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MS-TGA of ancient glasses: an attempt to determine the manufacturing conditions (I)☆

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Abstract

Gas release profiles of manmade glasses produced under different manufacturing conditions show significant differences. Recently produced glasses reveal a strong influence of the melting conditions, the raw materials and the fining additives on the gas release profiles. The knowledge of these relationships also allows conclusions to be drawn with respect to the manufacturing process, the raw materials used and the fining agents of ancient glasses. Three types of Ramesside coloured glass samples, blue-green [b-g], olive [o], and pink [p] from the eastern Nile Delta, San el Hagar (Tanis), Egypt, were investigated [Archaeometry 39 (2) (1997) 355]. Significant differences between the three glasses were observed. The so-called temperature of bubbling allowed the minimum of melting temperature to be determined which is different to the temperature data of the softening point measured by Thermomechanical Analysis (TMA) [b-g] 580°C, [o] 594°C, [p] 608°C [2]. A comparison of investigations of the Amara glass samples from a Petrie Flinders collection in Berlin should be published in another paper shortly.

Furthermore, significant differences in the raw material ([g] carbonates > hydrates; [o] carbonates > hydrates; [p] hydrates > carbonates > hydrates) were observed. Additives in the glass batches were different in quantities: NaCl and sulphate $\geqslant$ [o] > [p]. Gas release profiles are suitable tools for the identification of vitreous samples of unknown origin. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: MS-TGA; Ramesside coloured glasses; Gas release profiles; Degassing equipment

1. Introduction

The origin and development of ancient glasses has been investigated in different ways. The chemical composition allows discrimination between different glass types produced from different raw materials and exploration of the technological conditions of their production. The ancient glass houses have experience in producing soda-lime–silica glasses from the evaporite mineral trona $Na_3(CO)_3(HCO_3)_x{\cdot}2H_2O$, limestone and quartz. A major source of trona (soda), which was earlier used as a detergent, are the evaporate deposits of the Wadi El Natrun lake between Cairo and Alexandria, Egypt. In the outer zones of the summer precipitation of the respective lakes large crystals of thenardite (Na_2SO_4) together with halite (NaCl) and trona are formed.

The proportion of halite contamination in hand-picked trona is expected to range between several and more than 10% Brill, [3]. Soda of the Egyptian anti-

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quity (15–18th dynasty) as reported by Geilmann [4] contained 0.5–39% NaCl. That means sulphate and chloride content is common in the early Egyptian glasses [3].

In an attempt to determine the concentration of volatile compounds like chlorine and sulphur species in silica melts, gas release profiles are used. The temperature ranges of degassing is controlled by the raw materials, the melting additives and the melting conditions.

A special problem in glass production is the colour of ancient glasses. To produce clear glasses decolorizers are used, e.g. manganese or antimony oxides. However, some of earliest clear glasses contain no Sb or Mn and the decolorizer is unknown. Furthermore, amber coloured glasses were produced by lead or antimony additives, but a determination of the colouring ingredients in yellow glasses is quite difficult to obtain from the major element analysis. In particular, an iron-sulphide chromophore in the amber coloured glasses (only 0.01% S is necessary for this effect) is difficult to detect. In the present paper the possibility was tested for detecting the melting additives by evolved gas analysis (DEGAS). It is known from systematic studies that the degassing behaviour of manmade glasses is determined by the melting temperature and melting atmosphere, by the raw material and by the "fining" agents (purification agents to make the glass gas-free). With this investigation the use of the direct coupled evolved gas analysis system (DEGAS) should be tested as a tool of ancient glasses in archaeology.

2. Experimental procedures

The degassing profiles have been obtained by the use of a thermobalance in combination with a quadruple mass spectrometer (STA429 Netzsch and QMG2O2 Balzers). In the special devices the specimens were programme heated under vacuum in extreme non-equilibrium conditions. The short distance between sample and gas detection unit (not more than 20 cm) allow the determination of permanent gases and volatiles which have escaped from the sample without any reaction with the crucible and furnace material. In this configuration the analysis occurs by means of a DEGAS.

