + \nu_L$ H2O • ν_1/ν_3 OH+ν_2 OH	Bassanite ($CaSO_4.0.5H_2O$)
2900-2800 3300-3280 3090 1500-1800 1650 1550 1450 4330, 4260	• CH stretching • NH stretching • First overtone of amide II(ν_1) • little evident shoulder C=O • Amide I • Amide II • Amide III • ν+& (CH)	Organic binding
1100-1010 3600 4523	• Si-O stretching mode • OH stretching • Combination band ν +δ(OH)	Kaolin ($(AlSi_3,Si_4)O_{10}(OH)_2$)

1.5.1 Vase A

a) Egg points

Two different selected points were analyzed in the egg part (fig. 8). Both are considered to be white colored (RA_E1 and RA_E2). The IR spectra (appendix 3 fig. 25) show the presence of:

Fig. 8: IR white egg points in vase A, (RA_E1) in the front side of egg, and (RA_E2) in the inside border of egg.

- A sharp combination band (ν_1+ν_4) at 1798 cm^{-1} for RA_E1 and at 1788 cm^{-1} for RA_E2, respectively; a combination band, $\nu_1 + \nu_3$, centered at 2512 cm^{-1} with a shoulder at 2601 cm^{-1} for both points; an overtone $_3\nu_3$ and a combination $\nu+\delta$ (OH) at 4251 cm^{-1} for the point RA_E1. Those signals were attributed to Calcite ($CaCO_3$).

- A combination band ν_1/ν_3 OH+ν_2 OH at 5222 cm^{-1} in both points that indicate the presence of bassanite ($CaSO_4.0.5H_2O$).

- The Fundamental Si-O stretching mode at 1033 cm^{-1}, the double O-H stretching at 3623 and 3705 cm^{-1} and the combination band ν +δ(OH) at 4528 cm^{-1} in the point RA_E1 that indicate the presence of kaolin.

- The Doublet C-H at 2851-2929 cm^{-1}, the C=O at 1733 cm^{-1} and the amide I and II at 1650-1508 cm^{-1} that are to be attributed to the organic binder.

Despite the macroscopic similarity among the two points some differences between the intensity and the profile of some bands were observed: the double O-H stretching in point RA_E2 is not well observed (indicated by small arrows in figure 25) in point RA_E1. The spectrum of point RA_E1 lacks of the OH combination band at 4523 cm^{-1} of kaolin.

Moreover, the organic medium in this point is characterized only by the presence of amide I and II. This suggests that the organic binder in point RA_E1 is made of whole egg while in the point RA_E2 might be another protein binder **[55]**. The presence of a synthetic material, covering some of the combination bands of kaolin and some bands of the organic binder cannot be excluded. The molecular composition of the analyzed point is summarized in table 4.

Table. 4 the molecular composition of the egg points as inferred from IR spectra.

The analyzed points	IR molecular compositions
RA_E1	Calcite, kaolin, egg, bassanite
RA_E2	Calcite, kaolin, glue or casein, bassanite

b) White points

Four white points from the lid of vase A were analyzed. The points RA_L1 and RA_L2 are from the rear side of the lid (fig. 9b in appendix 4) and the points RA_L3 and RA_L4 are from the front side of the lid (fig. 9a in appendix 4). One white point, RA_B4, is located in the white part of the figure in the scene of body vase (fig. 10 in appendix 4).

The IR spectra (appendix 3 fig. 26) show the presence of:

- A sharp combination band ($\nu_1+\nu_4$) at 1798 cm^{-1} in the points RA_B4, RA_L1 and a lesser intense one in the point RA_L4; a band at 1788 cm^{-1} in the points RA_L2 and RA_L3. A combination sharp band, $\nu_1+\nu_3$, centered at 2512 cm^{-1} with a shoulder at 2601 cm^{-1} for all the points except for the point RA_L4 where it is a small band without shoulder; a weak and small band $_3\nu_3$ (CO_3^{-2}) and $\nu+\delta$ (OH) at 4248 cm^{-1} in the point RA_L4. Those signals were attributed to calcite ($CaCO_3$).

- A combination band ν_1/ν_3 OH+ν_2 OH at 5222 cm^{-1} in the points RA_L1 and RA_B4 indicate the presence of bassanite ($CaSO_4.0.5H_2O$).

- A combination band ν_1/ν_3 OH+ν_2 OH at 5164 cm^{-1}, $\nu_1+\nu_3$ SO_4 at 2126cm^{-1}, $\nu_2+\nu_L$ H_2O at 2232 cm^{-1}, a broad band of OH bending mode ν_2 at 1668 cm^{-1}. One resolved band for the antisymmetric stretching ν_3 mode of SO_4 at 1132 cm^{-1} appeared as inverted band, the antisymmetric bending ν_4 appeared as split of two resolved bands at 684, 626 cm^{-1}, the OH stretching at 3544 cm^{-1}in the points RA_L2, RA_L3 and RA_L4 indicate the presence of gypsum ($CaSO_4.2H_2O$).

- The fundamental Si-O stretching mode in the region 1012-1033 cm^{-1}, the double OH stretching at 3613 - 3695 cm^{-1} and the combination band ν +δ(OH) at 4528 and 4539 cm^{-1} indicate the presence of kaolin.

- The double C-H stretching in the regions 2850-2860 and 2920-2930 cm^{-1} in all the points, C=O at 1737 and 1733 cm^{-1} in all the points except RA_B4, amide I at 1648 cm^{-1} in the points RA_L1, RA_B4, amide II at 1518, 1508, 1518 cm^{-1} in the points RA_L3, RA_L2, and RA_B4 respectively, in addition to the presence of ν+& (CH) at 4320-4248 and 4330-4258 cm^{-1} in the points RA_L3, RA_L4, respectively. All of those bands identify the organic binder, whole egg **[53]**.

In the point RA_B4 the band of C=O might be covered by the intense band of the CO_3^{-2} from the mineral calcite **[55]**.

Bassanite is observed only in two points RA_L1 and RA_B4 while gypsum $CaSO_4.2H_2O$ is identified in the points RA_L2, RA_L3 and RA_L4. Its presence was inferred from the enhancement of the second order and combination bands in the region 1900-2200 cm^{-1} and the hydrated combination bands in the region 5140 cm^{-1} **[53]**. The calcite bands might be covered in the point RA_L4 by the presence of gypsum in higher amount as compared as to the other points RA_L3 and RA_L2 (appendix 3 fig. 27b). By comparing the spectra points that evidences the bands of bassanite and of gypsum (appendix 3 fig. 27 a, b) there is a splitting of the degenerate vibrations due to the presence of gypsum **[47]**. The enhancement of the combination bands in the range 1900-2700 due to the diffuse reflection is clearly evident in the RA_L2, 3, 4 points **[53]**

Table. 5 the IR molecular composition of the white points

The analyzed points	IR molecular compositions
RA_L1	Calcite, kaolin, egg , bassanite
RA_L2	Calcite, kaolin, egg , gypsum
RA_L3	Calcite, kaolin, egg , gypsum
RA_L4	Calcite, kaolin, egg , gypsum
RA_B4	Calcite, kaolin, egg , bassanite

c) Red points

Four red points were analyzed. Point RA_L5 is located in the red background of the front side of the lid (fig.9a in appendix 4), point RA_L11 is located in the rear side of the lid in a light red area (fig. 9b in appendix 4). The point RA_B1 is located in the pink background of the body, the point RA_B6 is in the brick area color in the figure (fig. 10 in appendix 4).

The IR spectra (appendix 3 fig. 28) show the presence of:

- A sharp combination band (ν_1+ν_4) at 1795 cm^{-1}; a combination ν_1+ν_3 sharp band, centered at 2512 cm^{-1} with a shoulder at 2601 cm^{-1}. Those signals were attributed to calcite ($CaCO_3$). The enhancement of the combination bands in the range 1900-2700 due to the diffuse reflection is clearly evident in the RA_L11 point **[53]**

- A combination band ν_1/ν_3 OH+ν_2 OH at 5212, 5200 and 5222 cm^{-1} in the spectra from the points RA_L5, RA_B1, and RA_B6 that indicate the presence of bassanite ($CaSO_4.0.5H_2O$).

- Combination bands ν_1/ν_3 OH+ν_2 OH at 5174 cm^{-1}, ν_1 + ν_3 SO_4 at 2133cm^{-1}, ν_2 +ν_L H_2O at 2225 cm^{-1}, a board band OH bending mode ν_2 as at 1658 cm^{-1}, one resolved band for the antisymmetric stretching ν_3 mode of SO_4 at 1122 cm^{-1} appeared as inverted band, the antisymmetric bending ν_4 appeared as split of two resolved bands at 705 and 637cm^{-1}. In addition, in the points RA_L11 the OH stretching at 3555 cm^{-1} indicates the presence of gypsum ($CaSO_4.2H_2O$).

- The fundamental Si-O stretching mode in the region 1018-1033 cm^{-1}, the double OH stretching at 3623 - 3695 cm^{-1} and the combination band ν +δ(OH) at 4528 and 4539 cm^{-1} in all the red points indicate the presence of kaolin.

- Sharp and double C-H stretching at 2850-2860 and 2920 cm^{-1}, C=O at 1735, 1730 and 1732 cm^{-1} in the points RA_L5, RA_B6, and RA_L11, respectively; amide I at 1658, 1689 and 1668 cm^{-1} in the points RA_L5, RA_B1, and RA_B6, respectively, amide II at 1569, 1518 cm^{-1} in the points RA_B1 and RA_B6 in addition to the ν+& (CH) band at 4322-4251, 4320-4250, 4321-4250 cm^{-1} in the points RA_L5, RA_B6 and RA_L11, respectively. All of those bands identify the organic binder.

Kaolin, calcite, organic binder and bassanite were identified in the body points RA_B1 and RA_B6 and the red lid point RA_L5. Gypsum was identified besides the main components kaolin, calcite and organic binder in point RA_L11.

Binder media is whole egg in the points RA_L5, RA_L11 and RA_B6. While in the point RA_B1 either a protein based binder can be indicated **[55]**. For the last point it can be drawn the hypothesis that another organic material that cover the surface result in a very tiny profile of CH bands and cause the absence of C=O absorption and of the OH bands of kaolin in the region 3600 cm^{-1}.

Table. 6 the IR molecular composition of the red points

The analyzed points	IR molecular compositions
RA_L5	Calcite, kaolin, egg, bassanite
RA_L11	Calcite, kaolin, egg, gypsum
RA_B1	Calcite, kaolin, egg or glue, bassanite
RA_B6	Calcite, kaolin, egg, bassanite

d) Blue greenish points

Two blue-greenish points from the lid RA_L9, RA_L10 were analyzed in the sinuous animal in an anguiform shape of the painting scene (fig.9a in appendix 4).

The IR spectra (appendix 3 fig. 29) show the presence of:

- A weak combination band ($\nu_1+\nu_4$) at 1788 cm^{-1}; a weak combination sharp band $\nu_1 + \nu_3$ centered at 2512 cm^{-1} with a small shoulder at 2591 cm^{-1}. Those signals were attributed to calcite ($CaCO_3$).

- A combination band ν_1/ν_3 OH+ν_2OH at 5202 cm^{-1} indicates the presence of bassanite ($CaSO_4.0.5H_2O$).

- The double OH stretching at 3623 - 3695 cm^{-1} and the combination band $\nu + \delta$(OH) at 4526 cm^{-1} indicates the presence of kaolin.

- Sharp and doublet C-H at 2850-2919 cm^{-1}, weak shoulder C=O at 1730 cm^{-1}, amide I at 1648 cm^{-1}, small doublet ν+& (CH) at 4322-4250 cm^{-1}. All of those bands identify the organic binder.

- Combination bands ($\nu + \delta$) of Si–O at 1887 cm^{-1} and tiny peaks at 1160, 1077 and 1010 cm^{-1}. All those peaks indicate the presence of Egyptian blue based on the study made by Miliani **[47]** and on reference **[58]**.

The main composition of the blue greenish points is kaolin, calcite, bassanite and organic binder.

Table. 7 the IR molecular composition of the blue greenish points

The analyzed points	IR molecular compositions
RA_L9	Calcite, kaolin, egg, bassanite, egyptian blue
RA_L10	Calcite, kaolin, egg, bassanite, egyptian blue

e) Yellow points

Three yellow points were analyzed from different areas in the lid and the body. Point RA_L6 in the yellow decoration in front of the lid (fig. 9a in appendix 4), point RA_B2 is located in the yellow dress of the figure in the body, point RA_B5 in the top yellow area of the body (fig. 10 in appendix 4).

The IR spectra (appendix 3 fig. 30) show the presence of:

- A combination band (ν_1+ν_4) at 1797 cm^{-1}; a combination sharp band, ν_1 + ν_3, centered at 2512 cm^{-1} with a small shoulder at 2601 cm. Those signals were attributed to calcite ($CaCO_3$).

- A combination band ν_1/ν_3 OH+ν_2 OH at 5222 cm^{-1} in the points RA_B2, RA_B5 that indicate the presence of bassanite ($CaSO_4.0.5H_2O$).

- A combination band ν_1/ν_3 OH+ν_2 OH at 5174 cm^{-1}, ν_1 + ν_3 SO_4 at 2133cm^{-1}, ν_2 +ν_L H_2O at 2225 cm^{-1}, broad doublet band of OH bending mode ν_2 at 1689 and 1627 cm^{-1}, one resolved band for the antisymmetric stretching ν_3 mode of SO_4 at 1122 cm^{-1} appeared as inverted band, the antisymmetric bending ν_4 is appeared as split of two resolved bands at 695, 637cm^{-1}, the OH stretching at 3544, 3435cm^{-1} in the point RA_L6 that indicate the presence of gypsum ($CaSO_4.2H_2O$).

- The fundamental Si-O stretching mode at the region 1021-1029 cm^{-1}, the double OH stretching at 3623 - 3695 cm^{-1} and the combination band ν +δ(OH) at 4528 cm^{-1} indicate the presence of kaolin.

- Weak and doublet C-H at 2851-2919 cm^{-1}, weak shoulder C=O at 1737 cm^{-1} in the point RA_B2, amide I at 1668, 1658 cm^{-1} in the points RA_B2, RA_B5 respectively in addition to the presence of small doublet ν+& (CH) at 4323-4250 cm^{-1} in all the points. All of those bands identify the organic binder: whole egg in the point RA_B2 and another protein binder, probably glue, in the points RA_L6, RA_B5 **[55]**.

Bassanite was identified in the points RA_B2, RA_B5 while gypsum was identified in the point RA_L6. Kaolin and calcite were identified in all the points.

Table. 8 the IR molecular composition of the yellow points

The analyzed points	IR molecular compositions
RA_L6	Clacite, kaolin, glue, gypsum
RA_B2	Clacite, kaolin, egg, bassanite
RA_B5	Clacite, kaolin, egg, bassanite

f) Gold and reddish points

Two points in the lid golden decoration were analyzed. Point RA_L7 is located in the reddish layer beneath the golden layer in the decoration of the lid and point RA_L8 is the golden point located in the decoration lid in the front side of the lid (fig. 9a in appendix 4).

The IR spectra (appendix 3 fig. 31) show the presence of:

- A weak combination band (ν_1+ν_4) at 1798 cm^{-1}; a combination weak band, $\nu_1 + \nu_3$, centered at 2512 cm^{-1} with a small shoulder at 2591cm^{-1} in the point RA_L8; a combination weak band, $\nu_1 + \nu_3$, centered at 2512 cm^{-1} without shoulder in the point RA_L7. Those signals were attributed to calcite ($CaCO_3$).

- A combination band ν_1/ν_3 OH+ν_2 OH at 5181 cm^{-1}, the evident combination and overtone bands for the SO_4^{-2} and H_2O in the range 2335-2126 cm^{-1}, one resolved band for the antisymmetric stretching ν_3 mode of SO_4 at 1112, 1101 cm^{-1} appeared as inverted band in the points RA_L and RA_L8, respectively; the OH stretching at 3404 cm^{-1} indicates the presence of gypsum ($CaSO_4.2H_2O$).

- Small and un inverted fundamental Si-O stretching mode in the region 1012-1023 cm^{-1} in the points RA_L7, RA_L8, the double OH stretching at 3613 - 3695 cm^{-1} and the combination band ν +δ(OH) at 4528 cm^{-1} indicate the presence of kaolin.

- Weak and doublet C-H at 2851-2919 cm^{-1}, amide I at 1617 cm^{-1}, amide III at 1450 cm^{-1}. Those bands identify the organic binder as another protein binder, possibly glue.

The two IR spectra of the reddish and golden points are very similar to each other. The reflectance from those two points mainly come from the diffuse reflection that could suggest that the particles of the surface (rough) have dimensions similar to the infrared radiation wavelength **[47]**. Neither Reststrahlen bands nor derivative feature bands were observed thus excluding the specular (surface) reflection **[47]**. All the bands of the IR spectra of those points are similar to the bands registered in absorption mode thus suggesting contribution of absorption from the golden layer and from the preparation layer beneath it. The main composition of those two points is gypsum and kaolin. Calcite is present but its weak bands suggest that it is covered by the gypsum layer.

Table.9 the IR molecular composition of the golden, reddish points

The analyzed points	IR molecular compositions
RA_L7 (reddish)	Calcite, kaolin, glue, gypsum
RA_L8(gold)	Calcite, kaolin, glue, gypsum

g) Stuccatura points

Two points from the intervention areas in the rear side of the lid RA_L12(fig. 9b in appendix 4) and in the orange area RA_B3 (fig. 10 in appendix 4) at the base of the body of vase A were analyzed.

The IR spectra (appendix 3 fig. 32) show the presence of:

- A weak combination band (ν_1+ν_4) at 1788 cm^{-1} and a combination weak band, $\nu_1 + \nu_3$, centered at 2512 cm^{-1} with small shoulder at 2591 cm^{-1} in the point RA_B3 while in the point RA_L12 it can be distinguished a weak combination band (ν_1+ν_4) at 1792 cm^{-1} and a combination weak band, $\nu_1 + \nu_3$, centered at 2512 cm^{-1} without shoulder. Those signals were attributed to calcite ($CaCO_3$).

