**Museum-Konservierung**

**Μουςειο-Προετοιμαστής**

**Museum-Conservatio**

**Documenta historiae**
**Band 11**

**München**

**2010**

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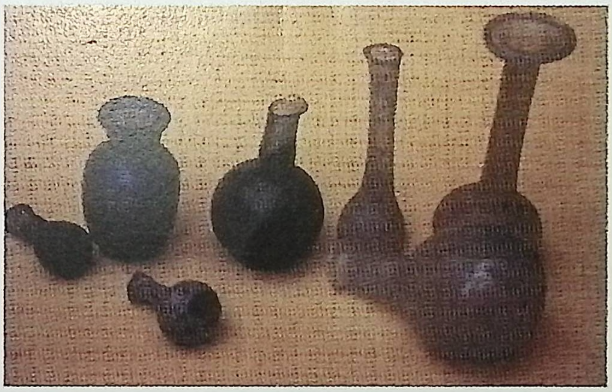

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# DOCUMENTA HISTORIAE

Nr. 11 2010

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ISBN: 978-3-86544-611-4 ISSN 1433-1691

**Herausgeber der Zeitschrift Documenta naturae im**
**Verlag (Publishing House) Documenta naturae - München (Munich)**

Dr. Hans-Joachim Gregor, Daxerstr. 21, D-82140 Olching
Dr. Marcel Schoch, Am Blütenanger 11, D-80995 München

Vertrieb: Dipl.-Ing. Herbert Goslowsky, Joh.-Seb.-Bach-Weg 2, 85238 Petershausen,
e-mail: goslowsky@documenta-naturae.de

Die Zeitschrift erscheint in zwangloser Folge mit Themen aus den Gebieten der Mediavistik, Alten Geschichte, Klassische Archäologie, Ägyptologie, Vorderasiatischen Archäologie, Vor- und Frühgeschichte und verwandten Wissenschaften.

Für die einzelnen Beiträge zeichnen die Autoren verantwortlich, für die Gesamtgestaltung die Herausgeber.

Gestaltung und Layout: Juliane Gregor und Hans-Joachim Gregor
Cover: Blown perfume vessels/ Thermohydrographs

**www.palaeo-bavarian-geological-survey.de; www. documenta-naturae.de**

**München 2010**

| Documenta historiae | 11 | p. 1-28 | 52 figs. | München | 2010 |
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# CORROSION PATTERNS AND CONSERVATION PROCESSES OR TECHNIQUES OF ROMAN GLASS VESSELS OF 1ST CENTURY AD FROM RHODES ISLAND, GREECE

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## ΠΕΡΙΛΗΨΗ

Τα γυάλινα αγγεία που επιλέγησαν για συντήρηση και αποκατάσταση προέρχονται από ανασκαφές της Ρόδου, που αποτελούσε ένα σημαντικότατο κέντρο υαλουργίας κατά την αρχαιότητα. Οι τεχνικές κατασκευής γυάλινων αγγείων στην περιοχή αυτή είναι συνήθως όλες οι μέχρι τώρα γνωστές κατά την αρχαία εποχή και απεικονίζουν με θαυμάσιο τρόπο την φαντασία και την ευρηματικότητα των υαλουργών της ελληνικής αυτής περιοχής, με αποτέλεσμα τις φιλοτεχνήσεις όμορφων αντικειμένων χρηστικών αλλά και διακοσμητικών, χωρίς να υπάρχει σαφής διαχωρισμός αυτών των δύο κατηγοριών. Οι επιδράσεις στην τεχνοτροπία ερχόντουσαν ταυτόχρονα από την ανατολή, με τα ονομαστά υαλουργικά της κέντρα (Συρία, Φοινίκη), το νότο με την μεγάλη υαλουργική παράδοση (Αίγυπτος) αλλά και τη δύση με τα νεώτερα εξαίσια επιτεύγματα υαλουργίας (Ρώμη).

Η ανάγκη αποκατάστασης αυτών των αγγείων προήλθε από την αναγκαιότητα μετάδοσης και διαχρονικότητα αυτών των τεχνικών, για να γίνουν και αυτά όπως και άλλα αρχαιολογικά ευρήματα αντικείμενο θαυμασμού, παρατήρησης και μελέτης από τις νεώτερες γενεές, συνειδητοποιώντας έτσι την πολιτιστική τους ταυτότητα από τα θαυμάσια αυτά δείγματα της ελληνικής πολιτιστικής κληρονομιάς.

## ABSTRACT

The study of the conservation and restoration of Roman blown glass cosmetic bottles from Rhodes, began with the gathering of historical - archaeological data and continued with the technological data of these archaeological objects. This important data about the ancient technology helps us understand the corrosion forms that might have occurred to these objects.

These forms of corrosion were confirmed macroscopically and microscopically. They included: dulling, crizzling, lamination, iridescences, pitting and crusting with biological deposits in almost all cases. The forms of corrosion were usually caused by the presence of humidity, temperature variations, crystallization of soluble salts in the excavation area and also during the storage of these objects.

After the forms of corrosion were identified, the appropriate conservation and restoration methods were selected. These included the analyses of the materials' structure and deposits, the pre-consolidation of the corroded surfaces, the extraction of the deposits, consolidation of the corroded surfaces and finally the joining of the broken pieces. As a last point, the appropriate conditions for the storage and exhibition of these glass vessels are being suggested.

**Keywords:** archaeological glass, corrosion, blown glass, conservation.

## INTRODUCTION - HISTORICAL DATA

Before the invention of artificial glass, the objects of value and high artistic quality were being manufactured from natural glass. Natural glasses were formed mainly by natural silicon casts that were mostly categorized geo-chemically within the acidic types that contain at least 65% of silicon dioxide ($SiO_2$) [10]. Obsidian could be considered as man's oldest contact with glass because of its macroscopic characteristics and structure that are similar to glass [13] (Fig. 1., Fig. 2.).

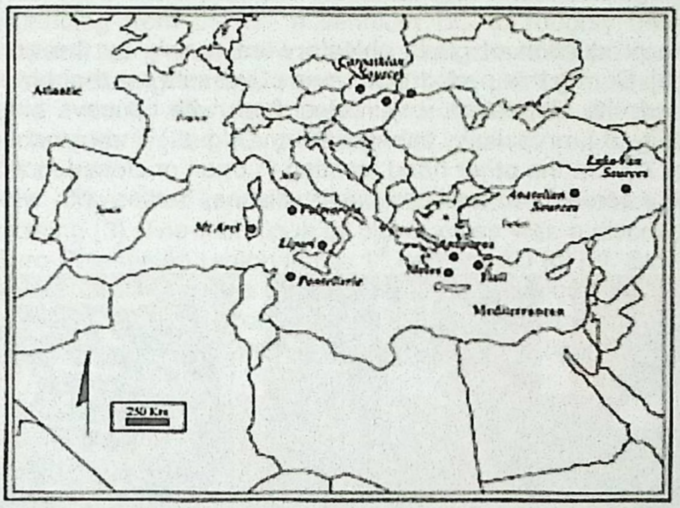


*Fig. 1. Map of Mediterranean Sea showing occurrence of obsidian [10].*

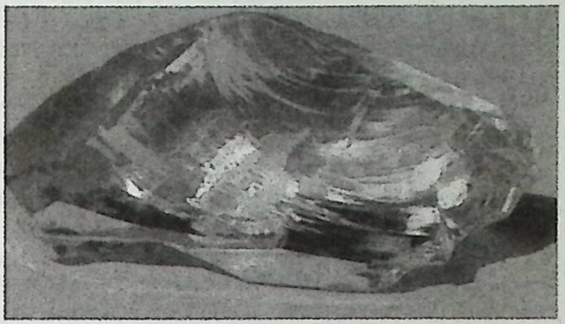


*Fig. 2. Sample of obsidian [10].*

The first glass objects were knives and peaks of arrows made from thin obsidian leaves; they date back to the beginning of the Paleolithic era [6].

From a technological point of view, glass is an inorganic material that is classified in shapeless solids. It is hard, fragile with a "conical" rupture, usually transparent or semi-transparent, homogeneous and isotropic [7]. Silicon dioxide ($SiO_2$), alkalis (Na, K), some alkaline earths (Ca, Mg) and aluminum (Al) are its main components. From the physiochemical perspective, it could be considered a "liquid" with exceptionally high viscosity and in ordinary conditions of temperature and pressure, presents the attributes of a solid material [1]. The manufacture of glass is ineffably connected with magic and religion and has been considered as a material with magical attributes. The basic aim of the glass manufacturer was to imitate precious stones, mainly lapis lazuli (Fig. 3.) and turquoise (Fig. 4.) [4].

*Fig. 3. Imitation of lapis lazuli [3].*

*Fig. 4. Imitation of turquoise [3].*

The precise chronology of the manufacturing and origins of hand-made glass is not evident. However, it is almost certain that it had been discovered in the eastern Mediterranean before 3.000 BC. It is reported by Pliny Senior that the traditional place for collecting sand suitable for the manufacture of glass was the estuary of the river Belus in Phoenicia. He also refers to another area for sand collection; this was the estuary of the river Volturnus, north of Naples. Pliny connects this area with the "modern" way of glass manufacturing (blown glass) which appears to have been used during Roman times [4]. In Egypt, glass was first encountered in the kingdom of Touthmosis III and, based on basic stylistic and analytic studies, it appears that the first craftsmen were from Asia [12] and probably from Syria [3]. The Egyptian name for glass was "iner en wedeh" or "aat wedhet" which when translated means, "stone that flows".

The techniques that were used for the production of glass objects were mainly by the core method and casting in open or closed molds [6]. During this period four types of vessels are thought to have been manufactured with the core method: the alabastron - cylindrical form with concave base (Fig. 5.), small amphora form - pear shaped (Fig. 8.), aryballos - spherical form (Fig. 6.) and oinochoe - a vase with a handle and a flat base [6] (Fig. 7.). On the other hand, casting in open or closed molds was used for the production of open vessels - containers, such as bowls, dishes, bottles with wide neck and tiles [6].

*Fig. 5. Alabastron [3].*

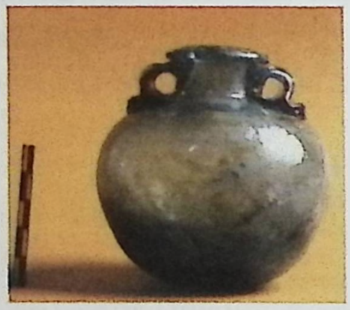


*Fig. 6. Global aryballos [8].*

*Fig. 9. Blown perfume unguentaria of candlestick type [8].*

*Fig. 7. Oinochoe [8].*

*Fig. 8. Small amphora [3].*

The revival of the glass manufacturing industry took place throughout western Asia, the near East and Mediterranean in the 9th BC [3]. The techniques that were used from the 7th through to the 9th century BC were similar to those of the Egyptians, but the types of vessels were hemispherical bowls and drinking vessels, with various decorations [3]. Apart from the two previous techniques, the technique of mosaic glass (Fig. 11.) was also used, albeit exclusively in western Asia and Mesopotamia. Important innovations were: the perfume cruet (alabastron), found in Cyprus, Italy and Palestine as well as small the amphora, the oinochoe e.tc..

The core method, as a technique of manufacturing glass unguentaria (perfume vessels), was used widely by all the glass workshops in the Mediterranean from 550 to 50 BC [3]. These vessels were used to hold perfume oils and cosmetics (Fig. 12.). The forms of older Greek ceramic and metal vessels gave their name to them [3]. The last phase of Mediterranean workshops of glass manufacturing that used the core method was during the Hellenistic period between the second half of the 2nd century and the first half of the 1st century BC. While the most popular vessels of this period were still mainly types of alabastron and amphora, they were smaller in size with a long neck [3]. At the same time as the core method, vessels were also frequently shaped by casting during the classic period (5th - 4th century BC), and just as frequently in the Hellenistic period from 3rd up to 1st century BC [6]. During the 3rd and 2nd century BC, the most characteristic technique is reported to be glass vessels with leaves of gold or silver enclaves between the two glasses layers [6],[3]. These were manufactured in Rhodes and illustrated the continuity of traditional Alexandrian products [6]. Finally, another technique that was developed in this period was the glass cameo that appeared from the end of the 1st century BC until the beginning of the 1st century AD [6].

The history of pre-industrial glass manufacturing can be divided into two periods: the first, extending from the 3rd millennium BC to roughly between 100 and 50 BC, where the craftsmen devised the process of transformation of natural primary materials in glass as well as the methods of manufacturing various vessels with the use of molds or with the configuration of glass melt around core, which afterwards was detached [16]. These time-consuming and particularly laborious techniques limited the production of glass to relatively small quantities and seldom allowed its wide distribution.

The most important innovation in the manufacturing of glass in antiquity was the discovery of blowing [3]. The technique of blown glass was a discovery that was likely to have emanated from the Syro-Palestinian region in the 1st century AD [6],[3]. Blown glass dates back to the 1st century AD until 4th century AD and is mainly a Roman technique [6]. The method of blowing was believed to be the motive for mass production and use of glass that could be implemented without any particular technological requirements or changes in the figure of the furnace [1] (Fig. 9. & Fig. 10.).

*Fig. 10. Blown perfume vessels [8].*

*Fig. 12. Core formed perfume vessels [3].*

*Fig. 11. Mosaic glass [3].*

The earlier discoveries of blown glass emanate from Jerusalem. Although the archaeological discoveries are located in the East, it is not evident whether the real free blowing was first produced there or in Italy. It is in Italy that earlier discoveries of blown unguentaria have been discovered, that date from the last fourth of the 1st century BC up to the first decade of the 1st century AD [1]. The small Italian unguentaria are similar to those from Syria, Palestine, Asia Minor and Cyprus [1] and they date back to the 1st century AD. Similar discoveries in Greece (Samothrake, Rhodes islands) are believed to be from the first half of the 1st century AD.

## RHODES' GLASS INDUSTRY

One of the most important and long-lasting centers of the glass industry in the Mediterranean, according to the archaeological bibliography on glass artifacts, is the island of Rhodes [15]. The glass in Rhodes dates back to the14th century BC [15]. The older finds were manufactured by the core method, but unfortunately most of them have been destroyed.

After the fall of the Mycenaean civilization, from the end of the 12th century BC up to the 9th century BC, the manufacture process of glass decreased in the Hellenic mainland. Rhodes, due to its geographic position, continued to possess an important place as a distribution center of new glass products from East to West up to the first half of the 6th century BC [13]. However, the abundance of glass utensils dating back to the end of the 6th century BC, has led researchers to assert that Rhodes flourished again as one of the most important manufacturing areas of the archaic and classic years in Eastern Mediterranean [15].

During the 3rd and 2nd century BC the manufacturing of glass objects presented outstanding results. The most characteristic technique of this period is reported to be the enclosure of gold and silver leaves between the two layers of a glass vessel [6]. With the discovery of the blowing method during the second half the 1st century BC on the coast of Phoenicia, blown glass was propagated in all the centers of glass production and also in new Mediterranean centers. In the southeastern Aegean, glass produced both with the blown method or with casting, was used for the production of utilitarian as well as luxurious vessels that decorated Roman villas in Rhodes and Kos [14]. Colorless, painted bulb-type and spherical ampoules used for holding cosmetics were discovered in the necropolis of Rhodes dating back to the early productions of the 1st and 2nd century AD [15].

From the roman vessels that have been found in Rhodes we can deduce that locally produced products were present at the same time as imported ones, even if the workshops from the early roman times have not yet been located. The archaeological finds though, imply that roman workshops existed during late antiquity. Samples of blown glass have been discovered and dated back to the late roman and early Christian years in the medieval city of Rhodes near the Ancient Agora [15]. Together with these indications, many utensils have been excavated. They include "prohous", "skyfous", plates and alabastron which cover all the typical groups of late antiquity up until Byzantine times. This shows that glass objects were also used at the Christian ceremonies [13].

