Centre for Archaeology Report

Analyses of Colourless Roman Glass from Binchester, County Durham

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Summary

Forty samples of Roman colourless glass tableware from Binchester, dating from the 1st to mid-3rd centuries AD, were analysed using ICP spectrometry. Parallels were sought amongst data gathered in similar studies of Roman glass from Colchester and Lincoln (Mortimer and Baxter, 1996; Heyworth et al, 1990). Some samples from the Colchester, Lincoln and Binchester groups were re-analysed using an energy dispersive spectrometer attached to a scanning electron microscope (SEM-EDS) and this established that the analytical variables within each set of ICP results differed slightly. The SEM-EDS data was used to compensate for these differences so that the ICP results could be compared.

The compositions of the glass samples from all three sites were broadly similar Higher concentrations of lead were found in certain types of 1st to 2nd century wares from all three sites. In contrast none of the mid-2nd to 3rd century wares contained in excess of 300ppm of lead. Samples from the same types of ware were often found to have more closely comparable compositions and a number of samples, particularly within the wheel-cut vessel and facet-cut vessel groups, were found to have distinctive compositions. The glass from Binchester, Colchester and Lincoln was compositionally distinct from the colourless Roman glass common in the Mediterranean region in the mid- to late-first millennium AD. However there were chemical similarities between some of the samples, with a green tinge, and the dark green HIMT glass seen from the 4th century onwards, the origins of which are unknown.

Keywords

Glass, Roman, analysis.

Introduction

Forty samples of Roman colourless glass tableware from Binchester, Co Durham, dating from the 1st to mid-3rd centuries AD, were analysed using ICP spectrometry by Nick Walsh, of Royal Holloway and Bedford New College, University of London, as described by Thompson and Walsh (1989). The samples were analysed for a suite of thirty major and trace elements (appendix, table 7). Professor Jennifer Price of Durham University and Dr Sally Worrell, of Winchester Museums Service, grouped the assemblage into five glassware types (counting cast vessels such as bowls, trays and plates as one group). The sample details are given in table 1.

Similar studies have been undertaken on colourless Roman glass, dating from the 1st to mid-3rd centuries AD, from Lincoln and Colchester (Mortimer and Baxter, 1996; Heyworth et al, 1990) and the data sets from each of these studies are compared in this report.

Table 1: Date, context and typological information on the Binchester glass samples analysed

ICP No.	Site	Context	SF No.	Date	Form	Cat. No
1	77	A380		late 1st-2nd C	wheel-cut cup	36
2	78	G3	1214	late 1st-2nd C	wheel-cut cup	37
9	77	A958		late 1st-2nd C	?wheel-cut cup	
17	78	A811		late 1st-2nd C	wheel-cut cup	35
22	78	A811	1063	late 1st-2nd C	wheel-cut cup	54
24	76	A1		late 1st-2nd C	wheel-cut cup	44
28	77	A458	884	late 1st-2nd C	wheel-cut cup	38
39	77	A216	719	late 1st-2nd C	wheel-cut cup	53
37	77	A81	410	late 1st-2nd C	wheel-cut cup	40
3	77	A93	486	mid-late 2nd C	facet-cut bowl	174
4	77	A458	885	mid-late 2nd C	facet-cut bowl	181
5	77	A95	470 / 473	mid-late 2nd C	facet-cut bowl	179
20	77	A2033		mid-late 2nd C	facet-cut bowl	177
34	77	A458		mid-late 2nd C	facet-cut bowl	178
7	79.2	A2573		65AD-early 2nd C	facet-cut beaker	
31	77	A407		65AD-early 2nd C	facet-cut beaker	25
38	77	A386	845	65AD-early 2nd C	facet-cut beaker	18
40	77	A411	863	65AD-early 2nd C	facet-cut beaker	28
8	77	A138	540	65AD-early 2nd C	facet-cut beaker	17
6	77	A406		65AD-early 2nd C	facet-cut beaker	21
10	79.2	A1583		65AD-early 2nd C	facet-cut beaker	23
12	77	A468	894	65AD-early 2nd C	facet-cut beaker	16
13	77	A407		65AD-early 2nd C	facet-cut beaker	25/29
14	78	A971A	1244	65AD-early 2nd C	facet-cut beaker	20
15	77	C40-60		65AD-early 2nd C	facet-cut beaker	22
16	78	A984	1332	65AD-early 2nd C	facet-cut beaker	24
21	78	A751	857	65AD-early 2nd C	facet-cut beaker	19
18	76	A43			unknown	
19	77	A2454		late 1st-early 2nd C	cast bowl	7
32	77	US	2817	late 1st-early 2nd C	cast bowl	8
35	79.2	A2454	2337	Late 1st-2nd C	cast bowl	6
33	79.2	A393	860	late 1st-early 2nd C	cast tray/plate	5
36	76	A49		late 1st-2nd C	cast plate/bowl	9
11	77	A524	939	late 1st-early 2nd C	cast saucepan/trulla	10
23	78.9	A1153	1523	3rd quarter 2nd-mid 3rd C	cylindrical cup	63
25	78.9	A876	1534	3rd quarter 2nd-mid 3rd C	cylindrical cup	57
26	76	A15		3rd quarter 2nd-mid 3rd C	cylindrical cup	73
27	77	A314	726	3rd quarter 2nd-mid 3rd C	cylindrical cup	75
29	77	A119	455	3rd quarter 2nd-mid 3rd C	cylindrical cup	66
30	78.9	A876	1528	3rd quarter 2nd-mid 3rd C	cylindrical cup	61

Results

Comparability of ICP data

Combining the Binchester, Lincoln (Mortimer and Baxter, 1996) and Colchester (Heyworth et al, 1990) results has the advantage of creating a large dataset for investigating trends and comparing the same types of ware from all three sites. However general dissimilarities were observed between the ICP data from each of these three studies. The most significant difference between the Lincoln glass samples and both the Colchester and Binchester data sets was the reported low soda (Na_2O) content of the Lincoln glasses (between 13.7 and 16.5wt%) (figure 1). The Binchester samples could also be differentiated as they reportedly contained less potash (K_2O), alumina (Al_2O_3) and iron oxide (Fe_2O_3) than the Colchester and Lincoln samples (figures 1-3). It was necessary to determine whether these differences were a result of analytical variables or if they were true compositional characteristics of the different glass groups.

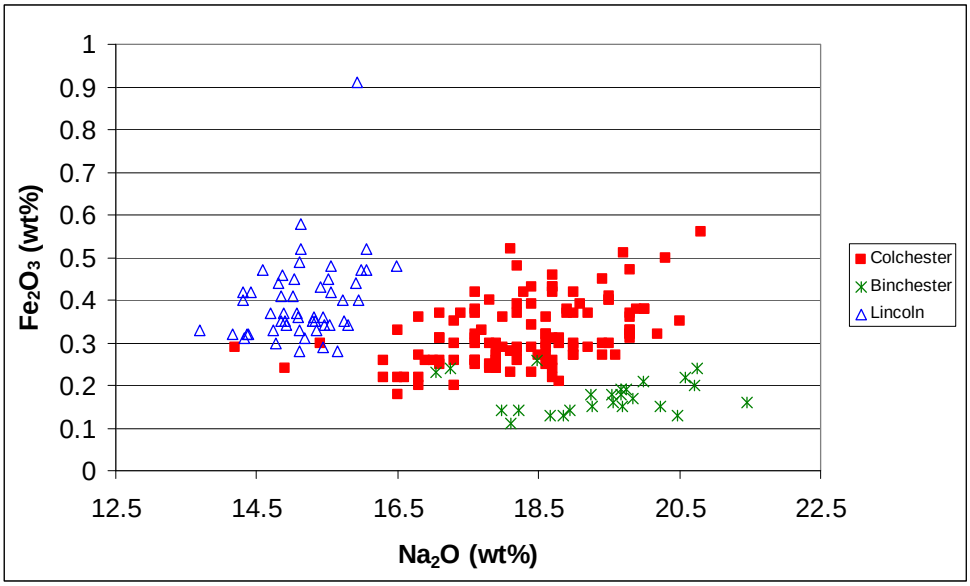

Figure 1: Plot of ICP data for soda and iron oxide for the Colchester, Binchester and Lincoln glass.

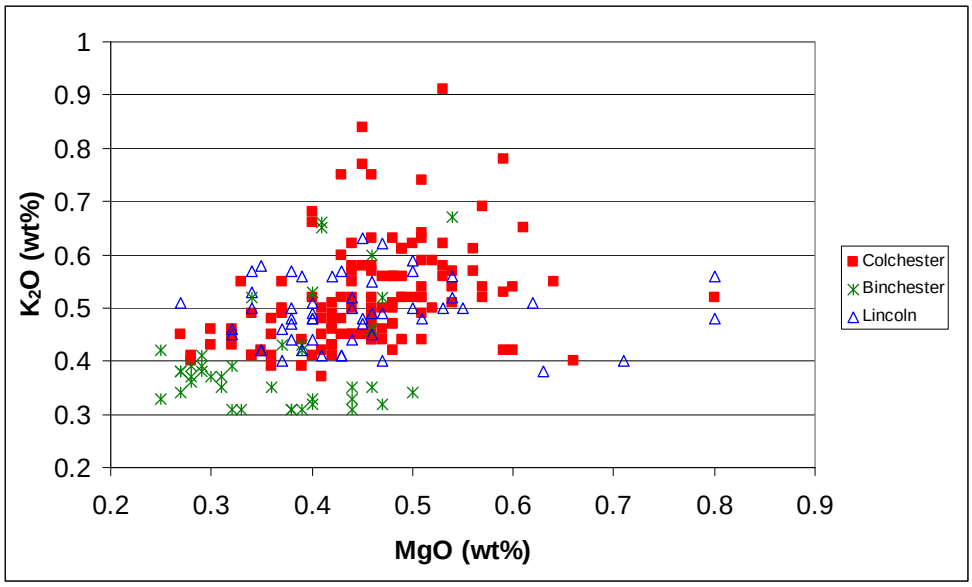

Figure 2: Plot of ICP data for magnesia and potash for the Colchester, Binchester and Lincoln glass

