

Section V. PIXE, microprobes

**COLORANTS IN GLASSES FROM ANCIENT SYRO-PALESTINE:
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 in use in archaeological research. 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 more than a dozen minor and trace elements of primary interest in glass studies; and, when run in a microbeam mode (with an analysis area of as little as 10^{-2} mm²) it can provide valuable spatial resolution in the study of individual regions of the color in multibanded glasses. This paper discusses the current operation of the Bartol PIXE facility, with emphasis on the use of customized selective filters which allow high sensitivity measurements for trace elements in glass matrices complicated by the presence of high levels of iron and lead. PIXE data recently obtained for multicolored pendants and beads from the Syro-Palestinian Bronze Age site of Beth Shan provides a practical application of these concepts.

1. Early glassmaking

The origins of man-made glass are uncertain. Glass beads appear in limited numbers in Mesopotamian archaeological contexts as early as the mid-3rd millennium B.C. Larger scale production, including the fabrication of vessels, is attested textually and archaeologically between 1600 and 1200 B.C., first in Upper Mesopotamia and spreading from there to Palestine and Egypt [1]. It has been suggested that glass was discovered during the early 2nd millennium B.C., when experimentation in the smelting of metal ores yielded glassy slags [2]. Alternatively, the innovation of glass may have been an outgrowth of prior advances in silicate technology, including the glazing of stone (particularly steatite) or of a crushed quartz body (faience), a technique which dates back to the 4th millennium B.C. in Mesopotamia and the Near East.

Both faience and glass are made from the same ingredients, only in different proportions – silica, an alkali flux (e.g., sodium carbonate or a potassium-rich plant ash) and a metal colorant. The earliest examples of glazed faience and stone are colored blue-green by cupric ions. Because of its higher silica/lower alkali composition, faience was fired to higher temperatures than glass – to about 900 °C rather than to about 650 °C. If a faience or stone glaze were separately applied, rather than effloresced from its silica body, it might well have had a composition before firing that was very similar to a glass batch mixture.

A significant development in glassmaking was the forming of vessels by applying softened glass around a core of clay and dung [3]. Such vessels appear about the same time in Mesopotamia and Egypt, and a flourishing

industry was established in Egypt during the late 16th century B.C., particularly at sites where large numbers of Canaanites were living. The innovative contributions of Levantine craftsmen during the early 2nd millennium B.C., as well as much later – a mid-1st century B.C. workshop in Jerusalem provides the earliest evidence for glassblowing [4] – suggests that core-forming of glass vessels originated in the Near East and was transferred from there to Egypt.

Many later developments in glass technology occurred in the Mediterranean basin and the Near East, e.g., lathe-cutting of Hellenistic vessels; the painting, enamelling and gilding of glass developed under Islamic rule; and the production of exceptionally clear Venetian “cristallo” glass with colored filigree decoration [5]. In these areas, soda-lime glass was used throughout the history of glassmaking, calcium serving as a stabilizer for the matrix. But modifications of the batch mixture were made from time to time. For example, before the 6th century B.C., antimony was exclusively used as an opacifier, and manganese was a colorant. Around the mid-6th century B.C., however, there was a decrease in magnesium and potassium in colorless glasses that was accompanied by an increase in antimony [6], with the latter in a reduced oxidation state serving as a decolorant. Between the 1st century B.C. and the 5th century A.D., low magnesia, colorless glasses were decolorized by manganese rather than antimony.

The development of novel colorants is especially characteristic of the Near Eastern silicate industries. The glasses and glazes colored with heavy metals, including lead antimonate yellow, manganic purple, and cobalt blue, that were first employed in Upper Mesopotamia in the mid-2nd millennium B.C. have

distinctive physical structures [7], and their trace element profiles sometimes point to specific ore sources. And Egyptian craftsmen during most periods were proficient in varying the sodium/potassium ratio to produce intense blue, or blue-green colors [8]. The Palestinian industries benefitted greatly from these technical advances to their north and their south.

2. Special features of the Bartol PIXE microprobe

PIXE spectrometry, by virtue of excellent sensitivity for the detection of relevant trace elements and its high spatial resolution, provides a very convenient means of characterizing all the variants on glassmaking outlined above. Over the past six years two of the authors (C.P.S. and S.J.F.) 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. [9,10]). Gains have been made primarily through the development of selective filters which, when included in the PIXE detection system, suppress the “pileup” and “sum peak” contributions from the dominant matrix element [11]. At the same time, however, the Bartol facility has been modified so that it can be operated in either a “minibeam” mode or a “microbeam” mode, i.e., gather data from an appropriate area on an artifact measuring either $\sim 50 \text{ mm}^2$ or $\sim 0.5 \text{ mm}^2$ [12]. The latter mode is well-suited to the study of glass vessels constructed from, or decorated with, thin bands of different color [13].

