ELEMENTAL ANALYSES OF NORTH AMERICAN GLASS TRADE BEADS

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Although European-made glass trade beads can be sorted into bead varieties and studied in that manner on the basis of physical attributes, much more information can be obtained about them by means of chemical analysis. Such analyses produce chemical fingerprints that may be compared and grouped. Bead varieties that have matching chemistries were made using the same ingredients that probably came from the same sources, suggesting that they were made in a specific manufacturing center and probably during the same approximate time period. Using this information may help to establish with which European nationals specific indigenous people were dealing and may perhaps even link archaeologically recovered beads to the European beadmaking houses from whence they came.

INTRODUCTION

The analysis of glass beads recovered from archaeological sites in northeastern North America began with typological classifications, based on the observed manufacturing technique, color, diaphaneity, shape, and decoration. The current definitive bead classification system for beads from this region was devised by Kenneth and Martha Kidd (1970), and was subsequently expanded by Karklins (1985).

Some polychrome glass bead varieties were manufactured and traded for only short periods of time, enabling researchers to developed variety-based chronologies for beads from archaeological sites that were in existence during the European contact period (e.g., Fitzgerald 1982; Hayes 1983; Kenyon 1984; Kenyon and Fitzgerald 1986; Kenyon and Kenyon 1983; Pratt 1961; Stark 1995). For beads that look different, even subtly, this approach works well, but for monochromatic beads, we may sort them by color, shape, and size, but this does not reveal their place of manufacture. Elemental analysis of these beads allows us to sort out what is different and what is similar in their glass chemistries, something which may eventually lead to a determination of which countries manufactured which beads.

A problem with elemental analysis is that the bead may be damaged during the process. Analytical techniques such as laser ablation ICP-MS (e.g., Gratuze et al. 1993) or neutron activation analysis (e.g., Gratuze et al. 1995; Hancock 2003) are therefore probably relatively appropriate, since they do little physical damage.

If we choose to use instrumental neutron activation analysis, we take whole beads for analysis. As long as we only analyze them for elements that produce short-lived radioisotopes that decay relatively quickly, the beads may be returned safely to their owners.

To describe glasses that were used to make beads, the important elements to be sought include the glass-forming elements such as calcium (Ca), aluminum (Al), manganese (Mn), magnesium (Mg), sodium (Na), potassium (K), iron (Fe), phosphorus (P), lead (Pb), and silicon (Si) together with the elements that produce coloring, including tin (Sn), antimony (Sb), arsenic (As), copper (Cu), cobalt (Co), nickel (Ni), gold (Au), and vanadium (V).

The elemental concentrations of >5-10 elements form a chemical fingerprint for each bead analyzed. Comparison of the fingerprints allows us to sort the beads into groups and/or follow specific bead compositions through time. Fortunately for archaeometrists, beads traded or given to the Native Peoples living in early eastern North America were generally interred with their owners, so that they generally tended to be buried within about forty or so years after their manufacture.

NEUTRON ACTIVATION ANALYSIS

The principles of neutron activation analysis (NAA) are published in full elsewhere (e.g., Kruger 1971; Neff 2000; Pollard and Heron 1996). Very briefly, the sample to be analyzed is inserted into a source of neutrons. While there, neutrons bombard the atoms in the sample. Since atoms primarily consist of empty space, most of the neutrons pass through the sample but some do hit the nuclei of atoms in the sample. Many of these bounce off. A tiny fraction of the nucleus-hitting neutrons coalesce with the nuclei of elements in the sample and form artificial radioisotopes of each element that was activated. As they are formed, the artificial radioisotopes begin to decay by emitting gamma-rays of characteristic energies (like radio station frequencies). The sample is subsequently withdrawn from the neutron source. After a suitable waiting time, to allow intense shorter-lived radioisotopes to decay, gamma-ray detectors are used to measure the number of gamma-rays emitted in a specific period of time and these figures are proportional to how much of a particular element was in the sample. Hence, by comparing the measurements we get from samples with those from elemental standards, we can get an elemental analysis of the original sample for a number of elements.

