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Pigments of the bust of Nefertete compared with those of the Karnak Talatats☆

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Abstract

The elaborate characterisation and specification of materials used for decorating statues and buildings can be achieved by means of complementary methods of investigation such as analytical light and electron microscopy, thermal analysis, X-ray and neutron diffractometry, and various types of spectroscopy. The results cannot only reveal the historically relevant exploration and refinement techniques of natural resources, but also the types of application on different supports. In addition deterioration and erosion processes can be monitored and eventually conservation and restoration procedures may be improved.

Here, we present results of investigations on materials, i.e. pigments which have been applied for the decoration of Nefertete's bust and—practically in the same period—for the illumination of the so-called Talatat blocks of the then dismantled temple erected at Karnak under the reign of Akhenaten. Special attention was paid to the blue pigments, which—in both cases—could be identified unambiguously by means of X-ray diffractometry and Raman spectroscopy with the so-called Egyptian Blue, $CaCuSi_4O_{10}$. Other materials used in the polychromatic decorations are iron oxides (red), amorphous carbon/ quartz (yellow) as well as the organic composite soot/bee wax mixtures (black). Obviously these mentioned pigments are chemically inert and therefore still visible, whereas other pigments such as green may have vanished more or less completely. In summary our investigations confirm and further reveal the skill of the Egyptian artisans and may elucidate a more detailed "life cycle analysis" of the used materials, spreading from the natural resources to the production and application and they finally may yield some useful hints for the advancement of our present reconstruction of historical developments in Egypt.

Keywords: Nefertete; Egyptian Blue; Raman spectroscopy; Accelerator mass spectrometry (AMS); Gas chromatography/mass spectrometry (GC/MS)

1. Introduction

In cultural historic terms the identification of the sources of functional materials used for decorating statues and buildings, i.e. of inorganic or organic pigments and colorants, is indicative for the technological

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skills, but also for the trade trajectories. A first discrimination has certainly to be done between naturally occurring materials exhibiting desired chromic properties and synthetic pigments such as Egyptian Blue or iron oxides exposed to various temperatures and atmospheres or black, i.e. soot from oil lamps or wood char. When ancient pigments are identified the chemical and thermal reactivity must be explored in order to re-identify the source or locality of the used pigments. For the ancient Egyptian civilisation Iversen [1] describes in extension the nouns for pigments applied in Karnak and other places. Special attention has been paid to the Egyptian Blue the colour of the eternal sky, which has been produced before 3000 B.C. A comprehensive overview on the studies on Egyptian Blue has been published by Delamare [2]. In this study, we focus on the characterisation of Egyptian pigments used in the polychrome decoration of Nefertete's bust and for the illumination of the so-called Talatat blocks of the (shortly after the death of Akhenaten dismantled) temple erected at Karnak under the reign of Akhenaten. We were not only interested in the composition of the materials, but also in the sources, i.e. in the localities where natural pigments have been found and in the production sites and technologies. As it is known many of the pigments in ancient Egypt proved to be chemically inert phases, even synthetic representatives like the Egyptian Blue, the recently found samples are still indicative. In order to gain an overview on the possible localities where natural minerals were found, isolated and later processed into pigments, one of us collected naturally occurring pigments during a rather time consuming and tedious campaign along the line Sakkara, Esna, Qurna and Assuan, as well as at other historical sites like Petra in Jordan and in the desert of Libya. The spectrum of the so disposable palette is remarkable [3]. These natural materials have been compared with pigments collected from Nefertete's bust and the Karnak Talatat, which have been described earlier [4–6]. We also characterised the black colorant of the pupil of Nefertete and compared it with recently prepared mixtures in order to find out the resources and the production manner of the original.