- A combination band ν_1/ν_3 OH+ν_2 OH at 5143 cm^{-1} and a small shoulder at 5065 cm^{-1} in the point RA_L12 and only band at 5154 cm^{-1} without shoulder in the point RA_B3, $\nu_1 + \nu_3$ SO_4 at 2126, 2116 cm^{-1} in the points RA_L12, RA_B3, respectively; $\nu_2 + \nu_L$ H_2O at 2225 cm^{-1} in the two points, OH bending mode ν_2 appears as a broad band at 1648, 1658cm^{-1} in the points RA_L12, RA_B3, one resolved band for the antisymmetric stretching ν_3 mode of SO_4 at 1132 cm^{-1} appeared as inverted band in the point RA_L12, the antisymmetric bending ν_4 appeared as split of two resolved bands at 715, 616 cm^{-1} in the point RA_L12 and 715, 606 cm^{-1} in the point RA_B3, the OH stretching at 3565, 3500cm^{-1} in the points RA_L12. All of those signals indicate the presence of gypsum ($CaSO_4.2H_2O$).

- The fundamental Si-O stretching mode at 1023 cm^{-1}, the OH stretching at 3675 cm^{-1} in the two stuccatura points that indicate the presence of kaolin.

- Sharp Doublet C-H in the region 2850-2919 cm^{-1}, C=O at 1737 cm^{-1} in addition to the presence of ν+& (CH) at 4330 and 4323 cm^{-1}in the points RA_L12, RA_B3, respectively identify the organic binder.

The main composition of the stuccatura points is gypsum. The presence of gypsum in these points affects the bands of the calcite that appeared as weak bands. Kaolin is one of the main components of the stuccatura points. The organic binder can be identified as whole egg.

Table.10 the IR molecular composition of the stuccatura points

The analyzed points	IR molecular compositions
RA_L12	Calcite, kaolin, egg, gypsum
RA_B3	Calcite, kaolin, egg, gypsum

PART III- Integration of the ARCHAEOLOGICAL results with the ARCHAEOMETRIC investigation results

CHAPTER V-Discussion

1. Pyxis vase (A)

From a close inspection of the results summarized in section II some information can be drawn.

As the ceramic body is concerned, basically iron and calcium were detected. Potassium, aluminum, titanium and silicon were also detected but due to physical (low emission yield, depth of penetration of X-rays) as well as instrumental reasons (low intensity of incident X-rays) the intensity of their emission lines is very low. This result indicates the presence of aluminum silicate, titania, iron oxides and calcium minerals as the components of the ceramic body. By complementing these results with those obtained by FT-IR, the presence of kaolinite and calcite was inferred. This suggests a temperature of firing lower than 650 °C in correspondence of which the transformation of kaolinite in meta-kaolin is complete **[59-61]**.
Calcium is ubiquitously present thus suggesting the presence of a preparation layer composed mainly by calcium compounds directly applied over the original ceramic body. The IR results indicate the use of whole egg as binder of the preparation layer. The detection of fluorescence lines of lead only in some points excludes the presence of a white lead preparation layer and indicates that it was applied only to obtain different hues in some coloured areas.
Strontium is another ubiquitous element joined with the presence of calcium both as a concomitant of calcium in the gypsum or as Celestine ($SrSO_4$) **[58]**. Its presence together with sulfur suggests the use of gypsum in the preparation layer.

The presence of calcite, as inferred by FT-IR, strongly suggests the use of this compound in mixture with iron compounds to produce a red layer over the preparation layer. Calcite justifies the different hues observed by visual inspection.

The tempera colors, whose use is confirmed by the presence of an organic protein fraction, have been applied over the above layers to produce figures and decorations.

The primary stratigraphy that could be suggested is represented in figure 9.

1.	**Ceramic matrix**
2.	**Preparation layer**
3.	**Red layer (iron oxides and calcite)**
4.	**Pigment layer**

Fig. 9: Scheme illustrate the stratigraphy of the layers of Pyxis vase A, from inner to outer.

The most notable result concerns the presence of bassanite in some points of the Vase A instead of gypsum. In fact, gypsum ($CaSO_4.2H_2O$) evolves into bassanite ($CaSO_4.0.5H_2O$) at temperature lower than 130 °C. Bassanite converts completely into anhydrite ($CaSO_4$) at a temperature higher than 400 °C. The hydration process from bassanite to gypsum is favoured by humidity higher than 50 %. The presence of bassanite indicates that the preparation layer has been deposited after the firing of the ceramic body and underwent a subsequent thermal treatment at low (c.a. 130 °C). The presence of gypsum in some point could be assumed as an indication of later intervention or retouches.
Notwithstanding the above evidence, the use in later intervention of organic pigments can be excluded since FT-IR does not indicate any functional group of common colorants.

The presence of an organic binder in the egg part of Vase A indicate that it has been prepared for decorations. Moreover, the presence of bassanite suggests that it is coeval to the remaining part of the vase.

2. Lebes Gamikos vase (B)

Unfortunately, on this vase only the campaign of XRF measurements has been performed. This allowed obtaining information on the pigments used. No detail about stratigraphy, molecule composition and intervention can be drawn from the above results.

CHAPTER VI

- **The palette**

The colors identified by visual inspection in painting and decorations of the Pyxis vase (A) were white, red, yellow, pink, orange, grey, black and bluish green. Generally, the preservation state of decorations is poor.

The XRF analysis allowed identifying peculiar elements for the various colored areas.

The results obtained for the white points in vase A, indicate the use of lithopone and calcite. The lithopone is a mixture of zinc sulfide (ZnS) and barium sulfate ($BaSO_4$) whose presence was based on the contemporary presence of Zn, Ba and S fluorescence lines in the XRF spectra. The lack of these contributions together with the presence of calcium, suggest the use of calcite as white pigment in some points.

The red color is rendered by the use of red ochre and of red lead (Pb_3O_4). The latter pigment was identified mainly inside the lid. It might be indicative of a restoration or of an intervention to improve aesthetics.

Concerning the yellow area, being iron the only characteristic element by XRF it can be guessed the use of yellow ochre ($Fe_2O_3 \cdot H_2O$). To render due flesh tones the presence of yellow ochre together with rose (mixture of hematite and calcite) can be conjectured in agreement with previous findings **[3]**. Different hues could be attributed to the use of lithopone in some points.

The golden decorations in both the lid and body have been realized by applying a golden leaf by means of a red bole beneath the metallic layer and the preparation layer.

No peculiar elements were found in the gray points whose elemental composition is almost coincident with that of the matrix.

Black color is characterized by the presence of copper thus suggesting the use of copper oxide to paint the black outlines of the figures even if the presence of black carbon cannot be excluded.

The copper was found in the blue greenish area thus suggesting the use of a Cu based pigment. The FT-IR spectra exclude the presence of azurite thus indicating the use of

Egyptian blue ($CaCuSi_4O_{10}$). This is confirmed by the presence of Si emission in the XRF spectra.

From the above findings the painted scene can be described, from a compositional point of view, as follows.

Mostly of the scene painted on the lid is not clearly observed due to the state of preservation. However, lithopone was applied in the painting the white area of the marine horse, the Egyptian blue for the ponytail or might be a blue sinuous animal. The yellow decoration surrounding the edge of the lid was mostly yellow ochre with several golden reliefs applied by means of red bole. The top back of the lid was in gray color without any distinctive color or pigment (appendix 4 fig. 11). The rear side of the lid was entirely covered with a white layer that impede the identification or even observation of any possibility presence of colored area.

The white dress of the female figure on the left and in some area of the female figure in the right on the body vase were painted by using calcite, the black copper oxide was used to repaint and redraw the outlines of the figures. Red ochre was applied as a dark red layer in the top rim in the surrounding decoration in which the golden leaf was applied. Yellow ochre mixed with calcite produced the yellow color used in painting the dress of the female figure that appeared seated in the middle of the scene (appendix 4 fig. 12).

The colors identified by visual inspection in painting and decorations of the Lebes Gamikos vase (B) were white, red, brown, gold and blue. Generally, the preservation state of decorations is poor. The scene of the Lebes Gamikos vase (B) was hardly observed due to loss of color. Decorations are present only in the body of vase.

The XRF analysis allowed identifying peculiar elements for the various colored areas.

The white area is essentially composed of calcium-based compounds. The red coloured areas are characterized by the presence of mercury in some points. This indicates the use of vermilion (cinnabar, HgS) **[62]** to render some hues over the background red composed basically by iron oxides.

The golden decoration was applied on a red bole layer **[63]**. No traces of silver are linked with the gold. This suggests the use of the pure gold metal without extraction or refining it. Therefore, it could consider as indication about the preciousness of this vase.

The brown area was characterized by the presence of manganese thus suggesting the use of manganese oxide (MnO_2) in mixture with brown ochre ($Fe_2O_3.H_2O$).

In the blue area, a notable high level of copper was identified besides nickel and lead. This finding suggests the use of a copper based blue pigment applied together with nickel oxide and lead oxide to give the wanted hue.

From the above findings it follows that the background of the painting is composed by iron oxides and calcite. Vermillion was used in painting the red chiton of the female figure in the middle of the scene. Calcium based pigment was applied in painting the faces of the two figures and probably the chiton of the second figure. Umber, brown ochre with manganese oxide, was applied in painting the hairs of the figures. A copper based pigment in mixture with nickel oxide was applied in the top of the vase as a background for applying small golden erotes (fig.13 in appendix 4).

All the pigments here identified were common in the ancient world. The palette characterizing both vases (Pyxis and Lebes Gamikos) is similar to that found in the investigation of the pigments on other Centuripe vases belonging to the Archaological Museum of Catania university **[64]**. Results were in a good agreement with those obtained by Riederer **[17]**, Deussen **[3]** and Richter **[10,12]**.

The study of the pigments in two Centuripe vases belonging to Libertini collection of the Archaeological Museum in Catania University **[64]**, was performed by using PIXE and XRD. The pigments found were red ochre, goethite, yellow ochre, hematite mixed with calcite, alizarin (which is the main component of madder lacquer) and the zinc white.

Riederer has investigated about the authenticity of eight Centuripean vases bought from the antiquarian through the investigation of the pigments used. The pigments identified were: yellow ochre, red ochre, golden leaves, kaolin, Egyptian blue, uncooked cinnabar, white lead, calcium white (white lime), umber.

The palette mentioned by Deussen in his doctoral dissertation***[3]** was red ochre or burnt yellow ocher, vermillion, yellow ochre, blue pigment obtained by finely crushed copper blue glass, umber and charcoal. Golden was found for the golden decorations.

Richter has identified the palette characterizing a Lekanis polychrome vase exhibited in the Metropolitan Museum of Art in New York **[10,12]**: red ochre mixed with chalk as background, yellow ochre, umber, chalk, finely crushed copper blue glass, cinnabar, lamp black.

*: see ref [3] Ch III. P124

- **Retouched areas**

Some intervention areas were identified during the prior visual inspection in both the lid and the body Pyxis vase (A). They appeared as an orange layer filling incisions and some lacunae between the different coloured areas. Measurements confirmed them and evidenced some other intervention areas.

Retouches were mainly composed of lithopone mixed with hematite and calcite. Black copper oxide was used to redraw and paint the black outlines of the figures in the painting scene of the vase A.

The stuccatura in both the lid and the body vase were identified by the presence of gypsum as indication of a restoration or a prior intervention.

Some differences were observed in Lebes Gamikos vase (B). In particular, zinc white besides the use of lithopone was found in the intervention area of the scene of the body vase.

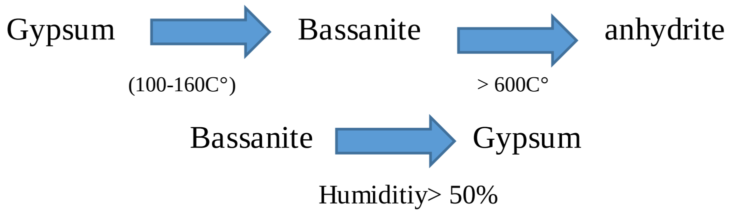
However, the most interesting result and in perspective the most useful result to identify later interventions, concern the presence of two mineral phases of calcium sulfate. Taking into consideration that bassanite ($CaSO_4.0.5H_2O$), the hemihydrate form of gypsum, was identified in the all the original body points and of the lid of vase A while gypsum ($CaSO_4.2H_2O$) was identified in intervention points in both lid and body, the presence of gypsum can be assumed as an evidence of intervention.

- **Painting technique**

Some information about the painting technique can be drawn from the above findings.

A protein fraction was identified as the organic binder in almost all the analyzed points in vase A. This confirms the use of the tempera painting technique to realize the scene and decorations. This is further confirmed by previous studies on Centuripean vases **[3, 10, 12, 17, 64]**.

The painting was applied over a preparation layer composed mainly by calcium sulfate beside calcium carbonate. The presence of bassanite indicates that this preparation layer was deposited on the vase after firing **[65]** to reduce its porosity and then it undergoes a thermal treatment. This was inferred once known that bassanite is the metastable phase that forms in a range of temperature comprised between 100 and 600 °C. The bassanite evolves to gypsum by a process favored by humidity.



This preparation layer was covered with a red background obtained by mixing between calcite and red ochre.

The figures were first drawn by a black or brown outline and filled with a white paint. Then the colors were applied by tempera technique **[3, 10]**.

The golden decorations were realized by applying golden leaves by the bole method.

Since no IR measurements were performed on the Lebes Gamikos vase (B), therefore no information about the use of organic binders can be drawn. Notwithstanding, it is reasonable to assume that the same painting technique has been used. Further investigations are needed on this vase.

- **Authenticity**

Tables 11 and 12 summarize the pigments suggested in the two vases and the criteria used to hypothesize them.

Table 11 Suggested pigments with the criteria followed on Pyxis vase (A)

Color	Criteria	Hypothesized pigments
White / front side lid	Zn,Ba,S	Lithopone ($ZnS+BaSO_4$)
White/ rear side lid	Ca	Ca based pigment
Blue (green shade)	Cu	Egyptian blue
Orange/ intervention area (stuccatura)	Fe, Ca, Zn,Ba,S	Lithopone ($ZnS+BaSO_4$) + iron oxide with calcite
Orange	Pb	Red lead Pb_3O_4
Red	Fe	Red ochre ($Fe_2O_3.H_2O$)
Gray	Fe,Zn,Ba,S	Lithopone ($ZnS+BaSO_4$) + iron oxide
Yellow/ in lid	Fe	Yellow ochre (Fe_2O_3)
Gold	Au	Gold leaf
Black	Cu	Copper oxide (CuO)
White/ in body	Ca	Ca based pigment
Yellow/ in body	Fe,Zn,Ba,S	Yellow ochre (Fe_2O_3)+Lithopone ($ZnS+BaSO_4$)

Table 12 Suggested pigments with the criteria followed on Lebes Gamikos vase (B)

Color	Criteria	Hypothesized pigments
white	Ca	Ca-based pigment
Red	Hg,S	Vermilion (HgS)
Pink	Fe,Ca	Mixture of hematite and calcium compounds
Blue	Cu,Ni,Ca	Copper blue pigment+ nickel oxide
Gold	Au,Fe	Gold leaf
brown	Fe,Mn	Brown ochre ($Fe_2O_3.H_2O$) +manganese oxide
Intervention area (stucco point)	Zn,Ba,S	Zinc white + lithopone

All the ochre pigments, iron oxides (yellow, red, and brown ochre) are considered to be ancient pigments used since prehistory unrespectful to the various techniques of painting because of their chemical inertia and easiness of mixing with other components **[62, 66]**.

The yellow ochre is the main pigment used in the Hellenistic period as a substrate for the application of the leaf of gold **[67].**

The application of the gold leaves on a preparation layer and the refining process on the Au is common to use in the Hellenistic and Roman periods **[51].**

The pink color, rendered by a proper mixture of pigments, was compatible with Hellenistic pigment **[3, 10].**

The Egyptian blue, a precious synthetic pigment, has been used only until Roman period. This pigment is no longer manufactured today **[66].**

Calcium carbonate as white pigment was basically used for painting grounds. It is known from prehistory and used until today. It is stable under ordinary conditions.

The red lead pigment was one of the earliest pigments artificially prepared and it is still in use. It was a favorite pigment of Byzantine and Persian illuminators and commonly used in European manuscripts and paintings **[66]**. Vermilion or cinnabar was known to the Greek and the Roman painters from the ancient times and has been used until 19th century **[66]**.

The pigments in the retouched areas are considered to be not ancient pigments and have not been used in the Hellenistic period.

The white zinc ZnO is a synthetic pigment and was introduced in 1782 **[68]** and appeared commercially in the 19th century. It has been used widely by the artists for making tints with other colors due to many properties such as it is a non-poisonous but mildly antiseptic compound **[69]** it is a fine pigment with very fair covering power property, relatively slow drying therefore it will not dry faster than the color under it **[70]**.

Lithopone has been used recently, it is considered to be a synthetic pigment and introduced in 1874 and still in use **[68, 71]**.

The black copper oxide was used for retouching the outlines of the figures aiming probably to make more attractive and hence to increase the value of the vase in the black market. It is not classified as a pigments from the Hellenistic period.

Since the two studied vases were probably found together in the so-called tomb 8 from the necropolis of Contrada Casino in Centuripe and since no available recorded information about the circumstances of findings or any documents asserting their originality has been detected **[3]** therefore we could only confirm that the vases are painted using pigments that were common in Hellenistic period and have been subjected to recent intervention works.

The preciousness of the Centuripe vases could be inferred since the use of precious pigments like Egyptian blue, vermillion and golden leaves in the decoration. This could suggest the use of the Centuripe vases in pompous wedding or funerary ceremonies **[72]**.

Conclusion

The pigments of two Centuripe vases Pyxis and Lebes Gamikos dated back to the early 2^{th} century B.C. have been investigated using portable XRF and reflectance FT-IR aiming to define the painting technique and to recognize the retouched areas and consequently identify the authenticity of the vases. In fact, they are reported to have been recovered in tomb 8 in necropolis Contrada Casino, Centuripe-Sicily, Italy without any recorded archaeological context.