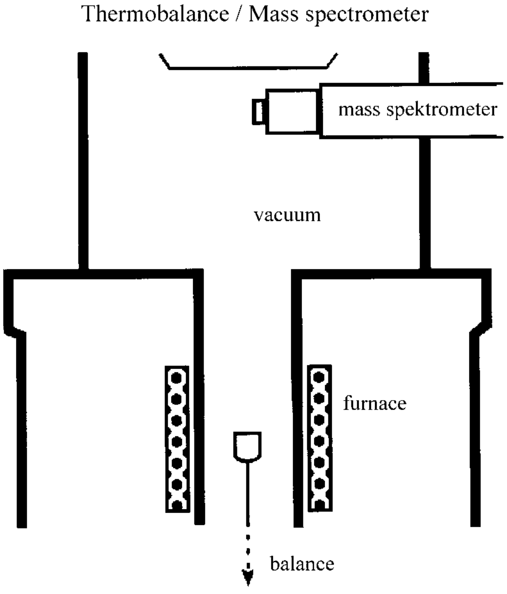

Fig. 1. Degassing equipment for high vacuum extraction.

The analysis of the three Egyptian glasses was undertaken, showing different degassing profiles of the encapsulated gases. In case of the Egyptian glasses, the thermal history and the raw materials could be different. The study was focused not only on the water release by heating, but also of other relevant gases like CO_2, CO, N_2, SO_2, HCl, HF, O_2 and hydrocarbons beside Na_2O.

The thermobalance has been tested with respect to degassing behaviour of the crucible and ceramic elements of the furnace. For this investigation alumina crucibles were used. The gas release was monitored in the temperature range from RT to 1500°C, although the following discussion is focused on the temperature range between 600 and 1200°C, the most interesting range with respect to glass forming process. The sample size varied from 10 to 100 mg. Single broken pieces were analysed without any handling. The heating rate was 10 K/min.

A detailed description of the equipment used (Fig. 1) was published in [5,6] Heide et al.

3. Results

Comparison of degassing profiles show that the three glasses have different degassing behaviour with respect of the chemical composition of evolved volatiles and in the temperatures of the maximum degassing rates.

When the samples are heated in a high vacuum, gases are liberated by diffusion and by bursting of bubbles. In the case of diffusion the partial pressure changes continuously with a smooth temperature maximum. Sharp spikes in the partial pressure curve indicate the bursting of bubbles. The number of such spikes and the intensity represents a relative value, permitting the comparison of extractable gas contents of the glass samples.

The following results are discussed:

- the correlation between the dehydration and decarboxylation ($H_2O^+ (m/z = 18)$, $CO^+ (mz = 28)$ and $CO_2{}^+ (m/z = 44)$; Fig. 2a–c);
- the correlation between the evaporation of Na and Cl species ($Na^+ (m/z = 23)$, $^{35}Cl^+ (m/z = 35)$, $H^{35}C1^+ (m/z = 36)$; Fig. 3a–c);
- the detection of hydrocarbons ($C^+ (m/z = 12)$, $CH_4{}^+ (m/z = 16)$ and the methane fragment $CH_3{}^+ (m/z = 15)$; Fig. 4a–c);
- the detection of fining agents (SO_2 fragment $SO^+ (m/z = 48)$ and S^+ or $O_2{}^+ (m/z = 32)$; Fig. 5a–c).

As shown in Figs. 2–5, the degassing of the specimens occurs in different steps. The H_2O-release in the temperature range from RT up to 700°C indicates a hydration of the glasses by alteration and is not discussed here in detail. The process is controlled by the rate of desorption. Above 800°C, CO_2, CO, SO_2, HCl, O_2, hydrocarbons and traces of water are liberated both in the form of bubbles (spikes) and by diffusion.

3.1. Blue-green glass

From the degassing runs in case of the blue-green glass, the formation of a melt results above 600°C from the first spikes in the H_2O and CH_4 release (Figs. 2a and 4a). No correlation exists between the H_2O, CO and CO_2-release; this means that water, carbon monoxide and carbon dioxide are formed as fluid species independent of each other (Fig. 2a). The evaporation by bubbling of NaCl is very distinct, as proved by the strict correlation of the $Na^+ (m/z = 23)$ and $Cl^+ (m/z = 35)$ spikes (Fig. 3a).

The identification of traces of methane is possible from the good correlation in the degassing temperature and spike intensity of the mass numbers 12, 15 and 16 (Fig. 4a). Furthermore the bubbling by SO_2 degassing (Fig. 5a) in the same temperature range (860–1140°C) as the NaCl evaporation (Fig. 3a) indicates sulphate content in the melt.