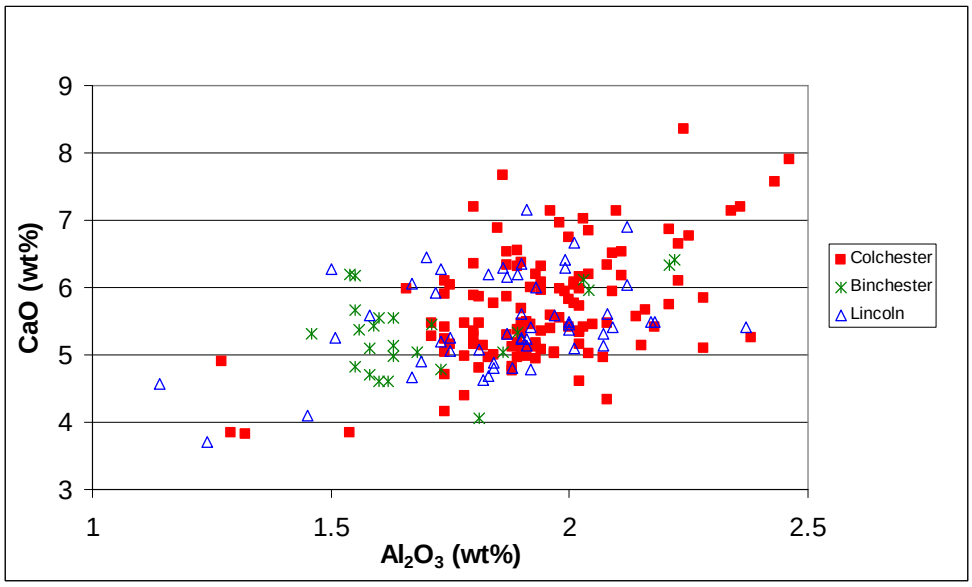

Figure 3: Plot of ICP data for alumina and lime for the Colchester, Binchester and Lincoln glass

SEM-EDS Analysis

Nine of the Binchester samples, 10 of the Lincoln samples and 6 of the Colchester samples, analysed previously using ICP, were obtained for re-analysis with a different technique, SEM-EDS spectrometry. (Additional samples from the Colchester group were sought but could not be obtained in the time available). The conditions used for analysis were an accelerating potential of 25kV, a beam current of 1.5nA and a counting time of 150s. Standard glasses of known composition were also analysed using SEM-EDS and the good agreement of the known and measured compositions is illustrated in the appendix, tables 5 and 6. On the basis of the analytical results for these glass standards, an SEM-EDS analysis would be anticipated to be within 4% relative of the Na_2O content, 14% of the MgO content, 20% of the Al_2O_3 content, 2%

of the SiO_2 content, 5% of the K_2O content and 6% of the CaO content. The detection limits for most elements measured by SEM-EDS was about 0.1% and 0.3% for Sb_2O_5. The SEM-EDS results for the re-analysed Binchester, Colchester and Lincoln samples (appendix, table 4) are compared to the ICP data (appendix, table 7) in figures 4 to 9 for some of the major elements. On each graph the line shows where the position of the data points would be if the SEM-EDS and ICP results were the same. The x-error bars represent the standard deviation for the SEM-EDS results for each sample. The analytical precision and error for ICP is usually quoted as 2-5% (Walsh pers. comm) and the y-error bars show 5% of each ICP result.