## TECHNOLOGY

The common use of the term "glass" coincides with the definition of Morey (1954): "glass is an inorganic material in the state of proportional liquids, but because of its high viscosity, it is considered as solid for practical reasons". Glass, as an inorganic material, is defined as the product of melting, which has been frozen to a solid condition without crystallization [7]. It is portrayed as a shapeless solid [6] that in the past was considered to have magic attributes.

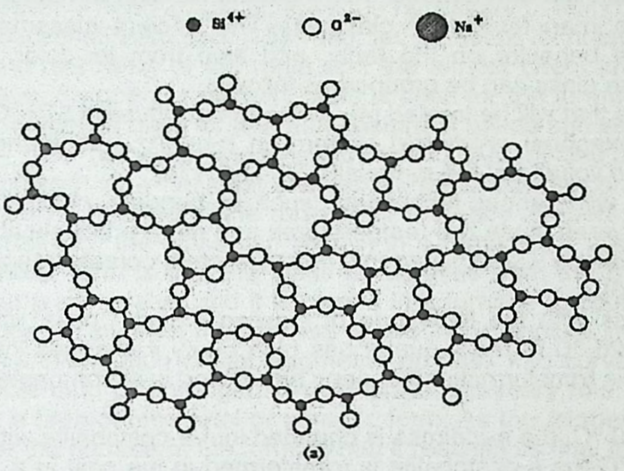
Raw materials for the production of ancient glass were silicon dioxide ($SiO_2$), calcium oxide (CaO) and alkalis oxides ($Na_2O$, $K_2O$) [12]. The main material for the production of glass is silicon dioxide that was mainly collected from sand. However, because the sand was mixed with many other materials, ancient manufacturers preferred to mine quartz or flint [5], [4].

Natural calcium can be found in the form of limestone, marble or chalk [12], but limestone as a source of calcium was only used when the other two sources of raw material did not contain a suitable quantity of calcium. It is most likely that the calcium was added indirectly [4], rather than on purpose [12], even if calcium is used today in the glass industry as a basic stabilizer of the sand and alkaline mixture [15]. Finally, the alkaline come from mines such as natron, known during antiquity in the Wadi Natrum in Egypt, (Fig.13.) Minor Asia, Macedonia, Thrace (near Philippous) and in Liti [15]. The alkaline also came from the sediments of drained lakes or from plants' ashes [12]. Potassium came from the ashes of various plants that belonged to the Salicornia plant family [12] and mainly grew in brackish grounds. These plants include the Salsola Soda and Salsola Kali [15] (Fig. 14.). Potassium was used as a main component in the manufacturing of medieval glass artifacts [15].

*Fig. 13. Wadi Natrum area in Egypt [15].*

*Fig. 14. The plant Salsola Soda (left) and the plant Salsola Kali (right) [15].*

It has been mentioned before that glass is created by the solidification of a melted solid without crystallization. If glass is compared with various other crystalloid materials, its structure is deprived of a regular geometric placement of various elements atoms within the network of shaping an atom [6]. This differentiation is observed in the case of silicon dioxide ($SiO_2$), which is found in crystalloid and in glazed forms [6]. The differences between the structure of crystalloid $SiO_2$ (c), the glazed $SiO_2$ (a) and glass $SiO_2$ - NaO (b) are illustrated in the next diagram (Fig. 15. & Fig. 16.):



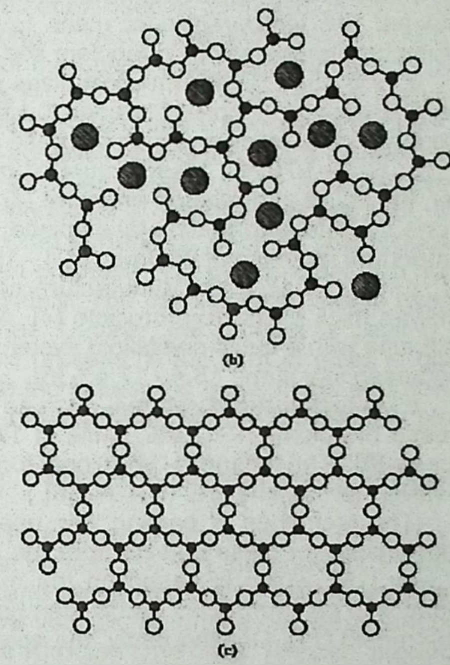


*Fig. 15. Glass net of silicon - oxygen (a) [6].*

*Fig. 16. Glass net of silicon -sodium - oxygen (b).*
*Crystal of mineral quartz (c) [6].*

The knowledge of the chemical structure and natural attributes of glass is paramount in understanding the process of deterioration, conservation and manufacturing technology. Glass manufacturing and glassmaking constituted two separate processes of production during antiquity, that up until recently, were not distinguished by researchers [15]. Pliny Senior, in his work Natural History XXXVI (p. 193, 194) reports about the manufacturing of glass: "They start a fire with light and dry timber, to which they add copper and soda, preferably Egyptian. (The glass), as well as the copper, melts in a row of furnaces and takes dark-colored shapes... After it has crumbled, melt it again in the workshop and decorate it... This was the ancient method of manufacturing glass" [4].

Glass manufacturing, with the fusion of raw material, was done in two stages that are also clarified by the sources:

1. Good mixture of raw materials, sand containing calcium and natron, which is slowly heated at 750 - 850 °C in simple ceramic crucibles or small containers. The result of this process was sand nitro, an intermediary product [4].
2. Crumbling and reheating of sand-nitrum at 1100 °C and adding colorings and opacifiers.

The second phase is completed with annealing, that is the progressive refrigeration of glass in the crucibles or containers [4].

Apart from these two stages, the process of coloration of glass also played an important role. The coloration was applied by specialized craftsmen [15].

The pigmentation of glass was applied in three manners:

a. With the presence of small quantities of metal oxides of precession, as cobalt (Co), copper (Cu), iron (Fe), nickel (Ni), manganese (Mn) etc., which were introduced to the mixture of the silicon network.

b. With the growth of colloid dissemination of soluble particles, as in the glasses of silver, copper and red-gold colour.

c. With the introduction of coloring materials in the glaze [6].

It is important to note that the manufacture of glass and its formation into an object are two different processes. As Pliny Senior reports in his book "Natural History XXXVI" "One is formed by blowing, another is formed on a wheel and another is turned like silver" [4].

Before the invention of the technique of blowing, glass production was depended on the characteristic of glass to return from its solid to its liquid form. This characteristic influences the configuration and the technique of the formation of ancient objects. Viscosity of glass depends on the composition of its components, as well as from the temperature. For example, at high temperatures (≈1050 °C), viscosity is low and allows the manufacture of glass [4]. The ancient glassmakers calculated the temperature of glass from its behavior on the tools, and also from its color. The manufacture temperatures of ancient soda type glass can be grouped as follows:

a. 505 - 590 °C: Warm-up of glass items that will be treated [4]. At the temperature of 573 °C we have the transformation of a-quartz with hexagonal crystalloid system, in b-quartz with triangular system, which is followed by an increase in the volume of the material 0,82 - 1,3% [6].

b. 625 - 970 °C: Manufacture of glass with various techniques, such as bending, casting with cullet, the spiral and rotation pressure [4]. Between these two temperatures and more precisely at 870 °C, one more transformation takes place: a-tridimite with a hexagonal crystal system comes along with an important increase of volume, 14,4 - 16% [6].

c. 970 - 1150 °C: Manufacture of glass with the technique of blowing and the possibility of gathering thick glass from crucible [4]. At 1025 °C, if the a-quartz has high purity it changes into a-cristobalite with a cubic crystalloid system. This transformation happens slowly and is accompanied by an increase in volume 15,4 - 17,4% [6].

d. At higher temperatures, such as 1470 °C, the a-tridimite is changed into a-cristobalite with an increase of volume 1 - 1,4%, while at 1726 °C the a-cristobalite is transformed in the cast in a slow process [6]. The changes from one form to another of $SiO_2$ have been revealed by studies with derivitive thermal analysis (D.T.A.) [6].

The technique of casting was used to describe the manufacturing method of transparent and semi-transparent glass objects from the early roman years. A variation of casting is the technique of lost wax [15], which is based on the manufacturing of an original wax object [4]. The prototype is molded with plaster or clay and is then heated. The melted wax was removed by passages at the base of the mould [11]. Consequently, the heated double closed mould (of plaster or clay) and intermediary wax wall was filled, through a crucible, with cullet glass or fragments that were melted by heating at lower temperatures (850 - 970 °C) [15]. This resulted in the melted glass forming the shape of a vessel inside the mould [15] (Fig. 17.). After the annealing, the mold was also removed [4]. The treatment of vessel was completed with cool abrasion.

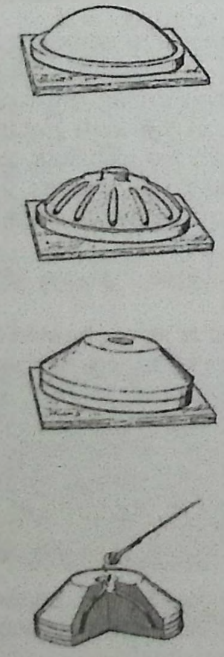


*Fig. 17. Mould glass formation [14].*

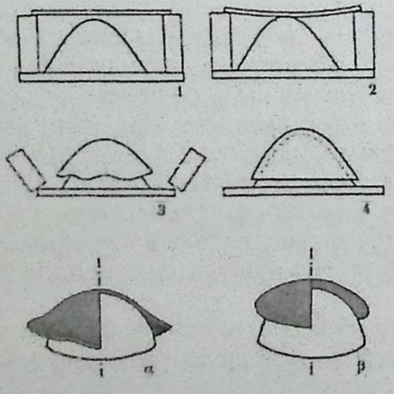


*Fig. 18. Technique of glass formation with bent in open mould [15].*

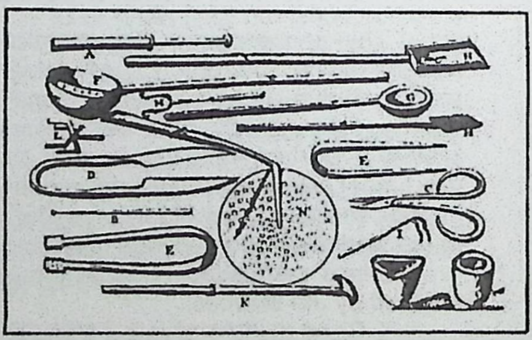


*Fig. 19. Tools for glass formation [11].*

Another technique of manufacturing glass objects was bending (Fig. 18.). This method allows the glass-maker to produce simple semi-spherical forms of vessels, mainly narrow, late-Hellenistic bottles or skyfous of Syro-Palestinian and Rhodian groups [15]. Glass disks are heated in a concave or a convex mold [4]; or bent with the help of a ceramic wheel, while () the object was finished with the help of polishers [15].

Latest research on the core technique indicates that the manufacture of transparent and non-transparent luxury vessels made wide use of open glow instead of glass-kilns. The former provide progressive heating and achieve the necessary bending and plasticity of glass, which are essential for its successful treatment [15]. Also, the pressure technique was often used in combination with casting for the fast filling of the mold and the almost direct imprinting of decorative elements on the glass surface. An open or bilateral mold is used for the formation of the object with pressure of thick glass. The method is used for the manufacture of beads and vessels [4].

The method of fusion is the technique of melting by heating two or more fragments of glass that are placed on a flat heat proofed surface. Fusion can be achieved when the glass remains for a relatively long time in the furnace at a steady temperature, in order for its surface to remain sticky. Alternatively, the glass can remain in a furnace for a short period at a high temperature [16]. If the desirable form is flat, the glass is removed from the fireproofed surface as soon as the process of fusion is completed and it is placed in a furnace to cool down gradually. On the contrary, if a curved surface is required, the process of casting is applied immediately. The casting technique is used for the transformation of flat fragments of glass into curved ones. Usually, the product of casting is a shallow mug or porringer. Gravity plays a primary role in this process. A flat item of glass is placed onto a fireproofed metal or ceramic form. As the temperature increases, the glass melts and flows to cover the surface of the form. When it reaches its final form, it is removed from the mold and is placed in a furnace to cool down slowly.

In order to prevent fluid glass from sticking on the form, the latter is covered before its use with a thin coating of baked clay [16].

It is likely that the technique of blowing had not yet been invented in the years of Pliny [7]. The invention of blowing glass, during the second half of the first century BC, on the coast of Phoenicia helped promote the widespread use of glass in the markets and transit centers of the Mediterranean. Rhodes boasts an important collection of early earless shallow vessels, bulb-type or overall ampoules of 1st half of the 1st century AD, and blown skyfous that imitate Rhodian type ones. Rhodes' production includes cosmetic bottles of candlestick type, many of which are deformed by manual laboratorial construction [13].

The glass production process includes two or three stages. First is the constructional or heavy work stage, at this point the glassmakers change the raw material in melted, clean limpid glass. In the second stage, the craftsmen or the artists shape the melted glass into an object. Sometimes, this is followed by a third stage where the object is decorated by using various techniques [16].

The blown glass can be carried out independently from the manufacturing process of melt glass because of the use of smashed glass or imported crude glass fragments or bars as source of raw material [16] (Fig. 20.). During the 1st century BC the blowpipe was invented, either in the roman province of Syria or in the Palestinian region. The basic tools for the treatment of glass, such as the blowpipe and the stick, have been use for centuries without having changed much from the ones that are used today [16] (Fig. 19.).

One end of the blowpipe is submerged into the melted glass, which is kept in the blast furnace where it collects a small amount of the glass mass. The glass sticks to the iron after being heated to 500 - 600 °C. With the blowing of air from the other end of the pipe, a thin walled glass "bubble" is formed. Wooden tools and pincers can shape this glass ball. During the whole process, the object is spun with a circular motion, in order to prevent it from "drooping" downwards and it is heated again in a furnace when is needed [5] (Fig. 21.).

In order to maintain the required temperature for the treatment of glass, the "bubble" is placed from time to time onto an iron bar, which is situated inside the kiln and is kept warm constantly [2]. The configuration of glass requires it to be in melted form so that it appears red or white in color. During the manufacturing process it is not possible for anyone to handle the glass with their bare hands and shape it as they wish. In contrast, one can only do that by using tools made of metal, stone or wood that have been previously placed in water [2]. Blowing, stretching, spinning, pressure, stinging, fission, engraving or cutting are involved in the treatment of glass (Fig. 22.). The finished glass objects should remain in a heated furnace for several days in order to cool down gradually [2].

*Fig. 20. Blowing process [11].*

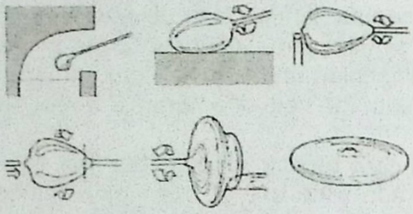


*Fig. 21. Blowing process [11].*

*Fig. 22. Blown Perfume vessels [8].*

Generally, there are three types of blown glass:

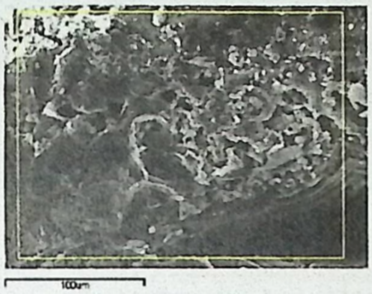
- The "free blowing".
- Blown in an open mould.
- Blown in a closed mould.