3.2. Pink glass

As seen in Figs. 2c, 3c, 4c and 5c, the degassing of the pink glass is quite different. The first degassing spikes are observable in the partial pressure profile of water up to 680°C (Fig. 2c). Partly mixed H_2O, CO and CO_2 bubbles are formed as seen from the coincidence in some of the peaks (Fig. 2c). The chlorine species are also connected with the formation of HCl (Fig. 3c).

In Fig. 5c, traces of SO_2 are also detected in correlation with $m/z = 32$ (escaped above 1060°C), more by diffusion than bursting of bubbles in comparison with Fig. 5a.

3.3. Olive green glass

The degassing profiles of the olive glasses (o-glass) are similar to the pink glasses (p-glass). Water escaped in big bubbles in the temperature range above 700°C up to 940°C (Fig. 2). The CO_2-release dominated with respect to CO. The degassing occurs by bursting of bubbles.

In Fig. 3b, in the olive glass obviously no correlation exists between Na and Cl, but a very good correlation exists between $m/z = 36$ and $m/z = 35$. This means that HCl escaped from the melt with a maximum rate up to 1080°C.

The degassing profiles of both the olive and the pink glasses in Fig. 4b and c shows that hydrocarbons are only formed in traces during the heating (unlike in the blue-green glass in Fig. 4a).

In these glasses sulphur escaped in voluminous bubbles in a temperature range above 1080°C (Fig. 5b). N_2 can be excluded from all degassing profiles on the basis of correlation between $m/z = 14$ and 28.