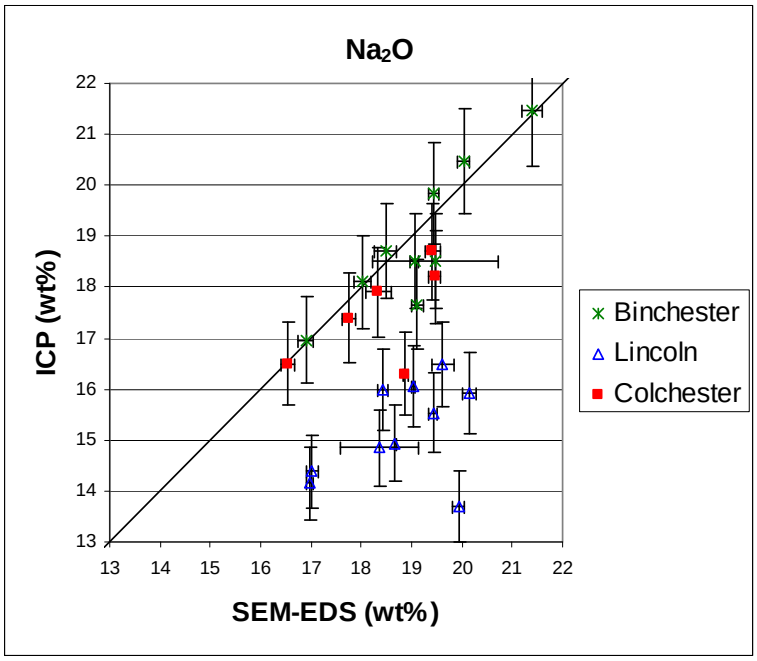

Figure 4: Plot of SEM-EDS data and ICP data for soda

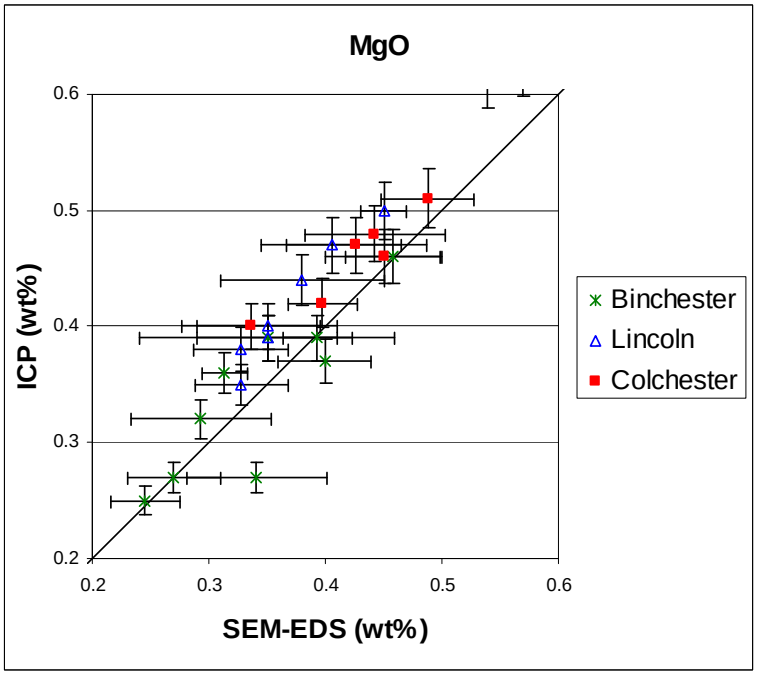

Figure 5: Plot of SEM-EDS data and ICP data for magnesia

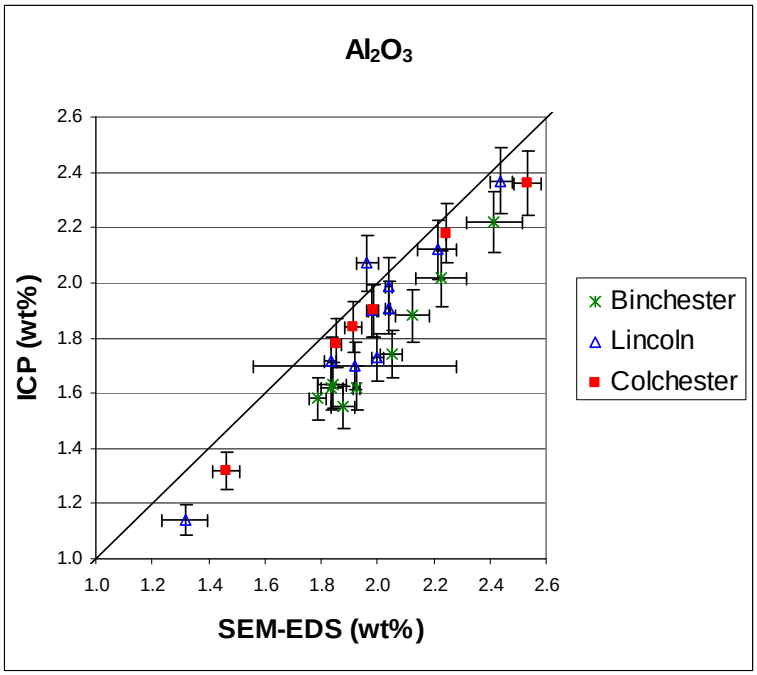

Figure 6: Plot of SEM-EDS data and ICP data for alumina

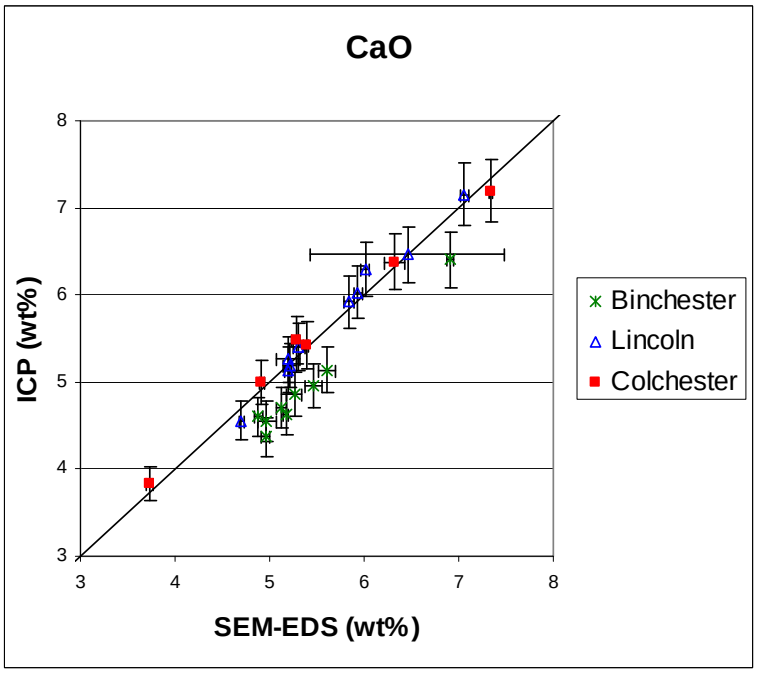

Figure 7: Plot of SEM-EDS data and ICP data for lime

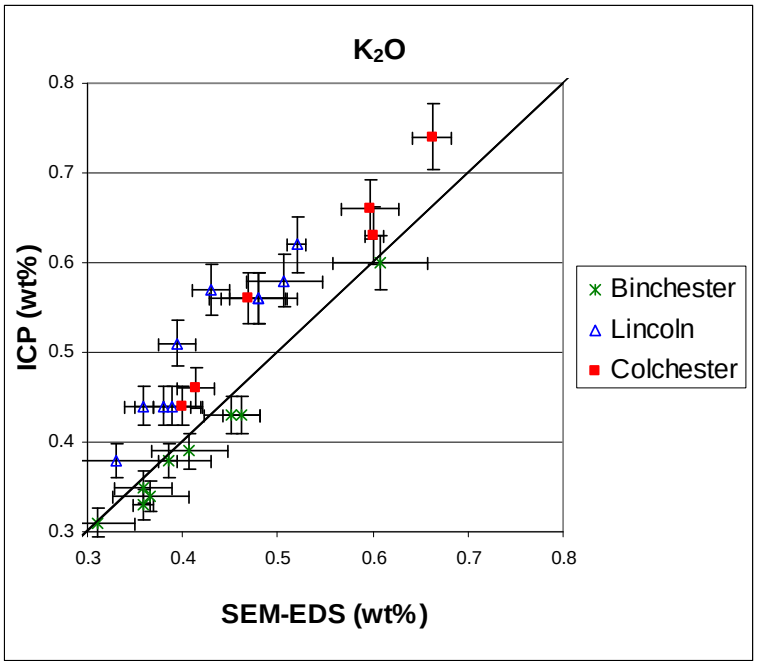

Figure 8: Plot of SEM-EDS data and ICP data for potash

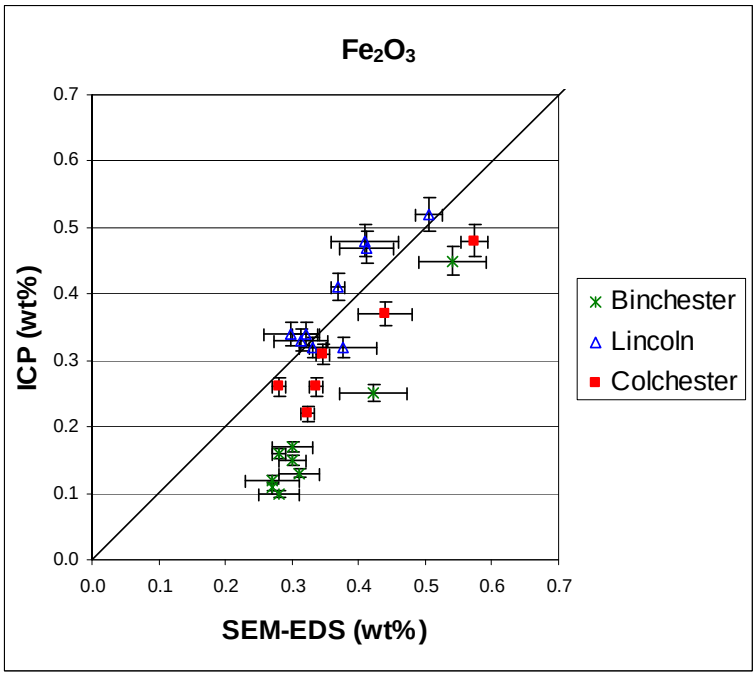

Figure 9: Plot of SEM-EDS data and ICP data for iron oxide

The soda contents of the Lincoln glass samples determined by ICP (Mortimer and Baxter, 1996) were much lower than determined by SEM-EDS whereas the magnesia and potash ICP values were slightly higher than those determined by SEM-EDS. For the Binchester glass, the alumina, lime and iron oxide contents determined by ICP were lower than determined by SEM-EDS. For the Colchester glass, the magnesia and potash values determined by ICP (Heyworth et al, 1990) were higher than measured by SEM-EDS, whereas the iron oxide and alumina ICP values were lower than determined by SEM-EDS.

Adjusting the ICP data

It was assumed that the shift between the ICP and SEM-EDS results for each element was systematic for all of the samples within each study and that linear trendlines through each set of data points on figures 4 to 9 would have a gradient of 1. On the basis of this assumption, adjustment factors that could be applied to the ICP data were calculated for the major elements in each study such that the trendline for the adjusted data would pass approximately through zero. This provided a rapid, although approximate, way of adjusting these large datasets so that they could be compared. However the error in this approach was greater for those elements where the linear trend was less pronounced, where many of the re-analysed samples contained similar amounts of that particular element and where fewer samples were obtained for reanalysis (as with Colchester). The adjustment factors used are listed in the appendix, table 3 and the adjusted Lincoln, Binchester and Colchester datasets are compared in figures 10 to 12. These figures can be contrasted with the unadjusted data in figures 1 to 3.

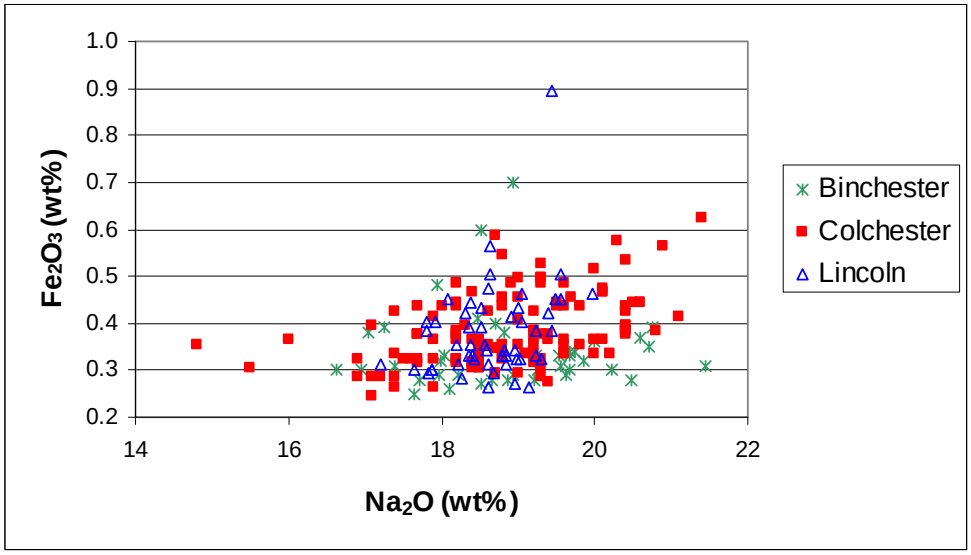

Figure 10: Plot of adjusted soda and iron oxide ICP data for the Colchester, Binchester and Lincoln glass.

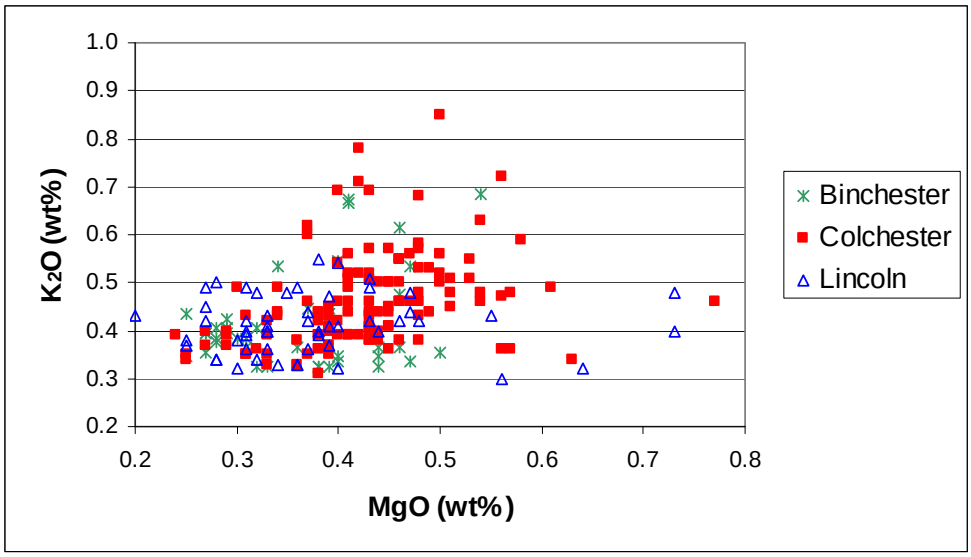

Figure 11: Plot of adjusted magnesia and potash ICP data for the Colchester, Binchester and Lincoln glass.