Beside the characterization of the pigments used for decoration and of the painting technique, the authenticity of the vases was one of the concerns, being the imitation of workshops of Centuripe vases widely prevailing. This is a consequence of their position as representative of rare relic from Hellenistic period. The vases are in a poor preservation state.

The pigments were identified using complementary non-invasive portable techniques (P-XRF and Total Reflectance FT-IR) that proved once again to be powerful techniques in performing non-invasive measurements in-situ. The measurements have been done in Salinas Archaeological museum in Palermo- Italy.

The Pyxis vase is constituted of three parts (egg, removable lid and body). The painting scenes were restricted on the front side of the lid and the body vase.

The palette of Pyxis vase was composed of red ochre for the background in the lid, pink color (hematite and calcite) for the background of the body scene, lithopone for the white area in the lid, calcite or chalk for the white area in the body, Egyptian blue for the blue greenish area in the lid, red lead applied inside the lid, yellow ochre for the yellow decoration, yellow ochre in different flesh tones in the yellow dress of the figure in the body, and golden leaf for the decoration in the lid and the body. The egg tempera technique was identified as the painting technique used in painting the Pyxis vase. Several retouched areas were identified in both the lid and the body through the application of modern pigments as lithopone. Overpainting areas was identified through the use of copper oxide in the body scene. Read lead was identified inside the lid that possibly was applied as a prior restoration work or an intervention work to give more worth.

The presence of kaolinite together with calcite suggests the firing temperate (650 ºC) for the cooking of the ceramic vase. Bassanite was identified as a plaster preparation layer of the painting in the body vase deposit after firing, while gypsum was identified as an indication of later intervention.

Only P-XRF analysis has been performed on Lebes Gamikos vase that has a non-removable lid. The pigments used and the retouched areas were identified. The palette used in painting the scene is composed of vermilion red for the chiton figure, pink color (hematite with calcite) for the background, calcite or chalk for the white figure, pure gold applied in a red bole layer, brown ochre with manganese oxide, Copper based pigment with nickel oxide for the blue area. The retouched area was identified by the use of modern pigment (white zinc).

The palette of the two vases has been found to be very similar to the palette used by the painters in Centruipe region in the Hellenistic period, as inferred from literature data.

Suggestion for future investigation on Centuripe vases in Salinas museum

1. IR measurements on Lebes Gamikos vase aiming to identify the painting technique.
2. More investigation on the blue greenish area in the lid of Pyxis vase A
3. More investigation on the blue area in Lebes Gamikos vase B
4. Further analysis to investigate the true composition of the pink background by using UV light or P-XRD.

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The great appreciation and the final thank gives to Professor Eugenio Caponetti for offering this work and for the full and effective supervision on the entire work.

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Appendix 1

Plate I


Fig. 1


Fig. 2


Fig. 3


Fig. 4

Plate II

Fig. 5

(a) (b) (c)

Fig.6 Fig. 7

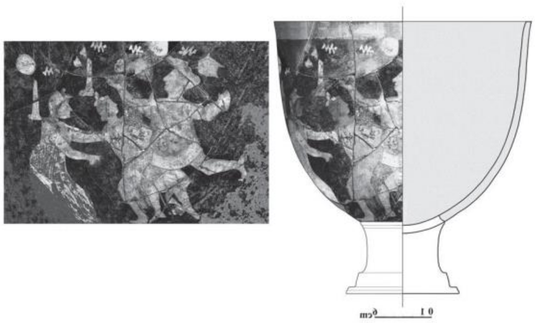


Fig. 8

Plate III

Fig. 9

Fig. 10

Plate IV

Fig. 11

Fig. 12

Fig. 13

Fig. 14

Fig. 15

Fig. 16

Figure captions in the plate (I, II, III, IV)

Fig.1: illustrates the decoration and the lekanis shape of Centuripe vessel in Salinas National Archaeological Museum-Palermo INV 2236, fully developed shape 4, no 57. The lid belongs to lekanis no 100 and put erroneously on this vessel.

Fig.2: lebes gamikos in Libertini 1934, Wintermeyer K78, INV. 46994 presented in Syracuse Museum

Fig. 3: pisside Collezione Mammana a fondo nero, Libertini 1926, Wintermeyer, K35, INV. 41493 in Syracuse Museum

Fig. 4: (a)bottle from 18bis tomb of the district Casino, Wintermeyer, K88 vessels Centuripe , INV. 49964 in Syracuse Mus.Arch.Naz. (b) Bottle no. 46, Syracuse, Mus. Arch. Naz., inv# 46995; Libertini calls this shape "lekythos a cocomero".

Fig. 5: illustrates the plastic decoration in lebes vessel (pisside, già Collezione Mammana) in Libertini 1926, Wintermeyer, K56, INV. 35946 in Syracuse National Museum.

Fig. 6: Pisside policroma con scena c.d. di "accademia di musica", già nella collezione Pisani e in seguito dispersa (ripr. Ad acquarello, da Libertini 1926) **[8]**.

Fig. 7: details of the main scene on the funerary vase, (Relaigh Vase) in North Carolina Museum of Art Bulletin **[7]**.

Fig. 8: La pisside cat. n. 203 (disegno di O. Pulvirenti) **[20]**

Fig. 9: Pisside policroma con scena cd. di epaulia: riproduzione grafica della pittura a seguito delle ridipinture modern (sin.) e ricostruzione delle figurazioni originarie (dx.). Berna, Antikensammlung (da Jost 1997) **[8]**.

Fig. 10: The Centuripe vessels as shown in Salinas Archaeological Museum in Palermo

Fig. 11: Pyxis vessel (A) in Salinas Archaeological Museum in Palermo, K57, no 81

Fig. 12: the lid of the Pyxis vessel (A) in Salinas Archaeological Museum. NI2237

Fig. 13: the final egg of the Pyxis vessel (A) in Salinas Archaeological Museum. NI2232

Fig. 14: the painting scene on the Pyxis body (A)

Fig. 15: Lebes Gamikos (B) in Salinas Archaeological Museum in Palermo NI2235, K82, no 71

Fig. 16: the painting scene on Lebes Gamikos vessel (B) in Salinas Museum NI2235

Appendix 2: XRF tables and table Captions

Vessel A

1. Egg points

Table. 1 Analyzed points and their position, color of the investigated area and guessed pigment as inferred from PXRF results for Egg in the vase A.

Analyzed points	Position	Color	suggested pigments
XA_E24	In side border edge under egg	White	No pigment
XA_E25	The rear side of egg	White	No pigment
XA_E26	The front side of egg	White	No pigment
XA_E27	Outside border edge egg	Gray	No pigment

Table. 2 PXRF results obtained from the egg points of vase A expressed as percentage of the net area.

Analyzed points	Area %														Ca/Fe
	Major elements		Minor elements												
	Fe	Ca	Sr	Ni	Ti	Si	K	Mn	Zn	Ba	S	Pb	Cu	Al	
XA_E24	55.09	30.80	4.03	1.42	1.81	1.70	2.76	0.80	0.56	0.20	0.21	0.05	0.25	0.12	0.56
XA_E25	49.04	38.60	4.27	1.28	1.40	1.38	1.80	0.66	0.25	0.24	0.43	0.10	0.19	0.14	0.79
XA_E26	56.60	28.13	5.53	1.70	1.89	1.76	1.36	0.75	0.36	0.45	0.69	0.07	0.27	0.25	0.50
XA_E27	56.13	30.41	4.57	1.42	1.76	1.31	1.81	0.62	0.39	0.33	0.64	0.10	0.23	0.09	0.54

2. White points

Table. 3 Analyzed points and their position, color of the investigated area and guessed pigment as inferred from PXRF results for white points in the vase A.

Analyzed points	Position	Color	suggested pigments
XA_L6	The upper part of the marine horse in front of the lid	White	Lithopone ($ZnS+BaSO_4$)
XA_L7	Marine Horse body in front side of lid	White	Lithopone ($ZnS+BaSO_4$)
XA_L17	The rear side of lid	White	Ca based pigment
XA_L16	Border inside the lid (incision)	Pale white	Ca based pigment
XA_L19	The rear side of lid	White red	Ca based pigment
XA_B1	Dress body of standing figure vase A	White	Ca based pigment

Table. 4 PXRF results obtained from the white points of vase A expressed as percentage of the net area.

Analyzed points	Area %														Ca/Fe
	Major elements		Minor elements												
	Fe	Ca	Sr	Ni	Zn	Ba	S	Mn	Ti	Si	K	Pb	Cu	Al	
XA_L6	33.39	21.40	4.22	1.28	23.43	9.85	4.30	0.67	-	0.58	0.47	0.23	0.20	0.05	0.64
XA_L7	54.74	21.98	4.54	1.39	6.34	3.85	2.08	0.87	0.95	1.11	1.62	0.12	0.23	0.14	0.40
XA_L17	32.92	51.22	4.29	1.32	2.40	1.11	3.27	0.46	0.44	0.91	1.06	0.18	0.17	0.10	1.56
XA_L16	33.78	48.17	4.39	2.25	0.73	0.27	6.29	0.66	0.64	0.25	0.62	1.63	0.31	0.02	1.43
XA_L19	43.27	45.11	4.14	1.31	0.34	0.29	0.54	0.51	1.22	1.05	1.59	0.12	0.21	0.1	1.04
XA_B1	30.56	55.29	4.35	1.52	1.52	1.32	1.00	0.58	0.50	0.65	0.93	0.59	1.15	0.04	1.81

3. Red points

Table. 5 Analyzed points and their position, color of the investigated area and guessed pigment as inferred from PXRF results for red points in the vase A.

Analyzed points	Position	Color	suggested pigments
XA_L4	Gap front side of the lid	Light red	Red ochre(Fe_2O_3)
XA_L8	Near the border of the front of lid	Pale red	Red ochre(Fe_2O_3)
XA_L18	Rear side of lid	Light red (pink)	Red ochre(Fe_2O_3)
XA_B2	Background vessel body A	Pink red	No pigment
XA_B6	the top rim of the vessel body A	Dark red	Red ochre(Fe_2O_3)
XA_L2	Front side of the lid (close to the edge)	Dark red	Red ochre (Fe_2O_3)

Table. 6 PXRF results obtained from the red points of vase A expressed as percentage of the net area.

Analyzed points	Area %														Ca/Fe
	Major elements		Minor elements												
	Fe	Ca	Sr	Ni	Ti	Si	K	Mn	Zn	Ba	S	Pb	Cu	Al	
XA_L4	50.79	36.08	3.53	1.18	0.66	0.80	1.16	0.45	2.48	1.65	0.71	0.10	0.17	0.12	0.71
XA_L8	49.00	38.14	4.26	1.46	0.98	1.17	1.30	1.17	0.69	0.55	0.56	0.13	0.26	0.19	0.78
XA_L18	44.42	42.22	4.40	1.27	1.00	1.01	1.72	0.74	0.64	0.40	1.58	0.07	0.19	0.13	0.95
XA_B2	39.05	47.02	5.17	1.93	0.74	0.80	0.84	1.09	1.39	0.74	0.49	0.22	0.30	0.10	1.20
XA_B6	55.77	28.83	3.94	1.91	1.75	0.69	2.46	0.74	0.75	0.42	2.15	0.07	0.33	0.05	0.52
XA_L2	55.66	34.46	3.72	1.13	0.88	1.13	0.99	0.58	0.27	0.14	0.35	0.21	0.20	0.21	0.62

4. Blue greenish points

Table. 7 Analyzed points and their position, color of the investigated area and guessed pigment as inferred from PXRF results for blue greenish points in the vase A.

Analyzed points	Position	Color	suggested pigments
XA_L1	The upper tail of the horse (or sinuous animal)	Blue greenish	Cu based pigment
XA_L3	The lower tail of the horse (or sinuous animal))	Blue greenish	Cu based pigment
XA_L21	Cross line in the rear side of lid	greenish	No blue pigment
XA_L22	Upper line in the rear side of lid	White greenish	No blue pigment
XA_L23	Lower line in the rear side of lid	White greenish	No blue pigment

Table. 8 PXRF results obtained from the blue greenish points of vase A expressed as percentage of the net area.

Analyzed points	Area %															Ca/Fe
	Major elements		Minor elements													
	Fe	Ca	Sr	Ni	Ti	Si	K	Mn	Zn	Ba	S	Cr	Pb	Cu	Al	
XA_L1	35.82	13.90	4.77	1.69	1.21	1.86	0.48	0.64	0.87	0.54	0.60	0.05	1.60	35.80	0.16	0.39
XA_L3	46.75	16.02	3.59	1.19	0.70	1.48	0.25	0.50	0.73	0.54	1.60	0.05	1.38	25.09	0.10	0.34
XA_L21	13.12	70.84	5.20	1.96	-	0.47	0.15	0.65	6.00	1.74	11.40	-	0.86	0.24	0.03	5.40
XA_L22	18.38	60.89	3.89	1.85	0.50	0.67	0.53	0.70	1.08	0.58	8.96	-	1.58	0.28	0.04	3.31
XA_L23	18.19	54.91	4.28	1.52	-	0.45	0.21	0.57	7.32	1.51	9.29	-	0.87	0.46	0.03	3.02

5. Orange points

Table. 9 Analyzed points and their position, color of the investigated area and guessed pigment as inferred from PXRF results for the orange points in the vase A.

Analyzed points	Position	Color	suggested pigments
XA_L5	The upper front of the lid	Orange	Lithopone ($ZnS+BaSO_4$) + mixture of (iron oxide+ calcite)
XA_L20	Line in the rear side of lid	Orange	Lithopone ($ZnS+BaSO_4$) + mixture of (iron oxide+ calcite)
XA_L12	Inside the lid	Dark Orange	Read lead Pb_3O_4
XA_L13	Border inside lid	Dark Orange	Read lead Pb_3O_4

Table. 10 PXRF results obtained from the orange points of the lid of vase A expressed as percentage of the net area.

Analyzed points	**Area %**													**Ca/Fe**
	Major elements		**Minor elements**											
	Fe	**Ca**	**Sr**	**Ni**	**Si**	**K**	**Mn**	**Zn**	**Ba**	**S**	**Pb**	**Cu**	**Al**	
XA_L5	35.05	29.73	5.36	2.20	2.16	0.14	0.76	15.78	3.91	3.79	0.54	0.36	0.03	0.85
XA_L20	41.79	32.55	5.11	1.63	1.45	0.51	0.61	8.99	3.20	3.11	0.22	0.46	0.05	0.78
XA_L12*	11.96	47.93	2.98	2.15	0.03	-	0.15	0.96	0.19	6.70	16.65	0.20	0.03	4.01
XA_L13*	13.13	52.87	3.19	1.74	0.06	-	0.17	0.96	0.24	8.89	12.50	0.16	0.02	4.03

*Due to the low intensity the experimental condition for the spectrum acquisition were 30 mA

6. Gray points

Table. 11 Analyzed points and their position, color of the investigated area and guessed pigment as inferred from PXRF results for grey points in the vase A.

Analyzed points	Position	Color	suggested pigments
XA_L9	Top surface back of the lid	Gray	Iron oxide+ small quantity of lithopone
XA_L15	Border edge inside the lid	Gray	Iron oxide+ small quantity of lithopone
XA_L14	Border edge inside the lid	Gray	Iron oxide

Table. 12 PXRF results obtained from the grey points of vase A expressed as percentage of the net area.

Analyzed points	Area %														Ca/Fe
	Major elements		Minor elements												
	Fe	Ca	Sr	Ni	Ti	Si	K	Mn	Zn	Ba	S	Pb	Cu	Al	
XA_L9	48.69	30.14	4.50	1.63	0.70	2.06	1.42	0.78	5.16	1.98	2.19	0.20	0.23	0.14	0.62
XA_L15	56.30	26.73	4.40	1.78	1.05	0.67	1.63	1.04	2.54	1.92	1.23	0.28	0.28	0.06	0.47
XA_L14	52.71	34.01	4.65	2.60	1.28	0.52	1.33	0.68	0.53	0.48	0.34	0.15	0.47	0.07	0.65

7. Yellow, Golden points

Table. 13 Analyzed points and their position, color of the investigated area and guessed pigment as inferred from PXRF results for yellow and golden points in the vase A.

Analyzed points	Position	Color	Hypothesized pigments
XA_L10 gold	Decorate border in front side of the lid	Gold	Golden leaf
XA_B5 gold	Decoration in the top rim of body vessel A	Gold	Golden leaf
XA_L11 yellow	Decorate border in the front side of the lid (the dolphin)	Yellow	Yellow ocher($Fe_2O_3.H_2O$)
XA_B3 yellow	The dress of the seated figure in the body vessel A	Yellow	Yellow ocher + small quantity of lithopone

Table. 14 PXRF results obtained from the yellow, golden points of vase A expressed as percentage of the net area.

Analyzed points	Area %																Ca/Fe
	Major elements		Minor elements														
	Fe	Ca	Sr	Ni	Au	Ag	Si	K	Mn	Zn	Ba	S	Pb	Cu	Al		
XA_L10 gold	59.26	19.36	3.30	1.43	11.59	0.02	0.59	0.99	0.43	0.18	0.19	0.53	0.36	0.59	0.14		0.33
XA_B5 gold	42.56	11.39	2.62	2.22	37.55	0.06	0.27	0.36	0.57	0.32	0.43	0.20	0.24	0.20	0.03		0.27
XA_L11 yellow	66.04	22.78	3.59	1.03	0.35	-	0.68	1.13	0.55	0.35	0.28	1.40	0.32	0.40	0.15		0.34
XA_B3 yellow	45.22	39.88	3.95	1.49	-	-	0.45	0.87	0.61	3.08	1.85	1.25	0.48	0.27	0.05		0.88

8. Black point

Table. 15 Analyzed point and its position, color of the investigated area and guessed pigment as inferred from PXRF results for black points in the vase A.