Free blown glass can be reheated reshaped with the use of a variety of methods. The enclosure of a glass mass into an open mold is one of the initial stages in the process of blowing, before the glass bubble acquires its bigger dimensions. This technique allows the heating and further configuration of the object [16]. The most important metal tools required for the manufacture and treatment of glass objects, apart from the pin of kiln and the ladle, are the following:

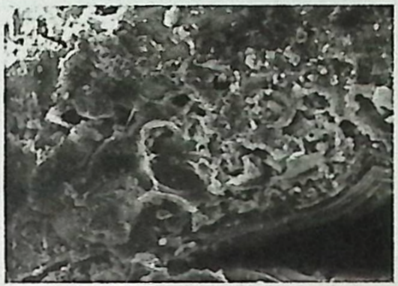
- The blowpipe.
- A pair of tongs.
- The shear.
- A type of "pincers".
- The circular scissors.
- The conjunctive iron tool for melting glass belts.
- A board which is like a small shovel [2].

Therefore, with the technique of blowing glass, it was possible to create thinner and clearer glasses. This has contributed to a big increase in the variety, form and number of small concave objects and, for the first time, bigger windows could be created [11]. In general, the first century after the invention of free blowing is characterized by the great decoration and stylish nature of the objects. They were usually made from simple transparent, light blue or greenish glass [1]. The roman glass that was meant to be for daily use, was green up to azure and sometimes yellow. Intensely colored glass also existed. Colorless glass has been known to exist since the first half of the first century AD and was considered to be more precious than the colored. It should be noted that the colors of ancient glass depend both on the chemical composition of the raw materials and on the production process [8].

**ANALYSES OF STRUCTURAL MATERIAL**
**Sample 1 (Y932)**
External

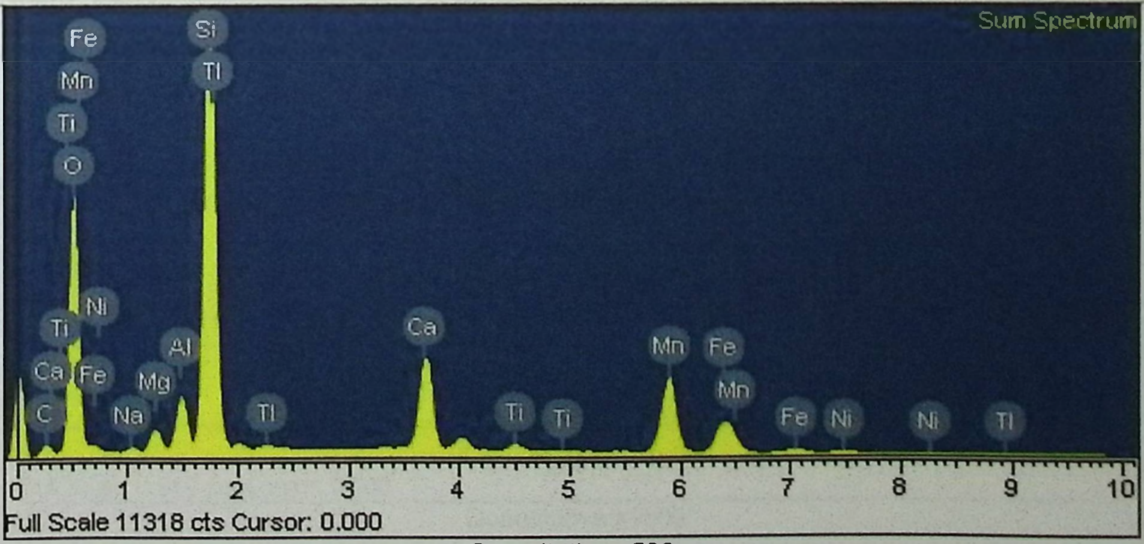


x500 Area



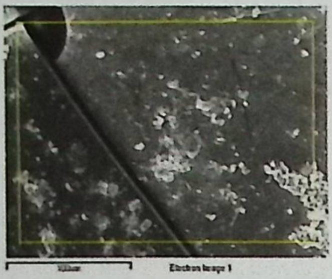
x500 Quantitative

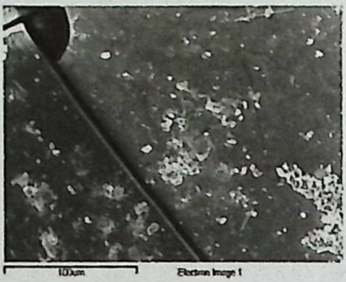
| Element | App | Intensity | Weight% | Weight% | Atomic % | Compd% | Formula | Number |
|---|---|---|---|---|---|---|---|---|
| | Conc. | Corrn. | | Sigma | | | | of ions |
| Si K | 28.74 | 0.7974 | 18.52 | 0.22 | 13.47 | 39.62 | $SiO_2$ | 1.71 |
| C K | 4.58 | 0.3366 | 7.00 | 0.55 | 11.91 | 25.64 | $CO_2$ | 1.51 |
| Mn K | 15.90 | 0.8196 | 9.97 | 0.15 | 3.71 | 12.87 | MnO | 0.47 |
| Ca K | 10.36 | 0.9854 | 5.40 | 0.08 | 2.76 | 7.56 | CaO | 0.35 |
| Al K | 3.03 | 0.7122 | 2.19 | 0.04 | 1.66 | 4.13 | $Al_2O_3$ | 0.21 |
| Fe K | 7.14 | 0.8378 | 4.38 | 0.10 | 1.60 | 5.63 | FeO | 0.20 |
| Mg K | 1.36 | 0.5965 | 1.17 | 0.03 | 0.98 | 1.94 | MgO | 0.12 |
| Na K | 0.46 | 0.6009 | 0.40 | 0.04 | 0.35 | 0.53 | $Na_2O$ | 0.04 |
| Ti K | 0.88 | 0.8304 | 0.55 | 0.03 | 0.23 | 0.91 | $TiO_2$ | 0.03 |
| Ni K | 0.72 | 0.8305 | 0.45 | 0.07 | 0.16 | 0.57 | NiO | 0.02 |
| Tl M | 0.77 | 0.6952 | 0.57 | 0.06 | 0.06 | 0.59 | $Tl_2O$ | 0.01 |
| O | | | 49.42 | 0.58 | 63.12 | | | 8.00 |
| Totals | | | 100.00 | | | | | |
| x500 Quantitative | | | | | | | Cation sum | 4.67 |



Quantitative x500

Internal

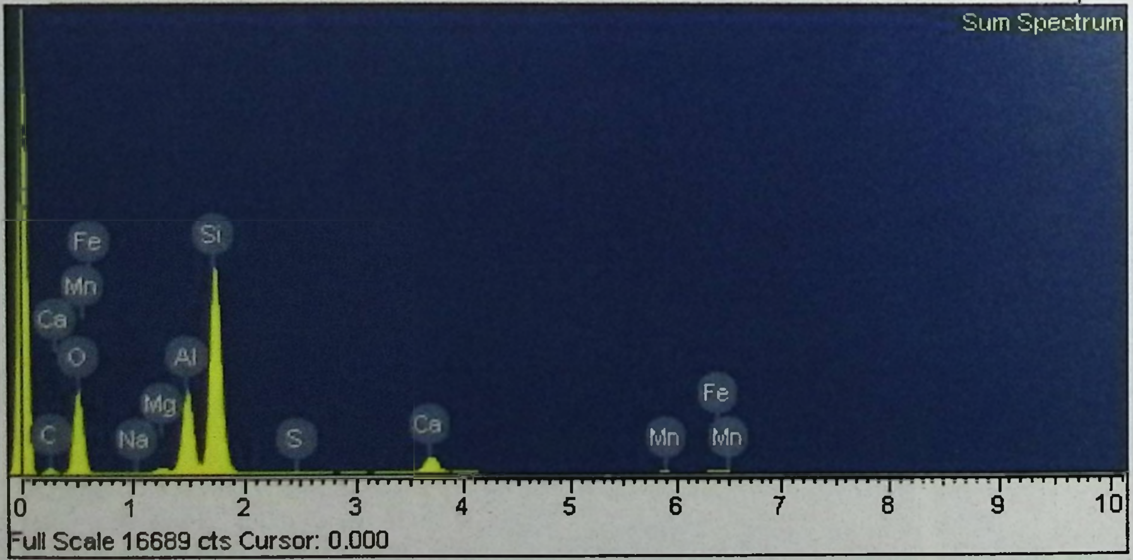




Quantitative x500

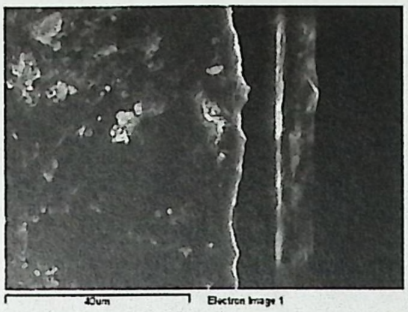
Area x500

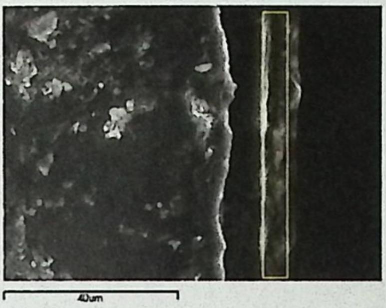
| Element | App | Intensity | Weight% | Weight% | Atomic % | Compd% | Formula |
|---|---|---|---|---|---|---|---|
| | Conc. | Corrn. | | Sigma | | | |
| Si K | 39.58 | 0.7985 | 27.73 | 0.39 | 19.21 | 59.32 | $SiO_2$ |
| Al K | 14.45 | 0.8395 | 9.63 | 0.15 | 6.94 | 18.20 | $Al_2O_3$ |
| C K | 1.72 | 0.2421 | 3.98 | 0.68 | 6.45 | 14.59 | $CO_2$ |
| Ca K | 5.21 | 0.9359 | 3.11 | 0.07 | 1.51 | 4.36 | CaO |
| Mg K | 0.77 | 0.7298 | 0.59 | 0.05 | 0.47 | 0.98 | MgO |
| Fe K | 1.44 | 0.8189 | 0.98 | 0.09 | 0.34 | 1.26 | FeO |
| Na K | 0.36 | 0.7624 | 0.26 | 0.05 | 0.22 | 0.36 | $Na_2O$ |
| Mn K | 0.58 | 0.8016 | 0.41 | 0.07 | 0.14 | 0.52 | MnO |
| S K | 0.21 | 0.7106 | 0.17 | 0.03 | 0.10 | 0.42 | $SO_3$ |
| O | | | 53.14 | 0.67 | 64.61 | | |
| Totals | | | 100.00 | | | | |
| Quantitative x500 | | | | | | | |



Quantitative x500

Section - Edge

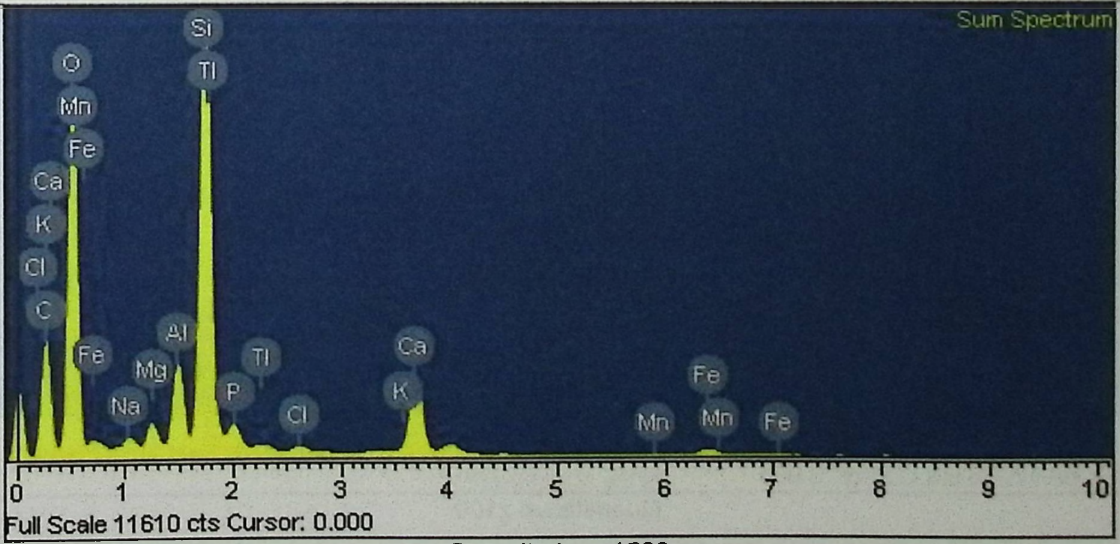




Quantitative x1500

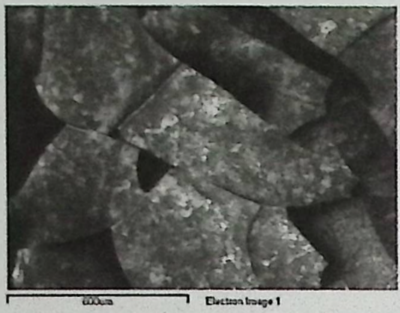
Area x1500

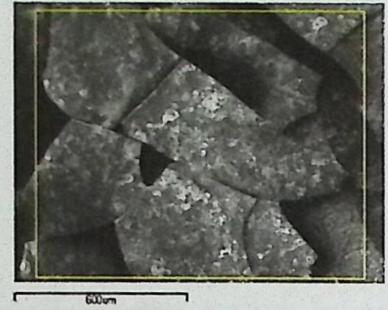
| Element | App | Intensity | Weight% | Weight% | Atomic % | Compd% | Formula | Number |
|---|---|---|---|---|---|---|---|---|
|  | Conc. | Corrn. |  | Sigma |  |  |  | of ions |
| C K | 37.54 | 0.4943 | 19.22 | 0.16 | 25.83 | 70.42 | $CO_2$ | 3.14 |
| Si K | 29.05 | 0.8247 | 8.91 | 0.04 | 5.12 | 19.07 | $SiO_2$ | 0.62 |
| Al K | 5.24 | 0.7473 | 1.78 | 0.02 | 1.06 | 3.35 | $Al_2O_3$ | 0.13 |
| Ca K | 8.55 | 0.9673 | 2.24 | 0.02 | 0.90 | 3.13 | CaO | 0.11 |
| Mg K | 1.59 | 0.6326 | 0.63 | 0.02 | 0.42 | 1.05 | MgO | 0.05 |
| Na K | 1.27 | 0.6457 | 0.50 | 0.02 | 0.35 | 0.67 | $Na_2O$ | 0.04 |
| P K | 2.10 | 1.0973 | 0.48 | 0.02 | 0.25 | 1.11 | $P_2O_5$ | 0.03 |
| Fe K | 1.28 | 0.8022 | 0.40 | 0.02 | 0.12 | 0.52 | FeO | 0.01 |
| Cl K | 0.37 | 0.7593 | 0.12 | 0.01 | 0.06 | 0.00 |  | 0.01 |
| Mn K | 0.30 | 0.7889 | 0.10 | 0.02 | 0.03 | 0.12 | MnO | 0.00 |
| Tl M | 1.07 | 0.7510 | 0.36 | 0.03 | 0.03 | 0.37 | $Tl_2O$ | 0.00 |
| K K | 0.20 | 1.0193 | 0.05 | 0.01 | 0.02 | 0.06 | $K_2O$ | 0.00 |
| O |  |  | 65.21 | 0.16 | 65.81 |  |  | 7.99 |
| Totals |  |  | 100.00 |  |  |  |  |  |
| Quantitative x1500 |  |  |  |  |  |  | Cation sum | 4.15 |



