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Investigation of Late 17th Century Crystal Glass

D Dungworth[1] and C Brain[2]

Summary

This report investigates the glasses used in the manufacture of fine tablewares (crystal glass) during the late 17th century and in particular the glass produced by George Ravenscroft who is traditionally credited with the invention of lead crystal. The review of the documentary evidence available shows that the glass for which Ravenscroft obtained a patent (in 1674) probably did not contain lead. There are no unequivocal documentary references to the use of lead for such glass until the 18th century. A range of glass vessels (52 samples) and production debris from a glasshouse (8 samples) were analysed. Most of the samples are lead glasses but thirteen are alkali glasses.

Keywords

Glass
Post Medieval

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Contents

Introduction

The 17th century saw many significant changes in glass production in Europe. In the early part of the century coal-fuelled furnaces were developed in England and towards the end of the century the first colourless lead glass (variously called ‘flint glass’ and ‘lead crystal’) was produced. These new technologies allowed Britain to become one of the leading glass producers. The origin of colourless lead glass is traditionally traced back to George Ravenscroft and his 1674 patent. However, the details of what Ravenscroft actually invented are obscure and there are almost no published quantitative chemical analyses of glass of this period. This report provides a detailed review of the documentary evidence relating to fine vessel glass manufacture during the 1670s and 1680s. This is necessary as Ravenscroft’s patent does not specify any ingredients for his glass. Indeed the first unequivocal link between lead and ‘flint glass’ does not occur until the middle of the 18th century. The report presents the results of the analysis of samples taken from a range of late 17th century drinking vessels.

Historical and Technological Background

Early Post-Medieval Glass

During the medieval and early post-medieval periods glass was produced in both northern and southern Europe. In northern Europe glasshouses tended to be situated in forest areas and made use of the ashes of the wood fuel as a flux to produce ‘forest glass’ (Hunter 1981). Some documentary evidence also suggests that other woodland plants (such as fern or bracken) were used (Cable 2001: 320–1). ‘Forest glass’ (*waldglas* or *verre de fougere*) tends to contain low levels of soda and high levels of potash. ‘Forest glass’ usually has a distinctly green colour due to the presence of iron oxide (from the sand or the plant ashes, or both). In southern Europe (especially Venice but also the glassmaking centre at Altare near Genoa) glasshouses used ashes from selected marine plants as a flux, such as *barilla* (Ashtor & Cevidalli 1983). These ashes were often washed to remove impurities and could be used to produce a colourless glass, called *cristallo* (Verità 1985). Venetian *cristallo* was imported by northern European countries and was certainly the more expensive and fashionable glass.

The demand for *cristallo* in northern European countries was high despite the high transport costs and the high rate of breakages during transport. During the 16th century northern European countries attempted to set up local glasshouses which could produce *cristallo* in imitation of that normally imported from Venice. The Venetian authorities tried to prevent the migration to northern Europe of skilled glassworkers but there do not appear to have been similar restrictions on the Altarian glassmakers and both centres were producing similar glass (Wilkinson 1968: 48). By the end of the 16th century glasshouses in Bohemia, Germany, the Low Countries and even England were employing Italian glassmakers to produce a colourless glass, an imitation of Venetian *cristallo*, often called *façon de Venise*, (Wilkinson 1968: 54–76; de Raedt *et al*. 1997). Altarian glassmakers, e.g. Da Costa, Odaccio and Dagnia, are prominent among the glassworkers in Britain during the 17th century.

There is extensive evidence for the manufacture of glass in England during the early part of the 17th century. In 1615 a patent (at this date an instrument which granted a monopoly) was issued to Sir Robert Mansell who dominated glassmaking until 1642 (Godfrey 1975). The nature of the glass industry during the Civil War and under the Commonwealth remains obscure but emerges more clearly after the Restoration of Charles II in 1660 (Charleston 1984: 97).

Glass Manufacture in England, 1660–1674

The return of Charles II in 1660 saw a rise in the documentary evidence relating to glass manufacture. Within months of Charles' return, the Duke of Buckingham entered into an agreement with one John de la Cam for the manufacture of 'christall de roach' for a period of ten years (Thorpe 1949: 138). However, the enterprise did not run for the full ten years, as by 1668 de la Cam was running a glasshouse in Nijmegen (the same town in which Da Costa and Odaccio worked together in a glasshouse, see below). It is likely that the agreement between the Duke and de la Cam was dissolved by 1662 as the Duke entered into a new agreement in that year with Clifford and Plowden for the production of glass (Charleston 1984: 98) This, like many subsequent late 17th century glass manufacturing agreements, was between a financial backer of high social standing and others skilled in the techniques of glass production. The agreements were often strengthened by obtaining royal patents; Clifford and Plowden obtained a patent for a 'new invention of making christall glasses', but no details are given (Hartshorne 1968: 221).

A number of patents were granted in the 1660s for the manufacture of glass. By this time the nature of patents had begun to change and they usually contained reference to some new quality of the glass produced (Hartshorne 1968: 221–223; Thorpe 1949: 139–140). However, the patents do not give detailed specifications as to what ingredients were used to make the glass. Patents still tended to give monopoly rights (for 14 years) and most were granted to the Duke of Buckingham (through intermediaries).

The Clifford and Plowden patent was surrendered in 1663 and a new patent was issued to Thomas Tilson (again through the Duke of Buckingham) which covered mirror plate as well as vessel glass but again provides no details as to how the glass was made (Hartshorne 1968: 438–9). In 1663 Bryan Leigh, Adam Hare, William Burroughs and Ralph Outlye petitioned for a patent for 'a way never yet before discovered, of extracting out of Flinte all Sorts of lookeing glasses, plates both Christall and ordinary and all manner of Christall glasse, farr exceedeing all former experiments both at home and abroad' (Hartshorne 1968: 222, 438). The use of flint as a source of silica in the manufacture of 'Christall' led to widespread use of the term 'flint' to describe the high-quality colourless glass regardless of the source of the silica (Charleston 1984: 114–115). Flint also became associated with lead glass even after the flint had been replaced by sand. Documents of the 1670s which contain references to 'flint glass' may be referring to lead glass or alkali glass.

The increase in glassmaking activity in the early 1660s was almost certainly influenced by the publication in 1662 of a translation (by Christopher Merrett) of Antonio Neri's 1612 *Art of Glass* (Cable 2001). This important work gave details of how to make colourless glass (*chrystall*) in the Venetian style. The *Art of Glass* also described how to make a variety of coloured glasses (in imitation of jewels) and in some cases made use of lead oxide. Lead oxide was only used for the manufacture of coloured glasses imitating precious and semi-precious stones. Neri's recipes for coloured lead glasses consisted of simply adding lead oxide to his conventional alkali frit (i.e. an alkali-rich plant ash such as polverine or rochetta heated with crushed quartz pebbles) and then adding small amounts of a suitable colourant (e.g. copper oxide). The proportions of alkali frit to lead oxide varies depending on the colour, but in most the lead oxide content would be in the range 40–60%. Neri stressed the need to calcine (roast) the lead to ensure that it was completely converted into the oxide and warned that if improperly calcined, ‘it returns to lead again, and by consequence the less breaks out the bottom of the pot . . . and lets all the metall run into the fire’ (Cable 2001: 164).