Analyzed points	Position	Color	Hypothesized pigments
XA_B4	The outline of the figures of the body vessel A	black	Copper oxide(CuO)

Table. 16 PXRF results obtained from the black point of vase A expressed as percentage of the net area.

Analyzed points	Area %														Ca/Fe
	Major elements		Minor elements												
	Fe	Ca	Sr	Ni	Si	Ti	K	Mn	Zn	Ba	S	Pb	Cu	Al	
XA_B4	35.25	33.55	5.51	1.91	1.29	0.69	0.74	0.55	1.87	2.06	1.20	0.88	15.73	0.15	0.95

9. Stuccatura point

Table. 17 Analyzed point and its position, color of the investigated area and guessed pigment as inferred from PXRF results for stuccatura point in the vase A.

Analyzed points	Position	Color	Hypothesized pigments
XA_B7	Stuccatura at the top of the body vase A	dark orange	Lithopone+ mixture of (iron oxide+ calcite)

Table. 18 PXRF results obtained from the stuccatura point of vase A expressed as percentage of the net area.

Analyzed points	Area %													Ca/Fe
	Major elements		Minor elements											
	Fe	Ca	Sr	Ni	Si	K	Mn	Zn	Ba	S	Pb	Cu	Al	
XA_B7	43.11	33.46	6.04	2.19	1.75	0.08	0.94	4.94	1.74	4.56	0.65	0.35	0.02	0.78

Vessel B

1. White point

Table. 19 Analyzed point and its position, color of the investigated area and guessed pigment as inferred from PXRF results for white point in the vase B.

Analyzed points	Position	Color	Hypothesized pigments
XB_B7	Background of the painting scene of the body vessel B	pale white	Ca based pigment

Table. 20 PXRF results obtained from the white point of vase B expressed as percentage of the net area.

Analyzed points	Area %														Ca/Fe
	Major elements		Minor elements												
	Fe	Ca	Sr	Ni	Ti	Si	K	Mn	Zn	Ba	S	Pb	Cu	Al	
XB_B7	41.19	46.83	3.52	1.44	0.85	0.44	1.35	0.80	0.68	0.48	1.88	0.15	0.24	0.04	1.14

2. Red points

Table. 21 Analyzed points and their position, color of the investigated area and guessed pigment as inferred from PXRF results for red points in the vase B.

Analyzed points	Position	Color	Hypothesized pigments
XB_B1	The dress of the figure in the body vase B	Red	Cinnabar (HgS)
XB_B2	The background of the scene of the body vase B	pink	Mixture of hematite and calcite

Table. 22 PXRF results obtained from the red points of vase B expressed as percentage of the net area.

Analyzed points	Area %															Ca/Fe
	Major elements		Minor elements													
	Fe	Ca	Sr	Ni	Ti	Si	K	Mn	Hg	Zn	Ba	S	Pb	Cu	Al	
XB_B1	26.87	44.58	4.20	1.62	0.24	0.42	0.81	1.67	13.34	1.91	1.27	2.46	0.27	0.24	-	1.66
XB_B2	29.80	54.62	4.69	1.39	0.38	0.66	0.97	1.80	0.21	1.19	0.86	2.05	0.18	0.18	0.09	1.83

3. Golden point

Table. 23 Analyzed points and its position, color of the investigated area and guessed pigment as inferred from PXRF results for golden point in the vase B.

Analyzed points	Position	Color	Hypothesized pigments
XB_B6	The decoration in the top of body vase B	Gold	Golden leaf

Table. 24 PXRF results obtained from the gold point of vase B expressed as percentage of the net area.

Analyzed points	Area %														Ca/Fe
	Major elements		Minor elements												
	Fe	Ca	Sr	Ni	Si	K	Mn	Au	Zn	Ba	S	Pb	Cu	Al	
XB_B6	53.29	24.77	3.38	1.29	0.42	0.78	0.34	11.12	1.25	0.82	0.92	0.44	0.37	0.05	0.46

4. Brown points

Table. 25 Analyzed points and their position, color of the investigated area and guessed pigment as inferred from PXRF results for brown points in the vase B.

Analyzed points	Position	Color	Hypothesized pigments
XB_B3	The hair of the first figure of the body vase B	Brown	Brown ocher($Fe_2O_3.H_2O$) +manganese oxide (MnO_2)
XB_B5	The top rim edge of vessel B	Brown	No pigment

Table. 26 PXRF results obtained from the brown points of vase B expressed as percentage of the net area.

Analyzed points	Area %														Ca/Fe
	Major elements		Minor elements												
	Fe	Ca	Sr	Ni	Ti	Si	K	Mn	Zn	Ba	S	Pb	Cu	Al	
XB_B3	44.11	37.69	6.08	2.12	0.72	0.61	1.69	1.43	1.17	0.93	2.12	0.49	0.40	0.13	0.85
XB_B5	41.17	42.86	2.51	1.52	0.94	0.73	1.98	0.53	1.01	0.67	4.01	0.41	0.23	0.06	1.04

5. Blue point

Table. 27 Analyzed points and its position, color of the investigated area and guessed pigment as inferred from PXRF results for the blue point in the vase B.

Analyzed points	Position	Color	Hypothesized pigments
XB_B4	The background of decoration in the top of the vase B	Light blue	Cu-based pigment+ nickel oxide

Table. 28 PXRF results obtained from the blue point of vase B expressed as percentage of the net area.

Analyzed points	Area %														Ca/Fe
	Major elements		Minor elements												
	Fe	Ca	Sr	Ni	Ti	Si	K	Mn	Zn	Ba	S	Pb	Cu	Al	
XB_B4	37.16	31.15	8.14	6.28	1.37	0.27	0.16	2.02	1.97	1.91	0.44	3.01	5.90	0.08	0.84

6. Stuccatura point

Table. 29 Analyzed point and its position, color of the investigated area and guessed pigment as inferred from PXRF results for stuccatura point in the vase B.

Analyzed points	Position	Color	Hypothesized pigments
XB_B8	The under area in the base of body vase B	brick orange	Zinc white + lithopone

Table. 30 PXRF results obtained from the stuccatura point of vase B expressed as percentage of the net area.

Analyzed points	Area %										Ca/Fe
	Major elements		Minor elements								
	Fe	Ca	Sr	Ni	Si	Mn	Zn	Ba	S	Pb	Cu	
XB_B8	10.53	23.55	4.76	1.77	0.08	0.34	39.94	12.28	4.73	1.08	0.69	2.24

Appendix 3 XRF & IR spectrums
XRF Spectrums

Vessel A

1. egg points

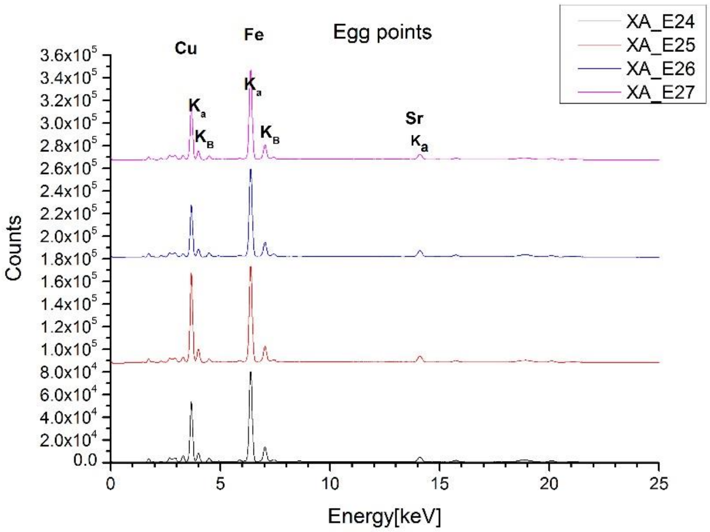


Fig. 1: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the egg points of vase A. Attribution of some of the lines to the emitting elements is shown.

2. White points

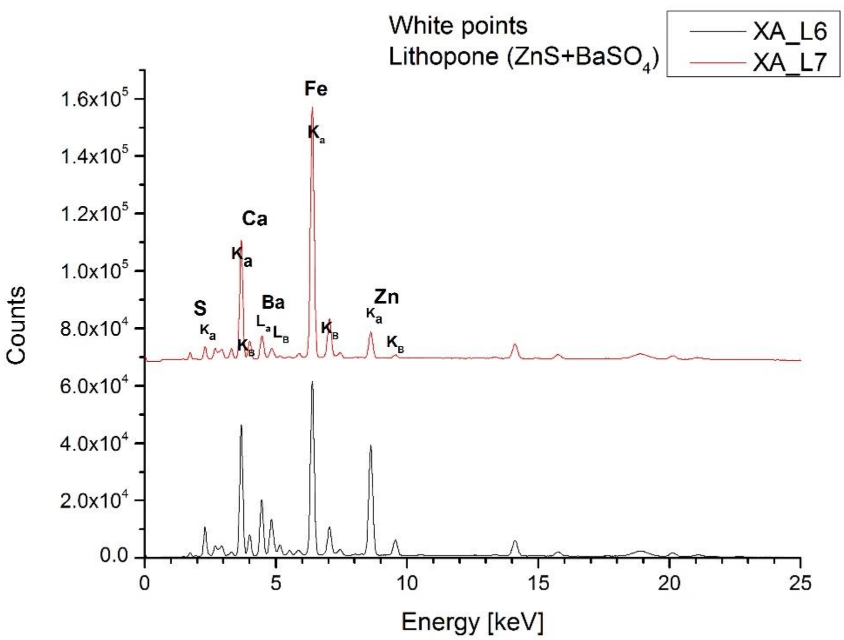


Fig. 2: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the white points of the front side of the lid of vase A. Attribution of some of the lines to the emitting elements is shown.

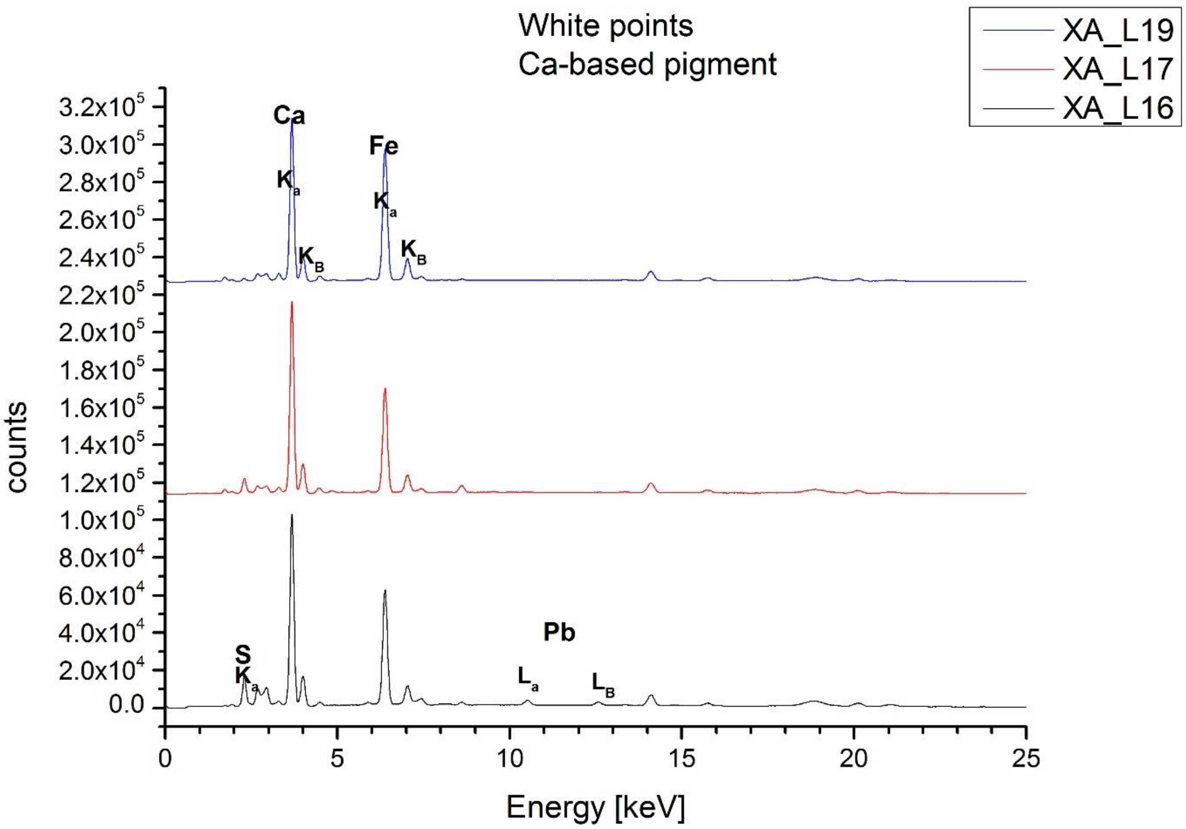


Fig. 3: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the white points of the rear side of the lid of the body of vase A. Attribution of some of the lines to the emitting elements is shown.

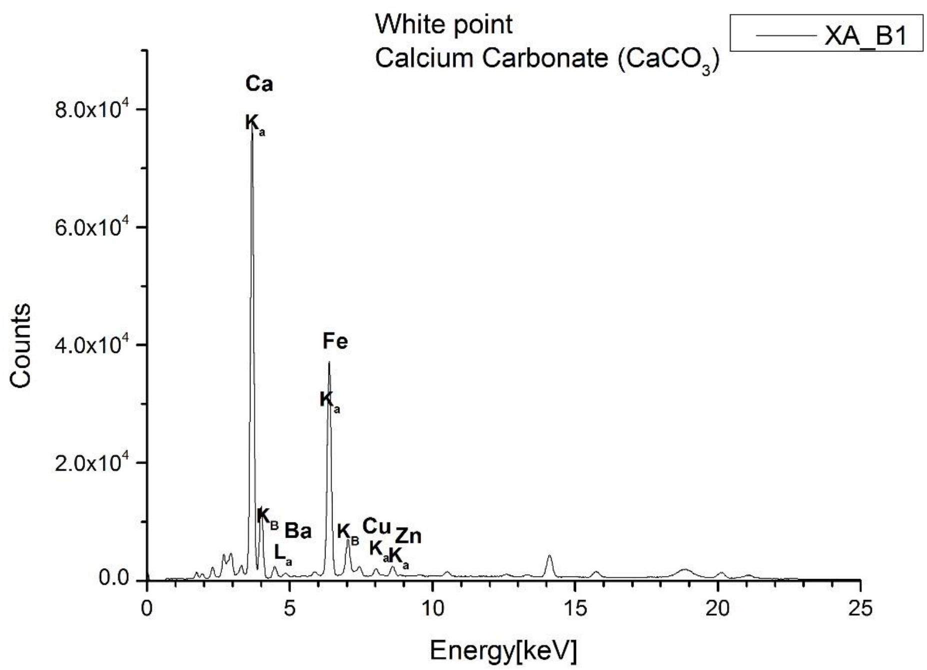


Fig. 4 XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the white point of the body of vase A. Attribution of some of the lines to the emitting elements is shown.

3. Red points

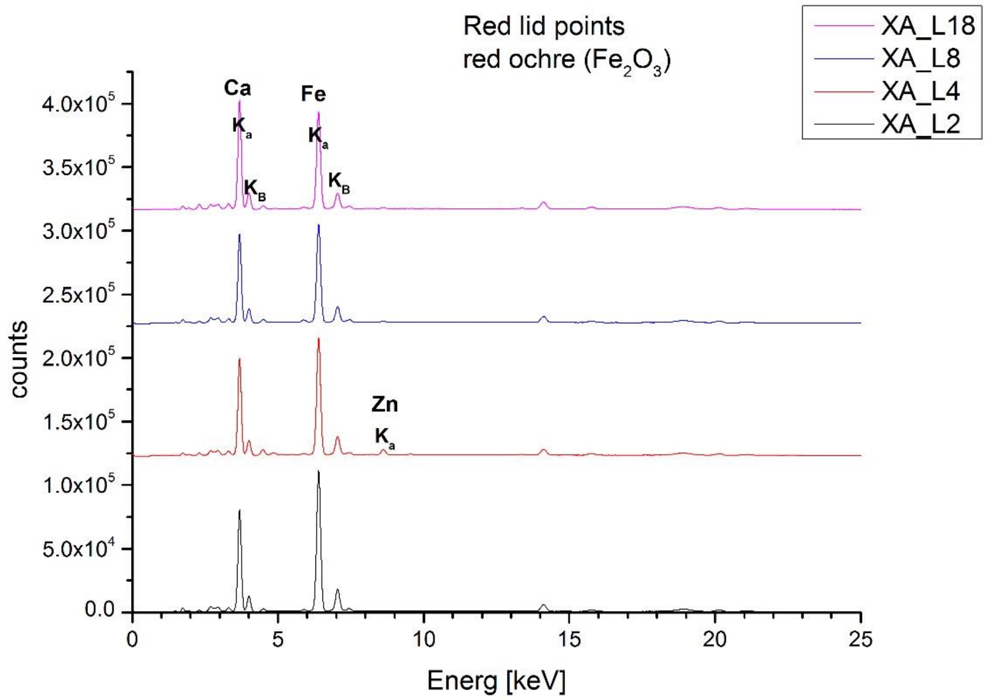


Fig. 5 XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the red points of the lid of vase A. Attribution of some of the lines to the emitting elements is shown.