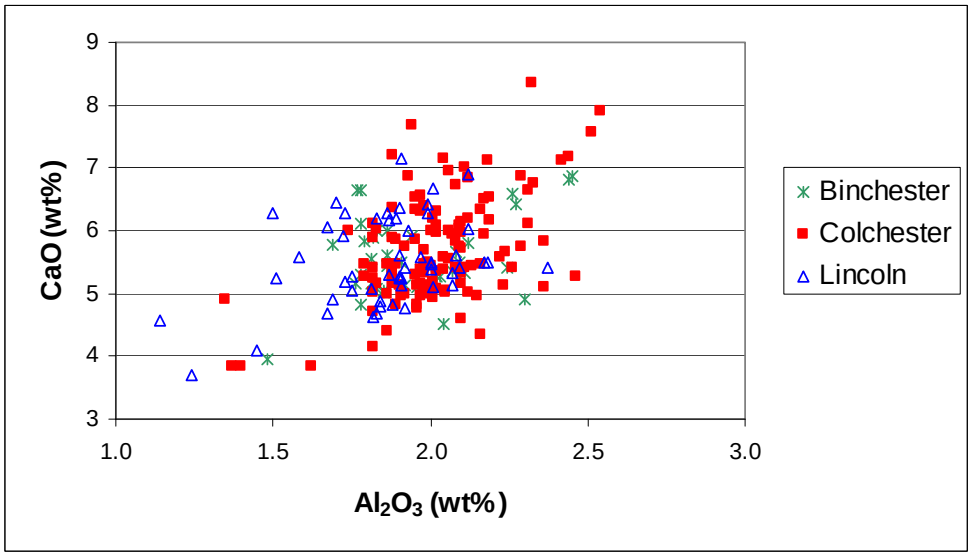

Figure 12: Plot of adjusted alumina and lime ICP data for the Colchester, Binchester and Lincoln glass.

Precision, error and reproducibility of analytical data

The methods used for ICP have been developed largely for the analysis of minerals and pottery. When analysing samples that contain elements in greater concentrations than typically encountered in these materials, large errors can be introduced if this is not taken into account. For example the ICP values for sodium in the Lincoln dataset are incorrect because the analytical programme used was not appropriate for materials containing in excess of 5-6wt% of soda (Walsh, pers. comm.). However the concentration of soda in the Binchester and Colchester samples was accurately quantified because the sample solution was diluted prior to analysis (Heyworth et al, 1990).

Problems can also arise when attempting to quantify elements that are not usually sought. An appropriate standard must be found in order to check for errors and to correct for drift during analysis of each batch of samples. Data for the element antimony and the rare earths may have been affected by this source of error (Heyworth et al, 1990 and Walsh pers. comm).

In techniques such as SEM-EDS, a low or high analytical total often results if errors have been introduced, warning of possible problems. However the analytical totals obtained for Roman glass using ICP analysis are always much less than 100% because silica, which comprises a large proportion of glass, is unfortunately lost in the sample preparation process used for ICP.

For a dataset to be useful in future research, the issue of the comparability of the results with those from other studies must be considered, regardless of the analytical technique used. To this end, glass standards of known composition are often included in programmes of glass analysis and it would be advantageous to adopt this practice for ICP studies, although some adaptation may be necessary to allow for the fact that the standard sample will be destroyed by analysis. As well as enabling errors and drift to be recognised and corrected, the inclusion of standards in each run would also provide an indication of reproducibility if both the known and measured compositions for the standards were published as part of the dataset. This would facilitate comparison of the results with those from other studies.

Interpretation of glass composition data

The glassware from Binchester, Colchester and Lincoln was categorised by type and the samples discussed in this report were taken from the categories listed in table 2. Late 1st to mid-2nd century cast vessels (including bowls and other objects), late 1st to mid-2nd century facet-cut or relief-cut/ground cups/beakers, late 1st to 2nd century wheel-cut vessels and late 2nd to mid-3rd century cylindrical cups were included in each of the three studies. In addition data is available for some late (mid-2nd to 3rd centuries) facet-cut vessels from Lincoln and Binchester and a group of early (late 1st to mid-2nd centuries) facet-cut bowls from Colchester. Facet-cut or relief-cut/ground cups/beakers, wheel-cut vessels and cylindrical cups were all produced by blowing followed by subsequent working of the form, such as grinding away the exterior of the blown blank in the case of facet-cut beakers.

Consistent differences were noted amongst the lead content results for different types of ware from all three sites. Therefore the samples have been categorised as high-lead, HL, (in excess of 300ppm lead) or low-lead, LL, (300ppm or below of lead) in table 2 and in the following discussion. (It should be noted that ‘high-lead’ is used as a relative term in this report and is not meant to indicate that the glass has a high overall lead content, such as in true lead glasses, which have a lead content in the order of 70wt% (Bayley and Doonan, 2000).

Table 2: The categories of glassware analysed in the Binchester, Lincoln and Colchester studies, including number of low lead (LL) and high lead (HL) samples.

Date	Binchester	Lincoln	Colchester
Late 1st to mid-2nd C	Cast vessels-5HL/1LL	Cast vessels-1HL/9LL	Cast vessels-4HL/15LL
Late 1st to mid-2nd C	Facet-cut or relief-cut / ground vessels-8HL/5LL	Facet-cut or relief-cut / ground vessels-7HL/ 3LL	Facet-cut or relief-cut / ground vessels-7HL/9LL
Late 1st to mid-2nd C			Facet-cut bowls-2HL
Late 1st to 2nd C	Wheel-cut vessels-2HL/7LL	Wheel-cut vessels-3HL/8LL	Wheel-cut vessels-15HL/14LL
Late 2nd to mid-3rd C	Cylindrical cups-6LL	Cylindrical cups-15LL	Cylindrical cups-53LL
Mid-2nd to 3rd C	Facet-cut vessels-5LL	Facet-cut vessels-7LL	

Selected major and trace elements for the different groups of ware have been plotted in figures 14 (soda and iron oxide), 15 (potash and magnesia), 16 (lime and alumina), 17 (lime and barium) and 18 (zirconium and vanadium). The results are summarised below and discussed in more detail by ware type in the appendix.

Glass composition

The 1st to 3rd century Roman colourless glass from Binchester, Colchester and Lincoln analysed in this study, referred to as the BCL group from here on, typically contained 4.5-7.5wt% lime, 1.5-2.5wt% alumina, 16.5-21wt% soda, 0.3-0.7wt% potash and 0.25-0.6wt% magnesia. There are few other analyses of colourless glass of similar date to the BCL samples with which to compare. A large set of compositional data has been gathered for colourless glass of the 4th to 8th centuries AD (Freestone et al, 2000 and 2002), including glass from production sites in Israel (Levantine I and Levantine II types) and Egypt (Egypt I and Egypt II types). Not surprisingly, given the spatial and chronological differences between these types of glass and the BCL samples, these types were generally compositionally distinct (figure 13). However the composition of the greenish HIMT (high iron, manganese and titanium) glass group of the 4th century and later, identified by Freestone et al (2002), was in some ways similar to that of the BCL group. For example, figure 13 shows that the lime and alumina contents are in the same range. Although the HIMT glass contained higher levels of iron, manganese, titanium, aluminium and magnesium oxides than typical for the colourless BCL glass, some greenish-tinged samples with increased concentrations of these elements were identified amongst the BCL group. This subset of the BCL glass is discussed in more detail later in this report.

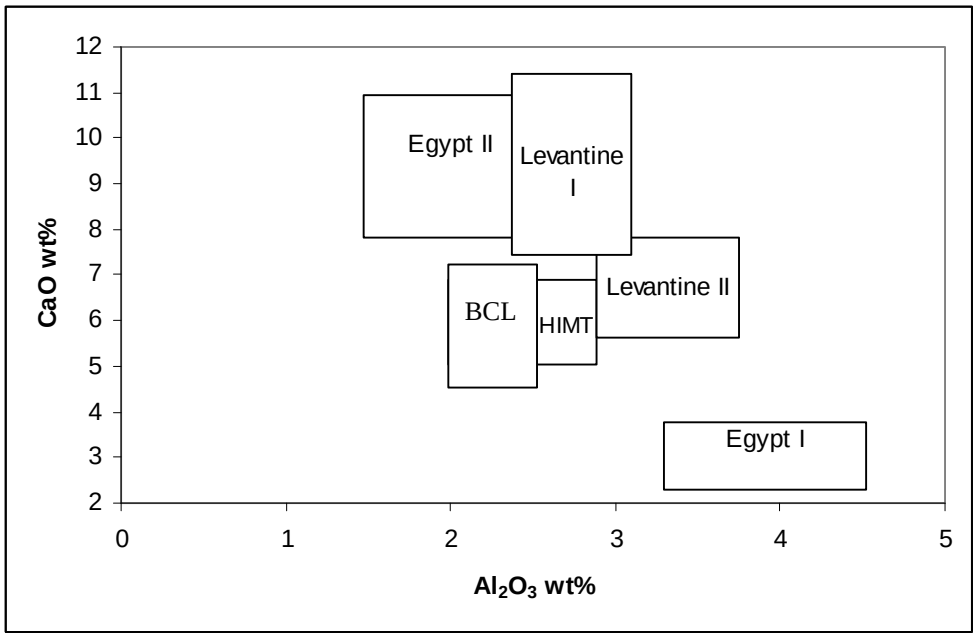

Figure 13: Lime versus alumina for groups of natron glass common in the Mediterranean region in the mid- to late-first millennium AD, identified by Freestone et al, 2002, compared to the adjusted data for the Binchester, Colchester and Lincoln glass samples from this study (BCL group).

Raw materials

The composition of glass is diagnostic of the raw materials used to produce it. The low levels of potash and magnesia in the BCL samples are indicative of a relatively pure mineral source of alkalis, such as natron, being used in their production rather than plant ashes. In addition, Freestone et al (2000, 73 and 2002) demonstrated that differences in the trace element contents of glass groups can be attributed to the geochemistry of the production areas. For example glass produced using Mediterranean coastal sand has characteristically low zirconium levels and high strontium levels, as the fresh shell in beach sands has a higher capacity to incorporate strontium. Glass made from inland sand, containing calcium carbonate derived from limestone, contains lower concentrations of strontium but higher concentrations of zirconium. The high concentrations of strontium (250-500ppm) and low concentrations of zirconium (10-40ppm) in the BCL glass are consistent with the use of beach sand in the production of the glass.

Glass production

No primary glass production sites dating to the 1st to 5th centuries AD have been identified. Most known production sites are in regions of the East Mediterranean, Syria-Palestine and Egypt and belong to a later date (Price, 2002). The furnaces at these sites were extremely large; for example those in Israel produced 8 to 9 tonnes of glass in each firing. The slabs of glass produced were broken up into “chunk glass” and probably transported to many glass workshops where objects were made. Lumps of glass have been found in shipwrecks of Roman date. Most of the BCL group samples were compositionally similar to each other, regardless of the type or date of ware or where it was recovered (Binchester, Lincoln or Colchester). This suggests that colourless glass of the 1st to 3rd centuries may also have been produced in large

batches at reasonably few sites, in a similar way to the model proposed for later glass production.