2. Experimental

Samples of natural minerals or mineral mixtures, which could have been used as pigments, were collected during a 9-month-period at different localities: at Petra (Jordan), on the Sinai peninsula and Mount Moses, in the Libyan Desert (Libya), in the White Desert (Libya) and along the Nile Valley at Sakkara, Qurna/Thebes, Western Desert/Thebes, Esna and Assuan. The samples were isolated, mortared, sieved and elutriated according to the antique techniques known from the literature. These standards were compared with original samples isolated from a Talatat (Museum of Berlin). They were characterised by X-ray diffraction, thermal analysis and Raman spectroscopy. The blue pigment, i.e. the Egyptian Blue collected from Nefertete's crown (Museum of Berlin) and two Talatat (one at the Museum of Berlin and the other at the original site, i.e. the temple of Akhenaten) were characterised and compared by means of Raman spectroscopy using a Renishaw Raman microscope, equipped with a Leica 50× objective and working with an Argon laser (wave length: 514 nm). The identification of the organic materials, i.e. the black colorant of the eye pupil of Nefertete's bust were determined by capillary gas chromatography and mass spectrometry (GC/MS) under electron impact (EI) conditions using a Finnigan 4510 system coupled to a Carlo Erba 4160 gas chromatograph unit (interface temperature: 360 °C). About 1 μg of sample dissolved in 1 μl octane was injected onto the capillary column (10 m × 0.3 mm, bonded dimethylsilicone phase) which was held at 126 °C for 1 min and then heated with 10 K/min to the final temperature of 350 °C. The mass spectra were recorded at 70 eV and 150 °C ion source temperature. The quantitative TG/DTA measurements of the enthalpy of the phase transition of quartz and the weight loss of the decomposition of limestone were done by the METTLER-TOLEDO Thermosystem, TA 8000 (Fig. 1).

The accelerator mass spectrometer for C-14 dating is shown in [8,9]. The investigation of the carbon black and bee wax mixture collected from Nefertete's eye is in detail described. The measured results are shown in Fig. 2.

3. Results

3.1. The inorganic pigments [3]

The collected and refined natural pigments were characterised by their optical appearance, i.e. their

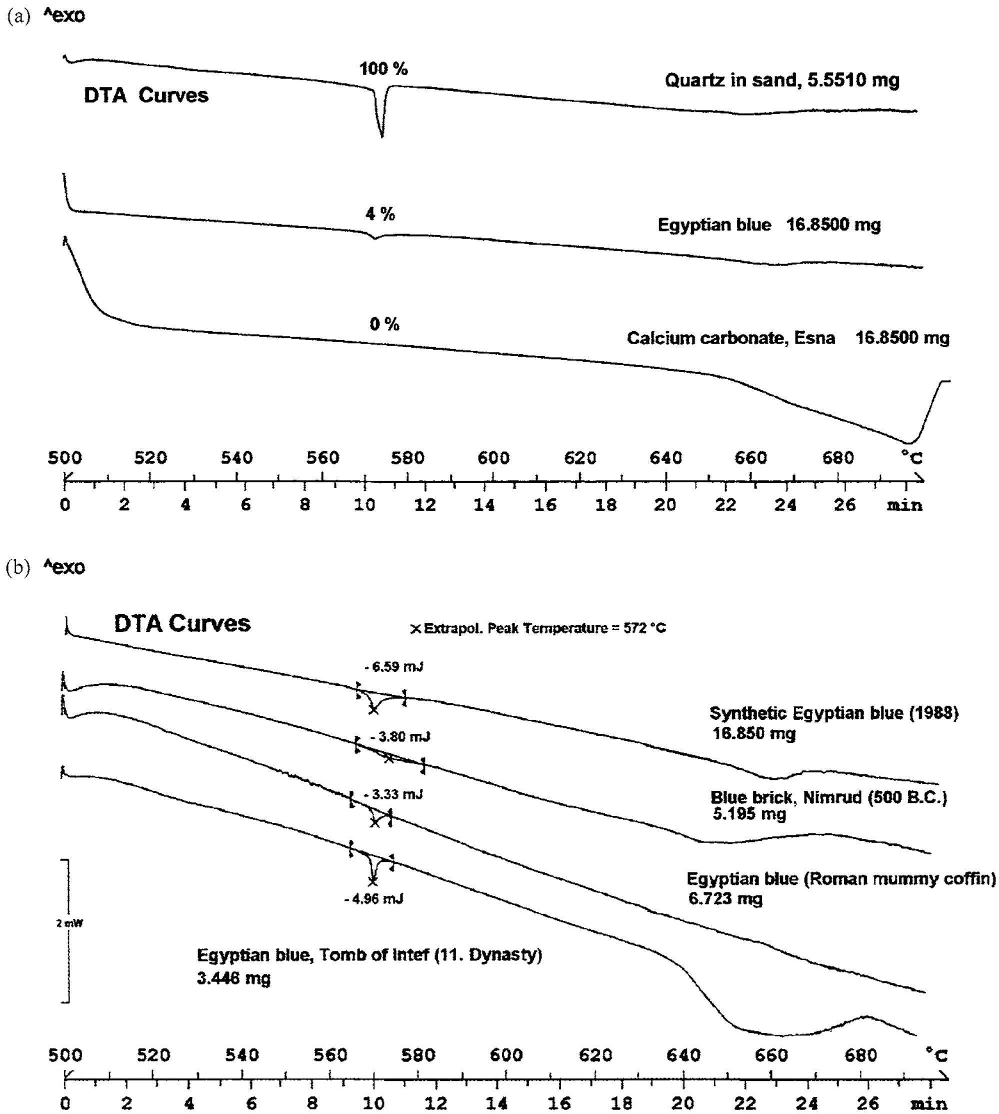
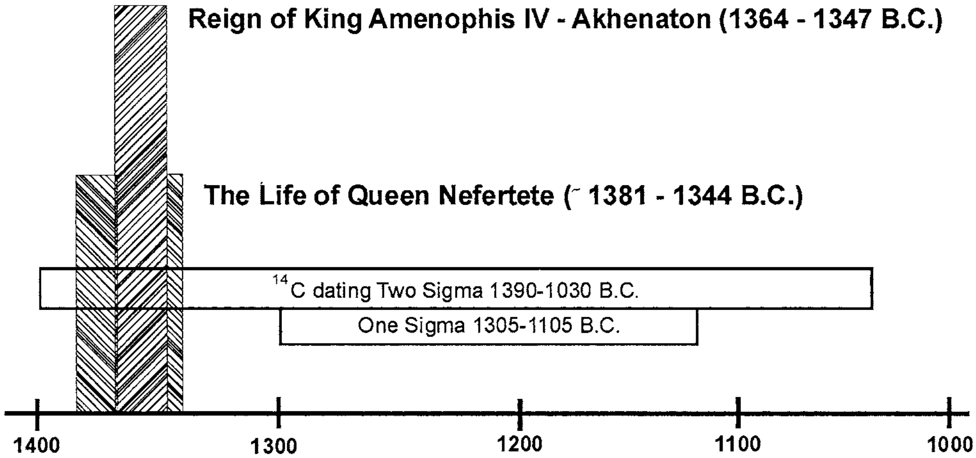


