CHEMICAL PROFILE OF GLASS TRADE BEADS FROM ARCHEOLOGICAL SITES IN TEXAS AND OKLAHOMA

CLAIRE C. DAVISON AND R. K. HARRIS

ABSTRACT

The results of x-ray fluorescence analysis of 18th and 19th century glass trade beads are presented. A chemical profile that appears characteristic of the beads is discussed.

Fifty-two glass trade beads from 18th and early 19th century archeological sites in Texas and Oklahoma have been analyzed by x-ray fluorescence (Table 1). The sites are, in chronological order, Womack, Gilbert, Vinson, Spanish Fort (Ayers Farm), and Devil's Canyon; probable dates for the sites are shown in Table 2. Although the degree of certainty varies, all are identified as Wichita Indian sites.

X-ray fluorescence, or any other method of chemical analysis, sheds light on the chemical ingredients of the artifact analyzed. A knowledge of the chemical ingredients can, in turn, serve as a basis for formulating other hypotheses; for example, hypotheses of artifact groupings (Davison, Giauque and Clark, 1971:651), trade routes, points of origin, artifact dating or site dating. For glass trade beads such studies aim particularly towards the ultimate ability to specify and date the manufacturing origins of the beads, to recognize all beads of the same origin — this may not be apparent visually — and to depict the factors that brought them to the archaeological sites. Such studies are in their infancy, and it was in the spirit of furthering them that we undertook the present pilot study of beads from Wichita sites.

The present study found that certain chemical features which are significant from the glassmaking point of view are characteristic of these beads throughout the time period represented. These four features are consistent with the dating of the beads. They constitute the chemical profile of the beads and are as follows:

1. **Antimony is in use.** Antimony (Sb) is a glassmaker's additive, used as an opacifying agent and also as a decolorizer. The study of glass history indicates that this element came into regular use by glassmakers in about the 17th to 18th century A.D. (Turner and Rooksby 1962; Neri 1662:82; Kunckel 1756:86). It had been used in antiquity, but apparently not in the medieval period (Turner and Rooksby, 1962; Sayre, 1963:263). Before the 17th to 18th centuries, tin seems to have been the conventional opacifying agent. However, after

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X-RAY FLUORESCENCE ANALYSIS OF GLASS TRADE BEADS FROM TEXAS AND OKLAHOMA[1]

Mn	Pb	Co	Bi	Sb	Sn	Site; Bead description; Type (Harris bead chart)[1]
2.3	0.02	nd	nd	0.14	nd⟨0.007	Gil.Ra3,1; black cane reheated; Type 96
2.9	0.12	nd	nd	0.23	nd⟨0.05	Vin.Li1,1; black cane reheated; Type 50
3.0	0.10	nd	nd	0.06	nd⟨0.02	SPF; black cane reheated; Type 96
3.6	0.19	nd	nd	0.14	nd⟨0.02	SPF; black cane reheated; Type 50
3.2	1.02	nd	nd	0.25	nd⟨0.02	SPF; black tubular cane, unreheated; Type 66
4.0	0.02	nd	nd	nd⟨0.04	nd⟨0.04	Dev.; black hexagonal multifaceted; Type 170
1.6	0.004	nd	nd	nd⟨0.02	nd⟨0.02	Dev.; clear purple hexagonal multifaceted; Type 156
na	very high	na	na	0.04	0.01	Dev.; clear green hexagonal multifaceted; Type 171
na	very high	na	na	0.14	0.14	SPF; clear green cane reheated; Type 83
na	very high	na	na	0.12	nd⟨0.07	Gil.Ra3,5; clear green cane reheated; Type 83
na	very high	na	na	na	na	Vin.Li1,1; clear green cane reheated; Type 83
na	very high	na	na	nd⟨0.05	nd⟨0.05	Vin.Li1,1; clear yellow cane reheated; Type 82
na	very high	na	na	0.3	nd⟨0.1	Vin.Li1,1; opaque yellow cane reheated; Type 81
na	very high	na	na	nd⟨0.05	nd⟨0.05	SPF; opaque white 4-sided olive, glassy; Type 102
na	very high	na	na	0.11	nd⟨0.06	SPF; opaque white wound olive, glassy; Type 101
0.03	0.02	nd	nd	3.7	⟨0.06	Wom.19A2-1; opaque white olive, porcelain-like; Type 2
0.24	0.01	nd	nd	9.4	nd⟨0.2	Wom.19A2-1; clear colorless over opaque white cane reheated; Type 5
0.23	0.02	nd	nd	7.8	nd⟨0.04	Wom.19A2-1; as above Type 5
0.21	0.02	nd	nd	6.4	nd⟨0.07	Gil.Ra3,1; as above Type 5
0.29	0.02	nd	nd	6.3	nd⟨0.13	Gil.Ra3,2; as above Type 5
0.24	0.03	nd	nd	5.2	nd⟨0.13	Vin.Li1,1; as above Type 45
0.46	0.04	nd	⟨0.02	5.2	nd⟨0.04	Gil.Ra3,1; as above, crackled surface; Type 5
0.05	0.04	nd	nd	7.5	nd⟨0.05	SPF; as above, not crackled, unreheated; Type 5
0.05	0.03	nd	nd	1.03	nd⟨0.05	Vin.Li1,1; clear colorless cane reheated; Type 49
0.21	0.29	nd	nd	0.28	nd⟨0.03	SPF; clear colorless cane reheated; Type 136
0.01	0.004	nd	nd	nd⟨0.02	nd⟨0.02	Dev.; clear colorless hexagonal multifaceted, opalescent; Type 139
0.03	0.17	0.03	0.007	4.1	nd⟨0.04	Gil.Ra3,2; cobalt blue opaque cane, reheated; Type 10
0.08	0.11	0.06	0.03	10.	nd⟨0.2	Wom.19A2-1; cobalt blue opaque cane, reheated; Type 10
0.04	0.06	0.07	0.03	8.2	nd⟨0.06	Wom.19A2-1; cobalt blue opaque cane, reheated; Type 11
0.12	0.05	0.02	nd	4.7	nd⟨0.06	Wom.19A2-1; gray opaque spheroid; Type 15
0.08	0.15	nd	0.02	6.2	nd⟨0.12	Gil.Ra3,2; gray opaque cane reheated; Type 47
0.11	⟨0.06	0.04	⟨0.07	0.05	nd⟨0.004	Wom.19A2-1; clear cobalt blue olive; Type 13