Lead content of colourless glass

The late 1st to 2nd century groups of ware, such as the cast vessels, facet-cut bowls, wheel-cut and facet-cut or relief-cut / ground vessels, all included some samples containing in excess of 300ppm of lead, referred to in this report as high-lead, HL.). When high-lead and low-lead samples of the same type of ware were compared, the sample compositions were similar in other respects (figures 14 to 18), suggesting that the variable lead contents are not characteristic of different production sites. However all of the cylindrical cups and facet-cut vessels, which are both types of ware assigned to the mid-2nd to the 3rd century, were of the low-lead type, LL, containing less than 300ppm of lead. Therefore the variation in lead content may signify different periods of production, with a transition between high-lead and low-lead types of glass taking place sometime between the late 1st to mid-2nd centuries.

As the concentration of lead in the high-lead BCL colourless glasses does not exceed 0.56wt%, it is unlikely to have had an observable affect on the properties of the glass, and so its addition may have been unintentional. Increased concentrations of lead and copper have been noted in glass that is thought to have been recycled frequently and consequently contaminated with different colourants (Freestone et al, 2002, 268). However, no significant relationship between the lead content and the concentrations of other elements in the BCL glasses could be found. As lead is unlikely to have entered the glass with the sand or alkali, other possibilities are that it was an impurity in an antimony compound added as a decolouriser or that it was present in cullet (Freestone pers. comm).

Roasted stibnite (Sb_2S_3) has been proposed as the source of antimony in calcium antimonate opacified glass (Mass et al, 1998; Rehren et al, 2003) and up to 1wt% antimony (Sb) was detected in the Binchester glasses. If the antimony compound added to colourless glass in the mid-2nd to 3rd centuries came from a different source to that used at an earlier date, a variation in lead content might have resulted.

Cullet used in the production of colourless glass would have been carefully selected to avoid contaminating the glass with colourants. However white glass, which is a colourless glass containing a white calcium antimonate opacifier, would probably have been suitable. Although most Roman white glass contained very little lead, the white glass on cameo vessels, and to a lesser extent mosaic vessels and cameo plaques or discs, commonly contained quite high concentrations of lead oxide (Bimson and Freestone, 1983; Freestone, 1990; Mass et al, 1998). The blue and white variety of cameo glass was rare and was made in the early empire, 25BC to 50/60AD, as was ribbon mosaic glass. Literature data indicates that the ratio of lead to antimony (Pb/Sb) in the lead-rich cameo white glass was about 4 to 1 (Bimson and Freestone, 1983; Freestone, 1990; Mass et al, 1998). However all of the colourless glass analysed in this study contained more antimony than lead, although the ratio varied. Therefore, if lead-rich white glass was the source of the lead in the high-lead BCL glass, it can only have contributed a small proportion of the antimony found in the same samples. The majority of the antimony is more likely to have been derived from the more common standard white glass cullet or by adding an antimony compound directly.

There are no high-lead samples amongst the mid-2nd to 3rd century BCL glassware but the antimony concentration range is similar to that found in the high-lead samples of earlier glassware. Therefore, if white glass cullet was also incorporated into colourless glass of the mid-2nd to 3rd centuries, very little of it contained high concentrations of lead by this time.

Distinct compositional groups

Although most of the BCL glass was compositionally similar, a number of samples with unusual characteristics were identified. Some variability in the composition of glass produced at a single production site would be expected, both within and between batches, due to factors such as the thoroughness of mixing and variability of the furnace temperature and the raw materials. The composition of the glass produced at a site may also have changed slightly over time. Therefore, where compositional changes are slight, it is difficult to determine whether these are a result of variables in glass production at a single site or the use of chemically distinct raw materials at different glass production sites. In this section, potentially distinct groups of samples are discussed.

One group of samples, including both low- and high-lead types, contained higher concentrations of iron (figure 14), manganese, titanium, aluminium (figure 16), phosphorus and magnesium oxides (figure 15). A trend towards increased levels of the trace elements zirconium, vanadium (figure 18), barium (figure 17), yttrium and the rare earth elements, such as cerium, was also noted. This group was particularly well represented amongst the wheel-cut vessels, many of which were described as having a greenish tinge, probably as a result of the increased iron content. The high-lead samples included a wide-rimmed bowl (Colchester 217) and wheel-cut cups (Binchester 39 and 22, Lincoln 13 and Colchester 456, 452, 447, 449 and 427 in particular). The low-lead samples included a rare cast handle fragment (*trulla)* from a bowl (Colchester 210) and more wheel-cut cups (Colchester 435, 460 and 428 and Lincoln 11). Some of the cylindrical cups also contained slightly increased concentrations of zirconium (for example in excess of 40ppm for the unadjusted Colchester dataset). Wheel-cut vessels and cylindrical cups have a more limited distribution, and are thought to be the products of workshops in the northwestern provinces (Baxter et al, 1995).

This group of samples appears to have been produced with variable sand that often contained a larger proportion of minerals or clay minerals giving rise to higher concentrations of certain elements. The increased phosphorus content of the glass may be due to the presence of rare earth phosphates in the sand (Freestone pers. comm). As the concentration of manganese oxide in the samples is correlated with other elements, such as iron, it is likely that the manganese entered the glass as a mineral component of the sand rather than being intentionally added as a decolouriser. The compositional characteristics of this group of samples, often described as greenish in colour, are similar to those of the green HIMT glass of the 4th century and later, identified by Freestone et al (2002) (figure 13). Although these types of glass were produced at different dates, the possibility that they have similar sources warrants further investigation.

Another possibly distinct compositional group, including both low- and high-lead samples, was characterised by lower concentrations of zirconium (figure 18) and barium (figure 17), slightly lower concentrations of alumina and lime (figure 16), and higher concentrations of potash (figure 15). The low-lead samples included base fragments of cast bowls (Colchester 222 and 224) and facet-cut vessels (Colchester 417, either a beaker or bowl, and Lincoln 45). The high-lead samples included two facet-cut bowls (Colchester 209 and 211) and three facet-cut beakers (Binchester 16 and Lincoln 52 and 49). The high-lead samples often contained unusually high concentrations of antimony as well. The furnaces producing this glass may have been located in a different area and used a different source of sand. Facet-cut bowls were much rarer than the plain bowls (Heyworth et al, 1990) and so might be traded further.

Two of the low-lead wheel-cut cups from Colchester (446 and 463) were atypical, containing low concentrations of soda (figure 14) and high concentrations of lime, alumina (figure 16) and phosphorus oxide. However with only two samples it is not possible to determine whether these constitute a distinct group. These samples are similar in composition to the 6th to 7th century compositional group Levantine I identified by Freestone et al (2002) (figure 13).

The mid-2nd to 3rd century facet-cut bowls from Binchester and vessels from Lincoln often contained slightly lower levels of potash (figure 15) and higher lime (figure 16) than the other groups of ware. However the trace element concentrations in these groups were comparable to the majority of the samples in this study and so the slight differences noted are more likely to be related to the later date of these wares, rather than indicating a different production site for the glass.

In figures 14 to 18, “facet-cut bowls” indicates the late 1st to mid-2nd century facet-cut bowls from Lincoln and “late facet-cut vessels” indicates the mid-2nd to 3rd century facet-cut wares from Lincoln and Binchester (see table 2).

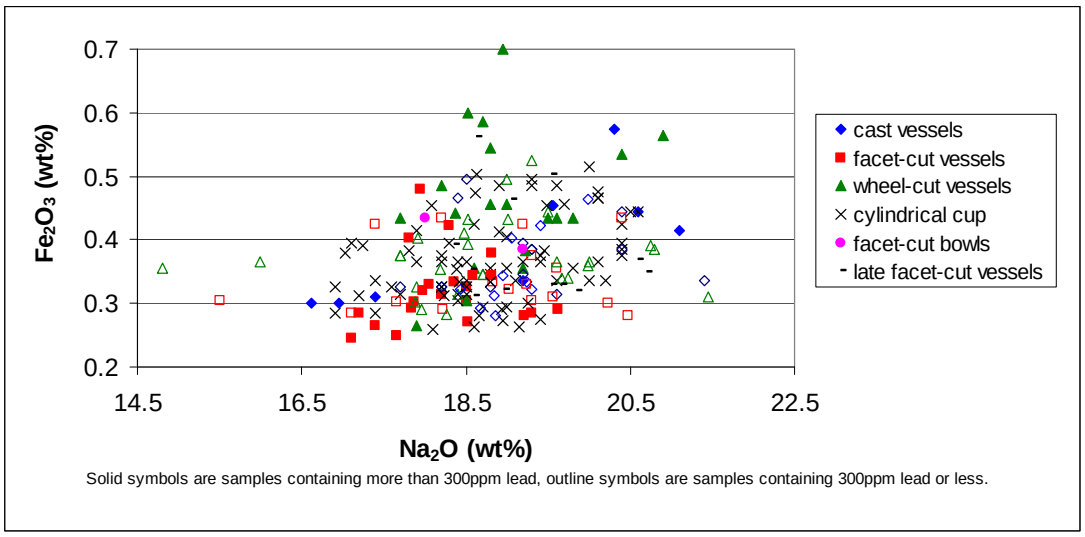

Figure 14: Plot of adjusted iron oxide and adjusted soda for the different types of wares from Binchester, Lincoln and Colchester

