COLORANTS USED IN ANCIENT EGYPTIAN GLASSMAKING: SPECIALIZED STUDIES USING PIXE SPECTROMETRY

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Proton-induced X-ray emission (PIXE) spectrometry has several practical advantages over other analytical techniques currently used in the study of ancient glass. It is nondestructive, it can conveniently determine a glassmaking recipe (i.e. the primary constituents used) within a single X-ray spectrum, it has superior detection limits for the minor and trace elements that are most influential in glass coloration, and, when run in a microbeam mode (with an analysis area as small as 10^{-2} \text{ mm}^2), it can provide valuable spatial resolution in the study of individual regions of decoration on multicolored vessels and jewelry. This paper discusses the current operation of the Bartol PIXE facility, with emphasis on the use of customized selective filters which allow high-sensitive measurements for trace elements in glass matrices complicated by the presence of high levels of copper, iron and lead. PIXE data recently obtained for artifacts and manufacturing debris from the New Kingdom workshop site at El-Amarna provides a practical application of these concepts.

1. Egyptian glassmaking and El-Amarna

The origins of man-made glass are uncertain. Glass beads, which were probably the accidental result of overfiring silicate composites, appear in very limited numbers in Mesopotamian and Egyptian archaeological contexts as early as the mid-3rd millennium B.C. But much-larger-scale production, including the fabrication of vessels, is only attested textually and archeologically from the early 2nd millennium B.C. onwards, probably beginning first in Upper Mesopotamia and spreading from there to Palestine and Egypt [1]. The innovation of controlled glassmaking may have been an outgrowth of prior advances in silicate technology, including the overglazing of steatite and a crushed quartz body, called faience [2]. The earliest examples of glazed faience and stone are colored blue–green by cupric ions. Additional impetus may have come, however, from the extensive experimentation in the smelting of metal ores (which yielded glassy slags) in the Near East in the early 2nd millennium B.C. [3].

Both faience and glass are made from essentially the same ingredients, only in different proportions – silica, an alkali flux (such as sodium carbonate or a potassium-rich plant ash) and a metal colorant. Because of its higher silica and lower alkali content, faience had to be fired to higher temperatures than glass, approximately 800–1000 °C versus 600–700 °C. If a faience or stone glaze were separately applied, rather than effloresced from a silica body, it might well have had a composition before firing very similar to a glass batch mixture.

A significant development in glassmaking was the forming of vessels by applying softened glass around friable cores of a clay/dung mixture [4]. The innovations in silicate technology introduced by Levantine craftsmen early in the 2nd millennium B.C. suggests that core-forming manufacture of glass vessels most likely originated here and was subsequently transferred to Egypt. The Egyptian silicate industry thereafter underwent a remarkable technological and stylistic transformation during the New Kingdom (circa 1550–1100 B.C.) and flourished at various sites (including Thebes on the middle Nile) where Canaanites from the Levant resided. Intricate glassmaking techniques were employed, using a wide array of frit and glaze colorants which were either imported or processed from native Egyptian ores.

El-Amarna, about 240 km south of Cairo, was built on virgin soil by the pharaoh Akhenaten (who reigned in the mid-14th century B.C.) as his capital city, to replace Thebes (about 240 km further south) as the center of Egyptian political authority. Glassmaking of Amarna represents a highpoint in ancient silicate experimentation, which must have required numerous craftsmen from all over Egypt and from abroad. Though the Amarna glass workshops themselves are no longer extant, scatters of glassmaking debris (e.g., fritting pans and shallow bowls for melting glasses and preparing colorants) indicate that it was located east and south of the great temple to Aten [5]. The various stages of the production process can be reconstructed from a variety of rolled-glass rods, flattened-glass strips, and ingot fragments of single-colored glasses, together with clay
molds. The latter were used to mass-produce a wide range of motifs – Egyptian hieroglyphs, fruits, deities, etc. – which were incorporated into tilework, jewelry and other decorative items.

The tour de force of Amarna glassmaking were the core-formed glass vessels, complete examples being found in the city buildings and fragments in the workshops. Multicolored details were achieved by dragging hot, viscous threads of glass off bulk rods and canes and running them across a vessel’s surface to produce wavy designs. Simple beads of various geometric shapes were made in a similar way, by winding threads of glass onto metal wires which could be easily extracted after cooling.

Novel use of glass colorants is especially characteristic of the glass and faience industry in Egypt at this time. For example craftsmen in Egypt were very proficient in varying the sodium/potassium ratio of the base glass recipe with copper as the colorant, to produce an intense light blue, green or blue-green [2]. Below, we look at the primary and secondary ingredients which formed the basis of the glassmakers’ “palette” at Amarna, at the same time identifying some of the elemental patterns which serve to characterize Amarna glassmaking.