The general features of the Bartol microprobe facility have been described in ref. [10] and are illustrated here in fig.1. Many of its 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 the achievement of a tightly-focused beam in the Bartol facility – the electrostatic quadrupole triplet (Q) – are provided in ref. [12]. The most

recent addition to the facility is an IBM-XT microcomputer fitted with the Nucleus Card, to manipulate the data prior to full treatment with the PIXAN peak-fitting program developed at AAEC, Lucas Heights [14].

Because of the diversity of glass composition, we have organized our PIXE analysis so that the facility is run 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 K_α and K_β X-rays from the elements with $11 \leq Z \leq 20$ (though weaker peaks in the higher energy region of the same X-ray spectrum do indicate what other elements may be present in the glass in significant quantities). This measurement provides immediate information on the main constituents of ancient glasses – silica, lime, soda, alumina, and potash.

b) As a), except that an Al foil filter of thickness 3.8 mg/cm^2 is included in the path of the X-rays entering the detection system, for the analysis of K_α and K_β X-rays from the elements with $20 \leq Z \leq 26$ (i.e., Ca, Ti, Cr, Mn and Fe). The Al foil eliminates the most intense sum peak we have to deal with in the analysis of a glass matrix, at 3.48 keV ($\text{Si } K_\alpha + \text{Si } K_\alpha$), and lesser sum peaks at 5.43 keV ($\text{Si } K_\alpha + \text{Ca } K_\alpha$), and 7.38 keV ($\text{Ca } K_\alpha + \text{Ca } K_\alpha$) (see fig. 2).

c) A 2.0 MeV proton beam energy is used, in conjunction with a complex group of filters (3.8 mg/cm^2 Al foil + 15 mg/cm^2 muscovite sheet + 7.5 mg/cm^2 V foil) for the analysis of the elements with $Z \geq 26$ (i.e., Fe and heavier). Low levels of lead and bismuth are determined during this measurement via the $\text{Pb } L_\alpha$ X-rays at 10.55 keV, and the $\text{Bi } L_\alpha$ 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 ($\text{Fe } K_\alpha + \text{Fe } K_\alpha$), and 8.14 keV ($\text{Fe } K_\alpha + \text{Si } K_\alpha$).

d) As c), except that the V foil filter is replaced by a brass one about 21 mg/cm^2 thick, for the analysis of the elements with $Z \geq 47$ (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

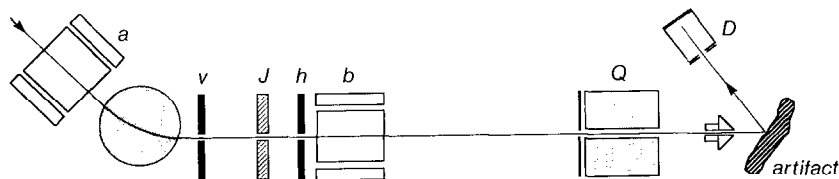


Fig. 1. A schematic of the Bartol PIXE microprobe facility. After partial collimation by the electrostatic X - Y steerer a, the proton beam passes through an analyzing magnet and an energy-selecting control slit (v). At this point, the beam has a rectangular cross-section, about $3 \text{ mm} \times 0.5 \text{ mm}$. An alignment unit intercepts the beam, so that the beam's quality can be assessed from the fluorescence it produces on a quartz window. Aperture h reduces the beam's height to about 0.5 mm before it is positioned by the magnetic X - Y steerer b to pass through the access aperture of the electrostatic quadrupole triplet (Q). This unit pinches down to beam close to a $50 \text{ }\mu\text{m}$ size, before a final collimation by a fine aperture in a kapton-sealed graphite tip. The detector D is a cooled Si(Li) crystal protected by a $7 \text{ }\mu\text{m}$ Be window (see ref. [13] for a detailed schematic).