Christopher Merrett’s commentary on Neri’s text offers some interesting observations on the use of lead in glass in 1662,

> Glass of Lead, ’tis a thing unpractised by our Furnaces and the reason is, because of the exceeding brittleness thereof. Lead, to glase their ware withal being the principal thing wherewith that glasing is made, is sufficiently known and practised dayly by the Potters, And could this be made as tough as that of Chrystalline ’twould far surpass it in glory and beauty of it’s colours, of which no man can be ignorant, that hath had any experience of this Metall.
> (Cable 2001: 373–4)

Merrett also repeats Neri’s warning that,

> Lead returning to it’s body, breaks out the bottom of the pots. Lead can hardly be so well calcin’d, but some particles thereof will remain uncalcin’d, which the heat of the furnace reduceth to Lead again.
> (Cable 2001: 375)

Despite the great improvements in the manufacture of glass in England during the late 16th century and the earlier part of the 17th century, the most prestigious glass remained that which was imported from Venice. Venetian glass consistently commanded higher prices than domestic glass (Godfrey 1975: 215–6; Charleston 1968: 66–7). In the late 17th century much of this trade was in the hands of the London Company of Glass Sellers who had originally been incorporated in 1635 but whose rights were confirmed by Charles II in 1664 (Thorpe 1949: 135). A remarkable collection of correspondence between two members of the Glass Sellers (Michael Measey and John Greene) and their manufacturer, Allesio Morelli of Murano, Venice from 1667 to 1672, provides details on the form of glass vessels imported (many are illustrated), as well as the quantities of glass required and numerous details about the quality of the glass and the shipping arrangements (Thorpe 1949: 147–150, 172–173; Hartshorne 1968: 228–233, 440–449). Greene finishes many of his orders with general instructions as to the quality of the glass and the way in which it is packed for the sea journey from Venice to London. Greene’s request for glass ‘of verrij Bright cleer whit sound Mettall’ (e.g. 10th February 1671, Hartshorne 1968: 444–5), shows that his main criterion was colourlessness. The quantities ordered were large; between February 1671 and May 1672 Greene ordered over 7600 drinking glasses of various sizes and styles. The demand for the glasses was high and Greene writes that Morelli should send those items that were available immediately with the remaining glasses to follow once they were produced. However, he became increasingly dissatisfied with Venetian glass: he warned that,

> . . . it will not be mij Interest to send to Venice for neither drinking Glasses nor Lookeing Glasses, for we make now verij Good Drinking Glasses in England
> (3rd May 1671, Hartshorne 1968: 447)

and complained about the Venetian glass sent to him,

> for truelj the last you sent me the Metall was indifferent good and cleer, but not so sound and strong as theij should have bin made
> (30th November 1672, Hartshorne 1968: 448)

The shift from Venetian *cristallo* glass to northern European imitations (*façon de Venise*) was also noted by Girolamo Alberti, the Doge of Venice's Secretary in London. In October 1672 he complained that,

> With regard to Venetian trade, I find that of glass is utterly ruined since the introduction here of the manufacture of mirrors and drinking glasses, by a privilege granted to the Duke of Buckingham.
> (Hinds 1939: 299)

In December 1672 Alberti referred to the import of Venetian drinking glasses and lamented that 'only 20 cases come to London in a year, instead of 300 as heretofore' (Hinds 1939: 330). In January 1674 he recorded that 'they already make crystal glass in perfection' (Hinds 1947: 195) and in June 1674 that the Venetian glass trade 'suffers from the extreme beauty of the English drinking glasses' (Hinds 1947: 264).

The Glass Sellers were acutely aware of the problems with importing Venetian glass, including the high level of duty that was liable for such imports, and the improving quality of domestic *façon de Venise* glass. In 1670 they began to negotiate with London glassmakers to secure a supply of 'white' glass (i.e. colourless glass) as a necessary step before applying for a ban on imported wares (Charleston 1984: 104). They ultimately secured a supply of suitable glass from George Ravenscroft.

George Ravenscroft and Glass Manufacture

Introduction

In 1674 George Ravenscroft was granted a patent for glass manufacture and the Glass Sellers entered into an agreement with him to buy all of the glass that he produced. It is widely accepted that Ravenscroft's 'invention' was lead glass but there are many details which remain obscure. Recent research has shed much light on the life of George Ravenscroft (e.g. Moody 1988; 1989; Rendel 1975), the nature of the patent that he obtained (MacLeod 1987), the glass that he produced (Charleston 1968; Watts 1975) and the activities of other glassmakers (Francis 2000). It is, nevertheless, frustrating that none of the contemporary documents describe the use of lead in the manufacture of glass.

Ravenscroft before glass manufacture (1632–1673)

George Ravenscroft (1632–83) was the second son of James Ravenscroft a successful merchant who thrived in the 17th century despite being a devout Catholic (Moody 1988: 199). James sent his sons to the English college at Douai in the Spanish Netherlands: George attended from 1643 to 1651. George then spent some time living and trading in Brussels before moving to Venice where he traded in various luxury goods (e.g. lace, glass, currants, sugar and brimstone), some of them already imported from the Levant. By 1666 he had returned to England to take over some of his father's business (Moody 1988: 200). He continued to trade with Venice and imported glass for the manufacture of mirrors.

Ravenscroft, the Savoy glasshouse and Da Costa

A 1677 agreement between Ravenscroft and the Glass Sellers records that Ravenscroft established a glasshouse at the Savoy in 1673 (Charleston 1984: 110). This was within the grounds of the old palace (and later hospital) and the location of a glasshouse is marked on a 1692 plan drawn by Sir Christopher Wren (Moody 1988: fig 2).

Alberti, the Venetian Secretary, records in September 1673, 'two new furnaces lately opened for very fine large crystal' (Hinds 1947: 116) and one of these may be the furnace at the Savoy. The Savoy glasshouse was visited 29 July 1673 by Robert Hooke and Christopher Wren. Hooke records that they visited,

> the new glashouse at the Savoy. Saw calcind flints as white as flower, Borax, Niter and tarter, with which he made his glasse he denyd to use arsenick he shewd pretty representations of Agates by glass &c
> (Robinson & Adams 1935: 53)

On Saturday 28 February 1674 Hooke further records that,

> Lazenby affirmed that he saw the man at the Savoy for making his crystal put into the pot first a Layer of borax, then a layer of Sand then of Niter
> (Robinson & Adams 1935: 89)

It is unfortunate that the diary entries do not say who the glassworker was; it is possible that it was Da Costa but there is no evidence of this. It is interesting that there appears to be no attempt to conceal the ingredients used in the glass recipe. There is no mention of the use of lead, despite the fact that Neri's recipes for the manufacture of artificial gems frequently make the use of large quantities of lead. MacLeod (1987: 798) suggests that the Savoy glassmaker kept the use of lead oxide a secret but given that the English translation of Neri's book had been published in 1662 it is unlikely that informed observers such as Hooke and Wren could not have deduced the use of lead if it was being used.