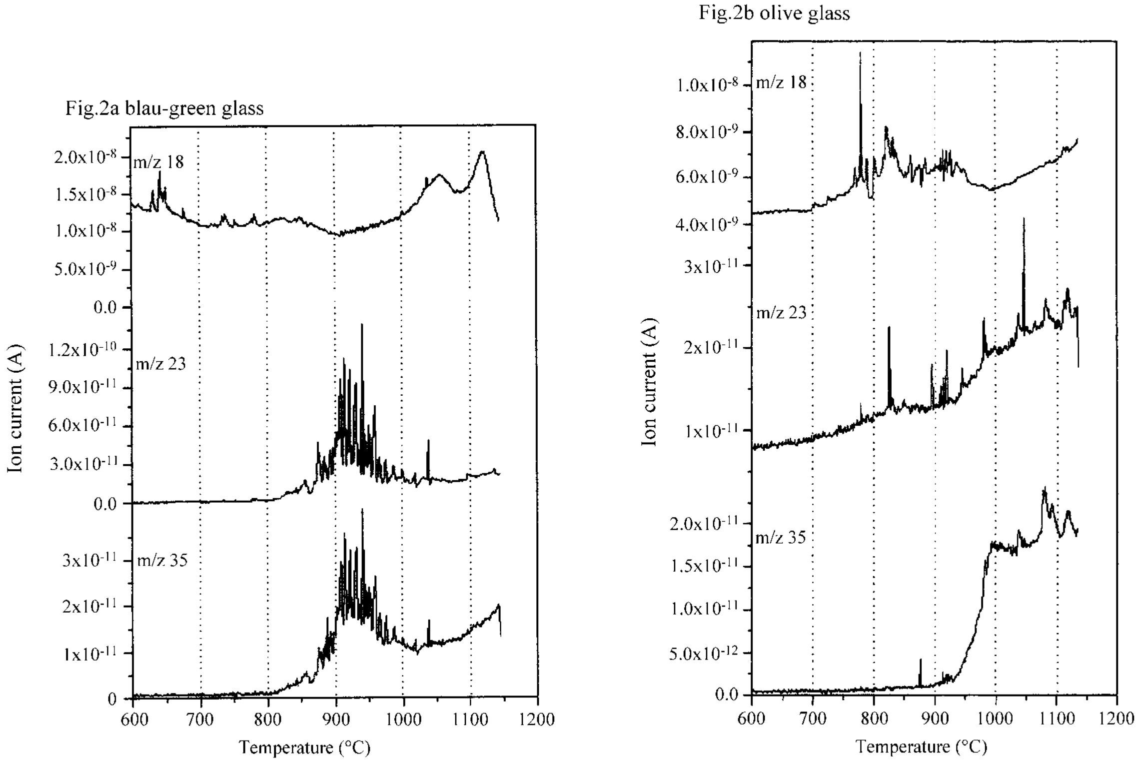
Fig.2a blau-green glass

Fig.2b olive glass

Fig.2c pink glass

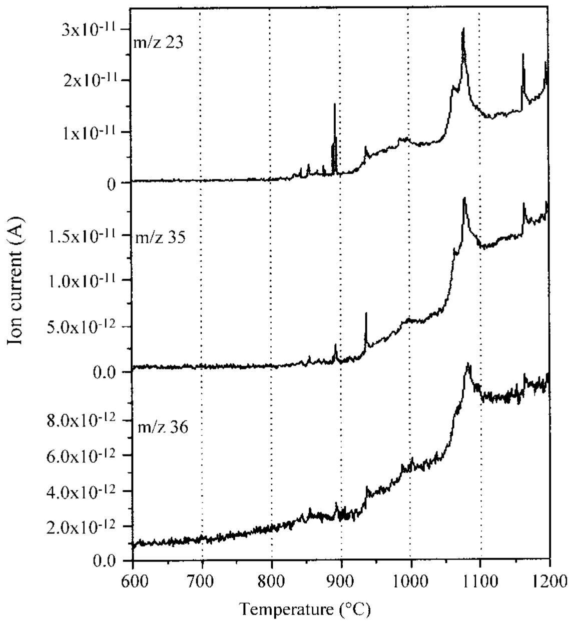

Fig. 2. MS-degassing curves of individual masses as H_2O^+ ($m/z = 18$), CO^+ ($m/z = 28$) and CO_2^+ ($m/z = 44$) of the (a) green-blue, (b) olive and (c) pink glass samples as a function of temperature by a mass spectrometer.