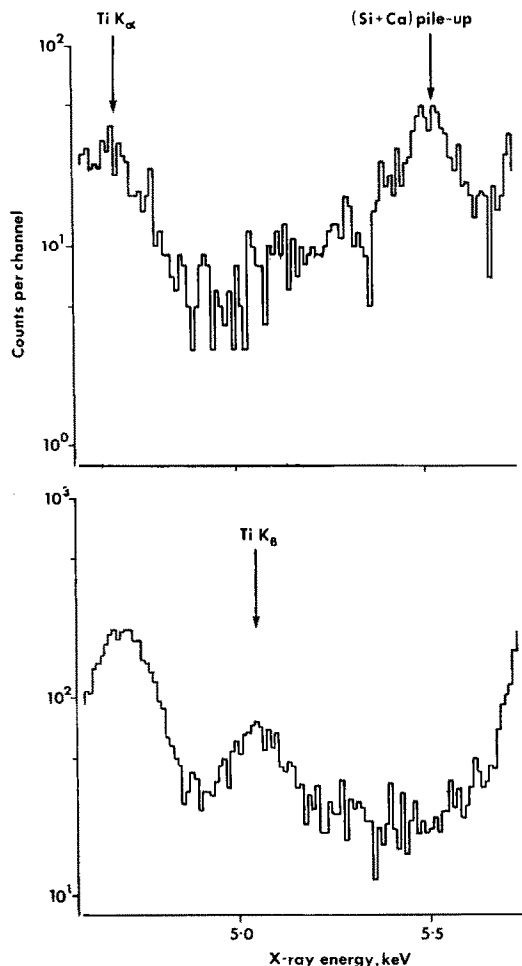


Fig. 2. Top: Part of the X-ray spectrum obtained during the PIXE analysis of a small brown glass cup from the Islamic site of Rayy, with a proton beam energy of 1.3 MeV and helium gas flowing across the gap between the glass's surface and the detector's window (as filter configuration a: see text). Bottom: As above, but with an Al foil filter (thickness, 3.8 mg/cm²) mounted in front of the detector's window (as filter configuration b: see text), and with the proton beam intensity raised about a factor of five. Note how this filter arrangement eliminates the "pileup" and "sum peaks" from the intense X-rays of the silicon and calcium constituents of the glass. The (Si+Ca) sum peak obscures the presence of trace levels of Cr (K_{α} : 5.41 keV).

added to lower the melting temperature of the glass-maker's mix [15], or if lead antimonate yellow was used as a colorant. The copper and zinc in the brass foil suppresses the three main Pb L X-rays (L_{α} , L_{β} , L_{γ} 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 ($PbL_{\alpha} + PbL_{\alpha}$); and so on). The removal of the sum peak at 25.22 keV ($PbL_{\beta} + PbL_{\beta}$) is particularly important

since it would otherwise obscure the main X-ray peak of tin (K_{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 for the kind of uncolored soda-lime glass used in antiquity as follows: (for an assumed matrix composition of SiO₂: ~75%; Na₂O: ~11%; CaO: ~7%; other alkali and alkali earths: ~6%; Fe₂O₃: ~1%)

under filter configuration b:

TiO₂: ≤ 44 ppm; V₂O₅: ≤ 54 ppm;

Cr₂O₃: ≤ 16 ppm; MnO: ≤ 20 ppm;

under configuration c:

PbO: ≤ 7.3 ppm; CoO: ≤ 48 ppm;

NiO: ≤ 8.0 ppm; CuO: ≤ 7.5 ppm;

ZnO: ≤ 8.5 ppm; As₂O₃: ≤ 5.8 ppm;

SrO: ≤ 18 ppm; MoO₂: ≤ 17 ppm;

MnO: ≤ 20 ppm; Ag₂O: ≤ 33 ppm;

SnO: ≤ 98 ppm; Sb₂O₅: ≤ 122 ppm.

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, the low energy tail of that element's K_{β} peak at 7.65 keV will always mask low levels of nickel (K_{α} : 7.48 keV); in a lead-rich glass, the Pb L_{α} peak at 10.55 keV will always obscure arsenic's K_{α} peak (10.54 keV), while the Pb L_{γ} peak at 14.76 keV will always partially overlap strontium's K_{α} peak (14.16 keV). Thus, for example, in a glass with as much as 40% lead oxide, the As₂O₃ detection limit might well be as high as 260 ppm. But PIXE detection limits are often one, if not two orders-of-magnitude lower than those attainable by alternative analytical tools in this kind of research [9], something which ensures that the data gathered from archaeologically-oriented programs (such as the Palestinian one summarized in the next section) are most detailed and informative.

3. Egyptian influences on glassmaking at Beth Shan

Egypt reinitiated significant contact with the Levant around 1750 B.C., with the rise of Semitic "Hyksos"



Fig. 3. *Left:* Glass flask (UM inv #29.105.784) from below the steps of Locus 1068 at Beth Shan. (The marker bar indicates 1 cm.) PIXE data for a white strip (arrowed) on the white and grey toroid decoration at the neck of the vessel:

Na₂O: ≤ 0.50%; MgO: 0.78%; Al₂O₃: 2.01%; SiO₂: 89.1%; SO₃: 2.86%;
 K₂O: 1.37%; CaO: 2.44%; TiO₂: 0.059%; Cr₂O₃: 0.024%; MnO: 0.014%;
 Fe₂O₃: 0.44%; CoO: ≤ 0.0064%; NiO: 0.0023%; CuO: 0.049%; ZnO: 0.017%;
 As₂O₃: 0.012%; SrO: 0.0094%; Ag₂O: ≤ 0.0047%; SnO: 0.061%; Sb₂O₃: 0.43%;
 PbO: 0.010%.