Quantitative x1500

Middle

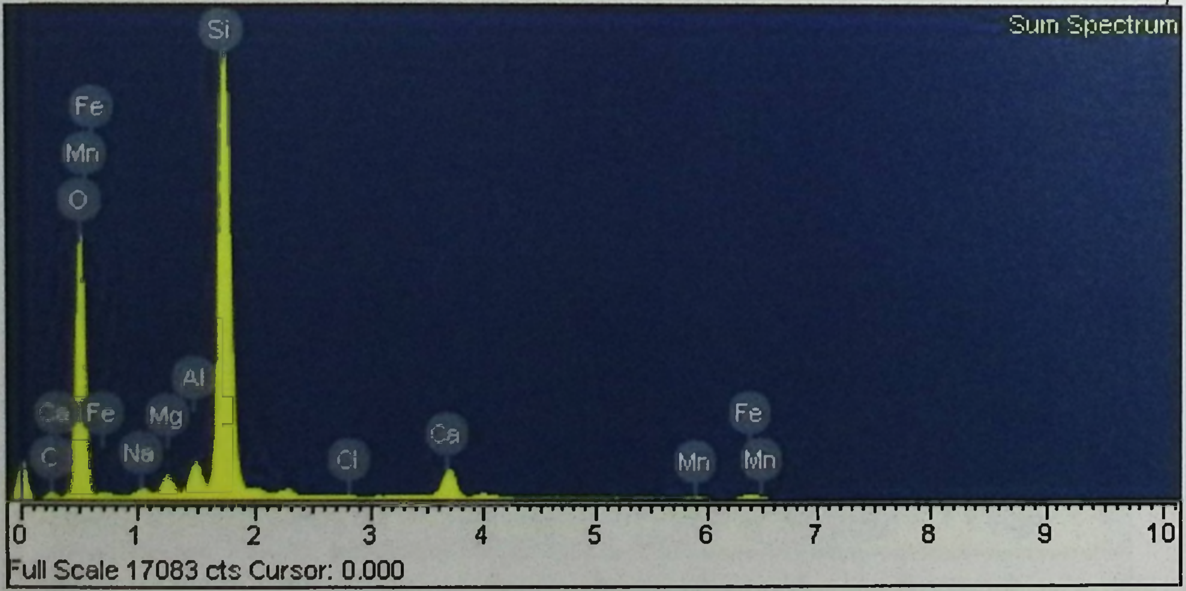




Quantitative x100

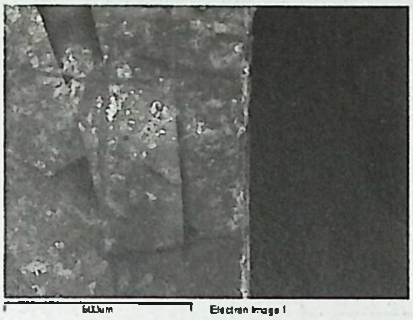
Area x100

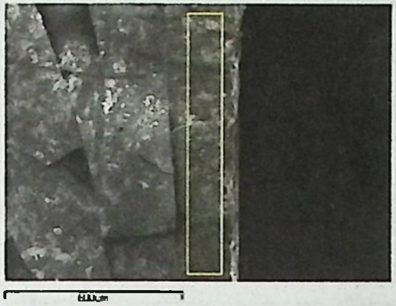
| Element | App | Intensity | Weight% | Weight% | Atomic % | Compd% | Formula | Number |
|---|---|---|---|---|---|---|---|---|
|  | Conc. | Corrn. |  | Sigma |  |  |  | of ions |
| Si K | 45.45 | 0.8747 | 34.25 | 0.31 | 23.85 | 73.28 | $SiO_2$ | 2.94 |
| C K | 1.21 | 0.2329 | 3.43 | 0.43 | 5.59 | 12.58 | $CO_2$ | 0.69 |
| Al K | 2.68 | 0.8180 | 2.16 | 0.05 | 1.57 | 4.08 | $Al_2O_3$ | 0.19 |
| Ca K | 4.26 | 0.9307 | 3.01 | 0.05 | 1.47 | 4.22 | CaO | 0.18 |
| Mg K | 1.92 | 0.7222 | 1.76 | 0.04 | 1.41 | 2.91 | MgO | 0.17 |
| Na K | 0.81 | 0.7609 | 0.70 | 0.05 | 0.60 | 0.94 | $Na_2O$ | 0.07 |
| Fe K | 1.38 | 0.8175 | 1.11 | 0.06 | 0.39 | 1.43 | FeO | 0.05 |
| Cl K | 0.18 | 0.6655 | 0.18 | 0.03 | 0.10 | 0.00 |  | 0.01 |
| Mn K | 0.36 | 0.8000 | 0.29 | 0.05 | 0.10 | 0.38 | MnO | 0.01 |
| O |  |  | 53.10 | 0.43 | 64.92 |  |  | 7.99 |
| Totals |  |  | 100.00 |  |  |  |  |  |
| Quantitative x100 |  |  |  |  |  |  | Cation sum | 4.30 |



Quantitative x100

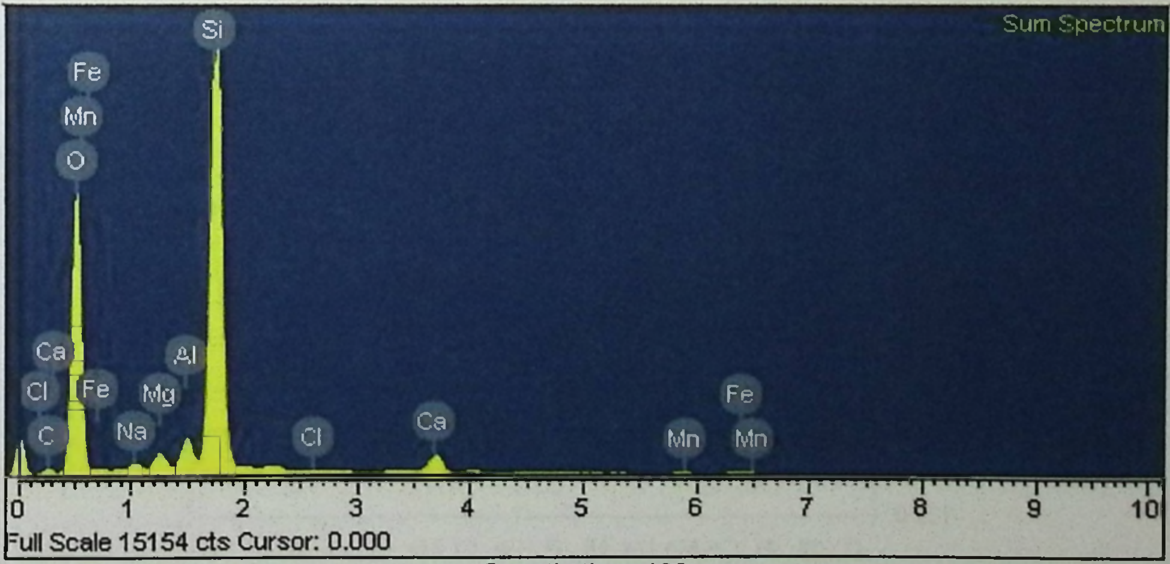
Before the edge



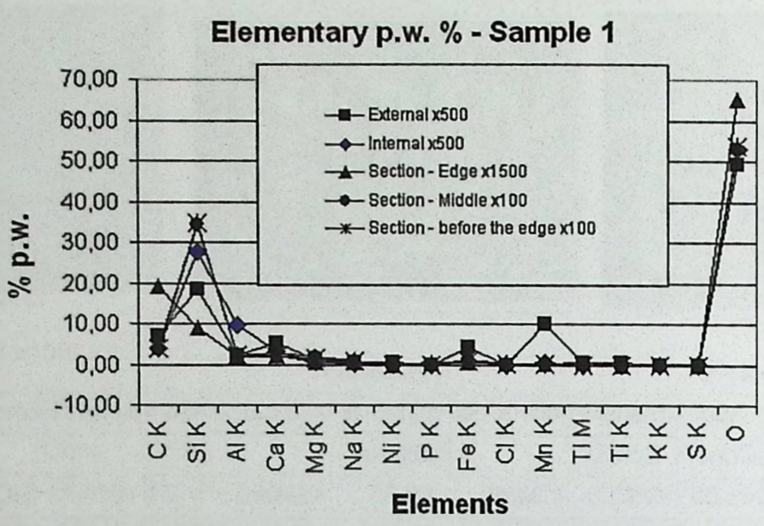


Quantitative x100 Area x100

| Element | App Conc. | Intensity Corrn. | Weight% | Weight% Sigma | Atomic % | Compd% | Formula | Number of ions |
|---|---|---|---|---|---|---|---|---|
| Si K | 45.65 | 0.8790 | 34.68 | 0.35 | 23.90 | 74.18 | $SiO_2$ | 2.93 |
| C K | 1.31 | 0.2313 | 3.79 | 0.49 | 6.10 | 13.87 | $CO_2$ | 0.75 |
| Al K | 2.61 | 0.8235 | 2.12 | 0.05 | 1.52 | 4.00 | $Al_2O_3$ | 0.19 |
| Mg K | 1.61 | 0.7240 | 1.48 | 0.04 | 1.18 | 2.46 | MgO | 0.14 |
| Ca K | 2.79 | 0.9286 | 2.01 | 0.05 | 0.97 | 2.81 | CaO | 0.12 |
| Na K | 0.92 | 0.7652 | 0.80 | 0.05 | 0.68 | 1.08 | $Na_2O$ | 0.08 |
| Fe K | 1.01 | 0.8171 | 0.82 | 0.06 | 0.28 | 1.06 | FeO | 0.03 |
| Mn K | 0.36 | 0.7999 | 0.30 | 0.05 | 0.11 | 0.39 | MnO | 0.01 |
| Cl K | 0.16 | 0.6634 | 0.16 | 0.03 | 0.09 | 0.00 |  | 0.01 |
| O |  |  | 53.85 | 0.48 | 65.17 |  |  | 7.99 |
| Totals |  |  | 100.00 |  |  |  |  |  |
| Quantitative x100 |  |  |  |  |  |  | Cation sum | 4.26 |



Quantitative x100

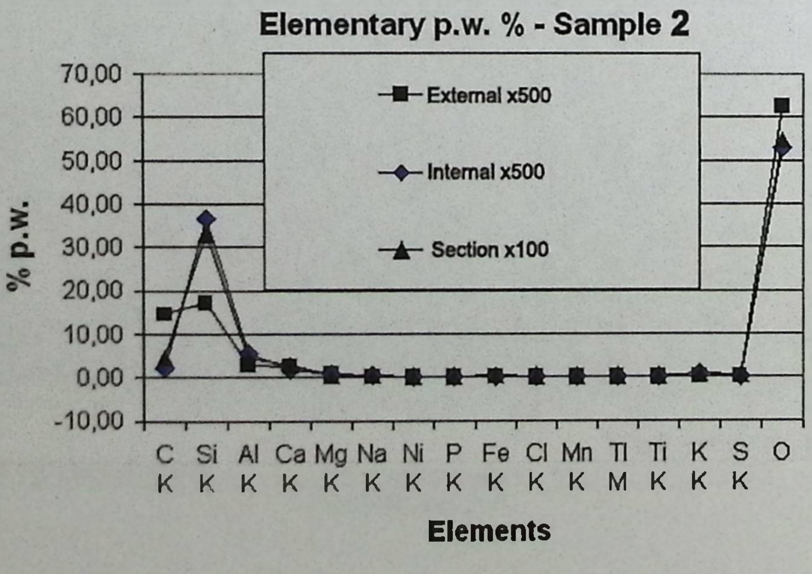


**CONCLUSIONS**

The following conclusions have been drawn from the previous element analysis:

1. The Si is generally low (<35%), very low (<10%) on the edge of section, very low in exterior and internal surface and low (<35%) in the middle of section and before the end of sample. This is because the material has been leached away by the intense humidity present.
2. The Na is very low (<1%) in all cases. This is because the material has been leached away by the intense humidity present.
3. The K is too low (≈0%), this is because the material has been leached away by the intense humidity present and also because of a possible lack in raw material.
4. Ca is also generally very low (<5%), perhaps a little higher in the exterior surface because of calcium salt crust formation.

**Sample 2 (Y931)**

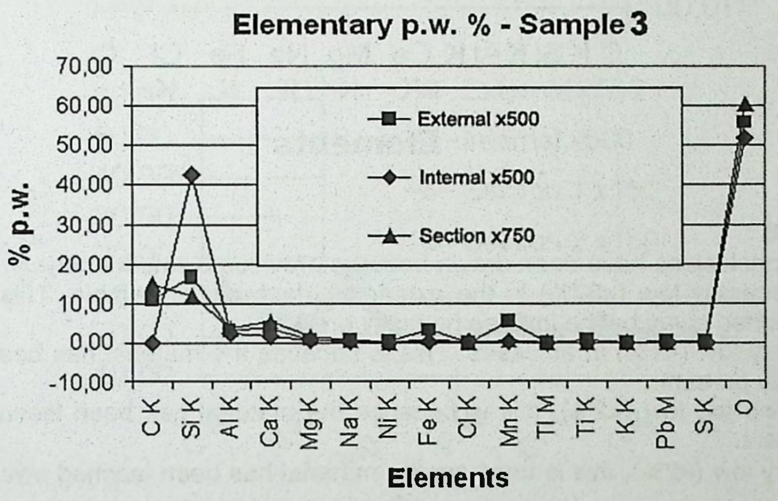


## CONCLUSIONS

The following conclusions have been drawn from the previous element analysis:

1. The Si is generally low (<37%) in the section and in the internal surface of sample and low (<17%) in the exterior surface of sample. This is because the material has been leached away by the intense humidity present.
2. The Na is very low (<1%) in all cases. This is because the material has been leached away by the intense humidity present.
3. The K is very low (≈0%), this is because the material has been leached away by the intense humidity present and also because of a possible lack in raw materials.
4. The Ca is also too low (<3%), but perhaps a little higher in the exterior surface because of the calcium salt crust.

**Sample 3 (Y934 A)**



## CONCLUSIONS

The following conclusions have been drawn from the previous element analysis:

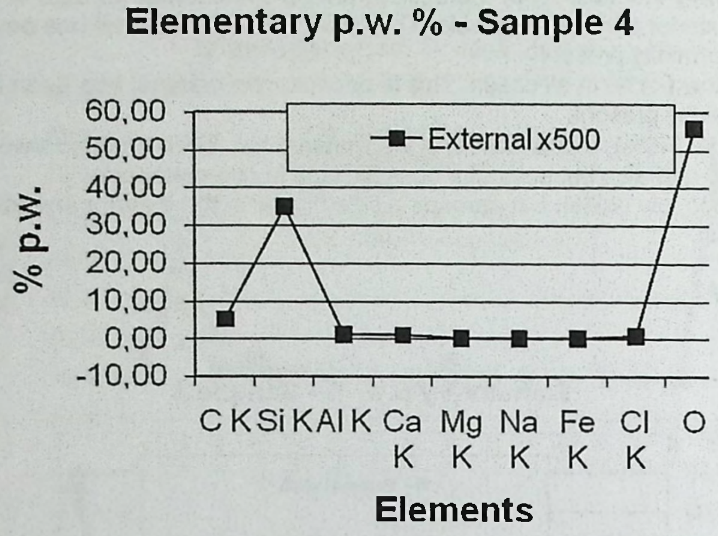
1. The Si is generally low (<42%) in the section and in the internal surface of sample and low (<17%) in the exterior surface of sample. This is because the material has been leached away by the intense humidity present.

2. The Na is very low (<1%) in all the cases. This is because the material has been leached away by the intense humidity present.

3. The K is very low (≈0%), this is because the material has been leached away by the intense humidity present and also because of a possible lack in raw material.