Fig.3a blau-green glass

Fig.3b olive glass

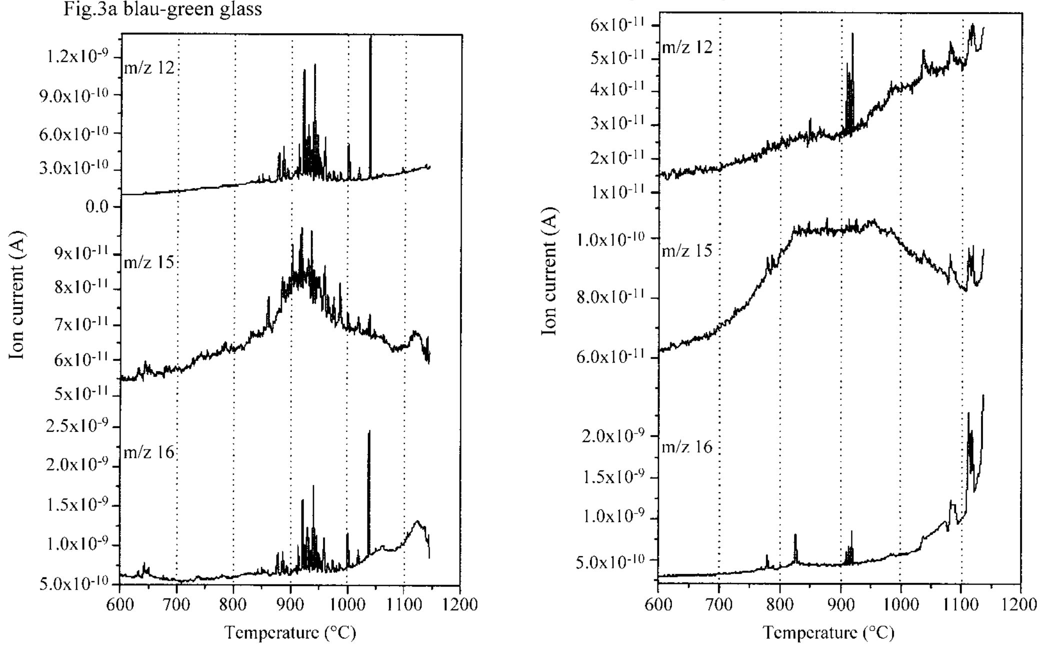

Fig.3c pink glass

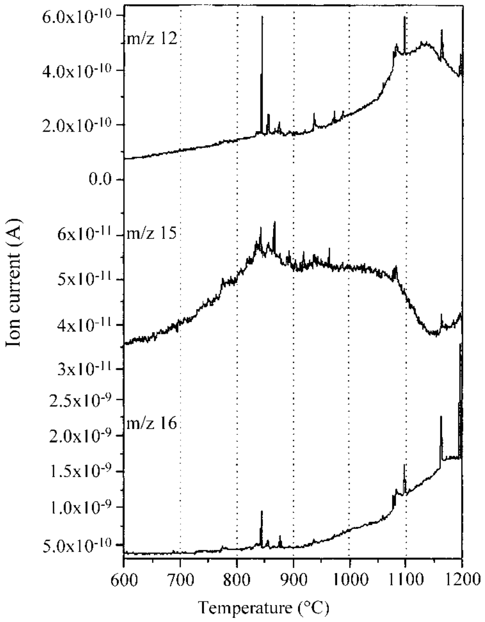

Fig. 3. MS-degassing curves of individual masses as Na^+ ($m/z = 23$), $^{35}Cl^+$ ($m/z = 35$), $H^{35}Cl^+$ ($m/z = 36$) of the (a) blue-green, (b) olive and (c) pink glass samples as a function of temperature by a mass spectrometer.