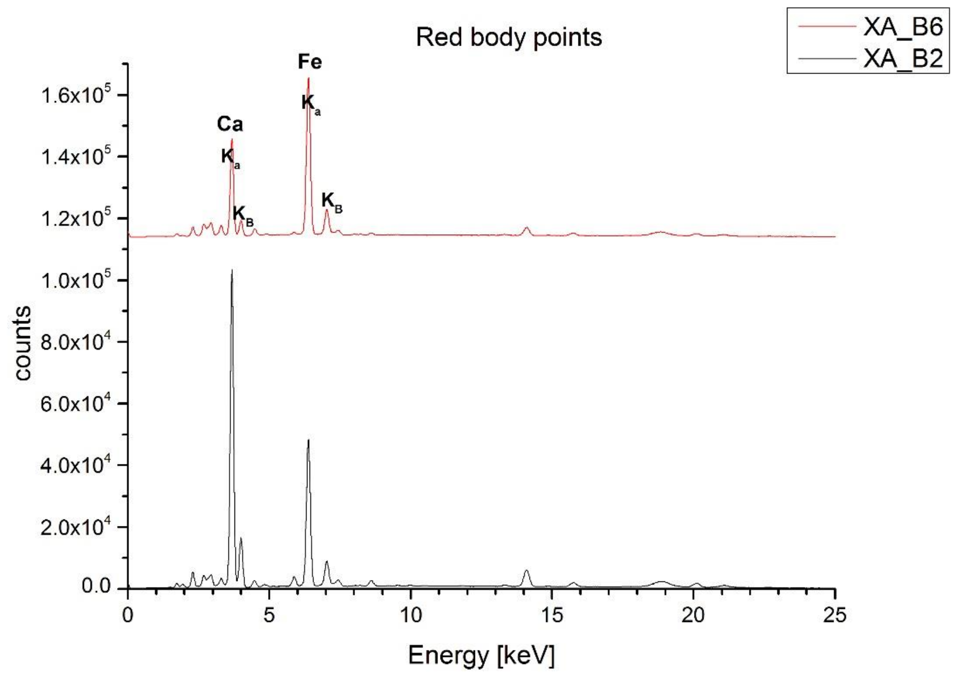


Fig. 6: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the red points of the body of vase A. Attribution of some of the lines to the emitting elements is shown.

4. Blue greenish points

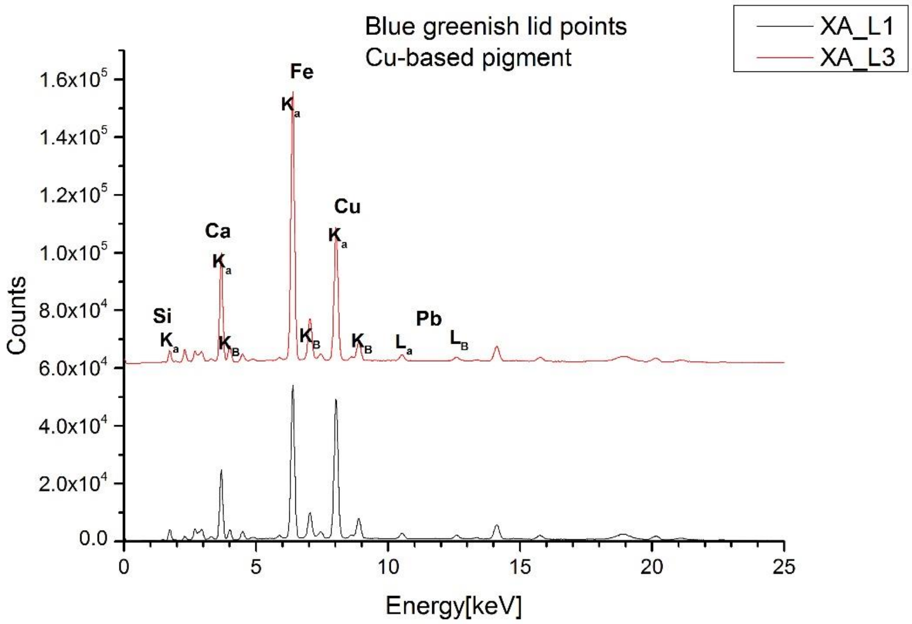


Fig. 7: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the blue greenish points of the lid of vase A. Attribution of some of the lines to the emitting elements is shown.

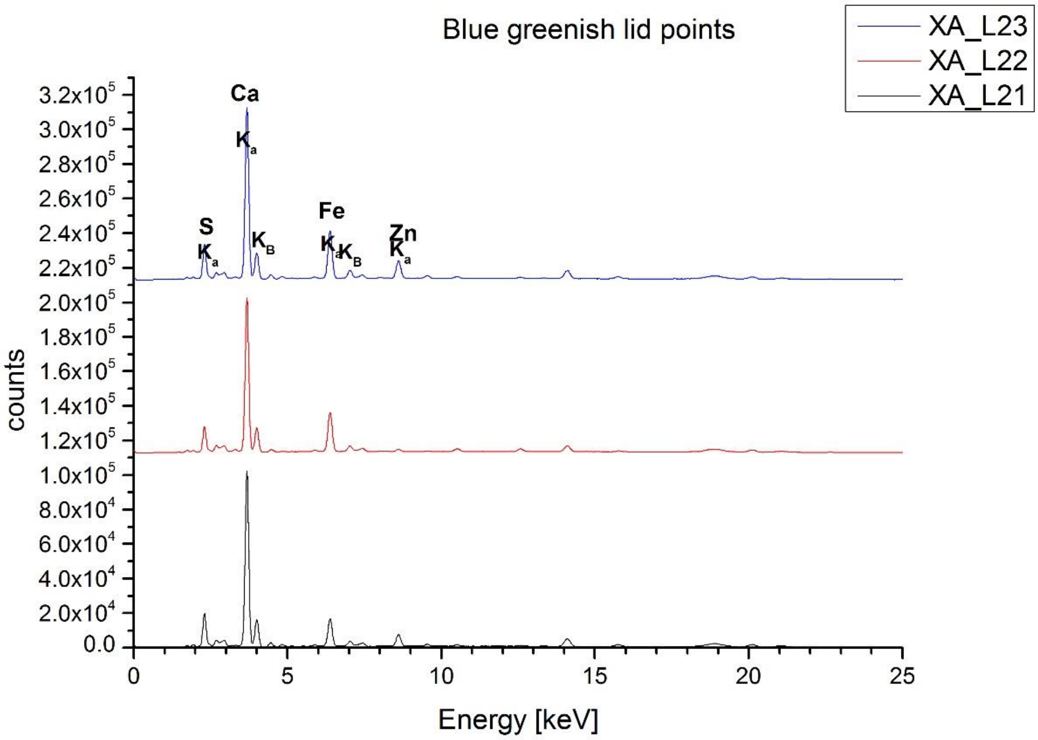


Fig. 8: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the blue greenish points of the lid of vase A. Attribution of some of the lines to the emitting elements is shown.

5. Orange points

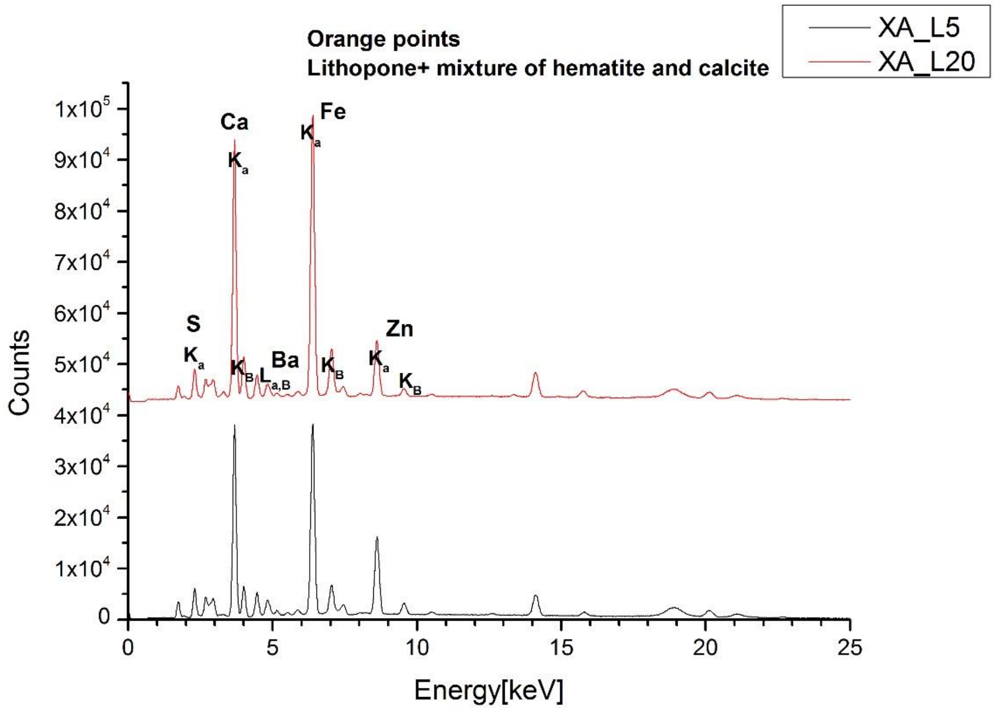


Fig. 9: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the orange points of the lid of vase A. Attribution of some of the lines to the emitting elements is shown.

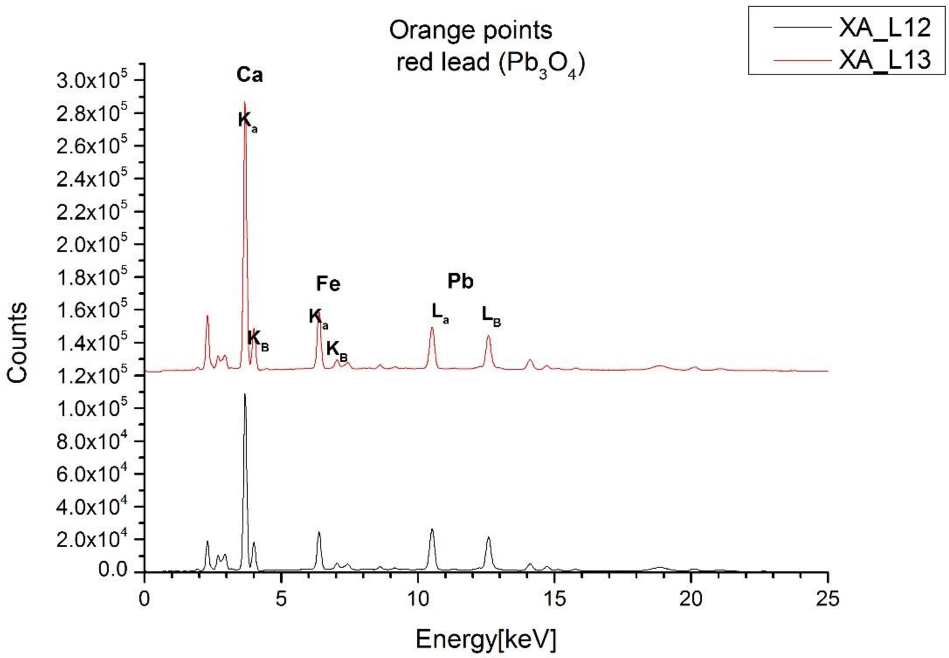


Fig. 10: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the orange points of the inside lid of vase A. Attribution of some of the lines to the emitting elements is shown.

6. Grey points

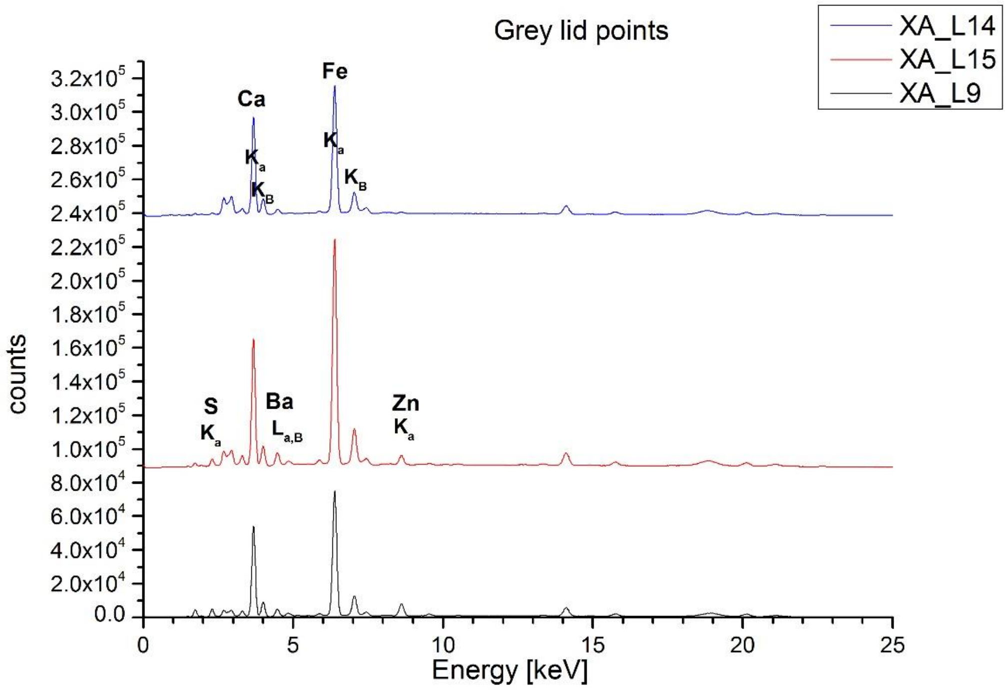


Fig. 11: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the grey points of the lid of vase A. Attribution of some of the lines to the emitting elements is shown.

7. Yellow, Golden points

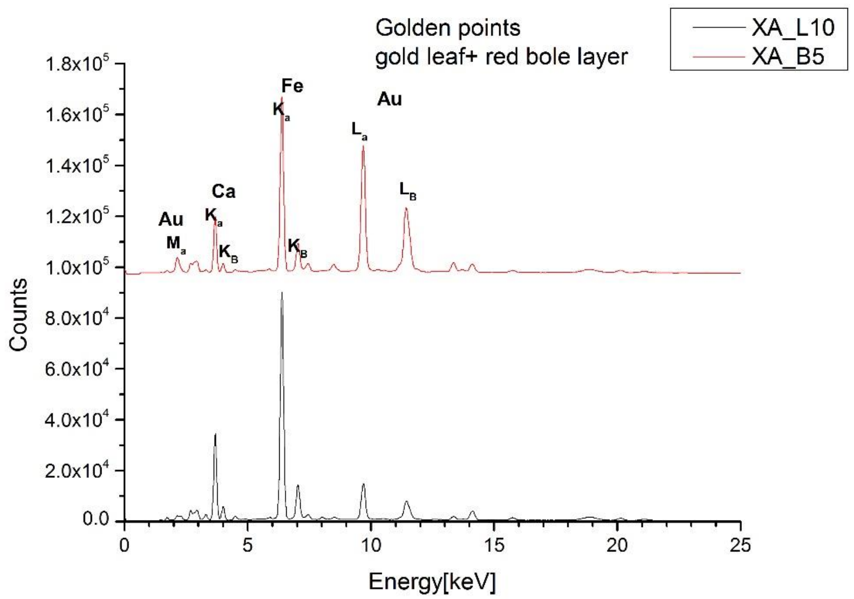


Fig. 12: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the golden points of the lid and body of vase A. Attribution of some of the lines to the emitting elements is shown.

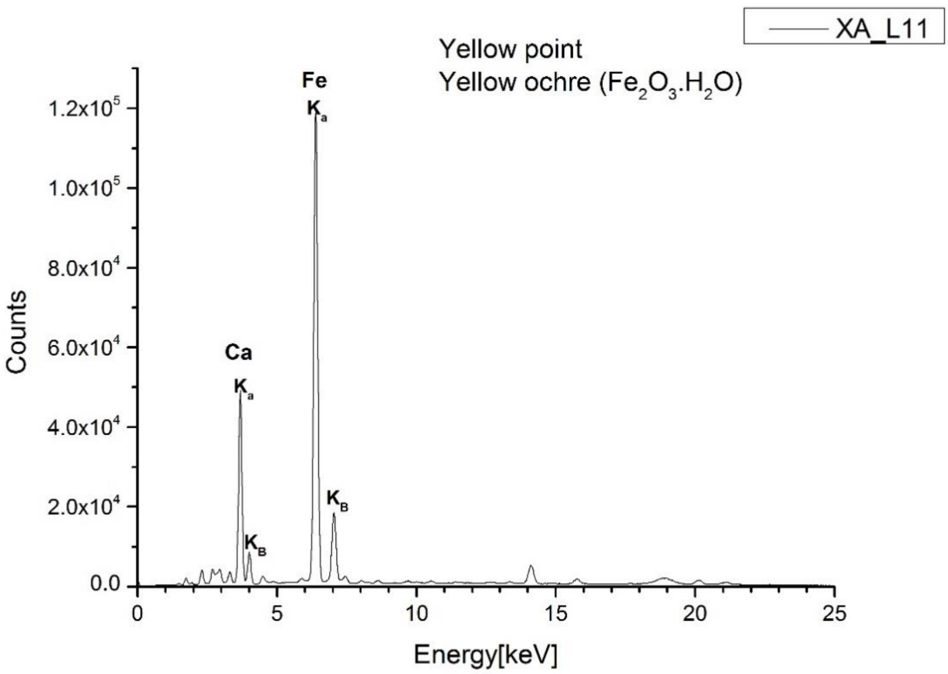


Fig. 13: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the yellow point of the lid of vase A. Attribution of some of the lines to the emitting elements is shown.