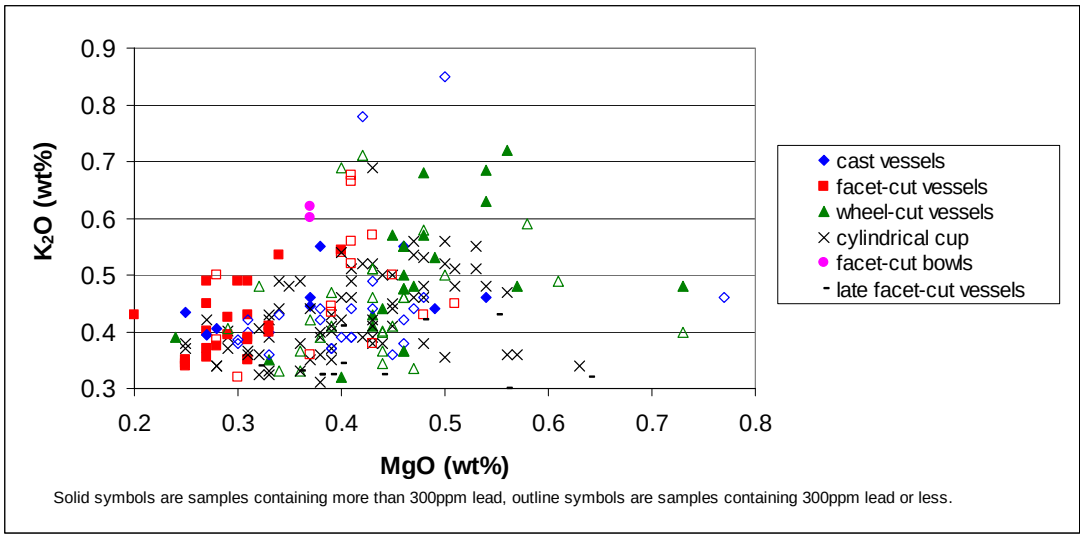

Figure 15: Plot of adjusted potash and adjusted magnesia for the different types of wares from Binchester, Lincoln and Colchester

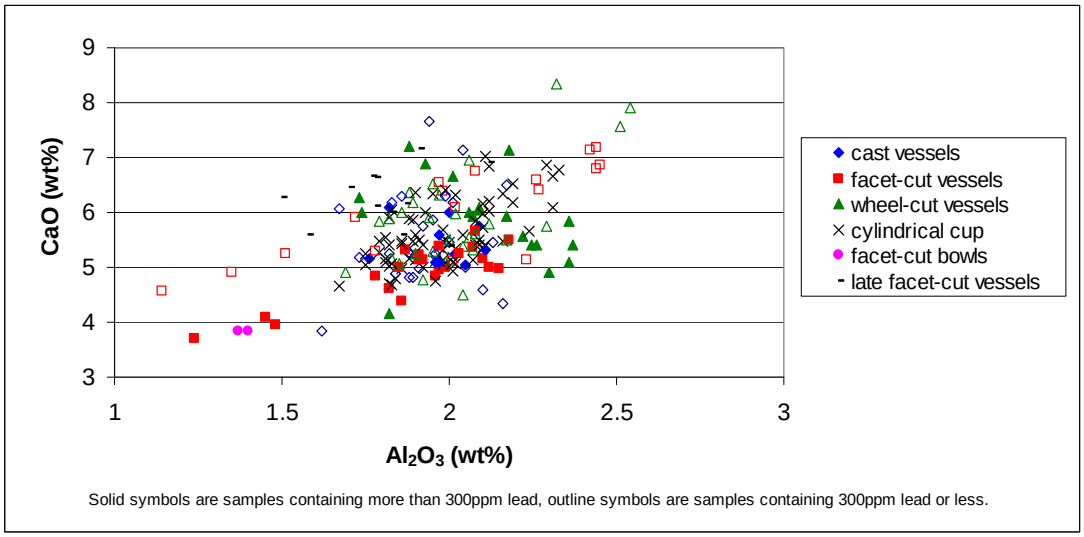

Figure 16: Plot of adjusted lime and adjusted alumina for the different types of wares from Binchester, Lincoln and Colchester

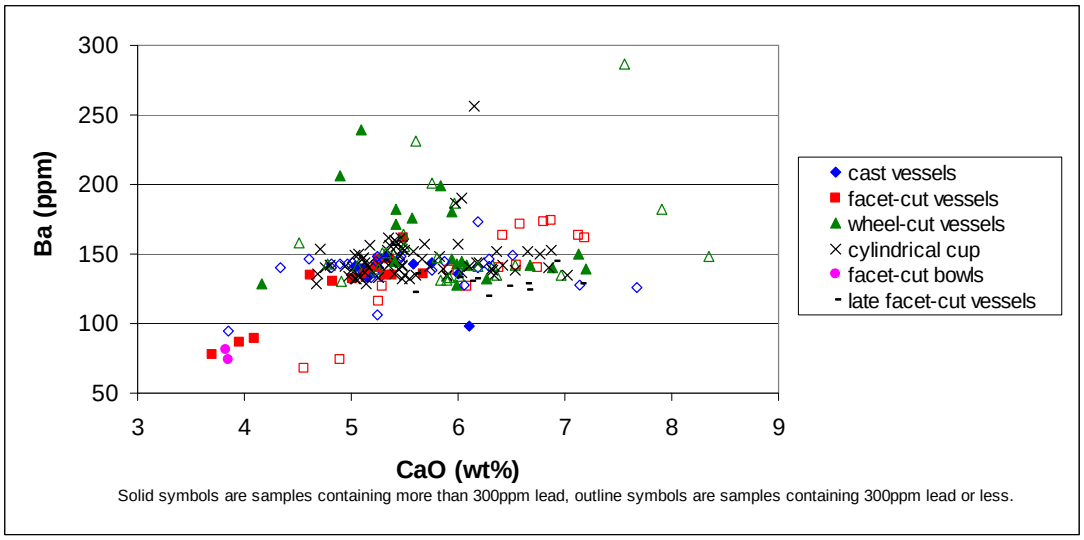

Figure 17: Plot of unadjusted barium and adjusted lime for the different types of wares from Binchester, Lincoln and Colchester

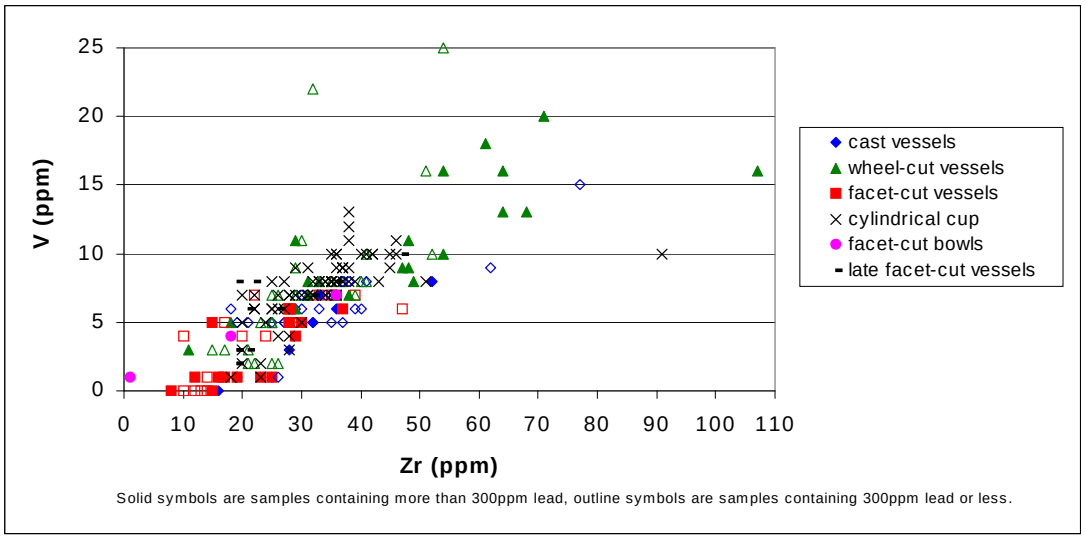

Figure 18: Plot of unadjusted vanadium and unadjusted zirconium for the different types of wares from Binchester, Lincoln and Colchester

Conclusions

In general the glass from Lincoln, Binchester and Colchester was chemically similar, regardless of the ware type or at which site the sample was recovered. This suggests that colourless glass may have been produced on a fairly large scale at a small number of sites in the 1st to 3rd centuries and the glass produced distributed as a bulk material to workshops where glass workers shaped it into vessels. It also indicates that furnaces in the same general area may have produced the glass, because chemically similar raw materials were used. Samples of the same type of ware were found to have the most similar compositions, regardless of where they were recovered, suggesting that vessels from particular workshops were probably widely distributed, supplying markets across Britain. However as yet there is no other archaeological evidence to support this model of glass production and distribution until a later date (Freestone et al, 2002, 258-259).

The characteristically low potash and magnesia content of the glass indicates that the source of the alkali fluxes was a mineral, such as the evaporite natron. This was probably combined with beach sand containing shell. Some groups of analysed samples had distinct chemical characteristics. In particular many of the wheel-cut cups had a greenish tinge and contained higher levels of iron than typical. The atypical composition of these samples is probably a result of the heavy mineral or clay mineral content of the sand used to produce the glass. There were similarities between these samples and the 4th century HIMT glass identified by Freestone et al (2002).

The groups of 1st to 2nd century wares analysed included both high-lead (in excess of 300ppm lead) and low-lead samples but all of the mid-2nd to 3rd century wares were low-lead. The concentration of lead in the glass may be related to the date of glass production and, if so, could be useful in establishing the production period of different forms of ware. The lead may have entered the glass with culllet or with an antimony compound used as a decolouriser.

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The ICP analyses were completed by Dr Nick Walsh, who also contributed to the discussion of the ICP technique. Professor Jenny Price and Dr Sally Worrell identified the different groups of ware for the Binchester samples. Many thanks to Professor Ian Freestone for providing ideas and very useful advice whilst discussing these results. Dr Hilary Cool, Dr Mike Baxter, Dr Mike Heyworth and Dr Catherine Mortimer were extremely helpful on the subjects of the Colchester and Lincoln glass studies. I am grateful to Lincoln Archaeology and Colchester Museums for permitting resampling of the material and in particular to Paul Sealey for his time in retrieving the Colchester samples.