Fig. 1. (a) Comparative DTA measurements of a mixture of quartz and determination of the amounts of the main constituents in the parent material. (b) Comparative DTA measurements of the portions of non-reacted quartz and calcite in ancient and new Egyptian Blue materials.

colour tone and by their phase composition. The phase analysis performed by X-ray diffraction and by Raman spectroscopy gave evidence for a rather large spectrum of different phases (and corresponding mixtures): quartz, SiO_2, hematite, Fe_2O_3, magnetite, Fe_3O_4, various iron hydroxides, gypsum, $CaSO_4 \cdot 2H_2O$, anhydrite, $CaSO_4 \cdot 0.5H_2O$, barite, $BaSO_4$, galena, PbS, limestone, $CaCO_3$, magnesium silicates, etc. could be isolated and identified at the various localities and, therefore, could have been utilised by the Egyptians (see Fig. 3a and b). The amount of quartz and limestone used as white pigment, i.e. as matrix for the chromic materials, was determined by quantitative TG/DTA measurements: the enthalpy of



Sample No.	Sample Description	Age	One Sigma	Two Sigma
AA 5530	Beewax - Queen Nefertete	2970 ± 60	BC 1305 -1105	BC 1390 -1030

Fig. 2. Accelerator mass spectrometry C-14 dating of the carbon black [9]/ bee wax mixture collected from Nefertete's eye [8].

the phase transition of quartz and the weight loss of the decomposition of limestone were used as measure. In Fig. 3, the course of a thermoanalytical measurement of such a mixture is exemplified for investigations on Egyptian Blue.