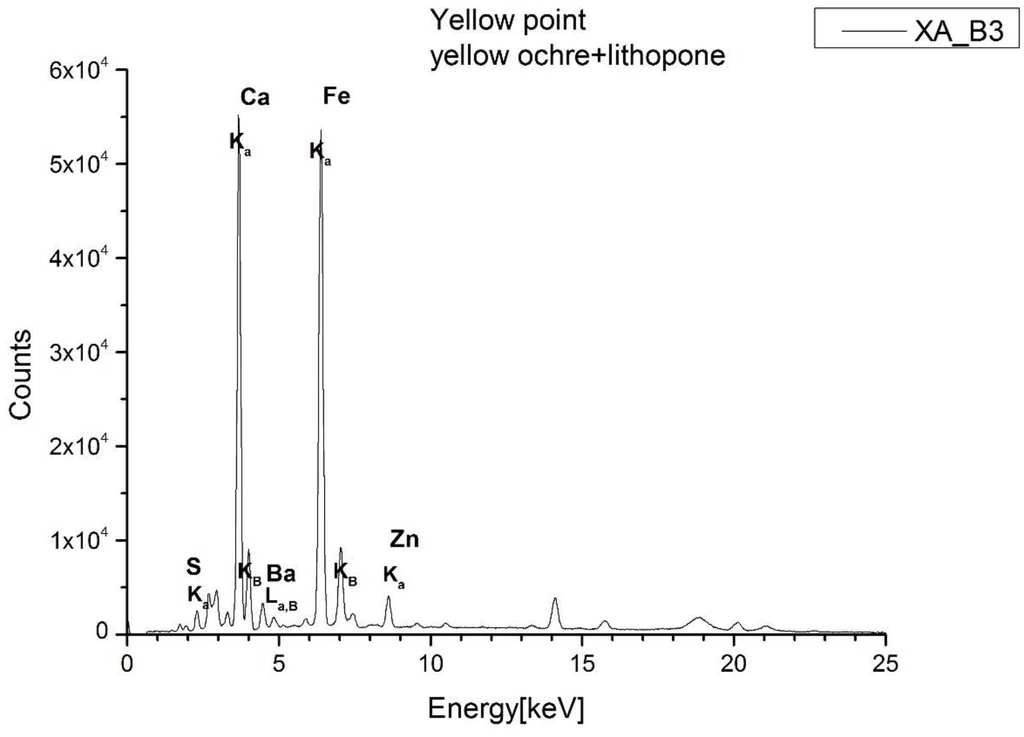


Fig. 14: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the yellow point of the body of vase A. Attribution of some of the lines to the emitting elements is shown.

8. Black point

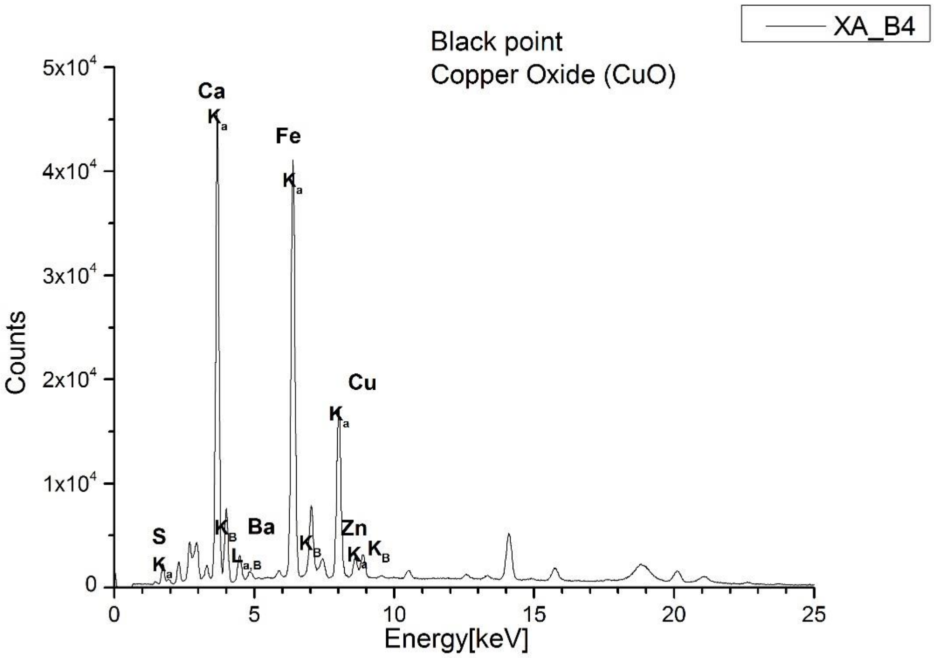


Fig. 15: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the black point of the body of vase A. Attribution of some of the lines to the emitting elements is shown.

9. Stuccatura point

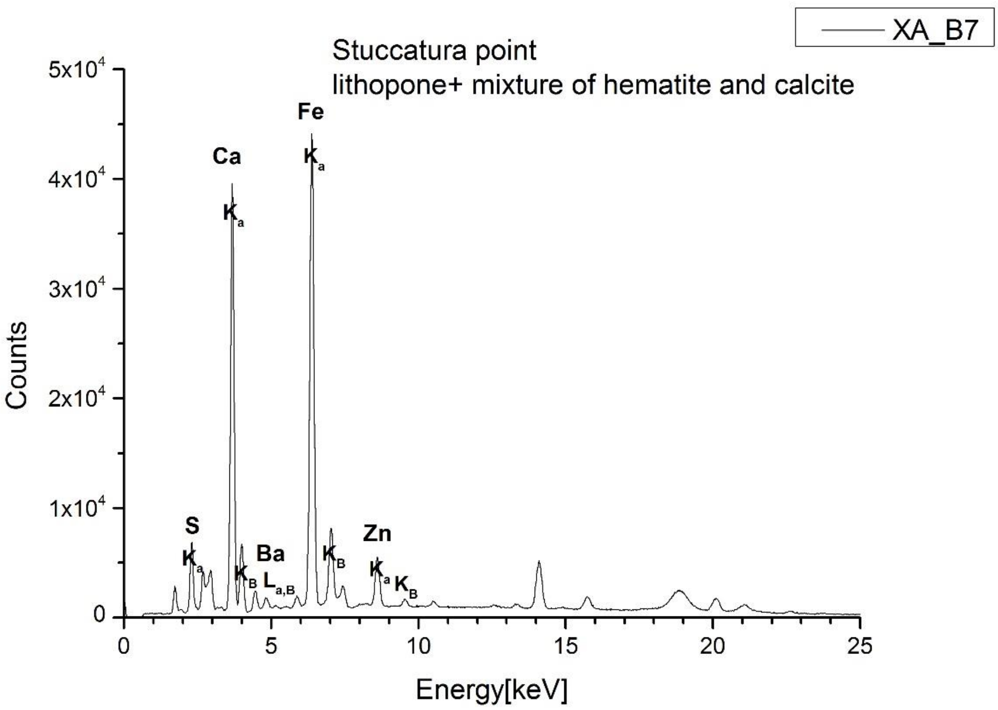


Fig. 16: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the stuccatura point of the body of vase A. Attribution of some of the lines to the emitting elements is shown.

Vessel B

1. White point

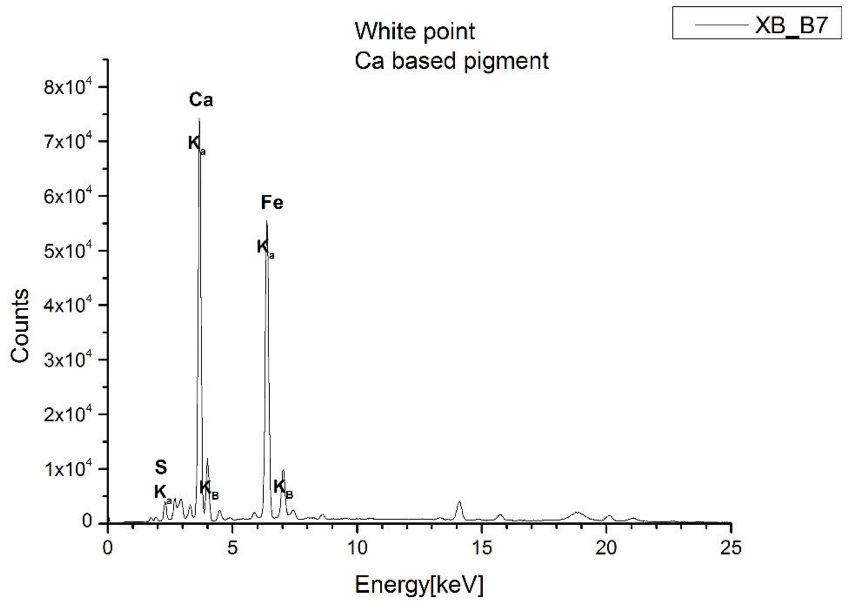


Fig. 17: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the white point of the body of vase B. Attribution of some of the lines to the emitting elements is shown.

2. Red points

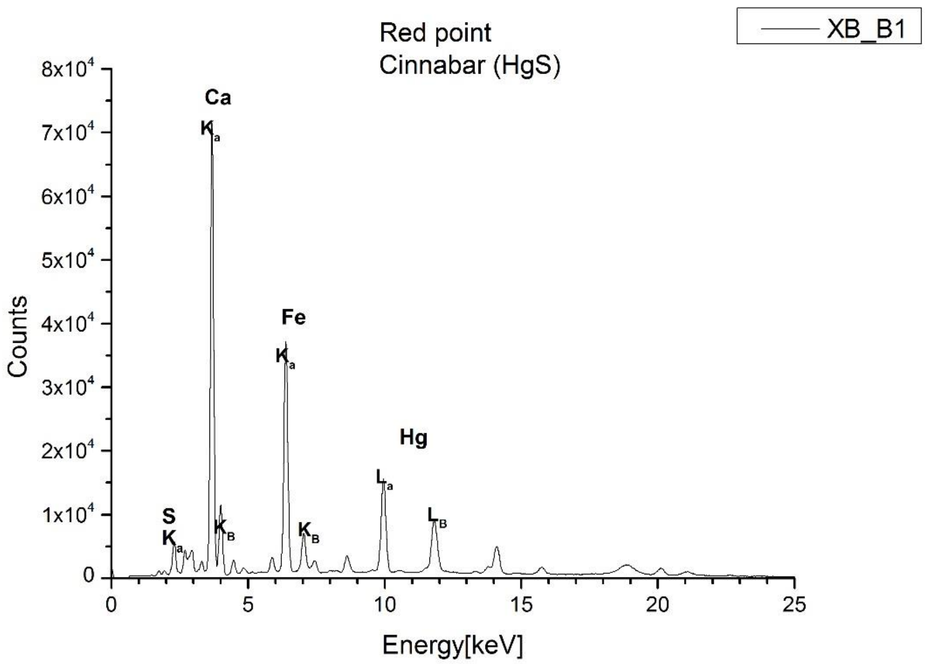


Fig. 18: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the red point of the body of vase B. Attribution of some of the lines to the emitting elements is shown.

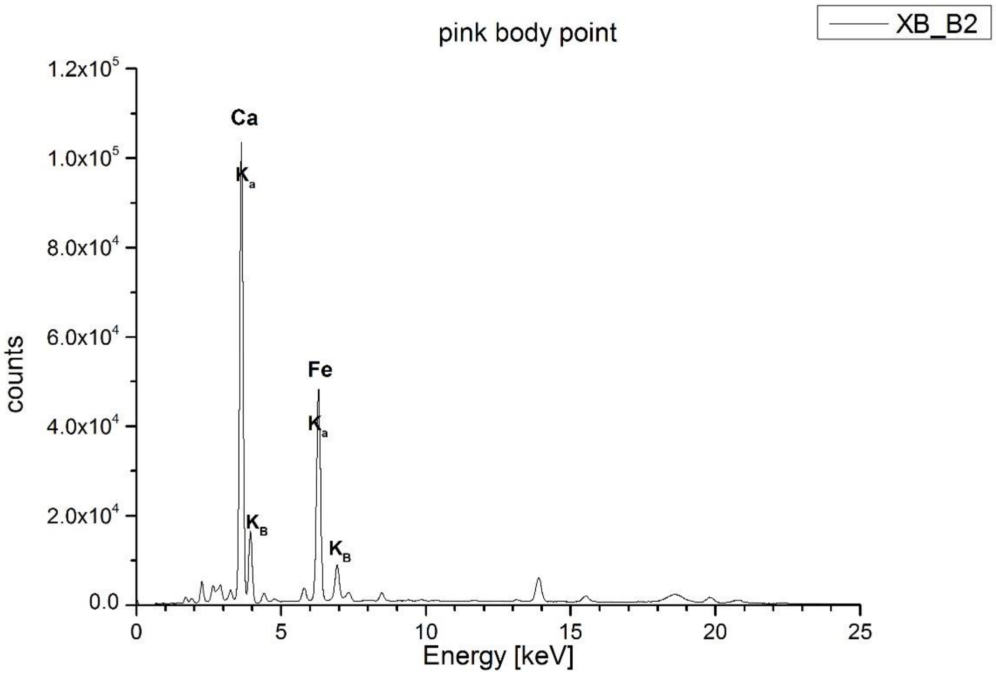


Fig. 19: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the red point of the body of vase B. Attribution of some of the lines to the emitting elements is shown.

3. Gold point

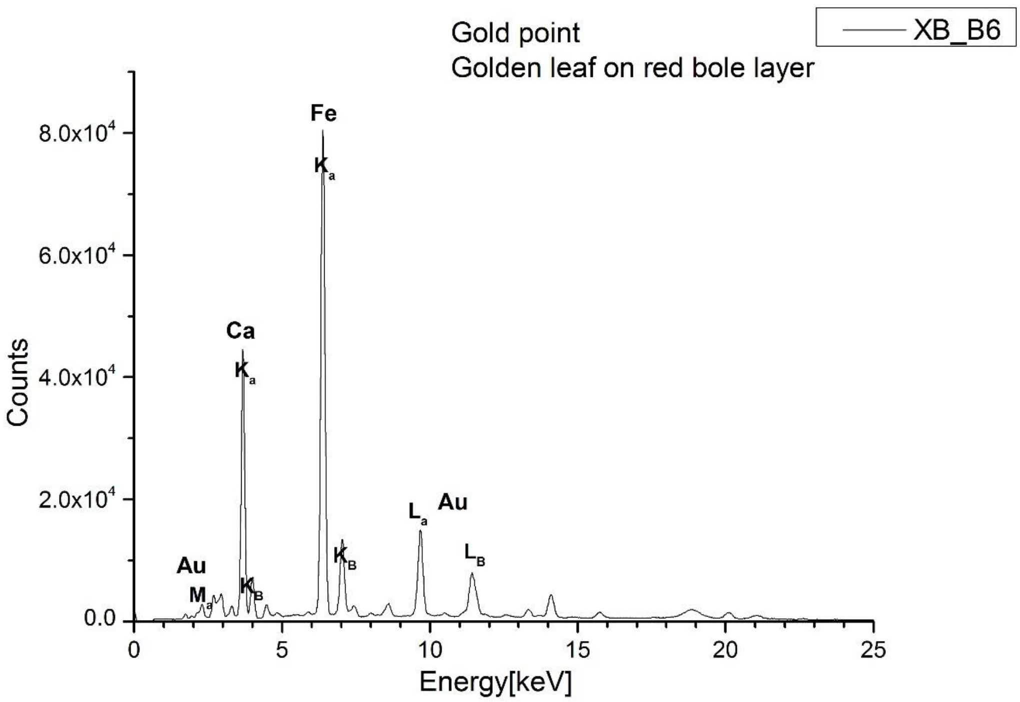


Fig. 20: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the golden point of the body of vase B. Attribution of some of the lines to the emitting elements is shown.

4. Brown points

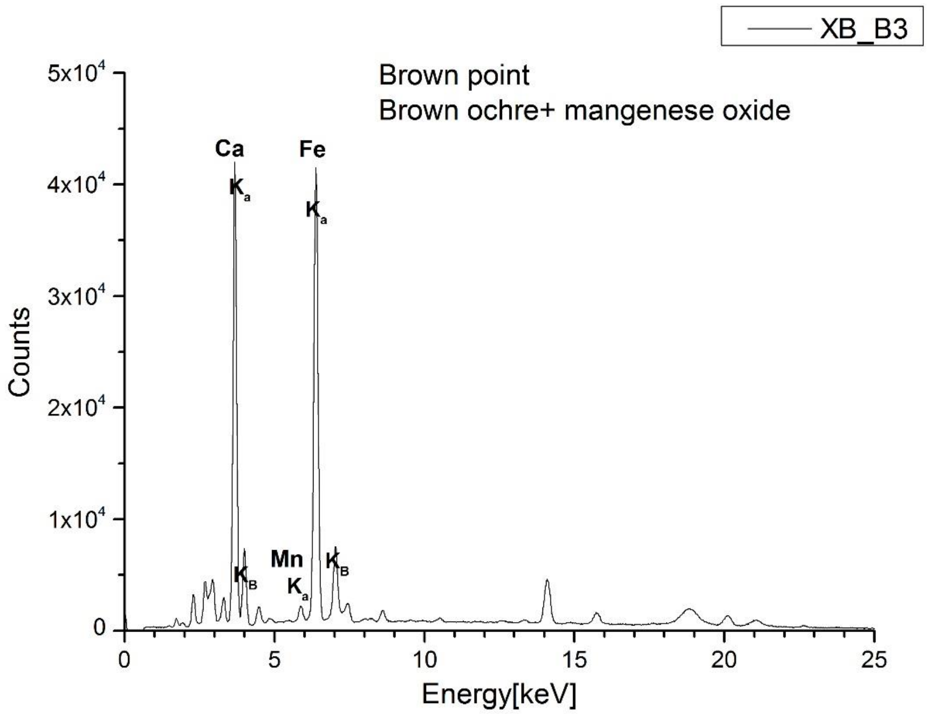


Fig. 21: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the brown point of the body of vase B. Attribution of some of the lines to the emitting elements is shown.