TABLE 1 (Cont'd)

Mn	Pb	Co	Bi	Sb	Sn	Site; Bead description; Type (Harris bead chart)[1]
0.05	0.06	0.04	nd	0.05	nd⟨0.01	Gil.Ra3,2; clear cobalt blue cane reheated; Type 77
0.14	0.01	0.03	0.02	0.10	nd⟨0.007	Gil.Ra3,5; clear cobalt blue cane reheated; Type 48
0.10	0.04	0.04	0.04	0.04	nd⟨0.008	Gil.Ra3,1; clear cobalt blue cane reheated tubular; Type 61
0.04	0.01	0.05	0.06	0.06	nd⟨0.02	Vin.Li1,1; clear cobalt blue cane reheated; Type 48
0.24	0.23	0.04	0.06	0.46	nd⟨0.008	SPF; clear cobalt blue cane reheated tubular; Type 48
0.10	0.03	0.03	0.04	0.03	nd⟨0.007	Gil.Ra3,1; translucent cobalt blue cane tubular, unreheated; Type 61
nd	nd	0.05	0.03	nd⟨0.009	nd⟨0.009	SPF; clear cobalt blue hexagonal multifaceted, no core; Type 130
0.03	0.005	0.03	nd	nd⟨0.01	nd⟨0.01	Dev.; as above Type 130
0.02	0.006	0.02	nd	nd⟨0.02	nd⟨0.02	Dev.; as above, with core; Type 132
0.68	0.05	nd	nd	0.15	0.05	Gil.Ra3,1; opaque red over green cane tubular, unreheated; Type 57
0.36	1.04	nd	nd	0.55	nd⟨0.08	Vin.Li1,1; opaque red over green cane, barely reheated; Type 51
tr.	0.02	nd	nd	0.02	0.009	Wom.19A2-1; blue-green opaque cane reheated; Type 12
0.14	1.5	nd	nd	2.7	nd⟨0.03	Wom.19A2-1; blue-green translucent cane reheated; Type 14
0.02	0.03	nd	nd	0.02	nd⟨0.008	Gil.Ra3,1; blue-green cane spheroid; Type 10
0.19	0.28	nd	nd	nd⟨0.03	1.67	Gil.Ra3,1; blue-green cane spheroid; Type 10
nd	0.02	nd	tr.	nd⟨0.01	nd⟨0.03	Gil.Ra3,2; blue-green cane spheroid; Type 46
0.02	0.02	nd	nd	0.11	nd⟨0.04	Gil.Ra3,2; clear blue-green cane unreheated; Type 80
0.02	0.03	nd	0.009	nd⟨0.04	nd⟨0.06	Vin.Li1,1; blue-green translucent cane unreheated; Type 80
0.02	0.05	nd	0.01	0.12	nd⟨0.05	Dev.; blue-green translucent cane barely reheated; Type 80