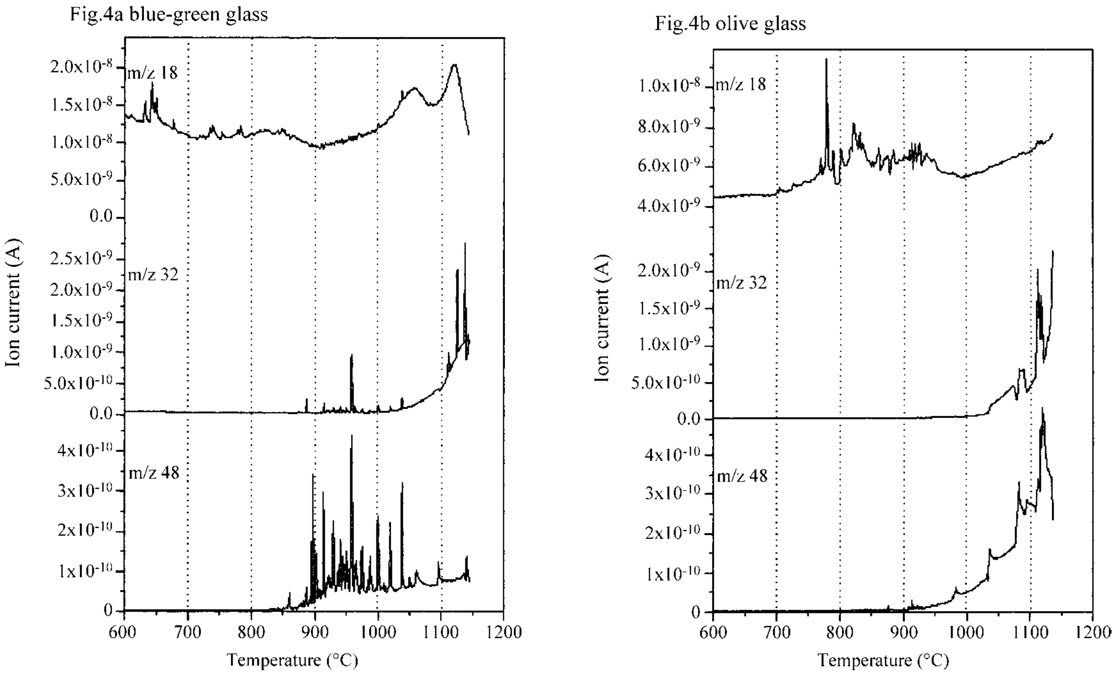
Fig.4a blue-green glass

Fig.4b olive glass

Fig.4c pink glass

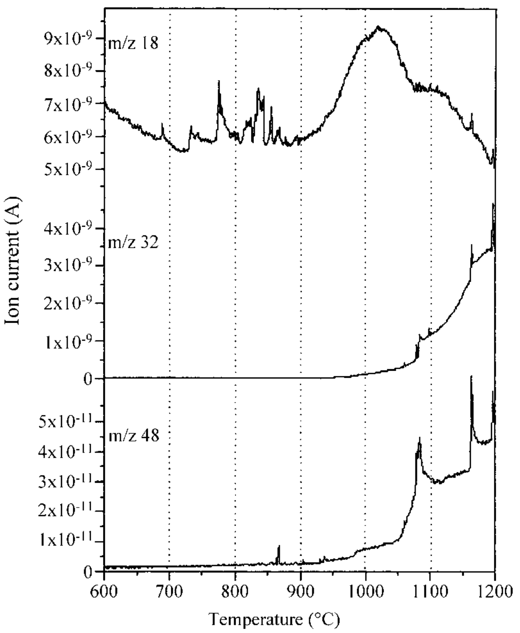

Fig. 4. MS-degassing curves of individual masses as $C^+ (m/z = 12)$, $CH_4^+ (m/z = 16)$ and the methane fragment, $CH_3^+ (m/z = 15)$ of the (a) blue-green, (b) olive and (c) pink glass samples as a function of temperature by a mass spectrometer.

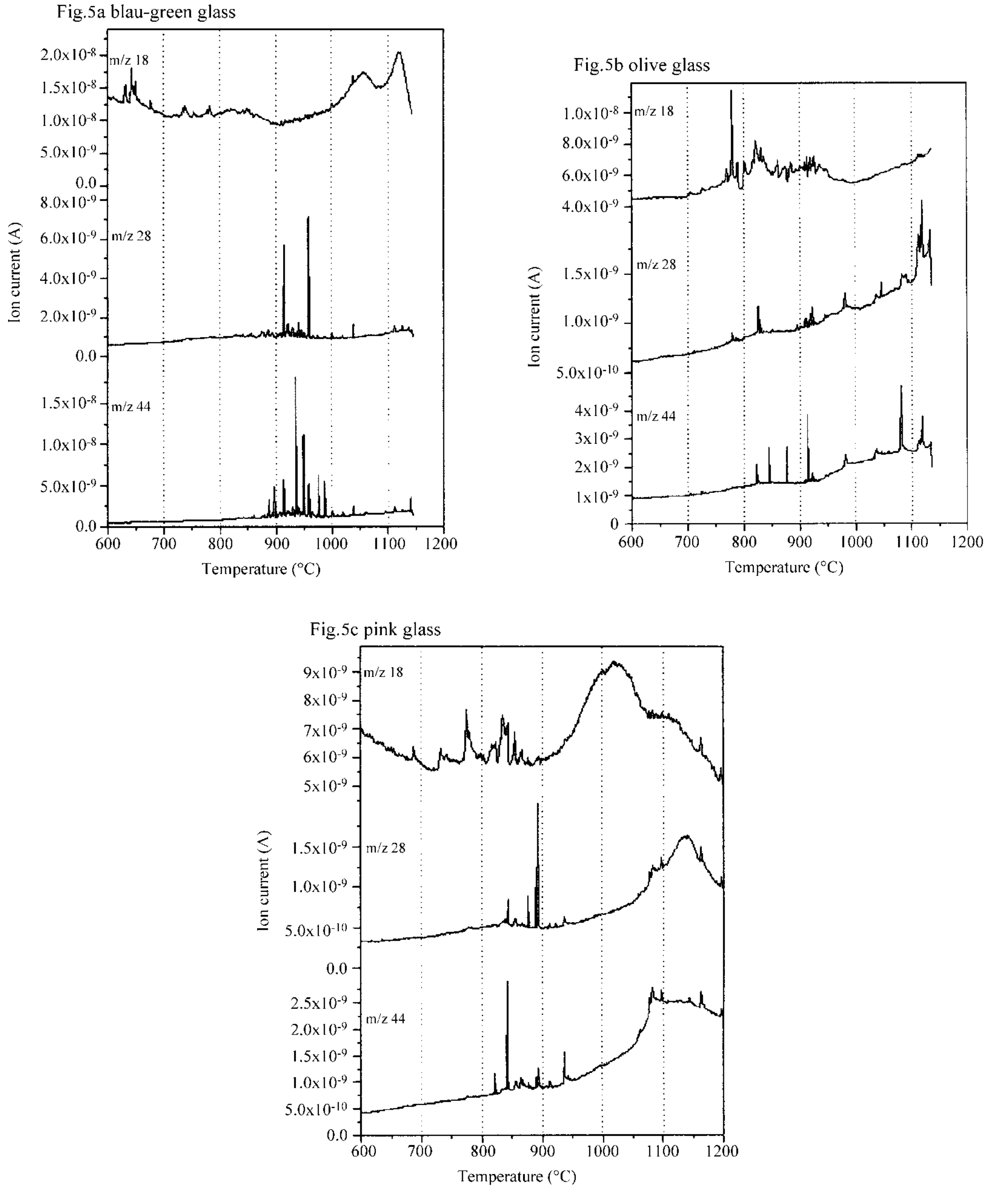

Fig. 5. MS-degassing curves of individual masses as SO_2 fragment $SO^+(m/z = 48)$ and S^+ or $O_2{}^+(m/z = 32)$ of the (a) blue-green, (b) olive and (c) pink glass samples as a function of temperature by a mass spectrometer.