Alberti, the Venetian Secretary, records on the 15th June 1674,

> It is above all necessary to prevent Venetian workmen from withdrawing to these countries as they bring their art with them. As the necessary materials are found here the English, in course of time, will perfect themselves in it. I am told that one Vicenzo, surname unknown, has come to London and intends to work there in the furnace of the Englishman Ravenscroft . . .
> (Hinds 1947: 265)

Ravenscroft does not explain why he became involved in the manufacture of glass but Moody (1988: 205) argues that his trade in Venetian glass had begun to suffer due to high import duties and so was faced with either abandoning the trade or entering into manufacture. Hindsight shows that he became engaged in manufacture but the Duke of Buckingham's patent for glassmaking still had some years to run. If

Ravenscroft was to produce glass then it would have to be an entirely new sort of glass. However,

> it is contrary to all we know of the 17th-century London business community and its ethos to imagine that a Levant merchant, of wealth and a necessarily high social status, would "descend" to the practice of a manual trade, glassmaking.
> (MacLeod 1987: 799)

It is more likely that Ravenscroft was a financial backer and that an Italian glassmaker (Da Costa) was the actual inventor of the glass that was patented. John Baptista Da Costa was one of two glassmakers from Altare (the other was John Odaccio Formica) who worked together in Nijmegen between 1665 and *c*.1672 (Francis 2000: 49). Both were later associated with lead glass industries: Da Costa in London and Odaccio in Dublin. Dr Plot, writing in 1676 (more of which below), credited the invention of the glass manufactured by Ravenscroft to Da Costa. The link between Da Costa and the invention of a new type of colourless glass is strengthen by Odaccio's application for a glassmaking patent in Ireland (Francis 2000: 50). This patent had almost identical wording to Ravenscroft's and was probably for a similar or identical glass.

The Savoy glasshouse was taken over by Francis Ravenscroft (George's brother) on 20th August 1676 and the lease notes that the fuel to be used was wood not coal (Rendel 1975: 68), despite the James I proclamation which banned the use of wood. The restriction on the use of coal at the Savoy was one which was in force throughout the city of London, and had been enforced for centuries (Watts 1990: 208).

Ravenscroft's Patent

On the 8th March of 1674 George Ravenscroft petitioned for a patent for glass production (Blackburne Daniell 1904: 194). As the Duke of Buckingham still held, in theory at least, a patent for the production of fine vessel glass, the petition received a detailed examination from the Attorney General Francis North (MacLeod 1987: 789). Ravenscroft claimed to have 'attained to the art and manufacture of a particular sort of Cristaline Glasses resembling Rock Cristall, not formerly exercised or put into use' (MacLeod 1987:789). The patent was for drinking glasses and specifically excludes mirrors as well as,

> other sorts of glasse of ancient fabrick, at present and for many years practiced or any other sort of glasse that shall be made by others
> (MacLeod 1987: 789)

Unusually, Ravenscroft asked for a patent to run for seven years rather than the usual 14 years. He also offered to lower the price of the glass once he had recovered his initial capital. North reported favourably on the patent application on the following day (9th March 1674), saying,

> [I] find that the glass mettle mentioned in the petition is of a finer sort, and made of other ingredients, than any other glass-houses in England have used, and in that respect may well be esteemed a new invention . . . the glasses thereby made do equalize if not excell those that are imported from Venice and France
> (MacLeod 1987: 789)

The King approved the application on the 19th March (Blackburne Daniell 1904: 206) and the patent was formally issued on the 16th May 1674 for a period of seven years. The patent states that Ravenscroft had produced “a perticuler sort of christaline glasse resembling rock christall” but provides no information about the composition of the glass or the techniques used in its manufacture (Hartshorne 1968: 454–6).

Ravenscroft’s patent is not unusual for its time in the lack of specific detail about the ingredients used and the method of turning these into glass. At this time patents were regarded as enabling instruments which gave the patentee a theoretical guarantee of exclusivity (MacLeod 1987: 784–5). Indeed there was little point in providing a detailed account of how the glass was made as there would be serious problems if it was necessary, at a later date, to prove that the patent had been infringed. Analytical chemistry was not sufficiently advanced in the late 17th century to allow the accurate assaying of the raw materials used in glassmaking, let alone the finished glass. In addition, the composition of raw materials often varied and slightly different materials could have been successfully substituted to achieve very similar ends. In theory, Ravenscroft would have been in a better position to maintain exclusivity for the glass if he concealed how it was made. The purpose of the patent may have been primarily as a defence against potential prosecution by the Duke of Buckingham.

Ravenscroft’s agreement with the Glass Sellers

The London Company of Glass Sellers saw that there was considerable potential in this patent and entered into an agreement (27th April 1674). The 1674 agreement does not survive but much of it was repeated in later agreements. The agreement with the Glass Sellers stipulated that they would buy all of Ravenscroft’s glass but that he would produce glass only for them (Charleston 1984: 111). In addition Ravenscroft was to have only one furnace with two ‘chairs’ (i.e. two teams of glass blowers).

The 1674 agreement, as well as later agreements, often stress that Ravenscroft’s glass was genuinely different to that produced by others: it was, ‘a sort of fine cristaline glasses in resemblance to rock crystal, far beyond any other used’ (MacLeod 1987: 790). The Company took a key role in the production of vessels and requested that one of its employees should specify the exact form, ‘Mr Moore knows better what is fitter to be made for the Trade both as to ffashion and size’ (Hartshorne 1968: 451).

The agreement with the Glass Sellers was renegotiated in September 1674 and Ravenscroft was allowed to set up a second glasshouse at Henley-on-Thames, with one furnace and two chairs (Charleston 1984: 111). The purpose of the Henley glasshouse is not clear but most have suggested that it was associated with the emerging problems of crizzling (more of which below). It has been suggested that Henley could have provided a more secluded location for further experiments with the batch ingredients in order to solve the crizzling problem (Barington-Haynes 1959: 159; Thorpe 1949: 156; Wilkinson 1968: 105). Alternatively, experiments may have continued at the Savoy while Henley produced alkali-based *cristallo* to meet the agreement with the Glass Sellers (MacLeod 1987: 792). It has also been suggested that Henley was a means to expand production beyond that agreed with the Glass Sellers, as the control of the Savoy glasshouse passed to Ravenscroft’s brother Francis (Watts 1975: 75). The Savoy glasshouse probably closed by May 1677 as it is not mentioned in the agreement with the Glass Sellers which restricted

Ravenscroft to a single furnace and Henley is mentioned in subsequent newspaper adverts.