4. The Ca is also too low (<5%), perhaps a little higher in the exterior surface because of the crust of calcium salt.

**Sample 4 (Y934 B)**



## CONCLUSIONS

The following conclusions have been drawn from the previous element analysis:

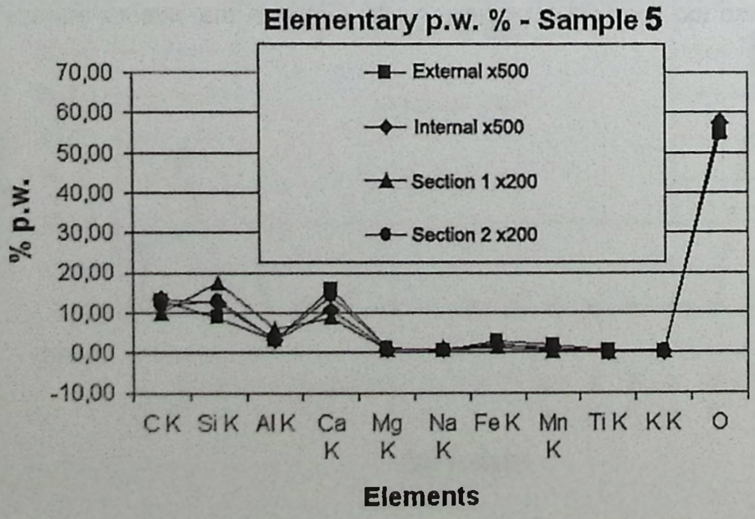
1. The Si is generally low (<37%) in the exterior surface of the sample. This is because the material has been leached away by the intense humidity present.

2. The Na is very low (<1%) in all cases. This is because the material has been leached away by the intense humidity present.

3. The Ca is also too low (<2%), this is because the material has been leached away by the intense humidity present.

4. The Al is very low (≈2%), this is because the material has been leached away by the intense humidity present.

**Sample 5 (Y941 big)**



**CONCLUSIONS**

The following conclusions have been drawn from the previous element analysis:

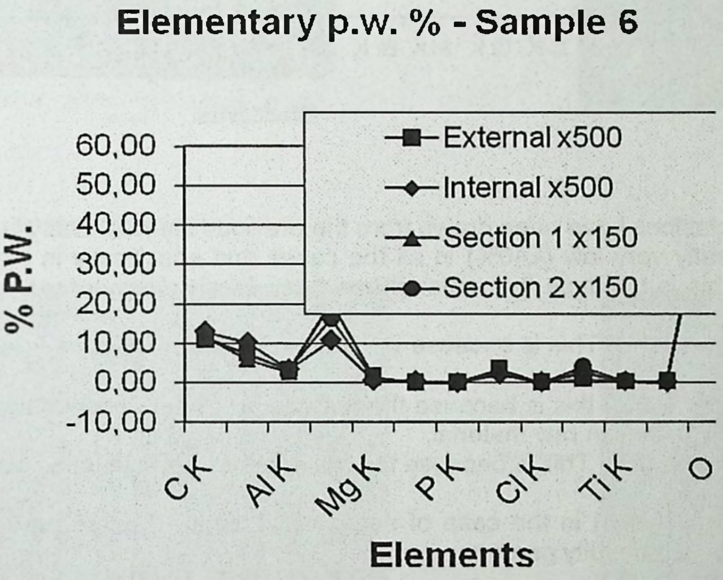
1. The Si is generally very low (<18%) in all the cases and specifically in the exterior surface of sample is very low (<10%).

2. The Na is too low (<1%). This is because the material has been leached away by the intense humidity present.

3. The K is really low (≈0%). This is because the material has been leached away by the intense humidity present, and also its lack in raw material.

4. There is a normal level of Ca, and it's especially high in the exterior surface in perhaps because the crust of calcium salt.

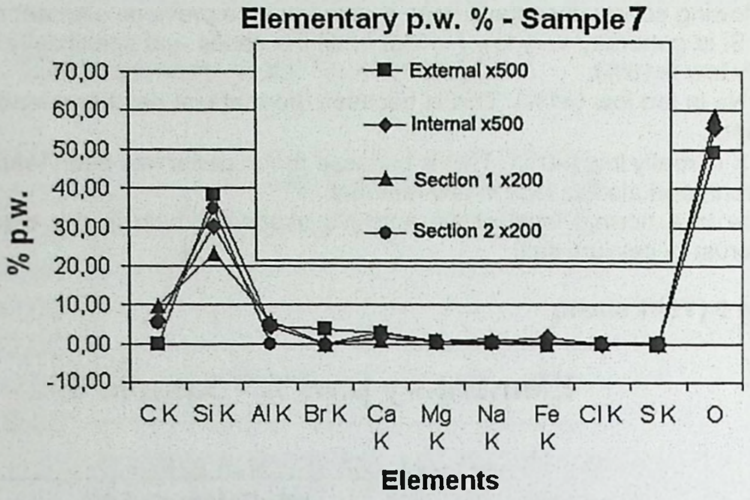
**Sample 6 (Y941 small)**



**CONCLUSIONS**

The following conclusions have been drawn from the previous element analysis:

1. The Si is generally very low (<10%) in all the cases this is because the material has been leached away by the intense humidity present
2. The Na is too low (<1%). This is because the material has been leached away by the intense humidity present
3. The K is really low (≈0%). This is because the material has been leached away by the intense humidity present, and also its lack in raw material.
4. There is a normal level of Ca it's especially high in the exterior surface, perhaps because the crust of calcium salt.



**Sample 7 (Y933)**

## CONCLUSIONS

The following conclusions have been drawn from the previous element analysis:

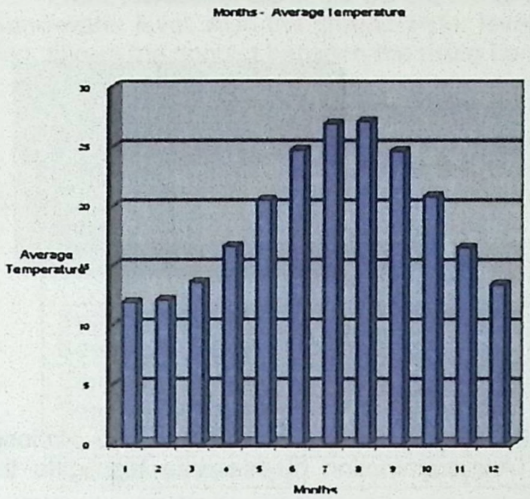
1. The Si is generally very low (<40%) in all the cases and specifically in the section 1 of the sample it is very low. This is because the material has been leached away by the intense humidity present.
2. The Na is too low (<1%). This is because the material has been leached away by the intense humidity present.
3. The K is really low (≈0%) this is because the material has been leached away by the intense humidity present and also its lack in raw material.
4. The Ca is very low (<5%). This is because the material has been leached away by the intense humidity present.
5. The Al is very low (<1%) in the case of section 2. This is because the material has been leached away by the intense humidity present.

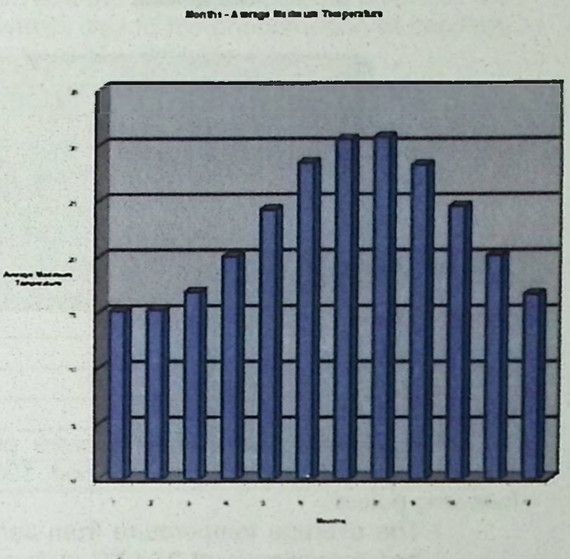
## ENVIRONMENTAL STUDY

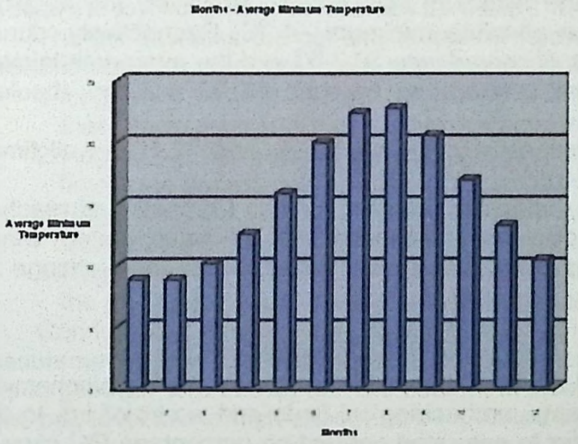
During the environmental study, data regarding winds, temperature and relative humidity from the area of the excavation was collected.

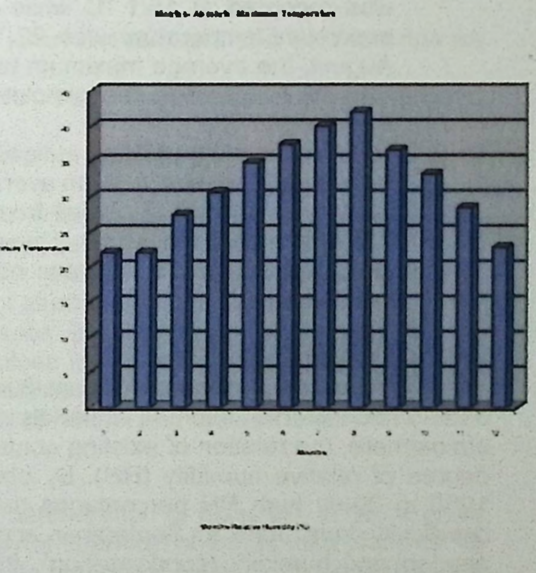
**Climate data - study.**

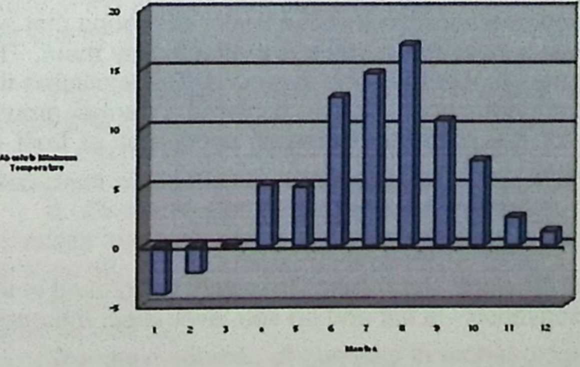
| MONTHS | AVERAGE TEMPERATURE | AVERAGE MAXIMUM TEMPERATURE | AVERAGE MINIMUM TEMPERATURE | ABSOLUTE MAXIMUM TEMPERATURE | ABSOLUTE MINIMUM TEMPERATURE | RELATIVE HUMIDITY (%) | HEIGHT OF RAINFALL | WIND DIRECTION |
|---|---|---|---|---|---|---|---|---|
| JANUARY | 11,9 | 15,1 | 8,8 | 22,0 | -4,0 | 70,1 | 149,6 | NW |
| FEBRUARY | 12,1 | 15,2 | 8,8 | 22,0 | -2,2 | 69,1 | 105,7 | NW |
| MARCH | 13,6 | 16,8 | 10,1 | 27,4 | 0,2 | 68,7 | 75,6 | W |
| APRIL | 16,6 | 20,0 | 12,5 | 30,6 | 5,2 | 66,5 | 27,8 | W |
| MAY | 20,5 | 24,2 | 15,8 | 34,8 | 5,0 | 64,4 | 18,6 | W |
| JUNE | 24,7 | 28,4 | 19,9 | 37,4 | 12,6 | 58,5 | 2,3 | W |
| JULY | 26,9 | 30,5 | 22,3 | 40,0 | 14,6 | 57,6 | 0,4 | W |
| AUGUST | 27,1 | 30,7 | 22,7 | 42,0 | 17,0 | 59,9 | 0,2 | W |
| SEPTEMBER | 24,6 | 28,2 | 20,5 | 36,6 | 10,6 | 61,4 | 5,8 | W |
| OCTOBER | 20,8 | 24,5 | 16,9 | 33,2 | 7,2 | 67,5 | 65,5 | W |
| NOVEMBER | 16,5 | 20,1 | 13,2 | 28,4 | 2,4 | 71,4 | 94,1 | W |
| DECEMBER | 13,4 | 16,6 | 10,4 | 22,8 | 1,2 | 72,4 | 157,4 | NW |

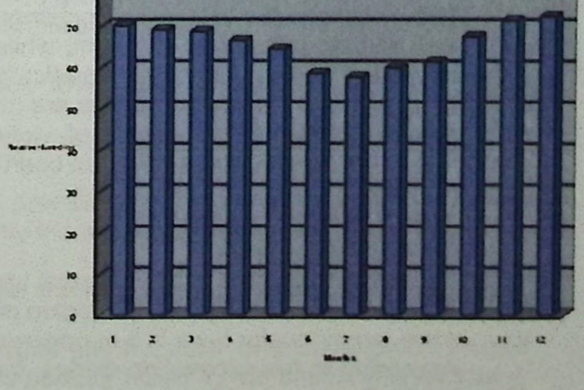

Months - Average Temperature
Average Temperature
0
5
10
15
20
25
30
1
2
3
4
5
6
7
8
9
10
11
12
Months


Months - Average Maximum Temperature
Average Maximum Temperature
0
5
10
15
20
25
30
35
1
2
3
4
5
6
7
8
9
10
11
12
Months


Months - Average Minimum Temperature
Average Minimum Temperature
0
5
10
15
20
25
1
2
3
4
5
6
7
8
9
10
11
12
Months


Months- Absolute Maximum Temperature
e Maximum Temperature
0
5
10
15
20
25
30
35
40
45
1
2
3
4
5
6
7
8
9
10
11
12
Months


Months- Absolute Minimum TemperatureA
Absolute Minimum Temperature
-5
0
5
10
15
20
1
2
3
4
5
6
7
8
9
10
11
12
Months


Months-Relative Humidity (%)
Relative Humidity
0
10
20
30
40
50
60
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80
1
2
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8
9
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11
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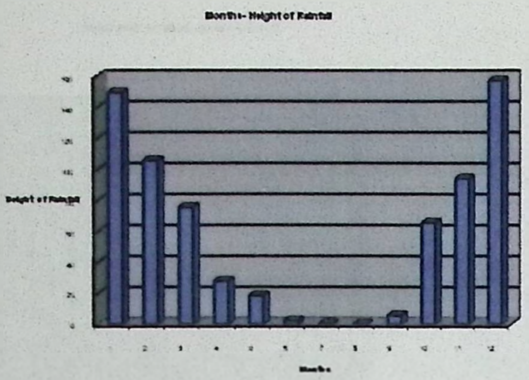
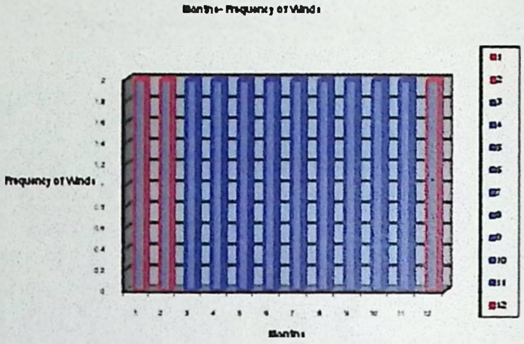
Months





The climate data elements were provided by the department of statistics of the National Meteorological Service for the period 1955 to 2004. An examination of this data highlights the following points:

1. The average temperature from January to December was a minimum of 11.9°C in January and a maximum of 27.1 °C in August. Also, the average maximum temperature for January was recorded at 15.1 °C while the average minimum was 8.8 °C. However, the absolute maximum temperature was 22 °C and the absolute minimum –4 °C. Respectively, during August, the average maximum temperature observed was 30.7 °C and the average minimum was 22.7 °C, while the absolute maximum temperature reached 42 °C and the absolute minimum 17 °C.
2. Relative humidity (RH%) indicated percentages of between 57.6% and 72.4% at all times throughout the year, with an average of 67 - 69%
3. The height of rainfall begins from 0.2 mm during the summer months (August) and reaches 157.4 mm over the winter (December). It also has to be noted that powerful western winds blow on the island all year round, apart from the winter period when they change to northwestern.