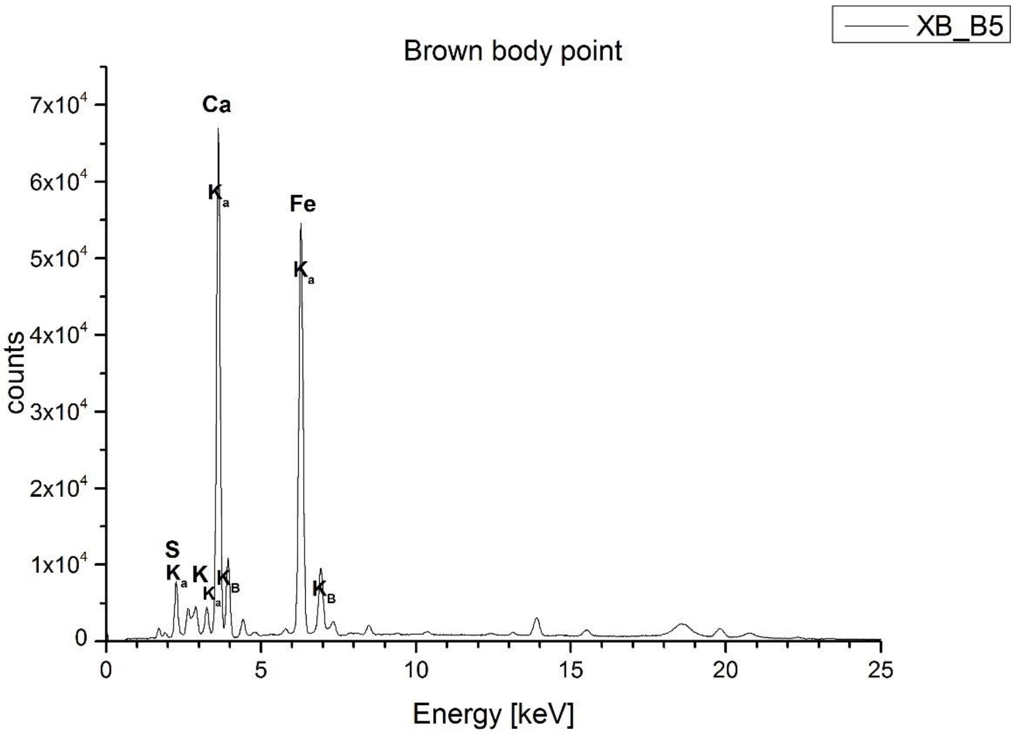


Fig. 22: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the brown point of the body of vase B. Attribution of some of the lines to the emitting elements is shown.

5. Blue point

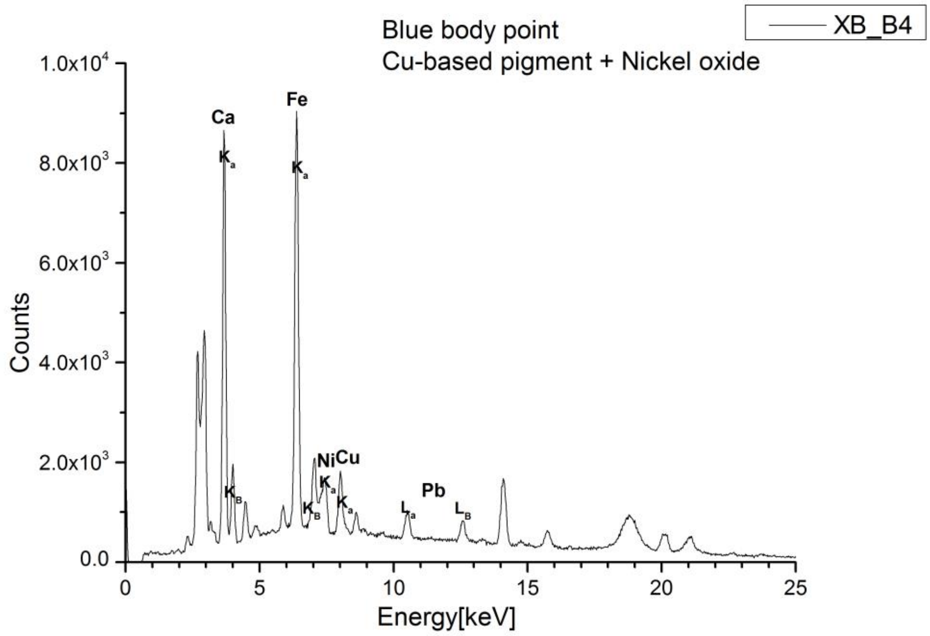


Fig. 23: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the blue point of the body of vase B. Attribution of some of the lines to the emitting elements is shown.

6. Stuccatura point

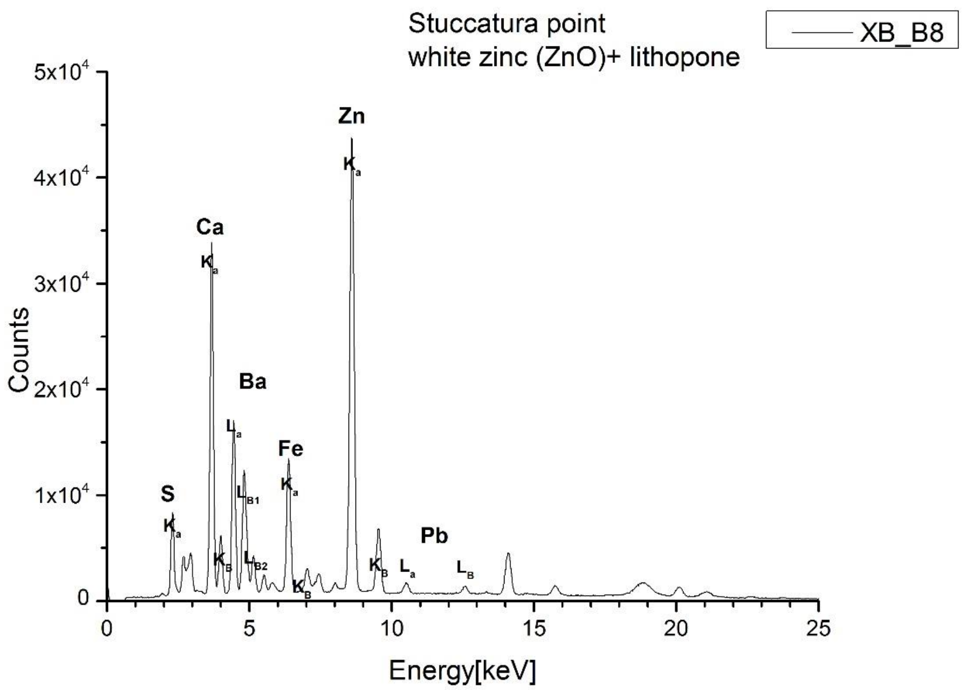


Fig. 24: XRF spectrum, Intensity (Counts in arbitrary units) vs Energy (keV) of the stuccatura point of the body of vase B. Attribution of some of the lines to the emitting elements is shown.

IR spectra

Vase A

1. egg points

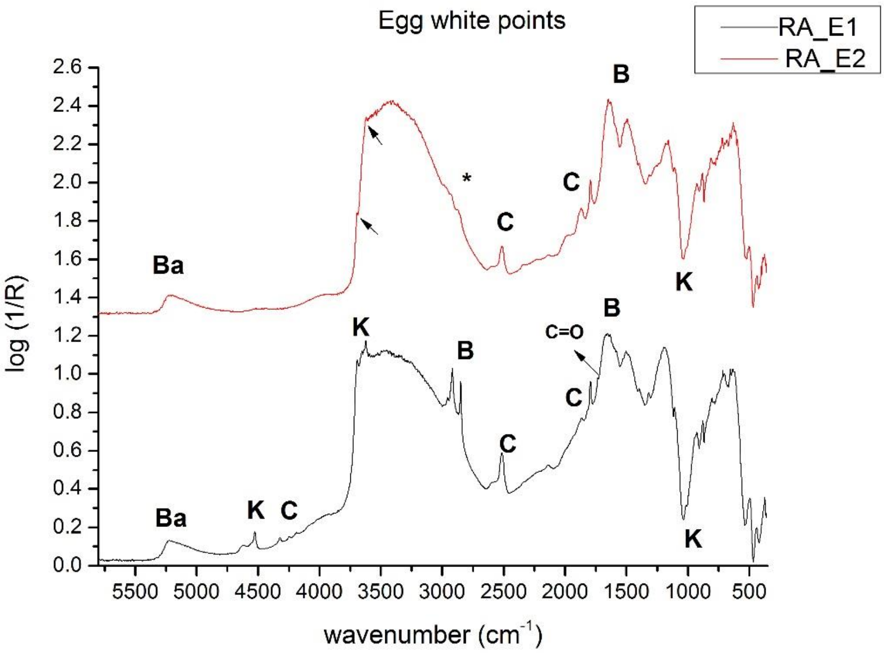
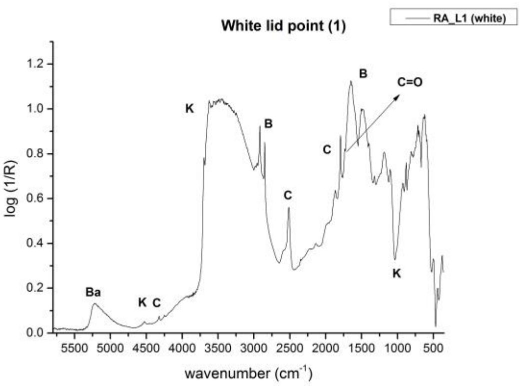
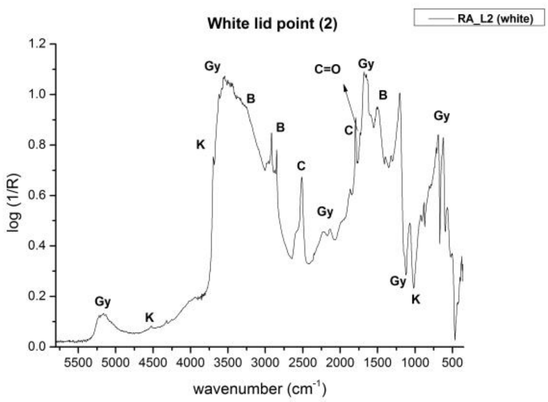


Fig. 25: reflection spectra of the egg points (RA_E1, RA_E2) in vase A characterized by k=kaolin, C= calcite, Ba=basanite, and B= organic binder

2. white points





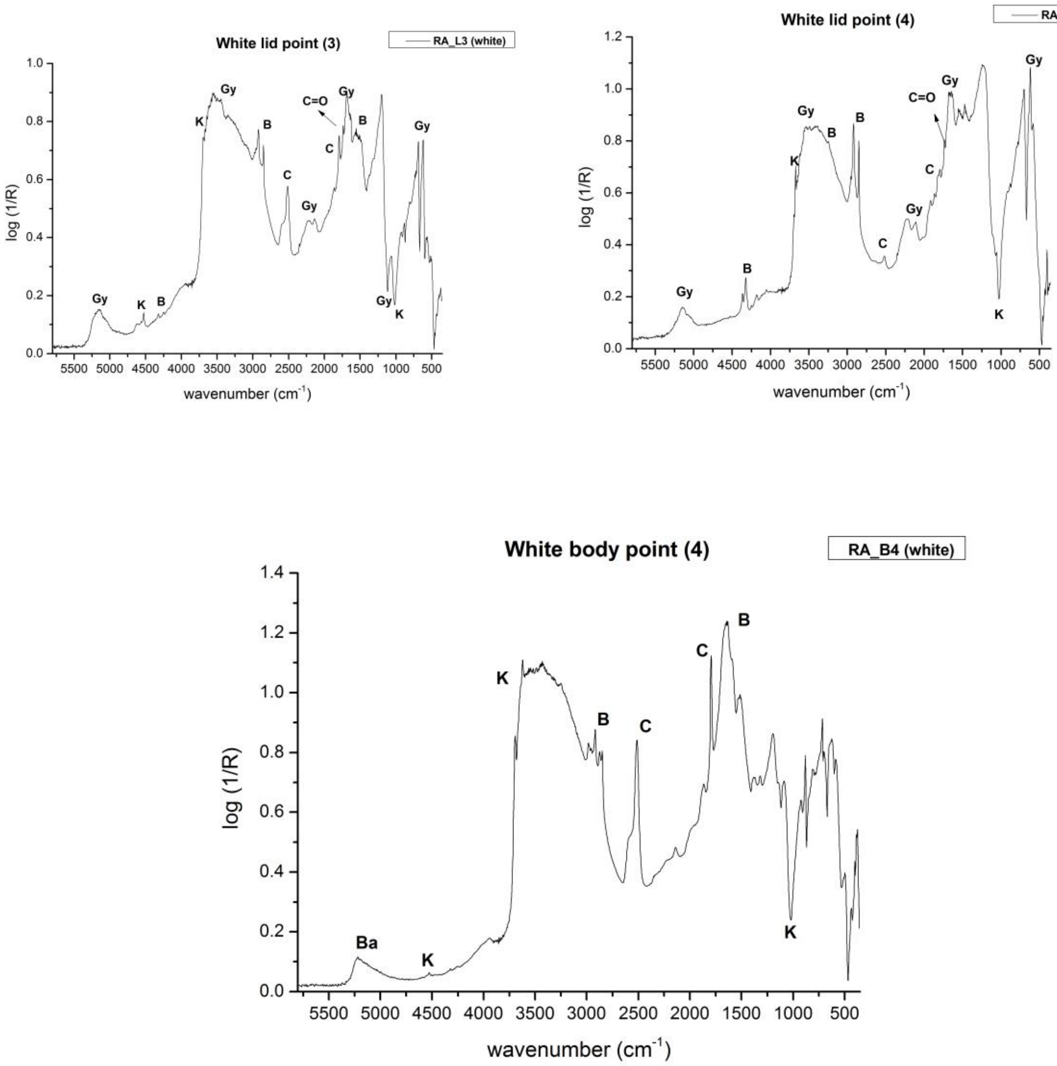
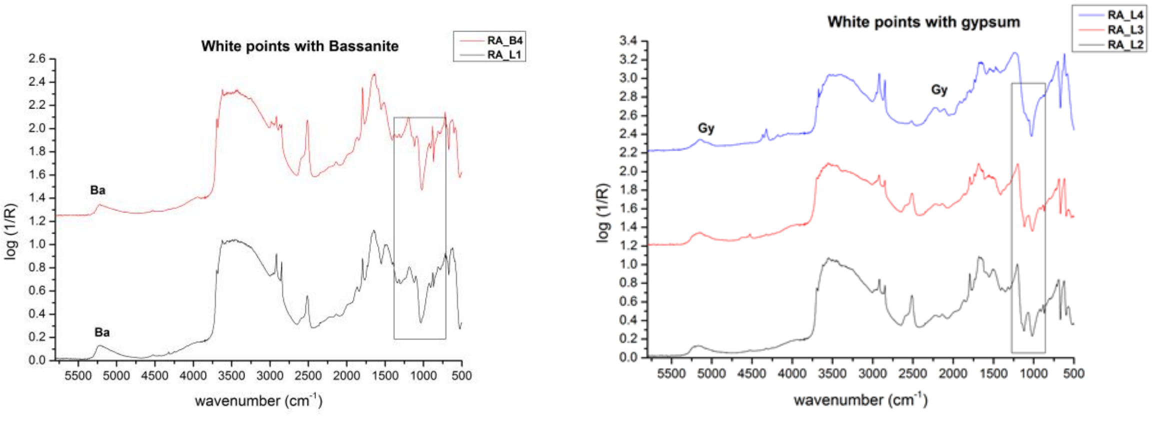


Fig. 26: reflection spectra of the white points (RA_L1, RA_L2, RA_L3, RA_L4, RA_B4) in the lid and body vase A characterized by k=kaolin, C= calcite, Ba=basanite, Gy=gypsum and B= organic binder



a) **b)**

Fig. 27: reflection spectra of the white points, a) for the white points with bassanite (RA_L1, RA_B4). b) for the white points with gypsum (RA_L2, RA_L3, RA_L4).

3. Red points

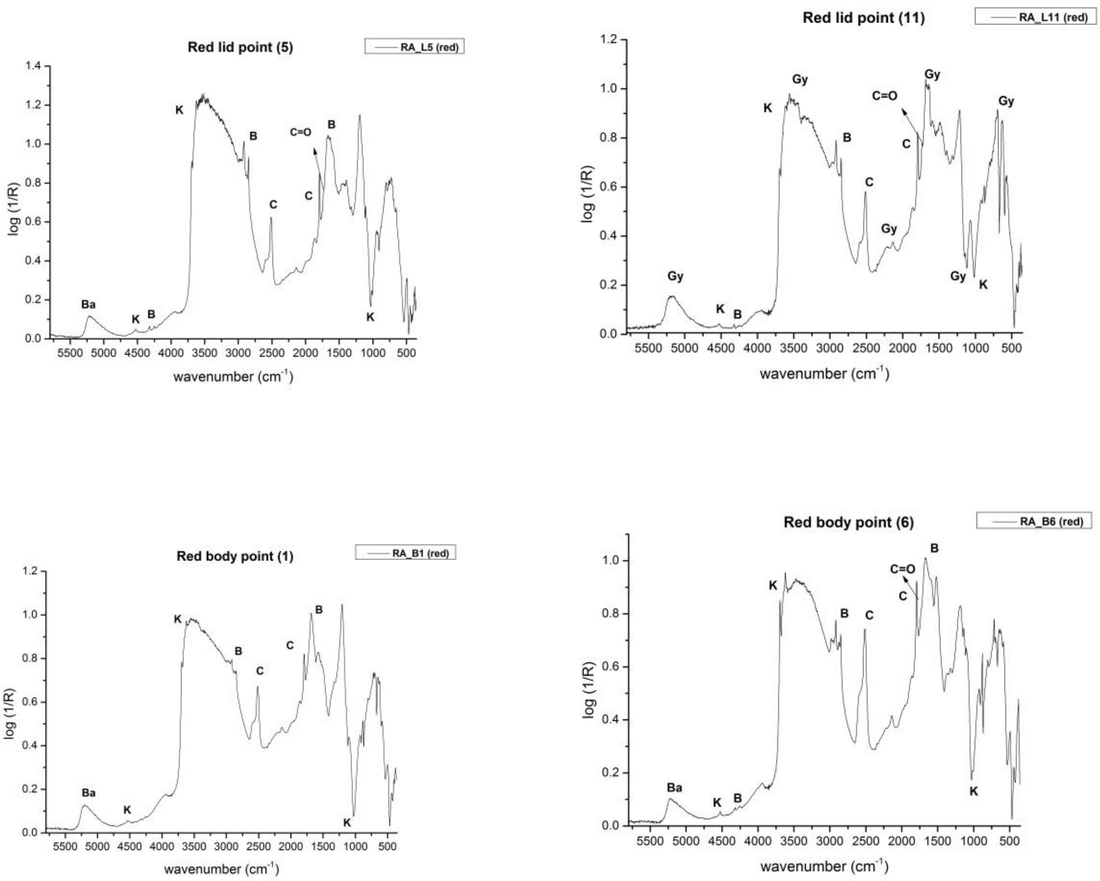


Fig. 28: reflection spectra of the red points (RA_L5, RA_L11) in the lid and (RA_B1, RA_B6) in the body of vase A characterized by k=kaolin, C= calcite, Ba=basanite, Gy=gypsum and B= organic binder