One needs access to a relatively intense neutron source, usually a research nuclear reactor, and a gamma ray spectrometer (sometimes a beta counter or alpha spectrometer). Along with the McMaster University reactor in Hamilton, Ontario, Canada is also blessed with having low-flux SLOWPOKE reactors at the University of Alberta in Edmonton, at the Saskatchewan Research Council in Saskatoon, at the Royal Military College of Canada in Kingston, at l'Ecole Polytechnique in Montreal, and at Dalhousie University in Halifax.

Nuclear reactors produce neutrons with a broad range of energies. There are three types of neutron activation reactions: (n,γ), (n,p), and (n,α). The first is generated by low-energy (<0.1 eV or thermal) neutrons, and the other two are produced mainly by epithermal and fast (>1MeV) neutrons. Although thermal neutron reactions are favored, some activation products may be produced from elements of different atomic number. For example, ^{28}Al is produced preferentially from aluminum by the thermal neutron reaction $^{27}\mathrm{Al}(n,\gamma)^{28}\mathrm{Al}$; from silicon by the epithermal neutron reaction $^{28}\mathrm{Si}(n,p)^{28}\mathrm{Al}$; and from phosphorus by the fast neutron reaction $^{31}\mathrm{P}(n,\alpha)^{28}\mathrm{Al}$. Although these reactions tell us that it is potentially horrible to try and analyze a matrix including Si, P, and Al, we may use the activation product ^{28}Al to analyze for Al in aluminosilicate materials, for Si in silica-rich, or doped, materials, and for P in bones. By using suitable neutron absorbers it is possible, but more time consuming, to distinguish between these cases, as described below.

Prior to a neutron activation analysis, beads of mass 5-10 mg are first cleaned ultrasonically, as required. They are stored individually in 1.2 ml polyethylene vials, and are irradiated serially for about a minute at a neutron flux of 2.0×10^{12} $\mathrm{neutrons.cm^{-2}.sec^{-1}}$. Five to seven minutes after neutron irradiation, the induced radioactivity is counted for five minutes using a hyper-pure germanium detector-based gamma-ray spectrometer. This produces analytical concentration data for Co, Sn, Cu, Na, Al, Mn, Cl, and Ca. The samples are recounted for 5 to 33 minutes the next day to measure the concentrations of the longer-lived radioisotopes of Na, As, Sb, and K. The sodium measurements are used to link both counts. Elemental concentrations are calculated using the comparator method. Beads of larger masses are irradiated at suitably lower neutron fluxes to make enough radioactivity for reasonable chemical analyses.

THE FINDINGS SO FAR

A student research project (Chafe 1986) started the sometimes-funded (but mainly not) glass bead analysis project that began at the SLOWPOKE Reactor Facility at the University of Toronto, moved to The Royal Military College of Canada, in Kingston, Ontario, and then to McMaster University in Hamilton. This initial work was expanded upon and eventually published (Hancock et al. 1994), and a number of general conclusions were drawn. Dark blue, cobalt-colored beads were readily separable from turquoise blue, copper-colored beads. Robin's egg blue beads were colored with cobalt and opacified with tin. In the dark blue beads, arsenic tended to increase with the cobalt, and manganese often occurred at concentrations much higher than in the turquoise blue beads. In the turquoise blue beads, for the Ontario Iroquois (Kenyon and Kenyon 1983), it was possible to distinguish Bead Period I beads from others by their low Ca (≤2%) content and to distinguish Bead Period II beads on the basis of their high sodium (>12.5%) content. Disintegration of low-calcium beads probably occurred by the leaching of alkali metals from the glass. Groups of samples of similar chemistry exhibited elemental concentrations that were precise to about ±10% to ±20% relative.

After the initial research, it was decided to tackle the analysis of monochromatic beads, progressing from blue to white to redwood (brick red), and finally to black and yellow.