**Conclusions.**

The presence of humidity constitutes one of the most important causes of the physiochemical deterioration of the structural materials of monuments, archaeological finds and works of art. In the atmosphere, the relation of existing contents in water to saturated content on percentage (%) gives a degree of relative humidity (RH). By observing the average RH per month, during the period from 1955 to 2004, high RH percentages have been noticed, although the height of rainfall decreases drastically from June to September and is quite low from April to May. According to the data of atmospheric humidity (condensation), the rainfall and the ground-water level (capillary rising), the result is likely to be a high percentage of relative humidity (RH%) in the ground.

With regard to the temperature changes, it is comprehensible that the layers of ground that are very deep remain untouched by them, while the layers near the surface are affected by them. The temperature in the deep layers is theoretically lower than that of the surface ground. This multiplies the problems, when the excavated objects are revealed and transported from a cooler to a warmer ground environment. Finally, in the region of excavation of the glass unguentaria, conditions of frost or particularly high temperatures have not been observed.

## TOPOGRAPHICAL DATA

### Ground-water lever.

According to studies of the National Institute of Geology and Mining Research, the ground in the city of Rhodes - and similarly in the region of the excavation - is flat and on sea level. Also, the upper level of the ground-water level is 5 m underground.

According to the excavation diaries, the artifacts that were used in this study were excavated at a similar depth.

Finally, petrographicly the ground is constituted by alluvium of certain dilouviac depositions (sand, gravel, mica) and also few neogenic rocks (clay, metamorphic).

**Conclusions.**

From the above elements we are led to the conclusion that the sea influences the height of the ground-water level. Also the ground-water level is too thin which, due to the phenomenon of capillary rising, allows the contact between the rising humidity and the level of excavation.

## ACIDITY - ALKALINITY - SALINITY OF GROUND OF EXCAVATION

Six samples were taken from the soil environment of the excavation. These samples were used for the measurement of pH, electric conductivity and concentration of sulphate ($SO_4^{2-}$) ions and chloride ($Cl^-$) ions. The results of these measurements appear in the following table:

| n/n | pH | Conductivity (μS/cm²) | $SO_4^{2-}$ (ppm) | $Cl^-$ (ppm) |
|---|---|---|---|---|
| **Sample 1 (Y931)** | **7,40** | **110** | **3,5** | **25,0** |
| **Sample 2 (Y932)** | **7,10** | **50** | **1,0** | **10,0** |
| **Sample 3 (Y933)** | **6,40** | **50** | **1,0** | **9,0** |
| **Sample 4 (Y934)** | **6,15** | **37** | **0,5** | **7,0** |
| **Sample 5 (Y941 small)** | **6,50** | **45** | **0,5** | **7,0** |
| **Sample 6 (Y941 big)** | **6,80** | **42** | **0,5** | **6,5** |

### Conclusions.

From the measurements of the soil samples that were taken from the surface of the objects' deposits the following conclusions can be drawn:

The pH indicates the content in ions of hydrogen ($H^+$) in an environment and it constitutes an important factor for an environment that contains water.

1. Regarding the first sample (unguentaria with record No Y931), the pH shows alkaline ground that shows a presence of calcium carbonate ($CaCO_3$).
2. Regarding the second sample (unguentaria with record No Y932), the pH shows light limestone ground.
3. Regarding the third and fourth samples (unguentaria with record No Y933, Y934), the pH shows acidic ground that implies a presence of aluminosilicates (quartz, clays etc.).
4. Regarding the fifth and sixth samples (unguentaria with record No Y941 small and Y941 big), the pH is light acidic to neutral, which means ground of aluminosilicates composition.

Conductivity asserts the concentration of soluble salts in a solution. According to the measurements, low conductivity has been observed that involves low concentration of chlorides and salts in general. This shows that the content in chloride ($Cl^-$) and sulphate ions ($SO_4^{2-}$) belongs mainly to the bed level that is high enough to be affected by the height of rainfall and the sea level.

## FORMS OF DETERIORATIONS

Humidity is the most important factor that leads to the deterioration of glass [6]. When a glass comes in contact with water or with a water solution, a number of chemical changes take place on its surface. At a later date, these reactions can penetrate the main body of the glass, depending on the quality of the surface that has been created. Certain surfaces are protected, while others are not, and their quality depends on various factors, mainly on the composition of glass and the pH of the glaze [5].

The processes of chemical reactions that take place when there is contact between a glass surface and a water solution can be described as follows:

1. Exchange of glass's cations with ions of oxon ($H_3O^+$) of the water solution, with diffusion that takes place within the already shaped diffusion layer.
2. Dissolution of diffusion layer controlled by the prevailing surface tendency. This process decreases the thickness of diffusion layer and consequently increases the effect of previous corrosive reactions [6].

What is more, with regard to the sodium glasses, the leaching of alkalis and silicon happens at the same time [5].

The main sources of humidity in archaeological glasses are the water of subsoil (ground-water level), the rain and the atmosphere (condensation) [9]. As already noted in the environmental study, the ground-water level is found to be quite high (5 m) and near to the depth that the artifacts were found (≈2 m). This fact had an immediate effect on the artifacts, as a result of the ground water capillary rise. But, still, the subsoil waters sweep mainly but not exclusively through the soil and the soluble components of the aluminosilicates, so that they contain ions of sodium ($Na^+$), potassium ($K^+$), calcium ($Ca^{2+}$), sulphates ($SO_4^{2-}$), chlorides ($Cl^-$) and silicates ($SiO_3^{2-}$) [9] which are dissolved in various proportions. In the case of Rhodes, the underground water is also connected with the sea.

This means that apart from the phenomenon of salt spray, by which salts are transported to the soil, important quantities of chloride and silicon salts can be found in the subsoil water itself. This is caused by the sea, for it is at the same hypsometric level as the ground.

It has already been noted that the high percentages of relative humidity encourage the creation of corrosion centers and the condensation of corrosion products on the glass surface. We have also mentioned that the growth of microorganisms can affect glass, both indirectly and immediately [6]. The various microorganisms can corrode the glass indirectly because of the water condensation on the glass surface that results in the creation of a corrosive environment [9]. Other studies have proved that the action of the microorganisms can cause the leaching of elements such as Sodium (Na), titanium (Ti), calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn) and aluminum (Al). Bio-deposits that are formed by their presence can cause changes on the diffusion, the conductivity and the natural behavior of surfaces with regard to the environmental conditions [6].

The contact between water and glass affects not only the glass surface, but also the chemical constitution of the water. Reactions take place that transform water into a light acidic or alkalic solution. This depends on whether the alkalis and the silicon dioxide leach off from the glass. The pH of the solution depends on the alkalis concentration, as well as on the ratio of alkalis oxides to silicon dioxide. These two factors change with the passage of time and consequently change the pH of the water solution [6].

The leaching away of silicon dioxide on the glass in the solution is very small and is continuous for pH lower than 9. However, it increases with the further increase of pH. More specifically, the solubility of silicon dioxide presents differences in the three regions of pH. In the first area, with pH<10, the solubility reaches roughly $6,31\times10^{-6}$ moles/lt with the shaping and the presence of orthosilicate acid ($H_2SiO_3$). In the second area with 10<pH<12 it has relatively high solubility as a result of the shaping and the presence of orthosilicate ions ($HSiO_3^-$). In the third area with pH>12 it shows higher solubility as a result of the shaping and the presence of silicate ions ($SiO_3^{2-}$) [6].

The leaching away of alkali in conditions with pH lower then 9, has been recorded to be linear and with no effect by the pH of the solution. For pH higher then 9 the process slows down as the pH increases. More specifically, the glasses that contain sodium are corroded under all the pH conditions; however it is worth noticing that corrosion rates tend to drop when the pH is higher than 9 [6].

Finally, the leaching away of calcium oxide is boosted under pH conditions lower than 10. On the other hand, when the pH is higher than 10 the oxides are more resistant to corrosion [6]. By measuring the pH of the samples' soil it is observed that the solubility of silicon dioxide in the first case is considered very low and continuous. On the other hand, intense corrosion of the samples has been observed by the leaching of the sodium and the calcium oxides that happen in conditions of low pH.

The following notes are taken from observations during the recording of samples from Rhodes:

**Perfume unguentaria with record No Y931:** These were fragments from two vessels. There was a neck, the body of one of them, as well as 21 fragments of very low thickness (0,5 -1 mm). Under macroscopic observation on the artifacts' surface, there was noted a deposition of clay (both inside and outside of the artifacts) and insoluble salts crusts. There was also an extended formation of lamination that resulted to iridescences.

**Perfume unguentaria with record No Y932:** They were also two unguentaria. From the fist one 32 fragments and 21 chips are saved, with a thickness of 2,5 mm. The second one consisted of only 11 chips with a thickness of around 2 mm. Depositions of clay (both inside and outside of the artifact) and hard crusts consisting of insoluble salts were also noted under macroscopic observation. Also noted was an extended formation of lamination that resulted in iridescences. Crizzling and pitting were observed on the surface, when examined under Scanning Electron Microscope (S.E.M.).

**Perfume unguentaria with record No Y933:** It was an unguentaria with an intact base and a neck with verge; also 19 fragments () with really low thickness (0,5 - 1 mm). Depositions of clay (both inside and outside of the artifact) and hard crusts consisting of insoluble salts were also noticed under macroscopic observation. Furthermore, extended formation of lamination, iridescences and biological decay had also been noted. Pitting was observed on the surface, when examined under Scanning Electron Microscope (S.E.M.).

**Perfume unguentaria with record No Y934:** This vessel was saved almost complete in two very thin pieces (1 mm). There were also three fragments from different unguentaria with thickness of 4 mm. On the one fragment depositions of clay (both inside and outside of the artifact) and hard crusts consisting of insoluble salts were noted under macroscopic observation. An extended formation of lamination and iridescences has also been observed. Pitting was observed on the surface, when examined under Scanning Electron Microscope (S.E.M.). On the second fragment, depositions of clay and dulling, along with surface irregularity, were noticed when observed by S.E.M.

**Perfume unguentaria with record No Y941**: These were also two artefacts. The big one had a neck with a verge and part of the base, along with 56 fragments with very low thickness (1 mm). Depositions of clay (both inside and outside of the artifact) and insoluble salts hard crusts were noted under macroscopic observation. Extended formation of lamination and iridescences had been observed, which was confirmed by the S.E.M. analysis. The second smaller unguentaria had one part of the neck and its verges as well as fragments of its base, along with 49 fragments 0,5-1 mm thick. Depositions of clay and hard crusts consisting of insoluble salts were also noted under macroscopic observation. What is more, an extended formation of lamination that resulted to iridescences was observed. Pitting and surface disintegration was observed on the surface, when examined under Scanning Electron Microscope (S.E.M.).

Generally, in all the above cases the same types of deterioration have been observed. These can be categorized as follows:

**Dulling.**

It is the most common form of corrosion, according to which a glass loses its initial lucidity and transparency, while it becomes progressively opaque (Fig. 23.). This type of corrosion can easily be distinguished from dulling that is caused by scratches or deposits [6].

**Crizzling.**

The crizzling of a glass can be the result of either pressure application on its surface, or spontaneous crizzling (without specific reasons) (Fig. 24.). In the case of the perfume unguentaria crizzling is the result of pressure application [6].

**Lamination.**

The creation of multiple layers on the surface is a form of corrosion according to which the glasses surface layers exfoliate (Fig. 28.). These layers are usually water saturated to a high percentage. In combination with fluctuations of humidity, this can lead to the shrinkage or the dilation of the layers, which results in the exfoliation of the glass surface [6].

**Iridescences.**

The term describes an optical phenomenon, when, due to its lamination, the glass presents a variety of colors, both in reflection and transit light [6] (Fig. 25.).

**Pitting.**

Pitting usually begins from the corroded nucleuses that are found on or under the surface of glass. It spreads in all directions under high speed, with an inside (?) direction, shaping circular cavities (Fig. 26.). Pitting is created under the defective regions of glass surface, and, regarding its size, it is classed as micro-pitting (d ≈ 0,1 - 0,2 mm), small pits (d ≈ 0,5-2 mm), large pits (d ≈ 2-4 mm) and very large pits (d<4mm) [6].

**Crusting.**

The formation of crust on a glass surface is related to the phenomenon of pitting. During the formation of the crust the surface of glass darkens in color, because of the presence of insoluble salts. When a surplus of calcium oxide is leached off the glass, it is deposited on the glass surface or between its deteriorated layers by forming a common phase.

According to other studies, during the corrosion of glass in the ground the alkalis, the alkaline grounds as well as certain other elements gradually lessen mass. On the other hand, aluminum, iron, titanium and certain other elements that form insoluble compositions, remain in the network of silicon dioxide (Fig. 27.).

*Fig. 23. Dulling.*

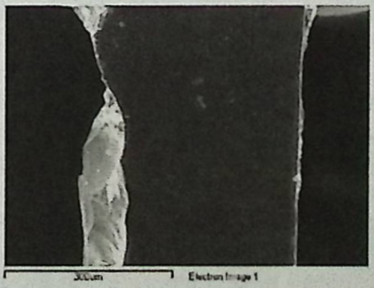


*Fig. 24. Crizzling.*

*Fig. 25. Iridescences.*

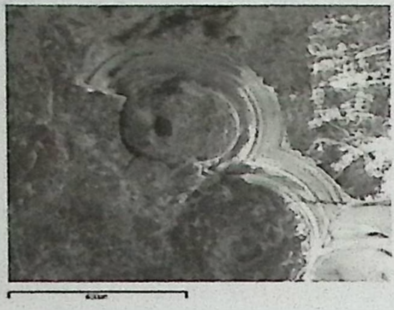


Fig. 26. Pitting.

Fig. 27. Crust.

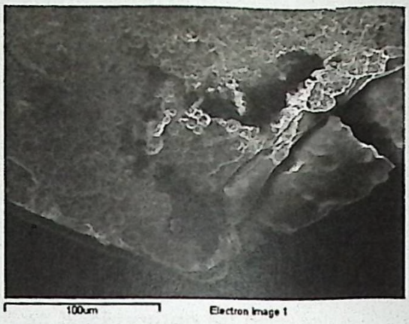


Fig. 28. Lamination.

## CONSERVATION PROCESSES

The conservation process of archaeological glass objects begins immediately the excavation, by immediately applying first aid measures. These measures are employed more systematically when the objects are moved to the laboratory.

No previous conservation work referring to the Rhodes vessels had been recorded. For this reason, we initially collected photographic documentation and recorded the objects as they were received (Fig. 29., Fig. 30., Fig. 31. & Fig. 32.); we also drew sketches of pieces that we considered to be significantly more important than the others. Afterwards, fragments of the vessels were used in the examination and material analysis of the objects, and the soil samples were utilized for the examination of the burial environmental conditions. It is important to note that no destructive analytical methods were used in the observation of the material structure of the objects, which resulted in the fragments being returned intact from the lab. The next step was to choose the suitable conservation methods and materials. As a result of the lamination decay the objects' surface had become extremely fragile. For that reason they were firstly consolidated with a low concentration solution of Paraloid B72 and acetone (Fig. 33. & Fig. 34.). The solvent was initially applied on its own to the surface and then the solution was periodically introduced and gradually increased, starting at 1% and rising to 4%. According to the bibliography the solvent that exists within the material's pores helps the resin's molecules increase their mobility and ability to penetrate the pores, as well as achieve even distribution of the consolidator within the material's mass.