4. Discussion and conclusions

As was shown by [7] from the degassing behaviour of soda-lime–silica glasses, conclusions can be drawn about the "fining conditions" and the raw materials from the gas released above 700°C. The volatile traces from the raw materials like carbonates, hydrates, hydroxides, escaped in a temperature range between

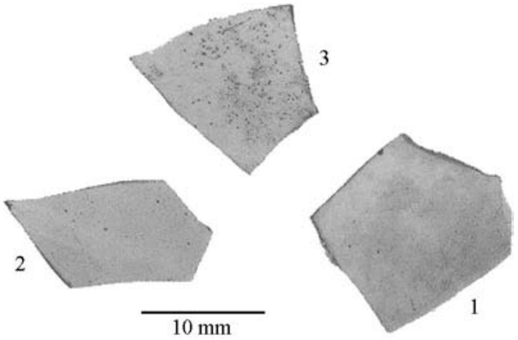

Fig. 6. Egyptian glass samples: (1) blue-green, (2) olive, (3) pink.

750 and 950°C. From the fining additives, a formation of volatiles occurs by chemical reactions above 1000°C.

The formation of bubbles and the bursting is possible in a viscosity range above the glass transition into the melt. Spikes in the degassing profile mark the formation of the glass forming melt.

In the case of the ancient Egyptian glasses we can conclude that carbonates are used as raw material (Fig. 6). The content of chlorine in the glasses is different (green>pink>olive). This is in a good agreement with the microprobe analysis (Table 1). In case of the pink glasses obviously a mixture of carbonates and hydrates was used as raw material.

The melting temperatures for the three glasses are not so different in the range between 600 and 700°C. The olive and pink glasses are generally in a good fining state, but there is no potential for reboiling processes during handling the glasses under the fire. It could be a hint that the glasses are produced in the same glasshouse. The redox state is in the blue-green glass. The formation of pink and olive glasses occurs under more oxidized conditions (more CO_2 than hydrocarbons).

The differences between the medieval wood ash and wood ash lime glasses are evident. Recent melting experiments producing common medieval glass composition of central Europe shows a relation between the degassing especially the formation of bubbles, and the melting conditions. In case of the synthetic melts the bursting of bubbles started above 1200°C. In this case the melting temperature was 1400°C for 13.25 h [8,9]. The bubble formation range in the medieval wood ash- and wood ash–lime-glasses was determined above 900°C. From this a melting temperature could be deduced above 1100°C. In case of the three Egyptian glasses from the bubbling range, a slightly lower melting temperature results (1000–1050°C). It may be that the lower melting temperature resulted from an addition of higher quantities of melting accelerators such as NaCl.

Table 1 presents data of the different glass types on the basis of very small specimens by a microprobe

Table 1
Chemical composition of different Egyptian glasses

Method of investigation	Blue-green		Olive		Pink	
	Microprobe	EDS[a]	Microprobe	EDS	Microprobe	EDS
SiO_2	83.50	67	74.09	65	76.66	67
TiO_2	0.28	n.d.[b]	0.58	n.d.	0.21	n.d.
Al_2O_3	3.62	3	4.35	2	3.18	2
FeO	2.09	1	6.50	2	1.63	1
MnO_2	n.d.	2	1.50	1.5	1.70	2
MgO	0.61	0.6	1.36	0.9	1.01	0.4
CaO	2.33	10	7.23	10	11.35	10
Na_2O	2.15	14	2.24	18	0.48	16
K_2O	1.98	11	0.74	0.7	0.82	0.5
Cl	1.80	0.5	1.16	0.9	1.34	1
P_2O_5	0.60	n.d.	n.d.	n.d.	1.00	n.d.
SO_2	0.51	0.7	0.57	0.6	0.77	1
Σ	99.47	100.8	100.32	101.6	100.15	100.9

[a] Semiquantitative EDX [1].