The comparison of these phases with samples collected from three different Talatat and of Nefertete's bust gave the following information. Whereas the materials of Nefertete's bust comprise gypsum and limestone (as ground) as well as hematite, orpiment, probably copper acetate (chemically reactive), the later specified synthetic pigment Egyptian Blue and the organic mixture soot/bee wax (pupil), the palette of the pigments used for the polychromic decoration of two Talatat of the Berlin Museum and one Talatat located at the original site elucidated some preliminary, but remarkable details: we identified quite unusual minerals like huntite (a magnesium calcium carbonate), magnesium silicate as well as zincobotryogen (basic zinc iron sulphate) and again Egyptian Blue. Whereas the redbrown colour of the arm of Akhenaten (see encircled domain on Talatat No. 753, Fig. 4) can be explained by the presence of zincobotryogen, the red pigment found on the Talatat

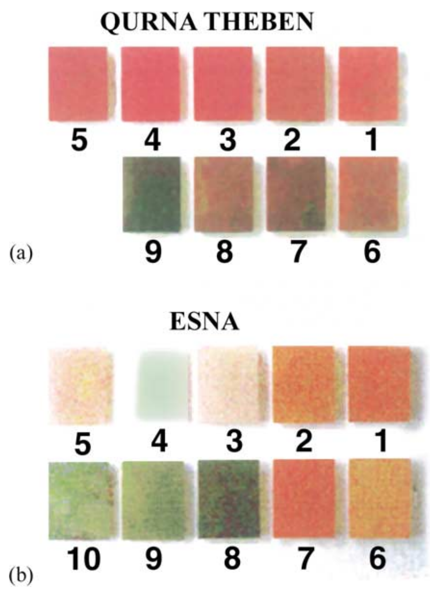


Fig. 3. Comparative studies of pigments fabricated from various sites and mineral resources. In (a), the site Qurna near Thebes is shown and a collection of different iron oxides/iron hydroxides pigments adopting finely graded colour tones are presented. In (b), a selection of pigments fabricated from mineral resources collected in Esna is shown.

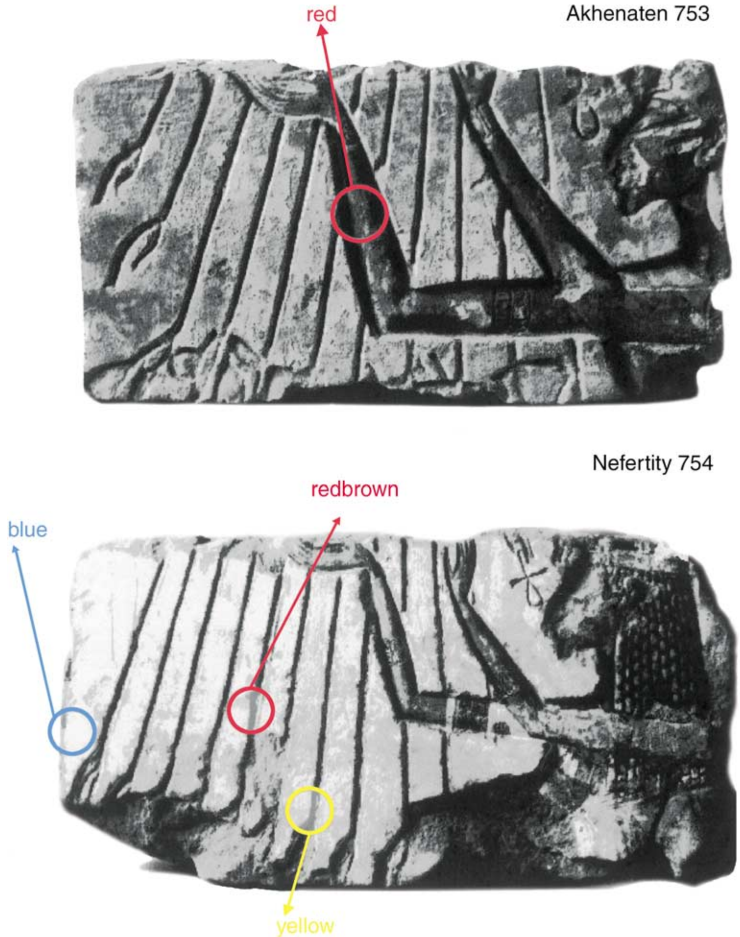


Fig. 4. Photographs of the two Talatat, No. 753 (Akhenaten) and No. 754 (Nefertete) of the Egyptian Museum, Berlin.

showing Nefertete (see encircled domain on Talatat No. 754, Fig. 4) is made up of huntite, a magnesium calcium mixed carbonate, which may contain iron and most probably of hematite. The yellow pigment on the Talatat showing Nefertete (see encircled domain on Talatat No. 754, Fig. 4) has been identified as a mixture of magnesium silicate and quartz. In summary, the X-ray diffraction studies gave evidence for a remarkable spectrum of different inorganic phases. Except from the synthetic Egyptian Blue, also present on the Talatat showing Nefertete (see encircled domain on Talatat No. 754, Fig. 4), the other pigments or mixtures can be found as mineral resources.