Right: Glass heart pendant (UM inv. #29.105.744) from Locus 1086 at Beth Shan. (The marker bar indicates 1 cm.) PIXE data for the white band (arrowed) at the upper rim:

Na₂O: ≤ 0.48%; MgO: 0.009%; Al₂O₃: 1.50%; SiO₂: 92.2%; SO₃: 0.056%;
 K₂O: 1.09%; CaO: 1.98%; TiO₂: 0.069%; Cr₂O₃: ≤ 0.0033%; MnO: 0.004%;
 Fe₂O₃: 0.29%; CoO: ≤ 0.0064%; NiO: ≤ 0.0018%; CuO: 0.11%; ZnO: 0.008%;
 As₂O₃: ≤ 0.0054%; SrO: 0.0040%; Ag₂O: 0.0054%; SnO: ≤ 0.013%; Sb₂O₃: 2.47%;
 PbO: 0.062%.

dynasties in the Nile Delta, and Palestine thereafter gradually assumed a subservient role to Egypt, as a forward defensive position and client state [16]. During the 13th century B.C., under the powerful rulers, Sety I and Ramesses II, Egyptian policy was directed towards creating a true colony, with a large Egyptian bureaucracy and military being brought in to control the local population and economy [17].

Of the many Palestinian communities affected by Egyptian imperialism, Beth Shan at the juncture of the Jezreel and Jordan Valleys underwent the most profound changes [18]. The site was transformed into an Egyptian military base by dismantling and leveling the area, and constructing a typical cluster of Egyptian buildings of the time – a residential sector of courtyard houses laid out along a grid pattern of streets, with a

temple, a “fortress” and “commandant’s house”. The proportion of Egyptian artifacts (about a quarter of the total assemblage) is the highest ever recorded at a Palestinian site.

Egyptian traditions are very evident in the Beth Shan silicate industry. Faience lotus chalices, which were common in a large hoard of silicate artifacts buried in the vicinity of the stairway leading to the altar room of the temple, were used to present food offerings to Egyptian animal deities. The masses of beads and pendants of both Egyptian and Canaanite types from near the stairway were probably strung together to form pectorals or collars that adorned temple personnel or a cult statue [19].

It is likely that a local variant of the industry existed at Beth Shan prior to Egyptian occupation. The glasses

and pre-prepared glassmaking ingredients (frits) were physically similar to standard Syro-Palestinian materials, although less common at Beth Shan than at other sites in the region. After the site was converted into an military garrison, however, faience of standard Egyptian type (which was lower fired than Syro-Palestinian faïences) became prevalent.

A more detailed chemical analysis of the silicate glazes and glasses using the Bartol PIXE facility revealed other significant details about their composition and place of manufacture. The minor elements associated with the colorants of the Egyptian-style and Palestinian beads and pendants were different from those of the vessels, all of the latter being exclusively Egyptian in style. The minor elements that were more prevalent in the vessel colorants – specifically, lead and/or tin associated with lead antimonate yellow/brown, calcium antimonate white, cupric blue-green, and manganic brown; and copper associated with cobalt blue – are also characteristic of vessel glazes and glasses definitely made in 13th century B.C. Egypt [8].

A white coloration that results from the depletion of all heavy metals occurs only on the vessels; the same colorant is documented in Egypt. However, the white colorant, calcium antimonate, is used in varying amounts for both vessels and small objects (e.g. the flask and the pendant shown in fig. 3). These differences, and several others which separate the trace element profiles of some of the colorants of the small objects from those of the vessels, substantiate the local manufacture of the former. But some Egyptian craftsmen must also have been present, to account for the very close stylistic and technological characteristics of the Egyptian-style beads and pendants to those of New Kingdom Egypt. That the craft of glassmaking was active at Beth Shan is clear from the pieces of misshapen and overfired glass and faïence found there, along with a cake of Egyptian Blue frit colorant, and a mold for a fluted bead or inlay. But the faïence and core-formed glass vessels, since they demanded far more technical expertise in their manufacture, were most likely made in Egypt at industrial installations such as that at el-Amarna [20], and exported to Beth Shan.

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