[b] Not defined.

analysis and EDS measurements. The alteration of the glass surfaces by weathering results in a poor reproducibility and changes the concentration of pathfinder elements. By means of DEGAS a separation between the alteration and the juvenile sample properties is possible. Detailed and systematic investigations are necessary to test the new possibility in the field of archaeometry.

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Appendix A. San el-Hagar (Tanis)

Situated in the northeastern part of the Nile delta, ancient *Dja'net* (Greek Tanis, modern San el-Hagar) (Fig. 7) was the residence and the burial place of the kings of the 21st and 22nd Dynasties. In the late period it became the capital of the 19th Lower Egyptian Nome. In the present state of our archaeological knowledge of the delta it is easily the most impressive ancient site there, and one of the largest. The problems which one encounters when trying to interpret the monuments of Tanis in order to trace its history epitomize the difficulties connected with all the delta sites. The most prominent excavators at San el-Hagar have been A. Mariette in the second half of the last century, W.M. Flinders Petrie (1883–1886) and P. Montet (1929–1951).

The salient feature of San el-Hagar is a large brick-built rectangular enclosure measuring about 430 m by

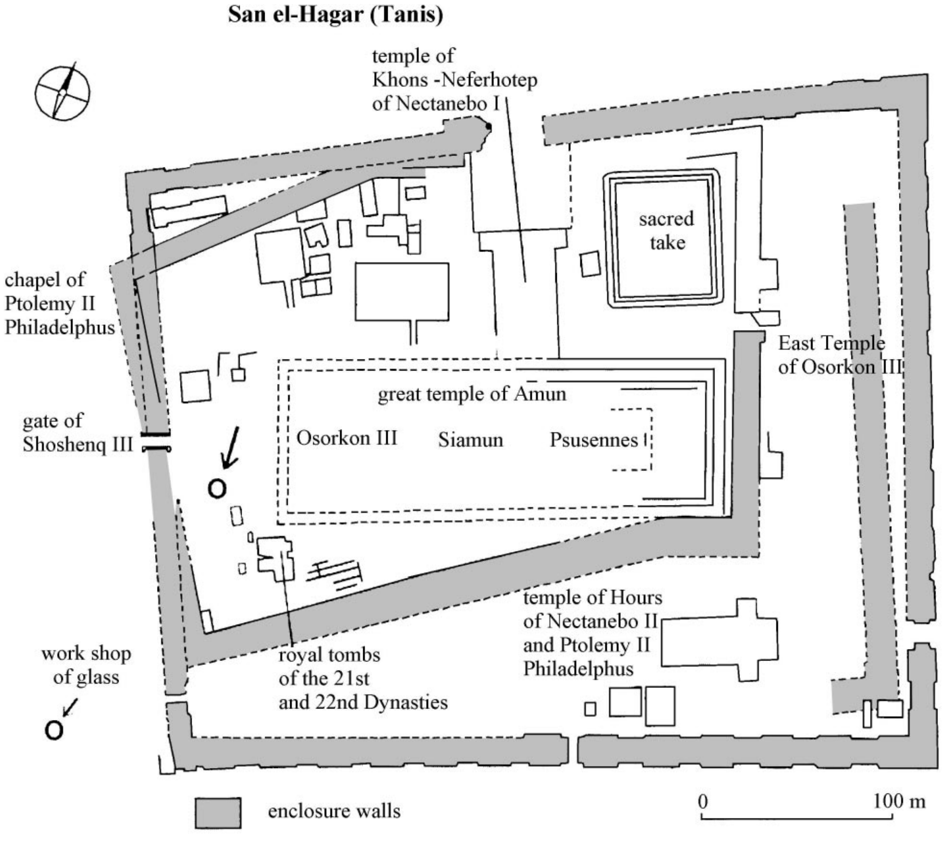

Fig. 7. A plan showing where the samples were found in the San-el-Hagar temple [10].

370 m. The enclosure walls were, amazingly, some 15 m thick and probably about 10 m high. Inside this precinct there is another inner enclosure with stamped bricks dating it to Psusennes I, which contains the great temple of Amun. Nowadays, the temple is a mass of inscribed and decorated blocks, columns, obelisks and statues of various dates, some of them even bearing the names of rulers of the Old and Middle Kingdoms (Khufu. Kephren, Teti, Pepy I and II Senwosret I).

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