Crizzling, Henley-on-Thames and Dr Plot

The first record of a problem with the crizzling that was occurring to Ravenscroft's glass is on the 3rd June 1676 when the *London Gazette* carried an advert which stated that the crizzling problem had been solved. Crizzling is a form of glass corrosion in which a network of fine cracks appears in the surface of the glass. As encountered by modern archaeologists and museum curators, this is usually a problem which has appeared in glass in the centuries since it was first manufactured. In this case, however, the crizzling seems to have appeared within months of manufacture. The fault must have taken at least a month or two to show itself; otherwise Ravenscroft would have been unable to sell glass or enter into an agreement with the Glass Sellers. The September 1674 agreement makes no mention of crizzling but many have interpreted the Henley glasshouse as a site for experimental work to solve the crizzling problem. That crizzling was a problem in 1674/5 is confirmed by the contemporary account written by Dr. Plot and published in April 1676. The relevant section of Dr Plot's *The Natural History of Oxfordshire* is quoted at length in Charleston (1984: 112). This states that 'the invention of making glasses of stones or other materials' was introduced into England by Da Costa, that Ravenscroft held the patent and that the glass manufacture was carried out by Hawley Bishop. Plot also says that the glass suffered from 'that unpardonable fault called crizzling'. Plot says that the glass had been made using calcined flints and a white sand and that to each pound of silica was added two ounces of nitre, tartar and borax. Plot implies that 'the ingenious Dr Ludwell' played some role in determining the batch composition but the meaning is unclear. Dr Ludwell (like Plot, Hooke, Wren and Merrett) was a member of the Royal Society with an interest in chemistry. It is certain that the limitations of late 17th century chemistry would not have allowed Ludwell to analyse either the mixed batch ingredients or the finished glass. Watts (1975: 73) has suggested that Ravenscoft and Bishop were manufacturing glass using a recipe devised by Ludwell but this is contradicted by Plot's statement that Da Costa introduced the technology. Alternatively Ludwell may have heard of the glass recipe used at the Savoy in 1673–74, experimented with it and then confirmed that it worked.

Plot's account states that the glassmakers were attempting to cure the crizzling problem by substituting imported quartz pebbles from Italy for the flints that had been used and reducing the proportion of alkalis. Plot is clearly of the opinion that the change in the source of the silica can have had little effect on crizzling and suggests that it is the 'abatement of the salts' which has cured the crizzling. Recent research into the crizzling phenomenon (more of which below) has shown that it is caused by the absence of stabilisers. Magnesia (MgO), lime (CaO) and lead oxide (PbO) can all act as stabilisers in glass but are not mentioned by Plot (or by Hooke when describing the Savoy glasshouse in 1673).

The list of fluxes added to the silica (nitre, tartar and borax) is identical to that given by Hooke for the Savoy glasshouse in 1673 and suggests that they were used in the manufacture of early Ravenscroft glass. Nitre (or saltpetre) is potassium nitrate (KNO_3) and was imported from India, primarily for use in the manufacture of explosives for military use (Watts 1990). Neri seems to use saltpetre only in the manufacture of nitric acid and not glass (Cable 2001). Mansell made some use of saltpetre as early as 1639 (Godfrey 1975: 158–9) but for what purpose is not clear. In 1666 saltpetre was supplied to the Duke of Buckingham's glasshouse at Vauxhall, but again the use to which it was put is not clear. The importing of saltpetre had been a Royal prerogative but in 1672 it became available commercially. Saltpetre was convenient both as a cargo and ballast for the sailing vessels making the trip from India to Europe. Tartar is potassium hydrogen tartrate ($KHC_4H_4O_6$) which forms naturally during the fermentation of grape juice into wine and crystallizes in the wine casks. Neri recommends the use of small amounts of tartar in the purification of the alkaline salt (Cable 2001: 61) as well as in some recipes for coloured glass used to make imitation gems. Borax, or sodium borate ($Na_2B_4O_7.10H_2O$), occurs as an evaporite deposit and was imported (e.g. from Tibet). Neri does not mention the use of borax but Kunckel's German translation of *The Art of Glass* (1679) does contain recipes for imitation gems using borax.

The ingredients given in the Plot account would give a glass containing the oxides of boron, sodium, potassium and silicon. The exact proportions of these oxides in the glass would vary depending on their purity and the extent to which they were calcined (Table 1). It has been widely accepted (e.g. Watt 1975: 76) that the recipe given by Plot would only produce a glass at excessively high temperatures (i.e. above 1300°C) which would be impractical for commercial glass production. However, this only applies if the ingredients received limited or no calcining. If the borax was calcined to the anhydrous form and the tartar to the oxide then it would be possible to form a glass at temperatures below 1300°C; temperatures that were regularly achieved in 17th century furnaces (Dungworth 2003: 37–9). Neri stresses the importance of calcining all raw materials and when referring to tartar qualifies it as 'well calcined' or even 'burnt' (Cable 2001: 248).

Table 1. Proportions of the oxides of boron, sodium, potassium and silicon in glasses made using the recipe given in Plot. The melting temperature (T_m°C) are estimated from Levin et al. *(1956: figures 6, 16, 227–9).*

Processing	**B_2O_3**	**Na_2O**	**SiO_2**	**K_2O**	**T_m°C**
No ingredients calcined	4.0	1.8	87.9	6.3	1460
Borax calcined	7.2	3.2	83.6	6.0	1370
Tartar calcined to carbonate	3.9	1.7	84.5	9.9	1390
Borax calcined and tartar calcined to carbonate	7.0	3.1	80.5	9.5	1300
Tartar calcined to oxide	3.7	1.6	80.1	14.7	1290
Borax calcined and tartar calcined to oxide	6.6	2.9	76.4	14.0	1210

Thorpe (1949: 157) believed that the Ravenscroft patent covered a glass which did not contain lead, and that lead only began to be added in late 1674 and early 1675 to cure the crizzling problem (cf. Barrington-Haynes 1959: 160). There is no documentary evidence to show that lead was added to the glass for which Ravenscroft obtained a patent. The accounts given by Plot and Hooke suggest that the glass was initially a borate-soda-potash-silica glass. More recent opinion, however, has tended to assume that even before 1675 and the emergence of the crizzling problem Ravenscroft's glass contained some lead (e.g. Watts 1975). Watts (1975: 72) argues that the timescale between the granting of the patent in 1674 and the public announcements that the problem had been cured in 1676 is too short to allow for radical changes to the glass batch composition (cf. MacLeod 1987: 779) and that the addition of even small amounts of lead would help to reduce the melting temperature of the glass. Watts argues that the glass as patented in 1674 contained a small proportion of lead, this glass later suffered from crizzling, and the problem was solved by increasing the proportion of lead oxide (cf. Moody 1989: 192). However, the idea that lead must have been present in Ravenscroft's glass in 1674 is predicated on a simplistic calculation of the batch composition of the Plot glass. If both the tartar and the borax were thoroughly calcined before weighing and inclusion in the batch, then it would be perfectly possible to make a glass using the Plot recipe. This would be 'just a potash borosilicate of unusual purity and transparency' (Moody 1989: 192). However, it would contain no network stabilisers and would tend to suffer from crizzling.

On the 18th September 1675 Ravenscroft was authorised by the Company to sell £400 worth of his stock of 'flint' glass made before 1st August of that year outside of England (Hartshorne 1968: 451–2). This implies that the quality of the glass made before the 1st August was noticeably worse than that made after and that it was no longer fit for the English market. On the 3rd June 1676 the Glass Sellers issued a certificate to the King and repeated this with adverts in the *London Gazette* to,

> certify and attest that the defect of the flint glasses (which were formerly observed to crissel and decay) hath been redressed severall months agoe and all the glasses since made have all proved durable and lasting as any glass whatsoever.
> (Charleston 1984: 113)

The advert is signed by Samuel Moore (the Company's representative) and Hawley Bishop and also mentions the 'distinction of sound discernible by any person whatsoever', which may be one of the earliest references to the ring produced by lead crystal when struck. The advert was repeated in July, October and November of 1676 and in October and November the advert also says that 'a seal or mark hath lately been set on them for distinguishing them from the former fabric'. The seal is not described and some of the plain seals on extant vessels may be examples from this period. Ravenscroft signed a new agreement with the Company on the 29th May 1677, which specified the use of a raven's head as the design for the seal. This agreement also restricted Ravenscroft to a single furnace with three chairs. It is usually assumed that it was the Henley glasshouse that was closed down as there is no further mention of it but the Savoy site is mentioned in subsequent newspaper adverts (Charleston 1968: 159; 1984: 125–6).