Seventeenth- to twentieth-century turquoise blue glass beads from sites in Ontario showed that different element concentration ratios could be used to sort the chronologies of turquoise blue beads over these centuries (Kenyon et al. 1995). A scatter plot of K/Na versus Cl/Na was the primary sorting tool. Traces of cobalt appeared in some of the Late French Regime beads (1660-1760), perhaps offsetting the lower copper levels in these beads, thus enhancing the blue color of the beads. Also, measurable amounts of tin were found in two early beads, and there were many cases of measurable quantities of both antimony and arsenic in later beads.

The Ontario-found turquoise blue bead chronological findings were applied to data from turquoise blue glass beads found at three sites in the Lac-saint-Jean region of Quebec (Hancock et al. 1996): Ashuapmuchuan, Chicoutimi, and Metabetchuan. Happily, the chemistry-based chronologies of the Quebec-found beads corresponded well with archaeological expectations. Again, cobalt at about the 200 ppm level appeared in early turquoise-colored beads, sometimes along with high levels of tin. Some of the later beads contained measurable levels of arsenic and measurable to high levels of antimony. It was gratifying to see that beads that physically looked alike matched in their chemistries.

At the Ashuapmuchuan site, a concentration of turquoise blue beads was found along with beads of other colors (Moreau et al. 1997). There was a fist-sized clump of beads and a dispersed association of beads. These two physical groupings produced only two distinct chemistries. It was proposed that the beads represented a bead-decorated bag filled with beads. Also, since the beads showed low concentrations of cobalt, it was thought that the time period of the beads should be in the Late French Regime (1660-1760), or perhaps the Early British Regime (1760-1840).

A study was made of cobalt-blue (royal blue or bright navy) beads from a glass beadmaking house in Amsterdam (ca. 1601-1610), and from the Neutral Grimsby (ca. 1625-1636) and Huron Ossonane (ca. 1636) sites in southern Ontario (Hancock et al. 2000). The Amsterdam beads produced two chemical groupings neither of which matched any of the data from the Ontario beads. This makes sense since the two Ontario sites were theoretically in the French trading sphere. Even though the Ontarioan sites are ca. 190 km apart, two separate groups of oval beads from Grimsby and Ossossane shared chemistries. A plot of arsenic versus cobalt inferred that the source of the cobalt was probably a cobalt arsenide ore that might have come from the Hartz Mountains of Germany.

White glass beads from the early-17th-century Auger site in southern Ontario produced four gross chemical groups that were based primarily on variations on the concentrations of potassium, sodium, tin, aluminum, and manganese (Hancock et al. 1999). The finding of early tin-opacified, turquoise-colored beads, followed temporally by antimony, and then arsenic, was confirmed using white glass beads from a number of sites in Ontario (Hancock et al. 1997). Tin opacification was used in the early 17th century; antimony starting in the late 17th century and extending into the 19th century; arsenic from the late 18th century onwards; fluorine in the late 19th century; and with none of the above, also during the late 19th century (Hancock et al. 1997).

The beads used by the Seneca of western New York state changed from tin-white to antimony-white in the second quarter of the 17th century (Sempowski et al. 2000). Beads very high in tin (>10%) were followed during the ca. 1625-1675 period by beads with ca. 3.4-4.2% tin. The primary reason for such low tin levels was that these beads had uncolored cores. Such cored white beads were only found in Ontario at the Orchid site (ca. 1625-1650) that is located near Fort Erie, Ontario, to the west of the Seneca lands (Hancock et al. 1997). Antimony-rich beads also came in uncored (ca. 3.0-4.5% Sb) and cored (ca. 1.0-1.6% Sb) varieties. Both kinds of beads generated multiple bead chemistries.

As previously mentioned, the purportedly decorated bag from the late-17th-century Ashaupmuchuan site in Quebec showed eight different antimony-white bead chemistries (Moreau et al. 2002).