Also, the use of solutions with increasing concentration facilitates the diffusion of the solution [6]. After each application the splinters were left to dry out on a sheet of Melinex (polyethylenterefthalic acid).

The next step was the cleaning of the fragments. The cleaning process involves the removal of soluble and insoluble deposits from the objects' surface. To begin with, we undertook a number of cleaning tests with deionised water, neutral detergents, various solvents and reagents in pulps. More specifically, deionised water applied with a cotton baton was used for the removal of soluble deposits. It was observed on application that the use of water ensures high solubility, and low penetration in the pores and in the corroded layers of the glass surface. After the application of various organic solvents (ethanol and white spirit), with a cotton baton, it was observed that the organic solvents caused low solubility, but high penetration. Thus, a combination of water - ethanol in proportion 1:1 was selected as the cleaning method for deposits.

For the removal of insoluble crusts various chemicals were used in the form of solutions and pulps. More specifically, solution 2% w/w E.D.T.A. (disodium salt of ethylendiamintetraacetic acid) with 2% w/w $NH_4HCO_3$ (ammonium bicarbonate) in deionised water was used. The solution was applied with a cotton baton. According to the bibliography, the action of bicarbonate salts lies both in the formation of insoluble carbonate salts with metal ions of crust, and in the creation of an alkaline environment, that encourages the removal of soluble salts that are contained in the crust. Therefore, it was observed that the solution softened the crust, which could then be removed by a mechanic method (with a scalpel). Also tested was a cleaning method using pulps of absorbant clays (sepiolite) with E.D.T.A. for the removal of calcium ions ($Ca^{2+}$) and magnesium ($Mg^{2+}$) (Fig. 35., Fig. 36. & Fig. 37. ). Once the pulp was applied, it was observed that the upper crust surface softened and could be removed relatively easily with a scalpel. Then the process of consolidation the fragile surface of glass splinters was initiated by successively covering them with low concentration solutions of acrylic resin Paraloid B72 and acetone. This was followed by the resetting of fragments, a process of joining and adhesion of the pieces using a highly concentrated solution of Paraloid B72 in acetone (Fig. 38. - Fig. 52.).

*Fig. 29. Vessel before conservation.*

*Fig. 30. Vessel before conservation.*

*Fig. 31. Vessel before conservation.*

*Fig. 32. Vessel before conservation.*

*Fig. 33. Pre-consolidation procedure.*

*Fig. 34. Pre-consolidation procedure.*

*Fig. 35. Cleaning procedure with pulps of E.D.T.A. and sepiolite.*

*Fig. 36. Cleaning procedure with pulps of E.D.T.A. and sepiolite.*

*Fig. 37. Cleaning procedure with pulps of E.D.T.A. and neutral paper.*

*Fig. 38. Fragments of vessel after cleaning.*

*Fig. 39. Fragments of vessel after cleaning.*

*Fig. 40. Fragments of vessel after cleaning.*

*Fig. 41. Fragments of vessel*

*Fig. 42. Fragments of vessel*

*Fig. 43. Fragments of vessel after*

*after cleaning.* *after cleaning.* *cleaning.*

*Fig. 44. Vessel after cleaning.*

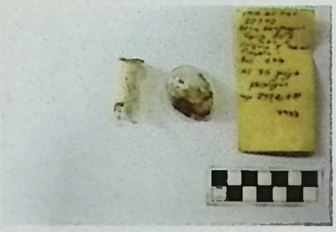


*Fig. 45. Fragments of vessel after cleaning.*

*Fig. 46. Fragment of vessel after cleaning.*

*Fig. 47. Fragments of vessel after cleaning.*

*Fig. 48. Joining procedure.*

*Fig. 49. Joining and adhesion procedure.*

*Fig. 50. Joining and adhesion procedure.*

*Fig. 51. Joining and adhesion procedure.*

*Fig. 52. Joining and adhesion procedure.*

## PROPOSED CONDITIONS FOR DISPLAY AND STORAGE

For the display of vessels, it is proposed to use showcases made of dehydrated material of silica gel and standard conditions; relative humidity 35 - 40%, temperature 21±1,5 °C, lighting 150 lux. For the storage of vessels, it is proposed to keep them in air-conditioned storage areas and placed in bookshelves with the following standard conditions; relative humidity <42%, temperature 18 - 23 °C, lighting <150 lux.

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|---|---|---|---|---|---|

# CONTROL OF RELATIVE HUMIDITY INSIDE A SHOWCASE WITH THE USE OF SATURATED SALT SOLUTIONS

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## ΠΕΡΙΛΗΨΗ

Σύμφωνα με τη βιβλιογραφία στον τομέα της συντήρησης έργων τέχνης, ο κύριος παράγοντας που πρέπει να ρυθμίζεται στο περιβάλλον ενός μουσείου είναι η σχετική υγρασία (RH). Τα επιθυμητά επίπεδα της σχετικής υγρασίας είναι περίπου στο φάσμα των τιμών 50% και 60% και σ' αυτή την περιοχή υπάρχουν λιγότεροι κίνδυνοι για τη διάβρωση των διαφόρων υλικών από τα οποία απαρτίζονται τα διάφορα έργα τέχνης. Η παρούσα μελέτη έχει σαν σκοπό να ρυθμίζει τη σχετική υγρασία σε μια προθήκη ενός εκθέματος, με τη χρήση και την παρουσία κορεσμένων διαλυμάτων διαλυτών αλάτων, έχοντας σαν αποτέλεσμα την ισορροπία του μικροπεριβάλλοντος της προθήκης. Πραγματοποιήθηκε ένας σημαντικός αριθμός πειραμάτων για την στατιστική επάρκεια της μελέτης και την αποτελεσματικότητα αυτών των διαλυμάτων. Το συνολικό συμπέρασμα είναι τα πολύ καλά αποτελέσματα από την παρουσία αυτών των διαλυμάτων διαλυτών αλάτων.

## ABSTRACT

According to key bibliography in the field of conservation, the primary factor that needs to be controlled in a museum environment is Relative Humidity (RH). The desirable levels of relative humidity typically range between 50% and 60%, as this range presents the fewest dangers for most materials. The present study aims to control the Relative Humidity by using saturated salt solutions inside a sealed museum case, in order to balance its microenvironment. A number of experiments were conducted in order to study the both effectiveness and the benefits of these solutions. The outcomes verify the excellent performance of the salts.

**Keywords:** relative humidity, corrosion, showcases, soluble salts solution, conservation.

## INTRODUCTION

Every museum environment needs to be controlled and regulated according to the exhibits housed in it, in order to fulfil the basic requirements for their protection. Museums choose their own individual methods for protecting the exhibits, according both to the needs of the objects, and the climate conditions they have to deal with. Relative Humidity affects every exhibit regardless of the material it is made of. Its fluctuations cause a dimensional alteration to the objects and thus a degradation of their properties.

Since certain exhibits need to be maintained taking specific environmental parameters into consideration, hermetically sealed cases are often used in museums. By reducing the fluctuations of the RH which may exist in the interior of the building, the objects are protected and a suitable microenvironment is created inside each case,

Despite the protection any sealed case may provide, there is always a certain amount of air inflow which leads to RH fluctuations inside the case. For this reason there are a number of buffers as well as climate control systems which are used either separately or in conjunction with each other in order to create an equilibrium. One of these methods consists of the use of saturated salt solutions, a method already used in various scientific applications. Its basic principle is the absorption or the evaporation of humidity in order for the equilibrium of the microenvironment to always be maintained (Stolow 1987). For example, if the RH is too low, the solution releases humidity into the environment, thus elevating the RH levels. On the contrary, if there is an increase of the RH levels in the environment, the solution absorbs a certain amount of humidity (Thomson 1986). Every salt solution provides a specific rate of RH ranging from the very low to the very high (fig. 1.) (Stolow 1987).

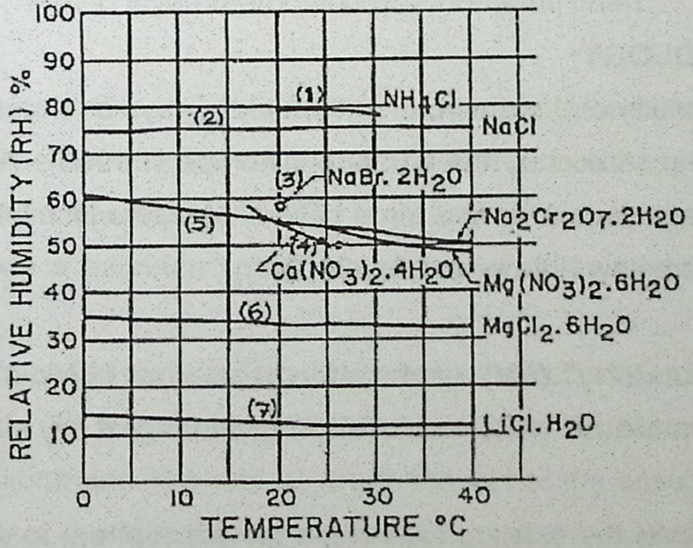

**Fig. 1.** Preservation of RH with saturated salt solutions, RH in function temperature graphs.

One of the limitations of the application presents is the fact that the salt crystals tend to creep to the walls of the case in which they are contained, therefore contacting the object directly. Another limitation is the fluid state of the solution which makes it difficult to move about (Thomson 1986). A less well known disadvantage is that salt solutions are not very effective as dehumidifiers. During the dehumidification process, the solution begins to absorb humidity from the air resulting to a certain level of dilution on its surface. The thinner solution which lies on the surface cannot be unified with the rest of the denser solution, resulting in an increase of the RH levels (http://www.oiml.org).

One of the advantages of this method is that the required solutions can be produced in large quantities. Furthermore, because of the non-soluble crystals in the solution, stability is provided without the need for constant replacement (Stolow 1987).

Designing the case may seem like a simple process, but careful consideration is needed in order to minimise the air exchange between the internal and external environment during the repeated opening of the case (Padfield 1966). In this way, protection is provided from the fluctuations of the RH levels, thus creating an appropriate microenvironment for the exhibit, while protecting it from pollution, dust and microorganisms. Such a case is suitable for special and unique artworks, but it is also an expensive and time-consuming construction (Lampropoulos 2003).

## TECHNOLOGY

The humidity of the environment should always be measured in order to control the humidity absorbed by the exhibits (Thompson 1986). The measurement of the amount of water vapour in the air is called "Absolute Humidity" and is measured as demonstrated below (Lampropoulos 2003):

**"Absolute Humidity" (AH) = saturation grams/ m$^3$ of moist air or**
**"Absolute Humidity" (AH) = saturation grams/kg of dry air**

The ratio of the existing vapours in the atmosphere to the saturated expression as a percentage gives the Relative Humidity (RH). RH can never be higher than 100% and is given by the following formula:

**Relative Humidity (RH) = [(amount of water in a given quantity of air)/ (maximum amount of water which the air can hold at that temperature)] x 100%**

The ratio among the Absolute Humidity (g/m³), the Relative Humidity (RH %) and the air temperature (°C) is presented by the hygrometric, or else, psychometric chart (fig.2). According to this chart, having the two out of the three variables as a given, makes it feasible for the third to be specified (Thomson 1986).

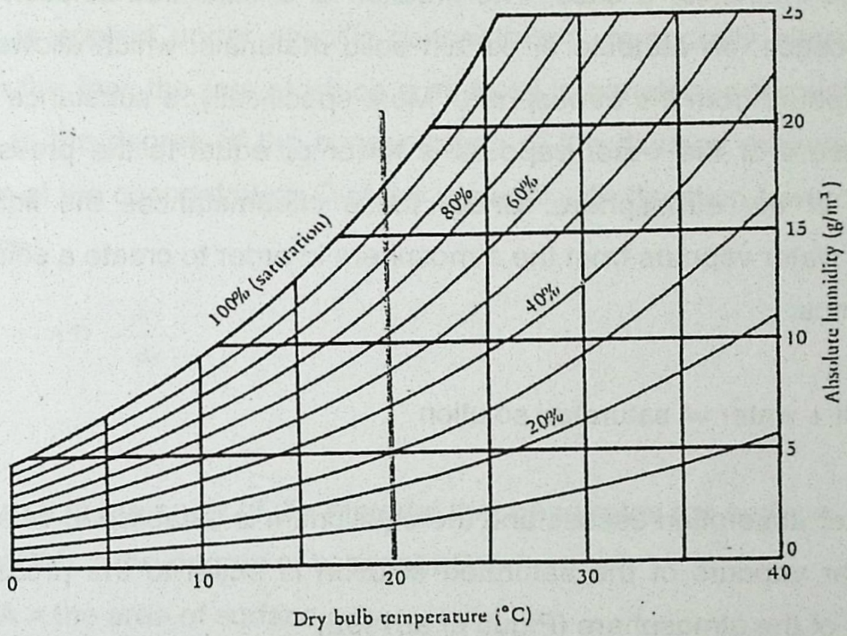

**Fig. 2.** Hygrometric and psychometric chart.

If there is a certain amount of air and water in a contained environment, the AH remains stable but the RH may vary. If the temperature increases, the RH decreases and if the temperature decreases, the RH increases. As a result, the air contained into a case or inside a museum space may become dryer or more moist (Cronyn 1990).

The conditions of the surrounding environment affect any case, no matter how well-sealed it may be. As a result, the RH in the interior of the case is affected by that of the external environment. The rate at which the RH of the case approximates the RH of the environment is of a declining exponential form and is given by the following mathematical formula:

$$-dC/dt = k(C-R)$$

Where C = the case RH at a given time "t".
R = the RH of the environment at a given time "t".

k = the constant of leakage speed.

The negative function suggests that the slope of the curve is negative when the (C-R) is positive and vice-versa (Thomson 1977).

The presence of the saturated salt solutions can stabilize the fluctuations of the RH in the interior of a case. The creation of a saturated solution is based on the deliquescence, an attribute of certain solid materials, which allows them to absorb water vapours from the atmosphere. More specifically, a substance is liquefied when the pressure of the water vapours is lower or equal to the pressure of the water vapours of the atmosphere. Under these circumstances the liquefied substance absorbs water vapours from the atmosphere in order to create a solution according to the balance:

$$\text{Salt} + \text{water} \rightleftharpoons \text{saturated solution}$$

The water absorption ceases and the equilibrium is established when the pressure of the water vapours of the saturated solution is equal to the pressure of the water vapours of the atmosphere (Pique et al.1992)

## ENVIRONMENT

Inside the case, there is always a certain exchange of air and water vapours from the external environment towards the interior of the case and vice-versa. The most significant cause for the fluctuations of the RH levels inside a case is the airflow (Lafontaine et al.1984).

The air exchange rate inside the case and the environmental space consists of an exponential nature. This rate is symbolized by "R" and is calculated according to the difference of the concentration of a gas between the internal of the case of $C_i$ and the surrounding space $C_r$, according to the following equation:

$$R = k.(Cr - Ci) \quad (1)$$

Where k = the leakage rate from the case.

Each gas has a specific rate "k" in a given case. Whether the rate of the air exchange is positive or negative plays an important role. When the "R" is positive it indicates that there is transfer towards the interior of the case. On the contrary, if it is negative this indicates a loss of air from inside the case. The constant “k” is directly related to time. As a result, when the concentrations are multiplied by time, the constant “k” represents the variation rate of the concentration (Brimblecombe et.al., 1983).