On 30th August 1678 Ravenscroft gave the Company six moths notice of his intention to terminate the agreement. Ravenscroft is likely to have continued producing glass at the Savoy for the Glass Sellers until February 1679, despite the fact that his patent would not expire until May 1681. The reasons for Ravenscroft terminating the agreement are not recorded but he continued to supply plate glass for looking glasses and coach windows (Moody 1988: 200).

After Ravenscroft

In anticipation of the termination of the agreement with Ravenscroft, the Glass Sellers signed an agreement in 1678 with two London glassmakers (Michael Rackett in the Minories and John Bowles and William Lillington in Stoney Street) for the supply of 'white glasses'. It is not clear whether Bowes and Lillington would have made alkali glass for the Glass Sellers or lead glass. On 22nd February 1682 (i.e. after the expiry of Ravenscroft's patent) the Glass Sellers entered into an agreement with Hawley Bishop for the supply of flint glass using Ravenscroft’s old premises at the Savoy. Hawley Bishop had worked for Ravenscroft and must have been familiar with the necessary ingredients. It is likely that both Bishop and other London glass producers began making lead glass after the expiry of Ravenscroft’s patent. Some glass makers appear to have continued to make high-quality glass using alkali fluxes. Henry Holden (a glass maker by royal appointment) advertised his wares as being ‘without any noxious ingredients’ which may be a reference to the fact that he did not use lead oxide.

Manufacture of lead glass spread outside London in the years that followed the expiry of Ravenscroft’s patent. Both Thorpe (1949: 161) and Vose (1980: 120) provide dates for lead glass production starting in Bristol and Newcastle-upon-Tyne in the 1680s and 1690s but without citing evidence (and sometimes contradicting each other). The archaeological evidence from the glasshouse at Silkstone, South Yorkshire (Dungworth 2003) shows production changed from a mixed alkali ‘white’ glass to a lead glass during the 1680s. The Glass Sellers sought to ban imports of so-called ‘country’ glasses into London during the 1680s. They argued that the ‘country’ glasses were of inferior quality and that the London consumer needed to be protected. It is perhaps more likely that those most in need of protection were the members of the Company of Glass Sellers.

It has been widely accepted that Ravenscroft increased the proportion of lead oxide (ultimately to 30%) in order to solve the crizzling problem (Barrington-Haynes 1959: 159–161; Charleston 1984: 115; Newton & Davison 1989: 60; Vose 1980: 118; Wilkinson 1968: 105) and that later glassmakers may have continued to increase the lead oxide content (Thorpe 1949: 158).

A national picture of English glassmaking in 1696 is provided by John Houghton’s *Letters for the Improvement of Commerce and Trade* (Hartshorne 1968: 457–8). Houghton lists 88 glasshouses, of which as many as 27 were producing flint glass. Houghton also recalls ‘the time when the Duke of Buckingham first encouraged glass plates and Mr. Ravenscroft first made flint glasses’. He also gives some information about the ingredients used in making flint glass,

> Our glass men for making the best flint glass use instead of powdered flints a very white sand such as we strow upon writing which is commonly brought from Maidstone in Kent & Isle of Wight, the common sand from Woolwich &c. with this sand and well purified potash the best christal glass is made.
> (Hartshorne 1968: 457–8)

Unfortunately, Houghton does not mention to use of lead in flint glass. However, documents prepared by glassmakers who petitioned Parliament for the appeal of the 1695 Act which taxed glass production, list ingredients produced in England,

> clay, sand, ashes, kelp, maggenees, coals, wood, and red and white lead
> (Buckley 1914: 54)

The 1698 will of Abigail Pilmey (who owned the Silkstone glasshouse) also lists red lead among the glassmaking materials (Ashurst 1992: 23).

Pellatt (1849: 34) provides a standard 19th century recipe: 1 cwt. carbonate of potash, 2 cwt. red lead or litharge, 3 cwt. sand washed and burnt, 14–28lbs.

saltpetre, 4–12oz. oxide of manganese. This would give a glass containing 12–14% K_2O, 51–53% SiO_2 and 34–35% PbO. Writing in the early 20th century, Marson gives a recipe for lead crystal which would contain 12% K_2O, 53% SiO_2 and 35% PbO (Marson 1918: 25). Modern lead crystal is usually manufactured to British Standard 3828, which provides compositional requirements for 'lead crystal glass' and 'full lead crystal glass'. The standard stipulates that lead crystal should contain at least 24% PbO and no more than 15% alkali oxides (with the sum of the alkali metal oxides, other than K_2O, not exceeding 2%). Full lead crystal should contain at least 30% PbO and no more than 12% alkali oxides (with the sum of the alkali metal oxides, other than K_2O, not exceeding 1%).

Previous Analytical Work

Very little scientific work has been carried out previously on late 17th century lead glass and most of the work which has been done provides limited information on the chemical composition.

Table 2. Lead oxide content of early lead glass determined by beta ray backscattering (after Emeleus 1960: table 2)

Date	Specimen	PbO%
c.1677	Sealed Ravenscroft mug	15
c.1677	Sealed Ravenscroft bowl	13
c.1677	Purple Ravenscroft Bottle (unsealed)	15
c.1677	Ravenscroft Jug (sealed)	33
c.1677	Fragment of Ravenscroft glass	18
c.1684	Coin glass (1684 coin in stem)	25
Late17th/early 18th century	Glass	23
Late17th/early 18th century	Covered glass	33
Late17th/early 18th century	Covered glass	33
Late17th/early 18th century	Medicine bottle	20
Late17th/early 18th century	Cruet	50+
Late17th/early 18th century	Bird fountain	30
Late17th/early 18th century	'God save Queen Ann' glass	27
Late17th/early 18th century	'God save King George' glass	23
Early 18th century	Coin glass (date on coin 1711)	25

Emeleus (1960) proposed that beta ray backscattering could be used to determine the lead oxide content of glasses and glazes and published the lead oxide results for fifteen late 17th century and early 18th century lead glasses (Table 2). Emeleus concluded that early lead glass (i.e. Ravenscroft glass) had lower lead oxide contents than later lead glasses. The beta ray backscattering method provides no information about the identity or quantity of other components in the glass (e.g. silica, alkalis or impurities).

Watts (1975) measured the specific gravity of seven lead glass vessels and from this estimated the lead oxide content of the glass (Table 3). The S-sealed vessel examined by Watts was sampled and analysed for this project (Sample 26). He suggested that the lead oxide content of early lead glasses increased over time. Estimating lead oxide content from specific gravity is a fairly imprecise method as the specific gravity may be affected by other components in the glass. Indeed, Watts' initial estimates of lead oxide content were lower than given in table 3 but he adjusted the values to take into account the boron that he presumed was in the glass.