4. Blue greenish points

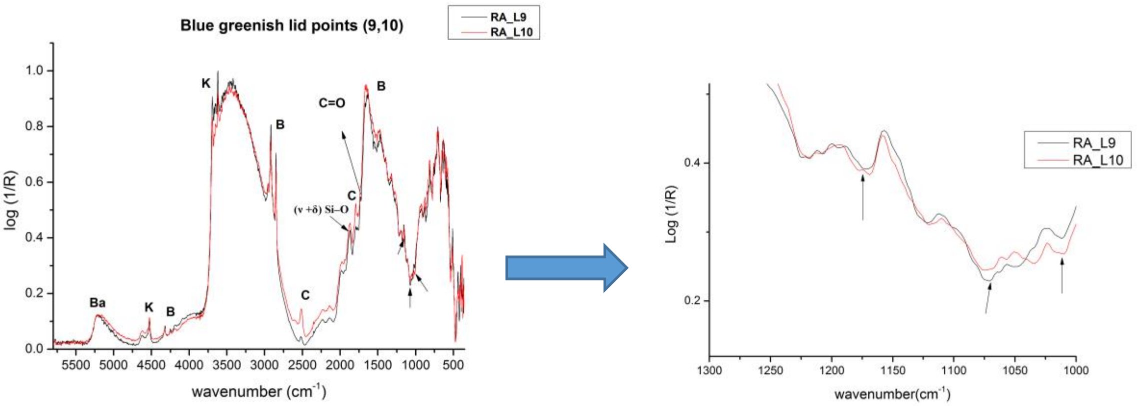
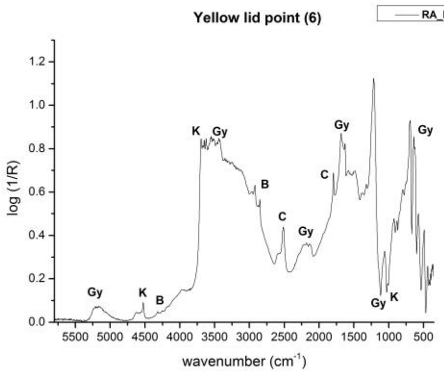
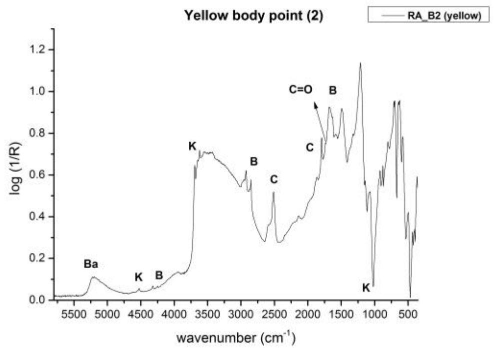


Fig. 29: reflection spectra of the blue greenish lid points (RA_L9, RA_L10) of vase A characterized by k=kaolin, C= calcite, Ba=basanite, and B= organic binder, arrows are indicated to Egyptian blue.

4. yellow points





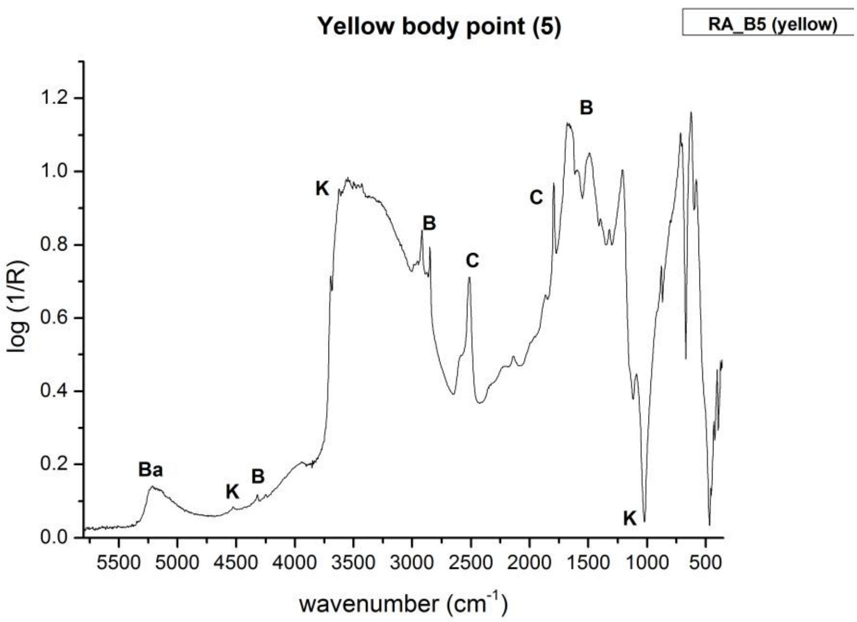
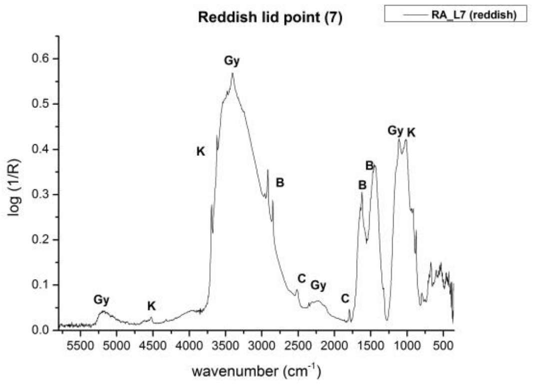


Fig. 30: reflection spectra of the yellow points (RA_L6, RA_B2, RA_B5) of vase A characterized by k=kaolin, C= calcite, Ba=basanite, Gy=gypsum, and B= organic binder.

5. Gold and reddish points



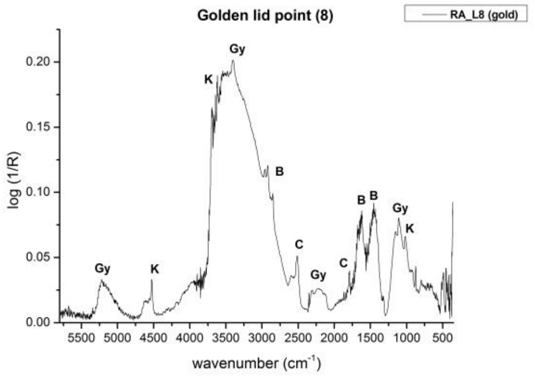


Fig. 31: reflection spectra of the reddish, golden points (RA_L7, RA_L8) of vase A characterized by k=kaolin, C= calcite, Gy=gypsum, and B= organic binder.

6. Stuccatura points

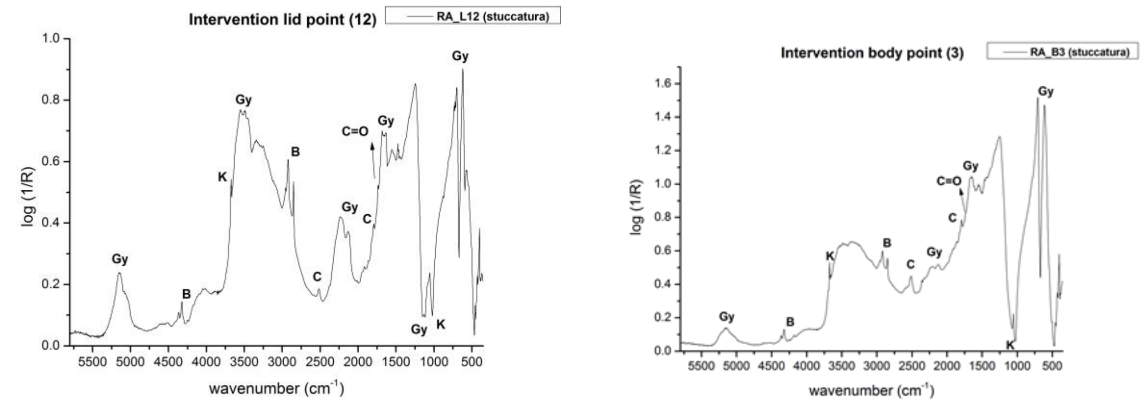


Fig. 32: reflection spectra of the stuccatura points (RA_L12, RA_B3) of vase A characterized by k=kaolin, C= calcite, Gy=gypsum, and B= organic binder.

Appendix 4 figures of vases

1. Finial egg
2. Lid
3. body

A

B

1. Lid
2. Body

Fig. 1: Centuripean vases. Pyrix vase A, Lebes Gamikos vase B displayed in Salinas Archaeological Museum in Palermo-Italy.

XRF analyzed points

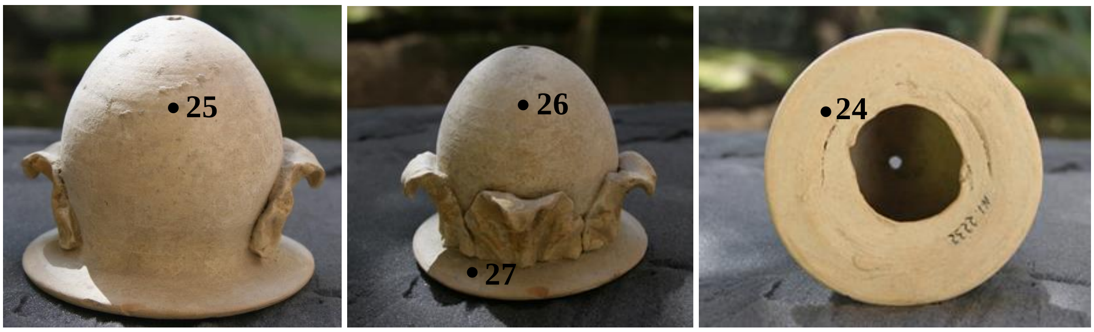


Fig. 2: XRF egg points in vase A

Fig. 3: XRF front side lid points from different colored areas in vase A. the colors are as following: blue greenish points (1,3), greenish point (21); red points (2,4,8); white points (6,7); orange point (5); background point (9); yellow point (11); golden point (10).

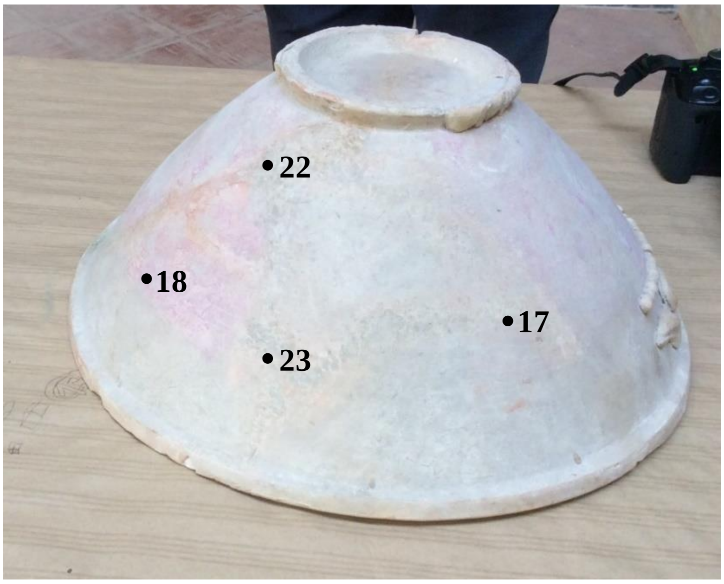


Fig. 4: XRF rear side lid points from different colored areas in vase A. the colors are as following: greenish points (22,23); red point (18); white points (19,17); orange point (20).

Fig. 5: XRF inside lid points from different colored areas in vase A. the colors are as following: white points (16); orange point (12,13); grey points (14,15).

Fig. 6: XRF body vase points from different colored areas in vase A. the colors are as following: white point (1); red points (2,6); yellow point (3); black point (4); gold point (5); stuccatura point (7).

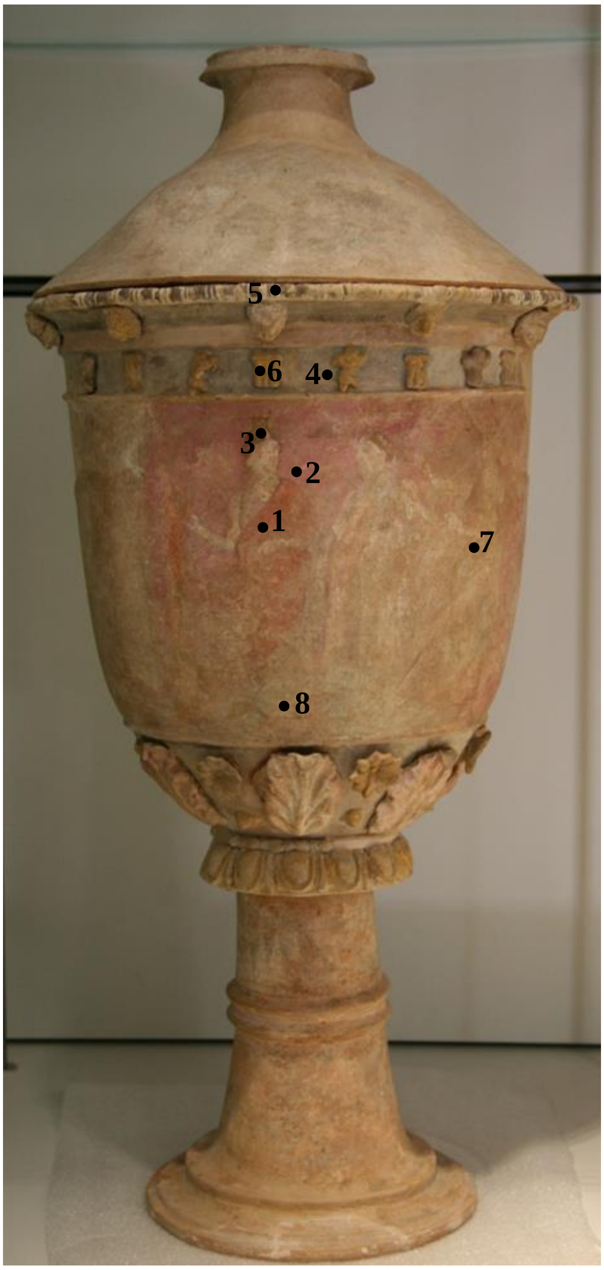
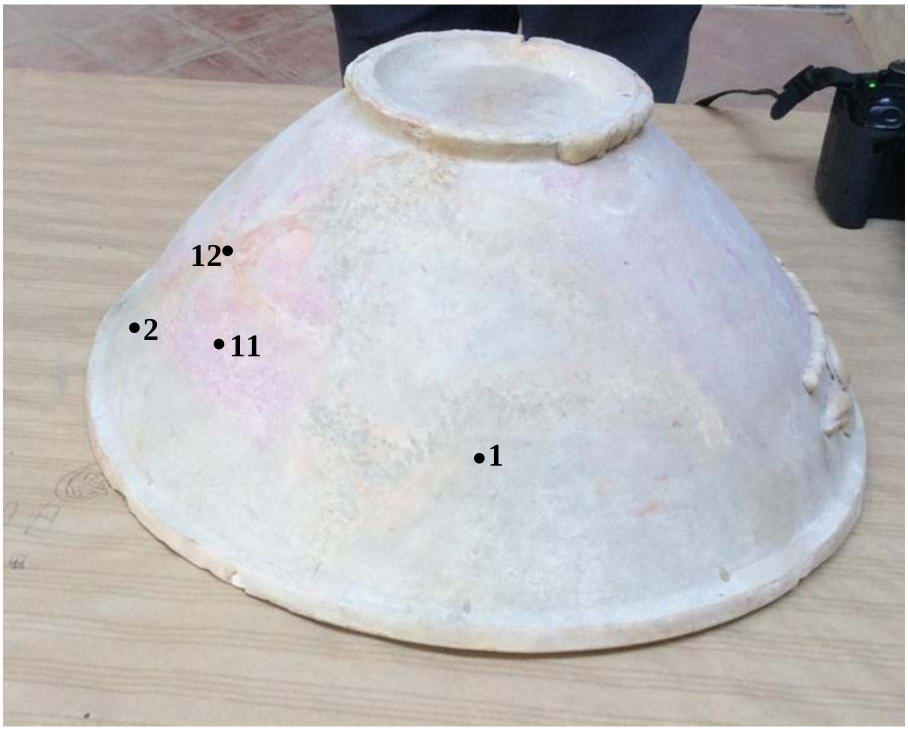


Fig. 7: XRF body vase points from different colored areas in vase B. the colors are as following: white point (7); red points (1,2); golden point (6); brown points (3,5); blue point (4); stuccatura point (8).

IR analyzed points

Fig. 8: IR white egg points in vase A, (RA_E1) in the front side of egg, and (RA_E2) in the inside border of egg.

a)



b)

Fig. 9: IR lid points in vase A, a) is the front side of lid with white points (RA_L3, RA_L4), green points (RA_L9, RA_L10), red points (RA_L5), yellow point (RA_L6), golden point (RA_L8), reddish point (RA_L7). b) is the rear side of the lid with whit points (RA_L1, RA_L2), red points (RA_L11), stuccatura point (RA_L12).

Fig. 10: IR body points in vase A. yellow points (RA_B2, RA_B5), red points (RA_B1, RA_B6), white point (RA_B4), stuccatura point (RA_B3).

Fig. 11: illustrates the palette used in painting scene in the lid of the vase A (Pyxis)

Fig. 12: illustrates the palette used in painting scene in body vase A (Pyxis)

Fig. 13: illustrates the palette used in painting scene in body vase B (Lebes Gamikos)