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Appendix

Adjustment factors

Adjusted value = ICP result + adjustment factor

Table 3: Adjustment factors applied to the ICP data

Site	Na_2O	Al_2O_3	CaO	K_2O	MgO	Fe_2O_3
Binchester	0	+0.23	+0.46	+0.015	0	+0.15
Lincoln	+3.5	0	0	-0.08	-0.07	-0.017
Colchester	+0.6	+0.08	0	-0.06	-0.03	+0.065

For example, Lincoln MgO adjusted value = ICP result – 0.07

SEM-EDS Analysis Results

Table 4: SEM-EDS results for selected glasses from Binchester, Colchester and Lincoln, mean of three analyses per sample, normalised

Site	ICP No.	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Sb_2O_5	PbO
Binchester	14	20.21	0.39	2.43	67.25	<0.1	0.45	6.97	<0.1	<0.1	0.31	1.90	<0.1
	11	18.61	0.40	2.15	71.87	<0.1	0.46	5.31	0.10	<0.1	0.42	0.63	<0.1
	9	21.56	0.31	1.85	70.03	<0.1	0.36	4.92	<0.1	<0.1	0.28	0.58	<0.1
	4	19.61	0.35	1.86	71.29	<0.1	0.31	5.66	<0.1	<0.1	0.30	0.50	<0.1
	39	19.55	0.46	2.24	70.53	0.11	0.61	5.48	0.11	0.24	0.54	0.44	<0.1
	32	17.67	0.36	2.14	72.59	<0.1	0.40	5.41	<0.1	<0.1	0.31	0.72	<0.1
	31	18.84	0.27	1.91	72.04	<0.1	0.37	4.92	<0.1	<0.1	0.27	1.16	0.17
	26	18.31	0.29	1.82	72.60	<0.1	0.42	5.20	<0.1	<0.1	0.27	1.03	<0.1
	8	19.06	0.25	1.87	72.40	<0.1	0.36	4.95	<0.1	<0.1	0.28	0.77	<0.1
Lincoln	2	19.16	0.54	2.05	69.40	<0.1	0.39	7.11	<0.1	<0.1	0.51	0.68	<0.1
	40	20.07	0.33	1.97	71.00	<0.1	0.36	5.24	<0.1	<0.1	0.31	0.62	<0.1
	51	19.56	0.38	1.84	70.86	<0.1	0.39	5.88	<0.1	<0.1	0.30	0.70	<0.1
	33	18.56	0.41	2.23	71.09	<0.1	0.52	5.97	<0.1	0.27	0.41	0.40	<0.1
	45	17.11	0.33	1.33	73.96	<0.1	0.51	4.73	<0.1	<0.1	0.38	1.52	<0.1
	22	18.51	0.57	1.93	71.36	<0.1	0.33	6.51	<0.1	<0.1	0.37	0.36	<0.1
	13	20.29	0.77	2.46	68.80	<0.1	0.48	5.35	0.25	<0.1	0.86	0.69	<0.1
	20	17.12	0.35	1.99	73.85	<0.1	0.48	5.23	<0.1	<0.1	0.33	0.51	<0.1
	3	18.80	0.35	2.01	71.98	<0.1	0.38	5.25	0.10	<0.1	0.32	0.78	<0.1
	1	19.76	0.45	2.05	70.04	<0.1	0.43	6.05	<0.1	<0.1	0.41	0.68	<0.1
Colchester	452	19.59	0.49	2.26	69.92	<0.1	0.67	5.42	<0.1	0.28	0.58	0.65	<0.1
	466	18.99	0.43	1.93	72.18	<0.1	0.40	4.95	<0.1	<0.1	0.34	0.73	<0.1
	402	16.66	0.45	2.55	70.56	<0.1	0.61	7.39	<0.1	<0.1	0.33	1.37	<0.1
	211(3139)	17.88	0.34	1.47	71.97	<0.1	0.60	3.76	<0.1	<0.1	0.44	3.01	0.41
	410	19.53	0.45	2.00	70.16	<0.1	0.47	6.36	<0.1	<0.1	0.35	0.59	<0.1
	498	18.45	0.40	1.86	72.80	<0.1	0.42	5.31	<0.1	<0.1	0.28	0.35	<0.1

Table 5: Known composition (in italics) of Corning standard A.

Standard	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	CuO	ZnO	SnO_2	Sb_2O_5	BaO	PbO
A	14.48	2.80	1.01	66.36	0.14	0.16	2.92	5.28	0.80	0.96	1.09	0.15	1.22	0.04	0.28	1.71	0.54	0.08

Table 6: Normalised SEM-EDS results for Corning A standard during analyses of samples from Lincoln, Binchester and Colchester as specified, average (number of analyses in brackets) and standard deviation

Site		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	CuO	ZnO	SnO_2	Sb_2O_5	BaO	PbO
Lincoln	Av.(6)	14.01	2.57	1.14	67.20	0.10	0.19	2.89	5.10	0.82	1.03	1.10	0.17	1.26	<0.1	0.22	1.69	0.47	<0.1
	StDev	0.06	0.06	0.02	0.13	0.05	0.04	0.05	0.04	0.03	0.03	0.05	0.04	0.06	-	0.09	0.09	0.06	-
Binchester	Av.(4)	14.27	2.51	1.14	66.93	<0.1	0.23	2.88	5.04	0.78	1.01	1.11	0.17	1.25	<0.1	0.30	1.69	0.52	<0.1
	StDev	0.07	0.07	0.08	0.13	-	0.03	0.02	0.08	0.05	0.04	0.05	0.02	0.05	-	0.11	0.11	0.02	-
Colchester	Av.(2)	13.91	2.56	1.10	67.15	<0.1	0.19	2.84	5.13	0.82	1.03	1.10	0.23	1.20	0.10	0.26	1.74	0.47	<0.1
	StDev	0.12	0.01	0.01	0.10	-	0.00	0.03	0.02	0.05	0.04	0.02	0.02	0.05	0.02	0.04	0.04	0.02	-

Table 7: Original ICP data for the Binchester samples (continued over page). Major elements (first 9 columns) in wt% oxide, other elements (remaining 21 columns) in ppm (parts per million) equivalent to μg/g.

ICP No	MgO	Na_2O	Al_2O_3	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Ba	Co	Cr	Cu	Li	Ni	Sc	Sr	V	Y	Zn	Zr	La	Ce	Nd	Sm	Eu	Dy	Yb	Pb	Sb
1	0.29	17.97	1.81	0.02	0.39	4.05	0.05	0.01	0.14	158	31	3	12	6	7	1	264	2	6	20	25	3	5	4	1.4	0.2	0.8	0.5	20	3018
2	0.46	20.76	1.89	0.02	0.46	5.34	0.06	0.02	0.24	147	27	5	12	7	8	1	394	2	7	19	26	4	7	5	1.9	0.2	1.0	0.6	93	3706
3	0.44	20.59	1.55	0.02	0.31	5.66	0.05	0.01	0.22	130	48	5	19	7	7	1	415	2	7	21	19	3	6	4	1.4	0.2	0.8	0.5	32	2979
4	0.39	19.85	1.63	0.02	0.31	5.14	0.05	0.01	0.17	136	42	5	17	6	6	1	366	2	7	18	19	3	6	4	1.5	0.2	1.1	0.5	23	2648
5	0.40	19.67	1.60	0.02	0.33	5.54	0.06	0.01	0.18	133	14	3	12	7	6	1	402	3	7	19	19	3	6	4	1.6	0.2	1.2	0.5	22	3326
6	0.41	19.56	2.03	0.03	0.65	6.12	0.04	0.02	0.16	171	19	4	9	6	6	1	395	0	8	17	13	4	6	5	1.9	0.2	1.1	0.6	109	6047
7	0.29	18.05	1.84	0.02	0.41	4.90	0.05	0.02	0.18	146	18	9	12	6	6	1	332	1	7	18	16	4	6	5	1.8	0.2	0.8	0.5	3377	7048
8	0.25	17.65	1.55	0.01	0.33	4.37	0.04	0.01	0.10	130	10	4	7	6	5	1	312	0	6	11	15	2	4	3	1.0	0.2	0.7	0.5	1394	4805
9	0.36	21.45	1.62	0.02	0.35	4.60	0.05	0.01	0.16	141	10	1	16	7	8	1	313	2	6	24	21	3	6	4	1.4	0.2	0.8	0.5	25	4606
10	0.41	19.24	2.04	0.03	0.66	5.96	0.04	0.02	0.18	163	27	5	10	7	6	1	368	1	8	17	14	4	6	5	1.9	0.2	1.1	0.5	113	7422
11	0.37	18.70	1.88	0.02	0.43	4.86	0.07	0.02	0.25	148	10	3	12	8	6	1	321	3	7	15	28	4	7	5	1.9	0.2	1.0	0.5	2091	4125
12	0.39	20.24	2.21	0.02	0.42	6.34	0.04	0.02	0.15	173	9	3	11	6	7	1	411	0	8	24	12	4	6	5	2.0	0.2	1.2	0.6	18	9018
13	0.28	18.22	1.55	0.02	0.37	4.83	0.03	0.01	0.14	127	14	5	5	6	7	0	324	0	7	14	10	4	5	4	1.8	0.2	0.7	0.5	11	7355
14	0.39	20.47	2.22	0.02	0.43	6.41	0.03	0.02	0.13	174	13	3	5	6	6	1	404	0	8	13	14	4	7	5	2.0	0.2	1.3	0.6	12	9020
15	0.31	17.98	1.80	0.01	0.37	4.80	0.06	0.01	0.17	146	17	4	12	7	6	1	398	1	6	18	17	3	6	3	1.4	0.2	0.7	0.5	2346	3296
16	0.34	18.82	1.25	0.02	0.52	3.49	0.04	0.02	0.23	87	12	3	12	5	7	1	304	0	5	17	8	3	6	4	1.4	0.1	0.8	0.5	4701	10299
17	0.46	19.99	1.63	0.02	0.35	5.55	0.06	0.01	0.21	134	34	6	12	7	7	1	400	3	7	19	15	3	5	4	1.5	0.2	0.9	0.5	44	2599
18	0.40	19.68	1.46	0.02	0.32	5.32	0.05	0.01	0.15	128	10	2	9	7	5	1	374	2	7	20	21	2	6	3	1.1	0.2	0.8	0.5	19	2469
19	0.28	17.39	1.79	0.02	0.39	4.80	0.04	0.01	0.16	140	15	7	8	6	6	1	318	0	7	14	16	3	6	4	1.5	0.2	1.0	0.5	3232	7180
20	0.38	20.71	1.55	0.02	0.31	6.18	0.06	0.01	0.20	129	17	5	10	7	7	1	453	3	8	19	21	4	6	5	1.9	0.2	1.1	0.5	37	3757
21	0.40	17.95	1.85	0.02	0.53	5.21	0.06	0.02	0.33	136	10	6	18	7	7	1	398	1	7	35	12	4	6	5	1.9	0.2	1.0	0.6	2068	8298
22	0.54	18.94	2.07	0.07	0.67	4.44	0.15	0.53	0.55	206	15	8	32	10	12	1	295	13	8	27	64	4	12	5	2.1	0.3	1.5	0.7	322	5335
23	0.33	18.94	1.60	0.02	0.31	4.61	0.05	0.01	0.14	135	14	3	12	7	6	1	289	1	7	22	18	2	5	3	1.1	0.2	0.8	0.5	33	5809
24	0.47	19.67	1.56	0.02	0.32	5.38	0.05	0.01	0.19	131	23	7	13	7	7	1	383	2	7	21	22	3	6	4	1.4	0.2	0.8	0.5	30	3021
25	0.32	19.26	1.58	0.02	0.31	5.09	0.06	0.01	0.15	132	9	4	9	8	6	1	347	2	7	14	23	3	6	4	1.5	0.2	1.0	0.5	21	2981
26	0.32	18.10	1.58	0.02	0.39	4.70	0.04	0.01	0.11	140	10	1	16	7	5	1	336	1	7	23	23	3	6	4	1.4	0.2	0.8	0.4	27	5242