2. Special features of the Bartol PIXE microprobe

PIXE spectrometry, with its excellent sensitivity for the detection of relevant trace elements and its high spatial resolution, provides a convenient means of determining the raw materials used in the variants on glassmaking outlined above. Over the past seven years two of the authors (CPS, SJF) have steadily refined the technique to optimize information retrieval for various archaeological materials (particularly bronze and debris created during the processes associated with its production – see refs. [6,7]). Gains have been made primarily through the development of selective filters which, when included in the PIXE detection system (fig. 1), suppress the “pileup” and “sum peak” contributions from the dominant matrix element [8]. At the same time, however, the Bartol facility has been modified so that it can be operated in either a “minibeam” or a “microbeam” mode, i.e. gather data from an appropriate area on an artifact measuring either circa 50 mm² or circa 0.5 mm².

The general features of the Bartol Institute’s microprobe facility have been described previously in ref. [10]. Many of the beam-controlling and -guiding components are very similar to those used by all PIXE facilities worldwide, and therefore do not require description here. The specifications of the one component which is crucial for achievement of a tightly focused beam in the Bartol facility – the electrostatic quadrupole triplet (Q) – are provided in ref. [9]. Appended to the facility is an IBM-XT microcomputer fitted with the Nucleus Card [11] to manipulate the data prior to full treatment with the PIXAN peak-fitting program developed at AAEC Lucas Heights [12].

Because of the complexity of glass composition, we have organized our PIXE analysis so that the facility is run sequentially in four configurations, as follows.

(a) With a helium gas stream bathing the artifact’s surface, a proton beam of 1.3 MeV energy is used to activate Kα and Kβ X-rays from the elements with 11 ≤ Z ≤ 20 (though weaker peaks in the higher-energy region of the same X-ray spectrum do indicate what other elements are present in the glass in significant quantities). This measurement provides immediate information on the main constituents of ancient glasses – silica, lime, soda, alumina, potash and magnesia.

(b) As (a), except with air and an Al foil filter of 3.8 mg/cm² thickness included in the path of the X-rays entering the detection system, for the analysis of Kα and Kβ X-rays from the elements with 20 ≤ Z ≤ 26 (i.e. Ca, Ti, Cr, Mn and Fe). The Al foil all but eliminates the most intense sum peak we deal with in the analysis of a glass matrix, at 3.48 keV (Si Kα + Si Kβ), and lesser sum peaks at 5.43 keV (Si Kα + Ca Kα) and 7.38 keV (Ca Kα + Ca Kβ).

(c) Now a 2.0 MeV proton beam energy is used, in conjunction with a complex group of filters (3.8 mg/cm² Al foil + 15 mg/cm² muscovite sheet + 7.5 µg/cm² V foil) for the analysis of the elements with Z ≥ 26 (i.e. Fe and heavier). Low levels of lead and bismuth are de-
terminated during this measurement via the Pb L\textsubscript{α} X-rays at 10.55 keV and the Bi L\textsubscript{α} X-rays at 10.84 keV, respectively. This filter configuration is particularly important if iron is a major constituent in a glass mixture, since it eliminates the sum peaks at 12.81 keV (Fe K\textsubscript{α} + Fe K\textsubscript{β}) and 8.14 keV (Fe K\textsubscript{α} + Si K\textsubscript{α}).

(d) As (c), except that the V foil in the filter is replaced by a brass one about 21 mg/cm\textsuperscript{2} thick, for the analysis of the elements with Z ≥ 47 (i.e., Ag and heavier). This last filter configuration is used only if lead is a major constituent in a glass, as would be the case if it was added to lower the melting temperature of the glassmaker's mix [13] or if lead antimonate yellow was used as a colorant. The copper and zinc in the brass foil suppress the three main Pb L X-rays (L\textsubscript{αα}, L\textsubscript{αβ}, L\textsubscript{αγ}, at 10.55 12.61 and 14.76 keV, respectively) while also eliminating the six sum peaks that will arise from combinations of these X-rays (at 21.10 keV for (Pb L\textsubscript{αα} + Pb L\textsubscript{αβ}), and so on). The removal of the sum peak at 25.22 keV (Pb L\textsubscript{ββ} + Pb L\textsubscript{αγ}) is particularly important since it would otherwise obscure the main X-ray peak of tin (K\textsubscript{α} at 25.27 keV).

With such a selective filter array in place, the proton beam's intensity can be greatly increased, with the consequence that the X-ray peaks of minor and trace elements of atomic number greater than the dominant element can be appreciably boosted, and therefore better resolved against the general spectral background. The relative levels of the charge density of the proton beam at the artifact's surface for the different filter configurations are typically set up as (a) : (b) : (c) : (d) = 1 : 5 : 80 : 250.