Table 3. Lead oxide content of early lead glass estimated from specific gravity measurements (Watts 1975)

Site/Museum	Description	Date	PbO%
V&A	Roemer (raven's head seal)	1674–1676	12.5–14.5
V&A	Wine glass (S seal)	1677–1681	12.5–14.5
Nonsuch	Wine glass (raven's head seal)	1680–1681	25
London	Wine glass, hollow ribbed stem	1681–1685	27
London	Wine glass	1681–1685	30
London	Wine glass	1681–1685	30
London	Wine glass	1681–1685	30

Mortimer (1991) analysed a late 17th century tapered stem vessel with a plain seal found at Billingsgate (this vessel is re-analysed here, sample no. 18). The vessel was crisselled with a yellowish tint and the chemical composition included 20% PbO, 13% K_2O and 63% SiO_2.

Lead glass working waste from the two late 17th century to early 18th century Yorkshire glasshouses excavated by Ashurst have been analysed. At Gawber a lead glass was found adhering to the inside of one of the early 18th century crucibles (Ashurst 1970). At Bolsterstone (Ashurst 1987) a variety of lead glasses may have been produced (Table 4). Three of these samples correspond well with the analytical results of the present programme (see below). The last two analyses in Table 4 do not match any of the lead glasses analysed here.

Table 4. Analyses of lead glass waste from Gawber and Bolsterstone (Ashurst 1970; 1987)

Site	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	PbO
Gawber	0.3	0.1	1.5	53.0	7.5	0.5	0.18	34.4
Bolsterstone	0.2	0.1	0.6	57.2	11.3	0.2	0.11	29.8
Bolsterstone	0.3	nd	0.3	55.1	7.8	0.6	nd	38.8
Bolsterstone	0.3	0.1	0.9	51.0	6.7	0.2	0.22	39.6
Bolsterstone	11.4	nd	nd	65.4	3.6	1.9	nd	17.7
Bolsterstone	12.0	nd	nd	65.1	3.7	2.0	nd	18.9

Recent excavations at the glasshouse at Silkstone, Yorkshire (Dungworth 2003; Dungworth & Cromwell forthcoming) that was operated between *c*.1660 and *c*.1700, recovered evidence for the production of lead glass. Numerous samples of vessel glass and glassworking waste were analysed using the same technique used for this project. This work showed that lead glasses replaced mixed alkali glass for the production of (non-bottle) vessel glass *c*.1680. Much of the analytical data from Silkstone is discussed below.

There are fewer published analyses of late 17th century glass outside England. Analytical work has established that 'Bohemian' crystal glass developed was a high-purity lime-potash silica glass and from the early 18th century Dresden glass contained minor (1–8%) amounts of lead oxide (Haase *et al*. 1987). Analyses of 16th and 17th century vessel glass from Amsterdam by Bronk *et al*. (1999) has shown that two are lead glasses. Unfortunately it is not known precisely when these two examples were produced.

Sample Selection

The aim of this research was to investigate the composition of glass vessels manufactured during the period 1665–1690 in order to shed light on the nature of the glass ‘invented’ by George Ravenscroft *c*.1674. To achieve this aim a range of glass vessels were selected for analysis (Table 5).

Table 5. Provenance and type of materials sampled
(NB. Three vessels from Guildford and two from Wells were sampled twice; one sample from the foot and one sample from the bowl of each vessel.)

Location	Vessel	Working waste
London	21	
Guildford	11	
Wells	4	
Oxford	1	
Northampton	1	
Hull	1	
Dublin	4	8
Jamestown, America	1	
Port Royal, Jamaica	13	
Total	**57**	**8**

Table 6. Vessels and samples with seals

Seal	Samples	Vessels	Sample numbers
Raven’s head	5	4	25, 30, 84, 101/102
S	2	2	26, 41
N	1	1	32
Boar/Bear	1	1	4
Bow & Lilly	1	1	27
Plain	2	2	18, 83
broken, missing, unidentified	6	4	19, 113, 42/115, 43/116
Total	**18**	**15**	

Chronology is the key to understanding what Ravenscroft may have invented and good evidence for date was the most important criterion in selecting samples.

- Vessels found in archaeological contexts can be dated by the artefacts or ecofacts they are found with (e.g. clay pipes and dendrochronology). In most cases, however, the archaeological dating of contexts is fairly imprecise.
- Some vessels have been found in hoards but many of these are from public houses and contain material which accumulated over a long period of time. The Gracechurch Street hoard is believed to be from a shop that burnt down in the Great Fire of London (1666), however, the hoard is not fully published.
- The surviving records of John Greene (in particular the drawings) provide information about glasses imported to England between 1667 and 1680 (British Museum, Sloane MSS 857, these have not been published in full but see Hartshorne [1968: plates 30–32] for a selection).

- The practice of adding seals to vessels was extremely short-lived; the earliest reference to the practice is in 1676 while the latest is 1684 (Charleston 1984: 124–5).
- The form of glass drinking vessels in the 17th century varied (Brain 2000). The shapes of the bowls and the feet of vessels remained fairly constant but the form of the stem joining the foot and bowl varied considerably. Some of these changes in vessel form are chronologically significant.

Samples were taken from drinking glasses which clearly dated before, during and after Ravenscroft's patent. Drinking vessels contemporary with Ravenscroft's patent included many examples with seals, including the famous raven's head seal.