The rate at which a substance is diffused via another is given by the second law of Fick that is applied under specific concentration, temporally altered conditions. According to this law, the rate at which a material is transferred through a surface is proportional to the degree of the concentration of the diffused material (dC/dx), i.e. the alteration of the concentration C of the material with direction towards x, vertically on the surface:

$$\frac{dm}{dt} = - A \cdot D \frac{dC}{dx}$$

Where m = the quantity of the material that penetrates the surface.

dC/dx = the degree of concentration.

A = the area of surface.

D = the factor of diffusion.

The humidity sources of the surrounding space vary and the condensation of the water vapours is one of them. Condensation is the phenomenon during which the water vapours (gaseous water) become liquid water droplets. In order for this to happen, the temperature of the environment should be lower than the dew point of the atmosphere, i.e. the saturation temperature of the atmosphere water vapours (ICCROM 1985, Lampropoulos 2003). In a given temperature, the amount of the existing water vapours is at a balance. Their concentration increases with the rise of the temperature and drops with its reduction (Padfield 1966).

## EXPERIMENT

The experiments were conducted using calcium nitrate hydrate $Ca(NO_3)_2 \cdot 4H_2O$ and magnesium nitrate hydrate $Mg(NO_3)_2 \cdot 6H_2O$ which stabilize the RH at the levels of 50% and 56% respectively. The RH and the temperature inside the case and in the surrounding environment were being monitored simultaneously by the use of two thermohydrographs (fig. 3.). The measurements were taken daily in the morning and in the evening.

**Fig. 3.** Thermohydrographs used for the monitoring of RH and temperature levels.

The diagram below shows some general characteristics of the specific forms of these two salt solutions (www.allanchem.com, www.inchem.org).

| **SPECIFIC CHARACTERISTICS** | **$Ca(NO_3)_2 \cdot 4H_2O$** | **$Mg(NO_3)_2 \cdot 6H_2O$** |
|---|---|---|
| Form | White crystalline | Colorless crystalline |
| Odor | Odorless | Odorless |
| Solubility (g/100 ml) | 660 (30 °C) | 125 (≈ 0 °C) |
| Density (g/cm) | 2,50 | 1,46 |
| Melting point (°C) | 40 | 89 |
| Boiling point (°C) | 132 | 330 |

In order to carry out the experiment, a cubical case was constructed with dimensions 40x40x40 cm. The material chosen was transparent plexiglas with thickness of 0.5 cm. On its upper side a rectangular aperture of 26x20 cm was designed so that the container and the thermohydrograph could be placed inside. This aperture was covered with a rectangular piece of the same material with dimensions 27x24 cm (fig. 4). During every experiment the aperture was sealed with silicon. This enabled the easy opening and closure of the case, every time changes had to be made to the solution. By way of precaution, the case can be designed in a way that there is access to the container with the solution without having to open the case, thus preventing the disruption of the environment inside the case (Piechota 1992).

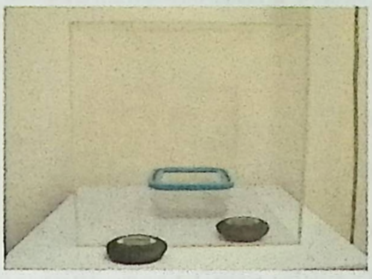

**Fig. 4.** General view of the experiment.

The reason for choosing plexiglas is because of the multiple possibilities it offers in its processing and formation, as well as its natural properties. This material is less dense and weights less than a piece of glass of the same thickness. Moreover, it is heatproof and soundproof. Plexiglas is characterized by a significant degree of endurance and stability, making it appropriate for external use (www.plexiglas.gr).

Some salts react with the container materials or the substances emitted by them, thus altering the composition of the solution and, as a result, the humidity balance. Therefore, the material of the container should be checked in order for it not to affect the microenvironment. Usually, in order to avoid this phenomenon, glass containers are used despite the fact that they are fragile (Astrup et al. 1990.). The glass container used had dimensions of 19x19x8 cm, was resistant to temperatures from -20 °C to 70 °C and had a plastic lid. Generally, it is preferable that the containers have an appropriate internal brim in order for the salt creeping and the contact of the solution with the object to be minimized. The creeping phenomenon is due to the manner in which salts are crystallized, the surface tension of the solution and the interfacial tension between the salt solution and the container (Astrup et al.1990). For this reason, a rectangular piece was removed from the plastic lid thus creating an internal brim (fig. 5). Alternatively, it is suggested to cover the containers with a special membrane through which the water molecules can penetrate, but the salt ions cannot (Stolow 1987).

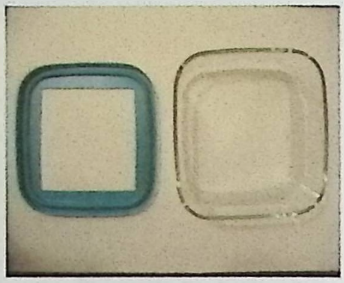

**Fig. 5.** The glass container used for the experiments.

When choosing the container, its surfaces should be smooth, while its shape should be wide and deep. This is due to the fact that the surface, together with the volume of the solution, affects the humidity control process, as the evaporation and the absorption of the water vapours take place at the surface of the saturated solution. Therefore, the bigger the surface is, the faster RH stability can be achieved. Respectively, the capacity of the container has to be large enough to accommodate the whole amount of water that is absorbed by air, especially during moist periods (Stolow 1987).

In order to create a saturated salt solution the following procedure takes place. Initially, the salt is diluted into purified water with constant stirring, which stops when no more salt can be diluted. It is important to note that, in some cases, the salt is added into water of a higher temperature than required, in order to attain a homogeneous solution. It then remains still for several hours until it reaches the desired temperature. (International Recommendation 1996). Moreover, the creation of deposit is observed, causing the solution to be saturated. Therefore, a stable balance is established between the water evaporation and the water vapour condensation, in the interior of a case or of a small space (Lampropoulos 2003).

The first experiment was realized using magnesium nitrate hydrate of purity ≥99%. In order to initiate the experimental process, the water inside the container should be at a temperature of approximately 0 °C, equivalent to the salt solubility. In order for this to be achieved, a thermometer with a range between -10 °C and 110 °C had to be used. The water was purified so that the maximum purity possible would be achieved.

Initially, 300 ml of water were taken which, according to the solubility of the magnesium nitrate hydrate, need 375g of salt in order for the solution to be saturated. During the stirring process, the container with the solution had to be placed, every now and then, in the freezer to ensure that its low temperature was maintained. When the saturated solution was placed in an environment of 25 °C, the deposit gradually diminished until it was completely dissolved. For this reason, more salt was gradually added until a certain amount of deposit was formed again. Therefore, according to our data, 125 g of magnesium nitrate hydrate had to be gradually added.

With the added salt the solution now reached a volume of 525 ml. Alterations were made to the volume of the solution during the experimental process, in order to reach the desired RH level. When the volume of the solution was: 525 ml, 300 ml, 100 ml, and 40 ml, the expected results were not achieved. When 40 ml of solution had remained, there was a minimal amount of deposit left at the bottom of the container. For this reason, 25g of salt were added, increasing the volume of the solution to 66 ml. This solution reached the desired consistency, as the case RH reached the level of 56%.

The second experiment was conducted by using calcium nitrate hydrate of purity 99-103%. According to the solution solubility, at a temperature of 30 °C, 660 g per 100 ml are required. Initially, 40 ml of water were taken, which need 264 g of calcium nitrate hydrate. As in the previous experiment, the water was purified and heated until it reached the required temperature. Salt was gradually added, while the solution was being constantly stirred. By the end of the experiment the total volume of the solution was 145 ml. In order to achieve our goal, the volume of the solution had to be altered. The volumes of the solution used were: 145 ml, 130 ml, 120 ml, 110 ml. At 110 ml the RH reached 50%, which was the initial objective.

## CONCLUSIONS

Inside a confined space, the RH demonstrates an exponential deterioration until it comes to an equilibrium with the humidity of the surrounding environment. As soon as there is an equilibrium between the internal and external environment, there is the danger for the stability of the RH to be negatively affected, should drastic changes to external conditions occur. This phenomenon was greatly noticed during the first experiment where magnesium nitrate hydrate was used. During the final stage, when the solution had a volume of 66 ml, a sudden temperature increase took place. As a result, the RH inside the case dropped significantly (fig. 6.). Therefore, the use of a material that can control the conditions of the surrounding environment is suggested, so that they remain fairly stable.

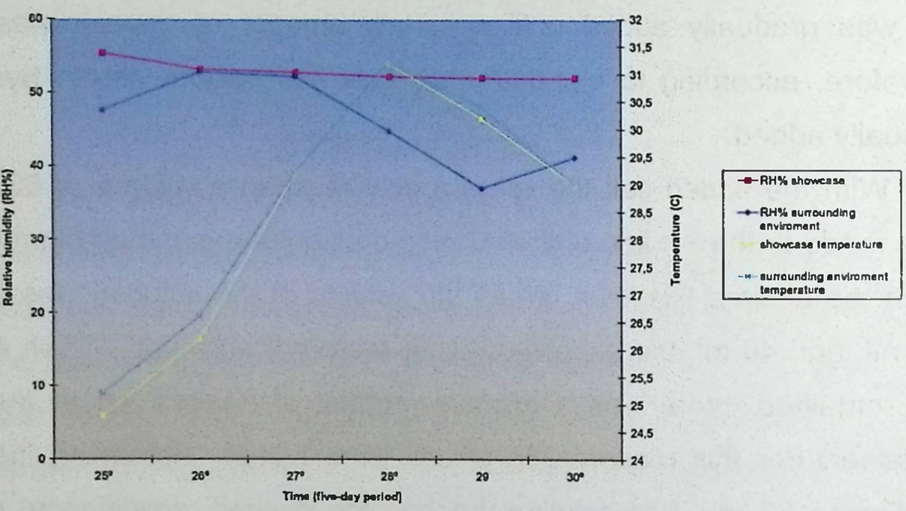

**Fig. 6.** As the temperature rises, the relative humidity begins to descend.

The creation of saturated salt solutions for the achievement of a stable RH in the interior of a case is not a simple procedure, but a rather complex one. Certain parameters that should be taken into consideration are: the chemical purity of the salt and water, the preparation of the solution, the quick restoration of an equilibrium, the preservation of the appropriate temperature during both the liquid phase and the gaseous phase, and the materials used to construct the case.

Should there be a small amount of foreign substances in the salt and the water, the RH changes due to the alteration of the solution composure. The same thing happens when certain substances are produced due to the salt staying inside the container. The solution should be over-saturated with an excess of non-soluble salt crystals, which will remain near the surface of the solution. This occured to the final solution of the magnesium nitrate hydrate, in which a certain amount of non-soluble salt was added, in order to achieve dense deposit at the bottom (fig. 7.). Based on this process, the second experiment with the calcium nitrate hydrate was conducted, paying particular attention to the non-soluble crystal layer formed inside the container.

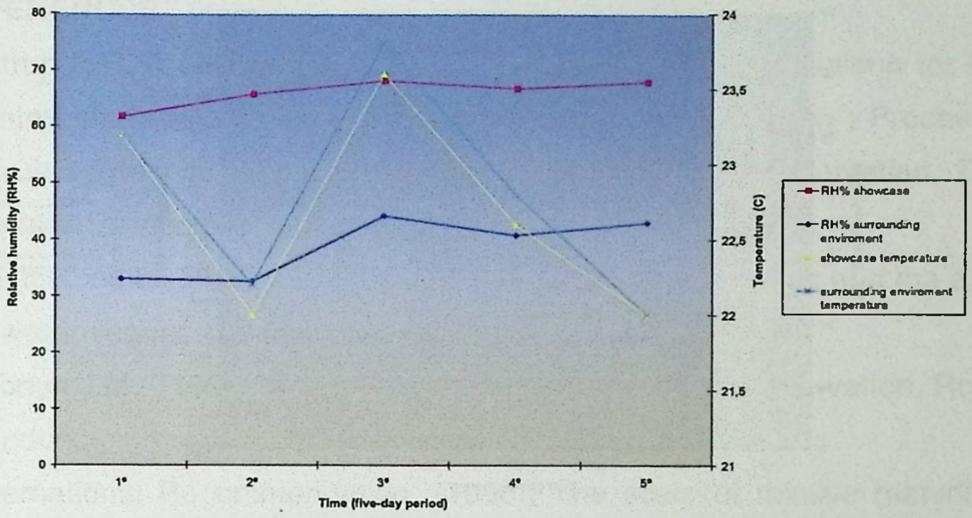

**Fig. 7.** Relative humidity began to stabilize when more salt was added.

In order for the RH to be stabilised faster, the surface of the solution should be fairly large. In this way, the space where the water vapours are contained is reduced and the air circulates over the solution. Alternatively, the use of many smaller containers may provide the same result, as the rate of absorption-evaporation of the water molecules occurs at the same speed. Moreover, it is necessary to consider the volume of the solution, which has to be large enough in order to provide the required amount of water vapours. Generally, the saturated solutions have an advantage over other controlling methods, as they do not need constant renewal.

The excessive amount of water in the solution may bring negative results, even if there are non-soluble grains of salt inside the container. These grains may eventually create a non-saturated solution, resulting to a higher level of RH. The above-mentioned phenomenon was obvious during the first experiment as the volume of the solution was disproportional to the size of the case, giving a 10% higher RH than the desired rate. When the volume of the solution was significantly reduced, a drastic drop of the RH levels was observed inside the case (fig. 8.). This affected the conduction of the second experiment, as the volume of the solution initially used was significantly reduced. Therefore, the initial RH levels were very close to the desired ones.

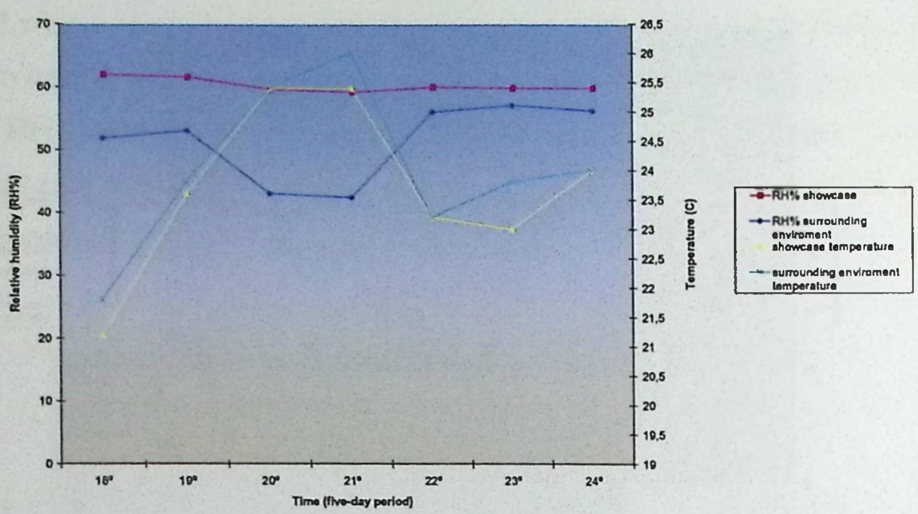

**Fig. 8.** The size of the case has to be proportional to the volume of the solution. Relative humidity increases or decreases according to this way.

By observing the two experiments, neither the magnesium nitrate hydrate, nor the calcium nitrate hydrate showed capillary creeping on the container's walls. According to Astrup et al (1990), the first salt is affected by the material of the container, as opposed to the second one. It is obvious that the magnesium nitrate hydrate did not present any signs of creeping, due to the glass container.

The overall conclusion of these two experiments is that saturated salt solutions provide RH stability in relation to external conditions. Fluctuations in the interior of the case were not completely avoided; however these fluctuations were much milder than the uncontrollable levels of fluctuations in the surrounding environment. Moreover, the fluctuations inside the case between morning and evening measurements were not significant. As far as the temperature levels are concerned, while they differed between the interior and the exterior of the case, they mostly demonstrated analogous fluctuations (fig. 8,9.).

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