[1]All data are given in percent. Results are estimated correct to within a factor of two, or perhaps larger where indicated. nd = not detected. The lower limit of detection of Mn, Co, and Bi is about 0.02%, and the lower limits of detection of Sn and Sb are given individually. na = not analyzed. Wom. = Womack; Gil. = Gilbert; Vin. = Vinson; SPF = Spanish Fort, Ayers Farm; Dev. = Devil's Canyon.

[2]Types are described in Harris and Harris (1967).

antimony came into use, the use of tin did not cease. Thus the presence of intentionally added antimony can aid in dating glass beads, although in this case the beads were already dated archeologically and the evidence from antimony merely serves to confirm the dating of the beads.

Antimony (or tin) may be considered intentionally added in glass when its concentration is in the tenth of percent range or higher. Besides being added intentionally, antimony may enter glass through cullet (scrap glass, which is usually included in new batches). Therefore in an antimony-using tradition one might expect to find that glasses which do not seem to contain intentionally added antimony still contain considerably more antimony than tin, and vice versa for tin-using traditions. By observing the ranges of concentration in Table 1, one can see which beads probably contain antimony as an intended additive. Where it may be considered unintended, it is still usually higher than the tin, which was almost never detected (Table 1).

2. **Manganese is used to achieve black.** There are several ways to achieve a black "color" in glass. In these beads the glassmakers apparently used manganese (Mn) in such high concentration that the purple color given by this element is dark enough to appear black. If the black beads are held to a strong light, the purple tint can usually be seen.

3. **Lead glasses occur.** Lead (Pb) glasses are one of the main types of glass, containing tens of percent lead oxide. In the lead glasses analyzed here, the amount of lead was not determined, beyond the fact that it was very high. It is estimated to be some tens of percent in the high-lead beads.

4. **Bismuth is often present in beads colored by cobalt.** Presumably the bismuth (Bi) is associated with the cobalt (Co) mineral, an association which is not unusual mineralogically. However, the presence of bismuth is not generally characteristic of most of the glass beads encountered in the experience of one of us (C.D.) except for the set of beads here discussed.

TABLE 2

SOURCES OF SAMPLES

Site[1]	Probable date[1]
Womack (Texas)	Possibly c. 1719
Gilbert (Texas)	c. 1750-1775
Vinson (Texas)	c. 1775-1800
Spanish Fort, Ayers Farm (Texas)	c. 1759-1820
Devil's Canyon (Oklahoma)	c. 1820-1836

[1]See Harris and Harris (1967).

Other remarks. The beads were also analyzed for iron, nick copper, zinc, arsenic, rubidium, strontium, and, in some cas barium. These elements show no remarkable features comparable the four listed above. The iron is usually in the tenths of percent ran of concentration; nickel was rarely detected; copper, when used as additive, was in the tenths of percent range of concentration, a otherwise usually was present in the hundredths of percent ran zinc was usually present in the hundredths of percent range; arse was often detected in the hundredths of percent range, particularly cobalt blue beads but also in various other colors; rubidium w occasionally detected in the hundredths of percent range of conc tration; and strontium was consistently present in the hundredths percent range. Trace amounts of barium were noted in some, but n all, of the black and purple beads.

Sub-periods within the span of some 130 years represented by th beads are not distinguished on the basis of the present chemical da It may well be possible to distinguish sub-periods with chemi analyses more extensive and precise than these. Sub-periods ha been distinguished on the basis of (a) chronological changes in t frequency of bead styles and (b) documentary evidence, in anotl report (Harris and Harris 1967:156-158).

Of the above four features only two might be detected by the n chemist bead consumer. These are the use of manganese in bla which gives it a purplish tint, and the use of lead glass, which ma the lead glass beads heavier than other beads of the same size. The u of antimony rather than tin and the presence of trace bismuth are n detectable by the senses.

It seems likely that the two undetectable features and perhaps four reflect the practices of the manufacturers (probably Europe

rather than the preferences of the consumers. It is hoped that future investigations may shed light on whether the chemical profile outlined here may be typical of 18th century glass trade bead production generally, or may be diagnostic of a particular manufacturing tradition, and to what extent, if any, it may be influenced by consumer preference.

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