3.2. The Egyptian Blue found on the Talatat and on Nefertete's bust

Egyptian Blue has been found on Nefertete's bust [6,7] as well as on the Talatat. A comparison by means of Raman investigations confirm (see Fig. 5 and Table 1) that the synthetic pigments used are practically identical.

3.3. The black colorant of Nefertete's eye [8]

As black colorant of the pupil a mixture of carbon black and bee wax was used. Worms were found in the bee wax indicating the biological source. Gas

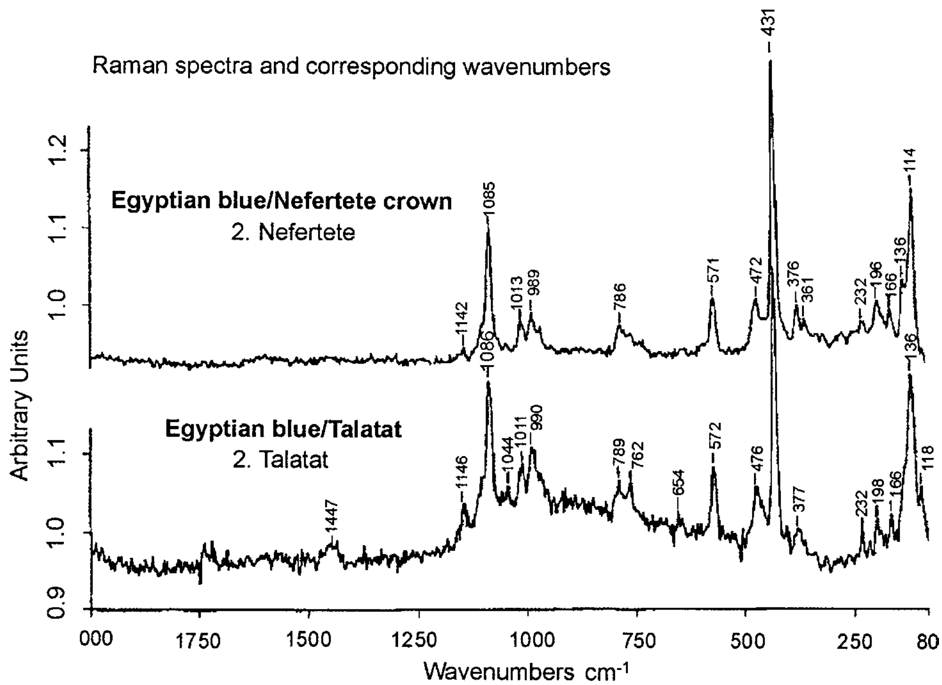


Fig. 5. Comparative Raman measurements of two Egyptian Blue samples collected from Nefertete's bust as well as from the Talatat.

Table 1
Comparative Raman data (in cm^{-1}) of Egyptian Blue collected from Nefertete's bust and from the Talatat No. 754 (see encircled domain, Fig. 3) as well as from a Talatat found at the original site in Karnak

Number	Cuprorivaite, Smithonian	1 Nefertete, Berlin	2 Nefertete, Berlin	1 Talatat, Luxor	2 Talatat, Luxor
1					1447
2		1142	1139	1146	1146
3	1086s	1085s	1082s	1085s	1086s
4	1040w				1044
5	1012w	1013	1011	1011	1011
6	992w	989	987	989	990
7	789w	786	784	786	789
8	762w		763		762
9					654
10	597vw				
11	571w	571w	568w	571w	572w
12	475m(sh)	472	471	472	476
13	430vs	431vs	429vs	431vs	431vs
14	377m	361	373	377	377
15	358m		358		
16	239w	232		232	232
17	200w	196		198	198
18		166		166	166
19	137m	136		136	136
20	114m	114m		118m	118m
21				95	95