Table 7 (continued): Original ICP data for the Binchester samples

ICP No	MgO	Na_2O	Al_2O_3	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Ba	Co	Cr	Cu	Li	Ni	Sc	Sr	V	Y	Zn	Zr	La	Ce	Nd	Sm	Eu	Dy	Yb	Pb	Sb
27	0.47	17.04	1.86	0.02	0.52	5.04	0.06	0.02	0.23	153	14	4	10	8	6	1	356	3	7	18	28	4	5	4	1.8	0.2	0.7	0.5	17	1990
28	0.44	18.48	1.71	0.02	0.33	5.46	0.07	0.01	0.26	133	21	3	15	7	6	1	354	3	7	24	21	3	7	4	1.5	0.2	1.1	0.6	29	3226
29	0.50	17.25	1.68	0.02	0.34	5.04	0.07	0.01	0.24	135	18	3	12	8	9	1	366	3	7	16	20	4	5	5	1.8	0.2	0.8	0.5	15	2478
30	0.31	18.66	1.63	0.02	0.35	4.98	0.06	0.01	0.13	139	19	2	11	12	5	1	345	2	7	16	20	3	6	4	1.5	0.2	1.0	0.5	14	2639
31	0.27	18.52	1.62	0.01	0.34	4.55	0.05	0.01	0.12	132	7	4	9	7	5	1	325	1	6	12	19	3	5	4	1.5	0.2	0.9	0.5	1446	7095
32	0.27	16.96	1.74	0.02	0.38	4.62	0.05	0.01	0.15	139	6	5	11	6	6	1	316	1	7	13	25	3	6	4	1.5	0.2	1.0	0.5	3236	7804
33	0.25	17.71	1.53	0.02	0.42	4.69	0.04	0.01	0.13	133	6	3	8	8	5	1	306	1	7	11	19	3	6	4	1.5	0.2	0.9	0.5	2082	9062
34	0.38	19.54	1.54	0.02	0.31	6.19	0.06	0.01	0.18	124	18	3	14	8	8	1	440	3	8	16	19	4	7	5	1.9	0.3	1.0	0.6	33	3361
35	0.27	16.62	1.73	0.02	0.38	4.64	0.05	0.01	0.15	139	11	6	12	7	7	1	312	1	7	13	16	3	5	4	1.5	0.2	0.9	0.5	3167	7588
36	0.30	18.86	1.73	0.02	0.37	4.78	0.05	0.01	0.13	148	7	2	11	7	6	1	321	1	7	21	26	3	6	4	1.4	0.2	0.8	0.5	33	5866
37	0.44	19.74	1.59	0.02	0.35	5.43	0.06	0.01	0.19	131	17	3	12	7	5	1	388	3	7	17	17	4	5	5	1.8	0.2	0.9	0.5	25	2900
38	0.29	19.63	1.74	0.02	0.38	4.92	0.05	0.01	0.14	135	6	5	10	7	5	1	324	1	7	13	25	3	5	4	1.5	0.2	1.0	0.5	1545	7587
39	0.46	18.52	2.02	0.07	0.60	4.96	0.10	0.24	0.45	171	7	8	21	7	7	1	375	11	7	24	29	5	11	6	2.2	0.3	1.4	0.6	777	4885
40	0.28	19.21	1.69	0.01	0.36	4.68	0.05	0.01	0.13	138	4	5	9	8	8	1	324	1	7	12	23	3	5	4	1.4	0.2	0.8	0.5	1473	7123

Results by ware type

Cast vessels (late 1st to mid-2nd centuries)

Three Binchester cast bowls and the fragments of a saucepan and a tray or plate (samples 11 and 33) contained in excess of 300ppm of lead, as did 4 of 19 Colchester cast vessel samples and one of the 10 Lincoln samples. The compositions of the high-lead bowls varied quite widely but because of the small number of samples, it was not possible to determine whether there were likely to be distinct groups present. The low-lead cast vessels, including the tray/bowl from Binchester (36), formed a tighter compositional group, although some atypical samples were present. For example Colchester low-lead sample 210, possibly a cast handle fragment from a bowl, contained high concentrations of soda, iron oxide and magnesia, increased concentrations of manganese oxide, vanadium and zirconium and was also described as greenish-colourless (Cool and Price, 1995, 39). Samples with similar compositions were identified amongst the wheel-cut vessels. Colchester low-lead samples 222 and 224, base fragments of bowls, were also outliers, characterised by low concentrations of zirconium and barium and to a lesser extent alumina and lime, and a high concentration of potash, similar to some of the facet-cut vessels (Colchester 417 and Lincoln 45). Colchester 215 contained unusually high concentrations of titanium oxide and zirconium.

Facet-cut bowls (late 1st to mid-2nd centuries)

The compositions of Colchester samples 209 and 211, from facet-cut bowls, were lower in lime and alumina but higher in potash, lead and antimony oxide than typical. They also contained low levels of barium and zirconium. These wares are compositionally similar to some other facet-cut vessels, including facet-cut beakers from Binchester (16) and Lincoln (52 and 49). Lincoln sample 49 is a biconical beaker, unusual in form and decoration.

Facet-cut vessels (cups / beakers) (late 1st to mid-2nd centuries)

Thirteen facet-cut vessels from Binchester, 16 facet-cut vessels from Colchester and 10 facet-cut vessels from Lincoln were analysed. Of these, 7 Colchester samples, 8 Binchester samples and 7 Lincoln samples were high-lead and formed a tight compositional group, characterised by low potash and magnesia, low iron oxide and fairly low lime. The low-lead samples were less tightly grouped and in general appeared to contain slightly more magnesia and lime. Three high-lead samples (Lincoln 52 and 49 and Binchester 16) and two low lead samples (Colchester 417 and Lincoln 45) were atypical, often characterised by lower concentrations of alumina, lime, barium and zirconium but higher concentrations of potash. Colchester 417 also contained a high concentration of antimony. These outliers were similar to atypical samples from the low-lead cast vessel group (Colchester 222 and 224) and the two late 1st to mid-2nd century facet-cut bowls from Lincoln.

Wheel-cut vessels (late 1st to mid-2nd centuries)

Nine wheel-cut vessels from Binchester, 11 from Lincoln and 29 from Colchester were analysed and had a wide range of compositions. Two of the Binchester samples (39 and 22), 15 of the Colchester samples and 3 of the Lincoln samples were high-lead. Many of the samples, both high- and low-lead, were described as greenish-colourless and contained higher concentrations of alumina, phosphorus oxide, iron oxide, titanium oxide, manganese oxide and magnesia than typical (for example Colchester samples 435, 460 and 428). Unusually high levels of zirconium, vanadium and sometimes antimony, barium and copper were often noted in these samples. The high levels of zirconium and iron oxide appeared to be more marked amongst the high-lead samples; of the samples containing more than 40ppm of zirconium, 5 were low-lead compared to 12 high-lead. There were also two distinct samples (Colchester 446 and 463) with low concentrations of sodium and iron oxides and high concentrations of lime, alumina and phosphorus oxide.

Cylindrical cups (late 2nd to mid-3rd centuries)

Six cylindrical cups from Binchester, 53 from Colchester and 15 from Lincoln were analysed. All of these were low-lead (the vast majority contained less than 100ppm of lead). The compositions of the cylindrical cups were variable, encompassing most of the compositional range seen for other types of wares. The majority contained less than 0.02% of manganese oxide but a small number contained more, up to 0.27wt% and these samples also had slightly increased barium, copper and zinc contents.

Late facet-cut vessels (mid-2nd to 3rd centuries)

Five samples from Binchester and 7 samples from Lincoln were analysed. The samples were all low-lead and were characterised by some of the lowest potash contents of all of the wares (0.3 to 0.4wt%). The samples also contained fairly high concentrations of lime and soda and fairly low concentrations of alumina. The Binchester samples formed a tighter compositional group than the Lincoln samples but in general wares from the two sites were compositionally similar.