Sempowski et al. (2001) studied the chemistries of opaque red (redwood) glass trade beads recovered from sites in Petunia in southern Ontario (ca. 1630-1650), in the Seneca territory in western New York (ca. 1610-1687), and from the Algonquian site of Ashaupmushuan in Quebec (ca. 1625-1700), as well as from a glass beadmaking house in Amsterdam (ca. 1601-1610). The data split into four gross chemistries, with the first two chemistries containing most of the pre-1655 beads and the last two chemistries containing mainly the post-1655 beads. The first three chemical groups contained measurable amounts of tin, with Group 3 beads containing both tin and antimony. This perhaps mirrors the transition from tin to antimony in white glass beads. Group 4 beads contained neither tin nor antimony and, as such, potentially reflect a technological change in the making of redwood beads. Chemical matches were found among beads from the four different geographic locations revealing the following connections: Amsterdam-Seneca, Amsterdam-Petunia, Amsterdam-Seneca-Petunia, Petunia-Seneca, and Algonquian-Seneca.

Two hundred and ninety glass beads and wasters from an Amsterdam beadmaking house (ca. 1601-1610) were characterized by their chemistries (Karklins et al. 2002). There was a diversity of colors: turquoise blue, royal blue, red, black, white, colorless, and gold. Apart from the gold-colored glasses (*see* below), all of the rest were soda-lime-silica glasses. Each color of glass produced multiple chemistries, illustrating clearly the diversity of material produced in one place over a relatively short period of time.

The 135 red glass beads in the collection all contained copper and tin and could be sorted into seven gross chemistries depending on whether the beads were cored, flashed, uncored, or multicolored. The 52 black/grey beads produced three different glass chemistries. The primary colorant was manganese in high concentrations. Eleven yellow beads split into three different coarse chemical groups. The notable features of these latter data are the very low levels of Na and K, and the low levels of Ca and Cl. These features imply that the yellow-colored beads were lead-silica glasses.

A beadmaking house in Middelburg, The Netherlands, was reputed to have operated during the last decade of the 16th century and into the early 17th century. Karklins et al. (2001) analysed an assortment of glass beads and rods of various colors. The glass beads and rods, which were chosen for their visual diversity, echoed that diversity in their chemistries. Apart from a single gold-colored glass rod of lead-silica glass, all of the other glasses were soda-lime-silica. Where opacification was expected, tin was used in all cases but two: a white bead (antimony) and a sky blue bead (cobalt/antimony). The presence of these two beads supports a closing date for the glass beadmaking house in the 1620s, after which time white glass beads that were opacified with antimony began appearing on Seneca sites in western New York (Sempowski et al. 2000).

CONCLUSION

The vast majority of the European glass trade beads analysed to date were drawn beads made from soda-lime-silica glass formulations, with fewer than several dozen wound beads of potash-lime-silica or lead-silica glass. It has been established that the colors of beads tend to translate into the inclusion of specific colorants and opacifiers into the glasses. Indeed, glass bead chemistries may be used as fingerprints for tracking glass beads. In a few cases, and with much effort, we can in fact trace glass bead chemistries from their place of manufacture in Europe to archaeological sites in North America. In many more cases, we can see how beads of similar chemistry were eventually dispersed in northeastern North America.

An expanded version of this article, with data for those who would like to see the evidence, is in preparation for inclusion in a book on the analysis of archaeological glasses (Hancock n.d.).

Before all of the analytical data alluded to above disappear, it would be beneficial to establish a user-friendly glass bead analysis data base that could be accessed by interested people. It would also undoubtedly be of value in the future to expand upon the numbers of analyzed beads from glass beadmaking houses in at least western Europe for the periods that are of interest to archaeologists. Unfortunately, these sorts of ventures are costly in expertise, time, and money. Nevertheless, since there are still groups of researchers analyzing glass trade beads from around the world, there is hope that some day these tasks may be completed. It would then be possible to present a more complete story of the manufacture and distribution of both drawn and wound European-made glass trade beads in North America and elsewhere.

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