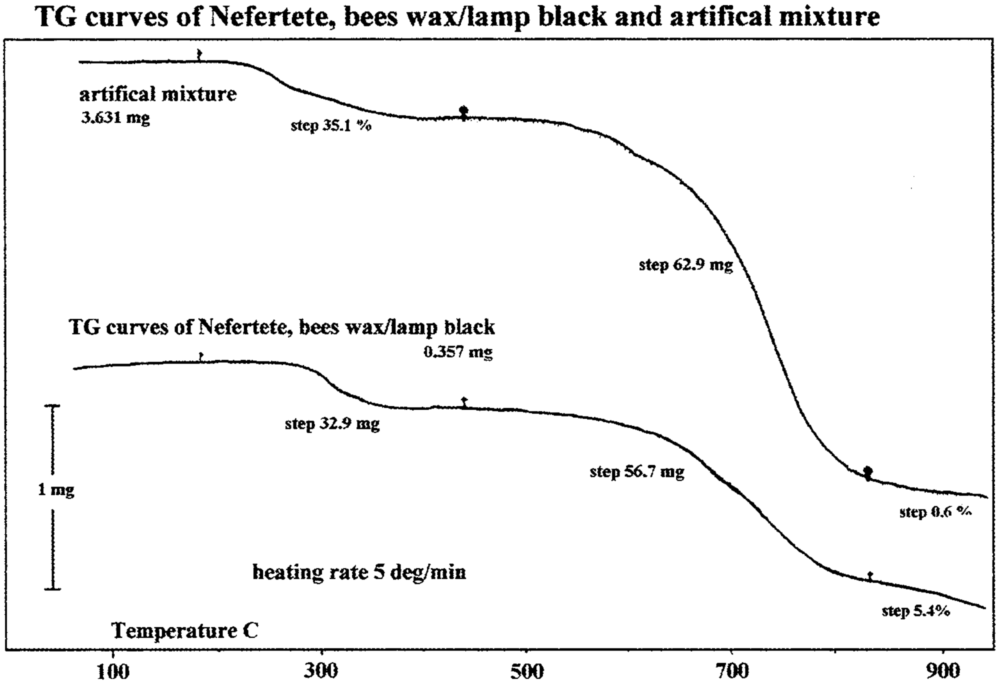


Fig. 6. Comparative thermoanalytical measurement of the thermal degradation of the carbon black/bee wax mixture collected from Nefertete's eye and prepared as imitate made up of oil lamp black and ancient bee wax.

chromatographic/mass spectrometric investigations elucidate the presence of palmitinic ester of myristil alcohol, indicative for bee wax as primary resource. In Fig. 6, the comparison between the thermal degradation of the original wax/soot mixture collected of Nefertete's eye with a phase mixture prepared from 3000 years old bee wax from the village of Deir-el-Medine (Ramesseum) and ancient soot from an oil lamp is shown. The findings indicate that analogous phase mixtures are present, i.e. the black colorant has been prepared as mentioned.

The detailed identification of the bee wax by GC/MS gave the following results: as one compound class a series of higher paraffins, namely $C_{27}H_{56}$, $C_{29}H_{60}$, $C_{31}H_{64}$ and $C_{33}H_{68}$ could be detected (data not shown). Their mass spectra show relatively abundant molecular ions and fragment ion series with intensity distributions characteristic for *n*-alkanes. The main components of the suspected wax binder were eluted at higher temperature. Their mass spectra show molecular ions at *m*/*z* 592, 620, 648, 676 and 704, respectively, and the corresponding mass chromatograms are represented in Fig. 7 (upper panel, A). All five spectra are dominated by *m*/*z* 257 ($C_{15}H_{31}COOH_2^+$, upper trace in mass chromatograms), which represents together with *m*/*z* 239 ($C_{15}H_{31}CO^+$) the acidic part of all five components. The mass differences to the molecular ions reveal the corresponding alcoholic parts of the esters as $C_{24}H_{49}OH$, $C_{26}H_{53}OH$, $C_{28}H_{57}OH$, $C_{30}H_{61}OH$ and $C_{32}C_{65}OH$. In addition in all spectra the corresponding $C_nH_{2n}^+$ and $C_n H_{2n+1}OCO^+$ ions as typical fragments involving the alkoxy group corroborate this assignment (e.g. *m*/*z* 336 and 381 for the case C_{24}). The main components are therefore C_{24}-, C_{26}-, C_{28}-, C_{30}- and C_{32}-esters of $C_{15}H_{31}COOH$.