Scientific Techniques

Sample Preparation

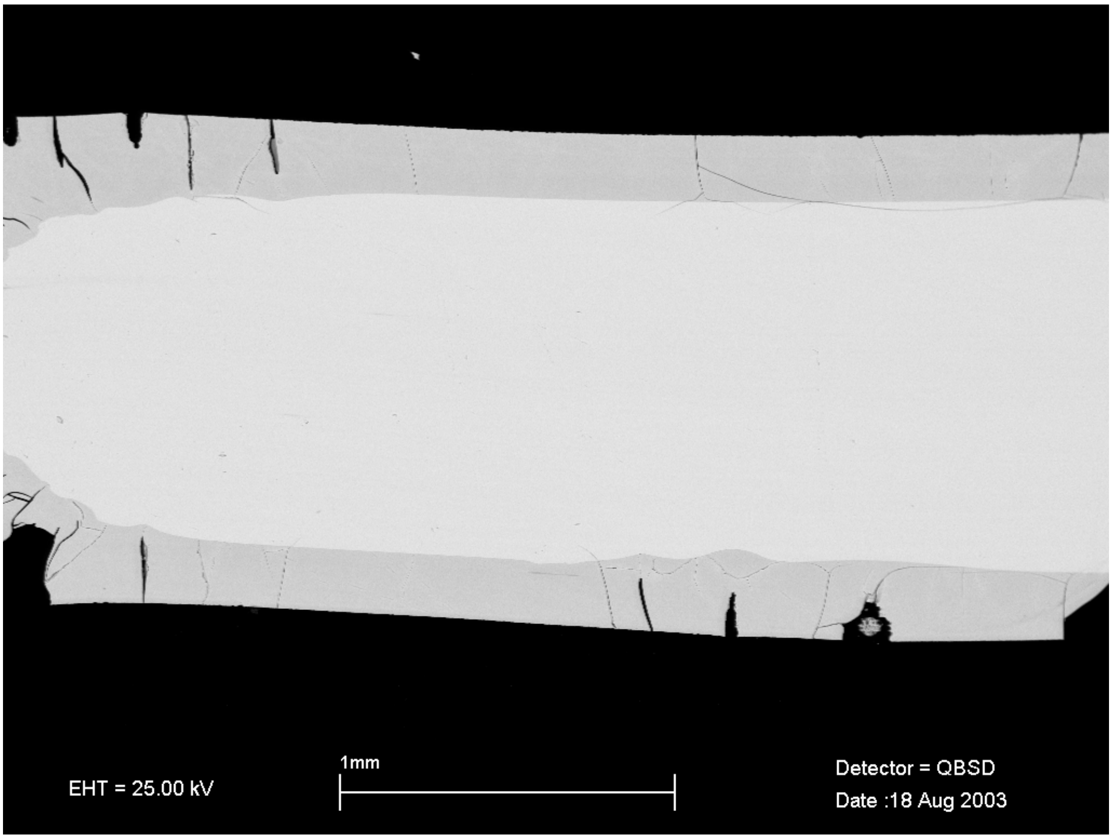

Figure 1. SEM image (back scattered electron detector) of crizzled lead glass (sample 37). The crizzled surface layer clearly shows as a slightly darker grey layer (with cracks) surrounding the core of uncorroded glass.

In order to fully understand the nature of the glass produced during this period it was necessary to determine its chemical composition. This cannot be achieved by analysing the surface of extant vessels as these may have suffered from corrosion or crizzling, which may have changed the chemical composition at the surface. However, it was also an aim of this research to examine the nature of crizzling in some early lead crystal glass. Therefore samples were taken which would allow the analysis of both the surface and core of a glass. This was achieved by cutting a small fragment of glass from each vessel using high-quality side-cutters. In most cases, the vessels sampled were incomplete or even fragmentary and so sampling in this way does not detract from the aesthetic value of the vessel, e.g. for display in a museum.

The glass samples were mounted in resin in cross-section (i.e. with both unaltered core and weathered or crizzled surface exposed). The mounted samples were polished to a 1 micron finish and carbon coated.

The mounted and polished samples were examined using a Karl Zeiss S440 scanning electron microscope (SEM). Both secondary electron and back scattered electron detectors were used to asses the condition and homogeneity of the samples. The back scattered electron detector was most useful as it allowed the identification of weathered surface layers as well as heterogeneity due to incomplete mixing of the glass. With a back scattered electron detector the brightness of different areas is proportional to their average atomic numbers. Thus corroded layers tend to be darker than the uncorroded core. Figure 1 shows a SEM image of sample 37: the bright central region is the uncorroded glass while the darker grey areas around this are the corroded or crizzled surface of the glass. The chemical composition of the glass was determined by analysing areas of core glass away from the corroded surfaces. If the glass is not homogeneous due to poor mixing of the molten glass then this can also be seen in SEM back scattered electron images (figure 2).

Analytical Technique

The chemical compositions of the samples were determined using an Oxford Instruments energy dispersive X-ray spectrometer attached to the scanning electron microscope (SEM-EDS). The SEM was operated at a voltage of 25kVolts and a probe current of 1.5nAmps. The Oxford Instruments germanium detector allowed for the simultaneous detection of all elements from oxygen to uranium, providing the elements were present above their detection limits (see table 7 for detection limits). Each spectrum was collected from an area approximately 100 by 200 microns for 100 seconds livetime. Each spectrum was calibrated using a cobalt standard and deconvoluted using the Oxford Instruments SEMQuant software (with phi-rho-z correction procedure). This made use of element profiles derived from single element or simple compound standards (pure iron, jadeite, etc). The profiles were standardised against appropriate glass reference materials (e.g. Corning standards). The results for the analysed glasses were not normalised. Table 7 shows the analytical errors and detection limits for the oxides.

Energy dispersive X-ray sprectrometry provides no direct information about the valence state of any elements present (e.g. metallic iron, FeO, Fe_2O_3 or Fe_3O_4). In each case, an appropriate valence state for the analysed material was chosen (largely following the valence state in the Corning glass standards) and the oxide weight percent calculated stochiometrically.

The germanium X-ray detector used to determine the chemical composition of the samples cannot detect the presence of boron. If a large proportion of boron is present in a sample this may be inferred from the low analytical total. The analysis of a fragment of modern pyrex laboratory glassware gave an analysed total of 85%; the missing 15% is likely to be boron oxide. Very few of the historic samples examined here gave analysed totals that were significantly below 100%. An attempt was made to determine if any boron was present in several of the samples using a wavelength dispersive X-ray detector[1], but failed to detect any (i.e. <1wt%).

Table 7. Errors and detection limits for each oxide

	error (1 standard deviation)	detection limit
Na_2O	±0.3	0.2
MgO	±0.3	0.2
Al_2O_3	±0.3	0.2
SiO_2	±0.7	0.2
P_2O_5	±0.1	0.2
SO_3	±0.1	0.2
Cl	±0.2	0.2
K_2O	±0.4	0.1
CaO	±0.3	0.1
TiO_2	±0.1	0.1
MnO	±0.1	0.1
Fe_2O_3	±0.1	0.1
CoO	±0.1	0.1
CuO	±0.1	0.1
As_2O_3	±0.3	0.4
SnO_2	±0.3	0.4
Sb_2O_5	±0.3	0.4
PbO	±0.3	0.4

Homogeneity of Samples

This report contains data about the chemical composition of the glasses examined and interprets differences in chemical composition in terms of recipes. It is therefore important that the analytical data provides a reliable indication of the composition of the glass.

The SEM images of the glass samples provide direct information about the homogeneity of the glass and in most cases the glass appears to be completely homogeneous. An example of the most heterogeneous glass (sample 19, see figure 2) was examined in detail in order to quantify the degree of heterogeneity. Linescans for lead oxide and potash through sample 19 (figure 3) show that the chemical heterogeneity of the glass (variance of 0.4–0.5wt%) only slightly exceeds the analytical precision (standard deviation of ±0.3–0.4) of the technique used (SEM-EDS).

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[1] Thanks to Oxford Instruments, High Wycombe for this work.