We have assessed minimum detection limits for the Bartol PIXE facility, based on run times of 5 to 20 min, for the kind of uncolored soda-lime glass used in antiquity as follows:

(1) for an assumed matrix composition of circa 75% SiO\textsubscript{2}, circa 11% Na\textsubscript{2}O, circa 7% CaO, circa 6% other alkali and alkali earths, and circa 1% FeO;

under filter configuration (b):

- TiO\textsubscript{2} ≤ 14 ppm, Cr\textsubscript{2}O\textsubscript{3} ≤ 16 ppm, MnO ≤ 20 ppm;

under filter configuration (c):

- PbO ≤ 7.3 ppm, CoO ≤ 48 ppm, NiO ≤ 8.0 ppm, CuO ≤ 7.5 ppm, ZnO ≤ 8.5 ppm, As\textsubscript{2}O\textsubscript{3} ≤ 5.8 ppm, SrO ≤ 18 ppm, Ag\textsubscript{2}O ≤ 33 ppm, SnO ≤ 98 ppm, Sb\textsubscript{2}O\textsubscript{5} ≤ 122 ppm.

Just how effective filter configuration (d) can be is indicated by the fact that the SnO detection limit only rises at a rate of about 1 ppm per percent of added PbO.

The use of these various filter configurations does not overcome several interference effects that will tend to raise the detection limits of specific elements in certain colored glasses. In a cobalt-rich glass, for example, the low-energy tail of that element's K\textsubscript{β} peak at 7.65 keV will always mask low levels of nickel (K\textsubscript{α}, 7.48 keV). But PIXE detection limits are often two orders of magnitude lower than those attainable by alternative analytical tools in this kind of research [6], something which ensures that the data gathered from archaeologically oriented programs (such as the Egyptian one summarized in the next section) are most detailed and informative.

3. The Amarna glass industry

Throughout the history of glassmaking in the Near East, a soda–lime glass was used, with calcium oxide serving as a stabilizer for the glass matrix. Modifications of the batch mixture were made from time to time, however, and early, experimental stages in glassmaking were no exception. The Amarna glasses, and glazes are characterized by high CaO levels (circa 8.2% on average, see fig. 2), approximately twice that of contemporaneous and later glasses from both Egyptian and the Eastern Mediterranean sites [14–20]. Although this might be partly explained by the prevalence of a certain colorant – calcium antimonate white – in the group, which also served as an opacifier [16], similarly elevated levels of MgO (circa 2.8% on average) points to the intentional addition of stabilizers to the batch mixture [17].

Heavy-metal colorants are especially distinctive of Amarna glasses and faience glazes. Computer clustering of the PIXE data for 13 oxides listed in section 2, along with related data for FeO, reveals a specific composition for each colorant (see the dendrogram in fig. 3). For example, all four yellow glasses studied here (YEL1–YEL4) owe their correlation to lead antimonate, and an outlier to this yellow subgroup (GRE1) owes its green coloration to a mixture of lead antimonate and cupric blue. Two cobalt-blue samples clusters quite close to the yellow subgroup, because they both contain a significant amount of lead antimonate as an additive. Similarly, the glasses in a white subgroup
The remaining glasses included in the dendrogram generally contain copper as an intentional additive, but are differentiated in terms of minor and trace elements. The VIO1 glass, for example, is colored violet by combining cupric blue (CuO, 2.6%) with low levels of MnO and CoO (0.17% and 0.16%, respectively). In one subgroup, the glasses BLU3 and BLU6 (colored by cupric ions) and RED2 (colored by cuprite) are opacified by calcium antimonate, and their tin levels are elevated, suggesting the use of bronze refuse as the source of the copper. In another subgroup, the faience glazes BLU1 and B/G1 (cupric ions) and RED 1 (cuprite) are not opacified by calcium antimonate, and their tin levels are nearly negligible. It might be proposed then that the glass and faience industries had separate workshops at El-Amarna, following different recipe traditions.

After Akhenaten's monotheistic revolution had failed and the worship of Amun had been reinstated at Thebes, the site of El-Amarna was largely abandoned. The glass and faience industry, however, continued to flourish in other parts of Egypt and its colonies abroad. But ongoing PIXE studies of later Egyptian silicate groups (from Tell El-Yahudiyyah and Thebes in Egypt proper, and the turquoise mining center of Serabit El-Khadem under Egyptian auspices in the Sinai) indicate that by the 13th century B.C. the Amarna "palette" had been modified. Distinct differences in batch recipes and colorants are best understood as resulting from local production at each site. For example, calcium-antimonate white is virtually nonexistent in the later groups, whereas a transparent glass/glaze which is depleted in heavy metals and often devitrified to a white color is more common. Probably reflecting the availability of local manganese ore, a black glaze at Serabit El-Khadem is characterized by very high levels of manganese and copper, in association with elevated tin, iron and barium. The PIXE analysis and statistical evaluation of the Egyptian glasses and glazes thus provides an efficient means of tracking the temporal course and geographical dimensions of a major ancient technology.

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References