A very similar distribution of the main components is observed for contemporary bee wax (see panel B). Not only the distribution but in addition the individual mass spectra show a high degree of similarity. The medium from the Nefertete's bust is, therefore, very likely composed of an ancient bee wax which contains very similar constituents as contemporary bee waxes.

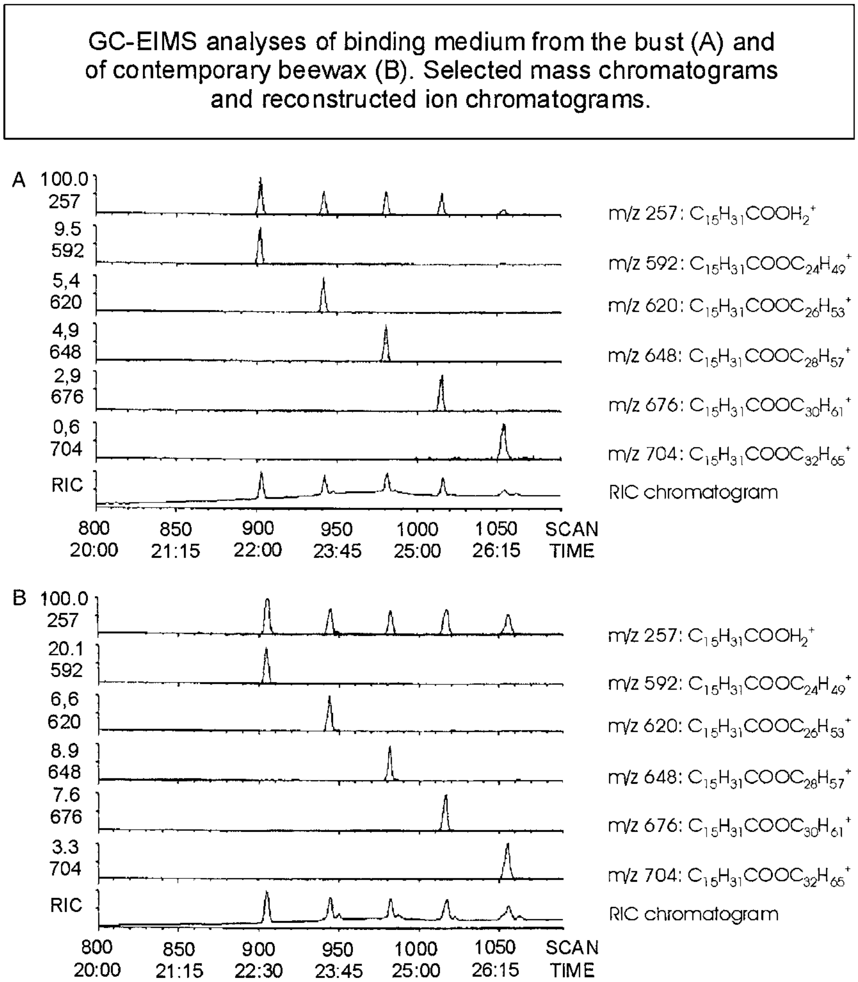


Fig. 7. Gas chromatographic/mass spectrometric investigation on different ancient bee waxes [7,10].

4. Conclusion

The findings of our investigations give some further insights into the skills of the Egyptians for collecting, preparing and applying pigments and colours. The initially mentioned perspective to trace the "life cycles" of the used and/or transformed materials from the natural resource to the artefact has to be commented: although many natural pigments have been collected and classified the palette of the colorants actually used is more versatile. Therefore, additional efforts have to be undertaken in order to compile a comprehensive understanding.

The application of complementary methods of investigation proved to be beneficial. Even if only minute amounts of specific samples are disposable, the careful inspection by different, if possible destruction-free investigations, the accurate knowledge of the site where the sample has been collected, and the generation of imitates allows—in the best case—concise interpretations of the ancient (civilisation) processes.

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