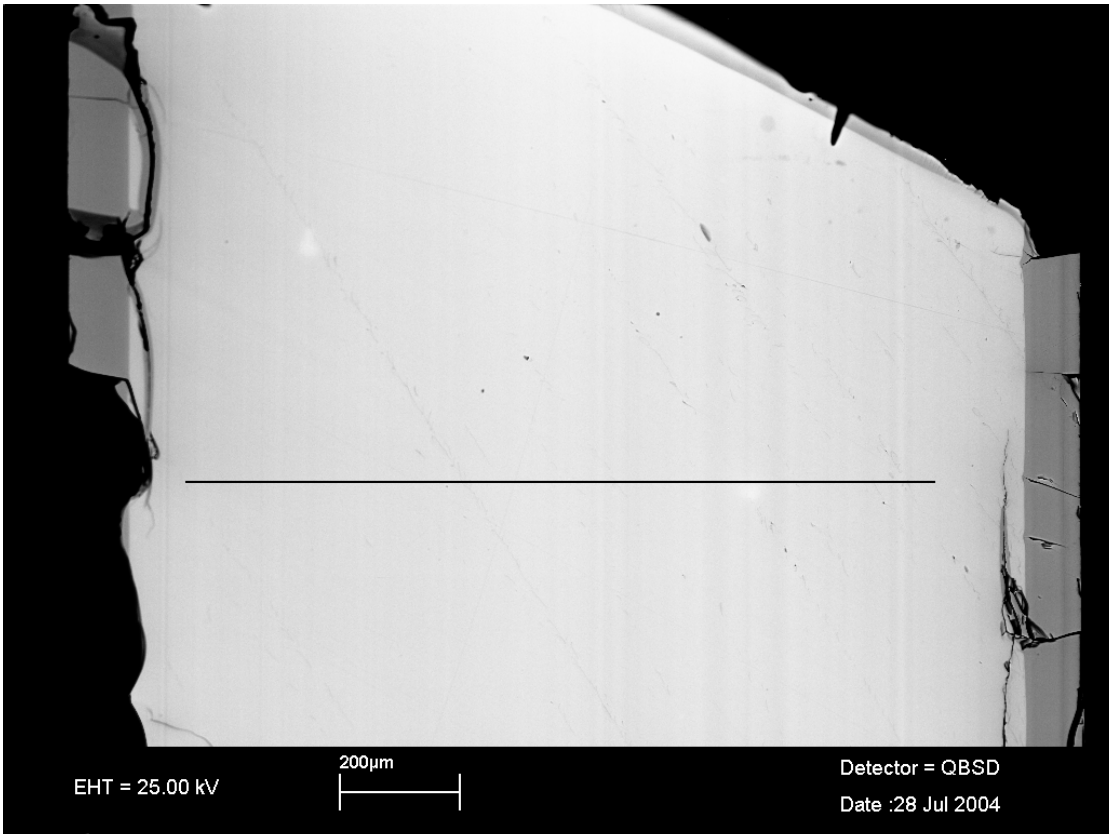

Figure 2. SEM image (back scattered electron detector) of sample 19 showing surface corrosion (dark grey layers to the left and the right) and some heterogeneity (slightly darker vertical lines within the glass. The horizontal black line shows the position of the linescans (see figure 3)

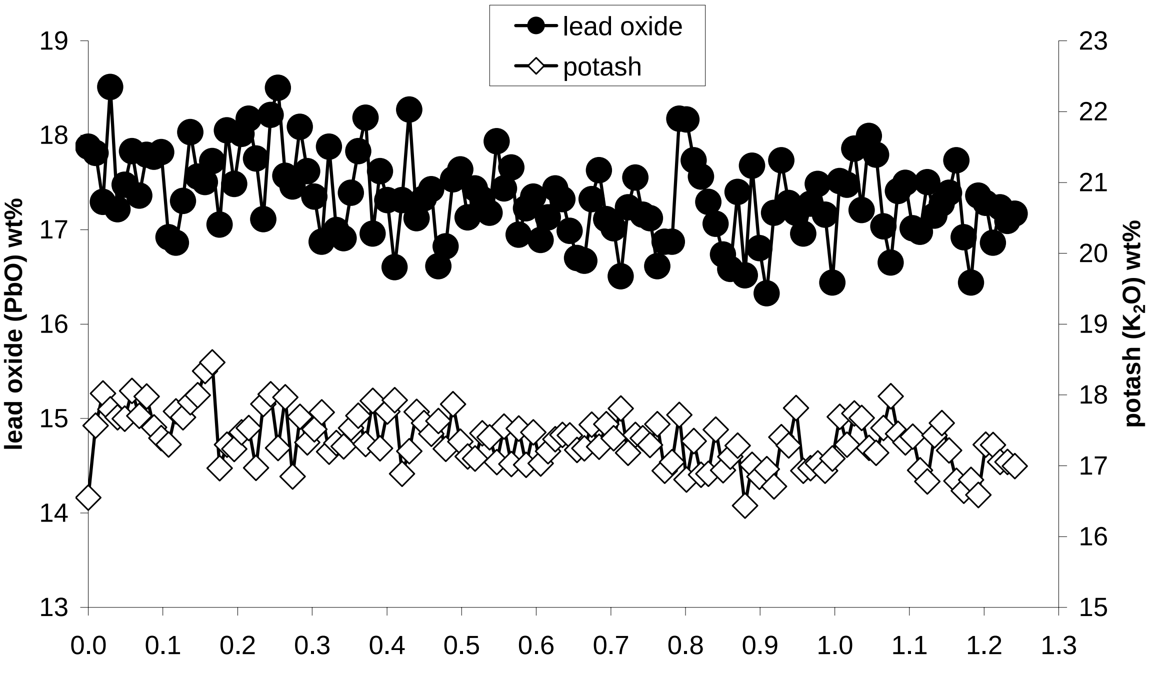

Figure 3. Linescan through sample 19 (for position of linescan see figure 2).

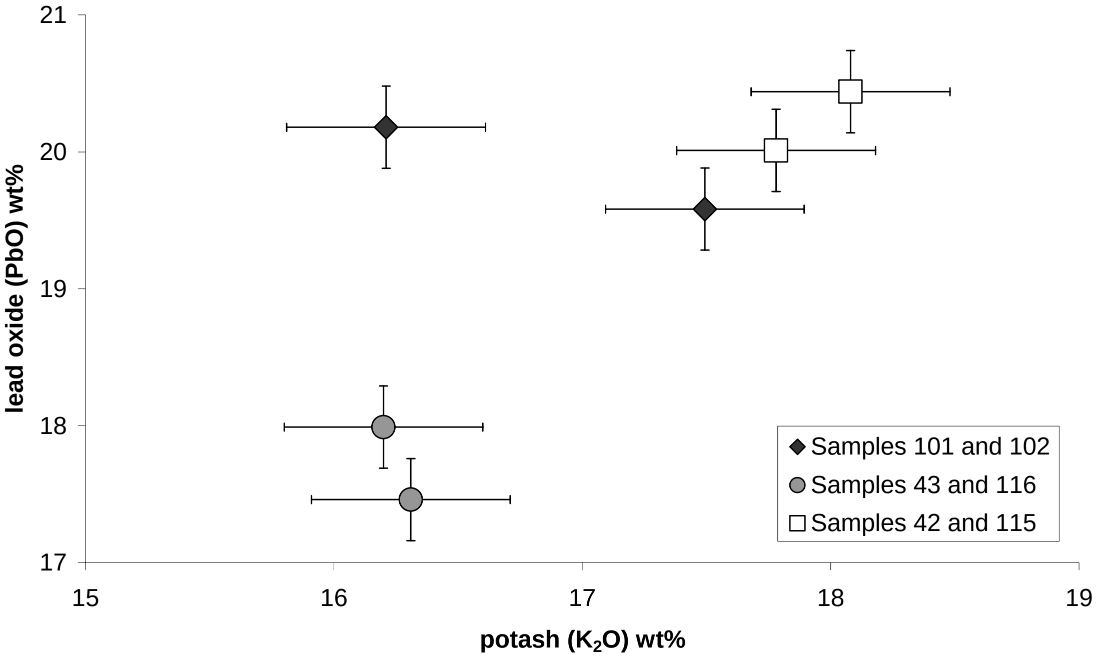

Figure 4. Potash and lead oxide contents of six samples taken from three vessels. The error bars show a single standard deviation (i.e. 68% probability).

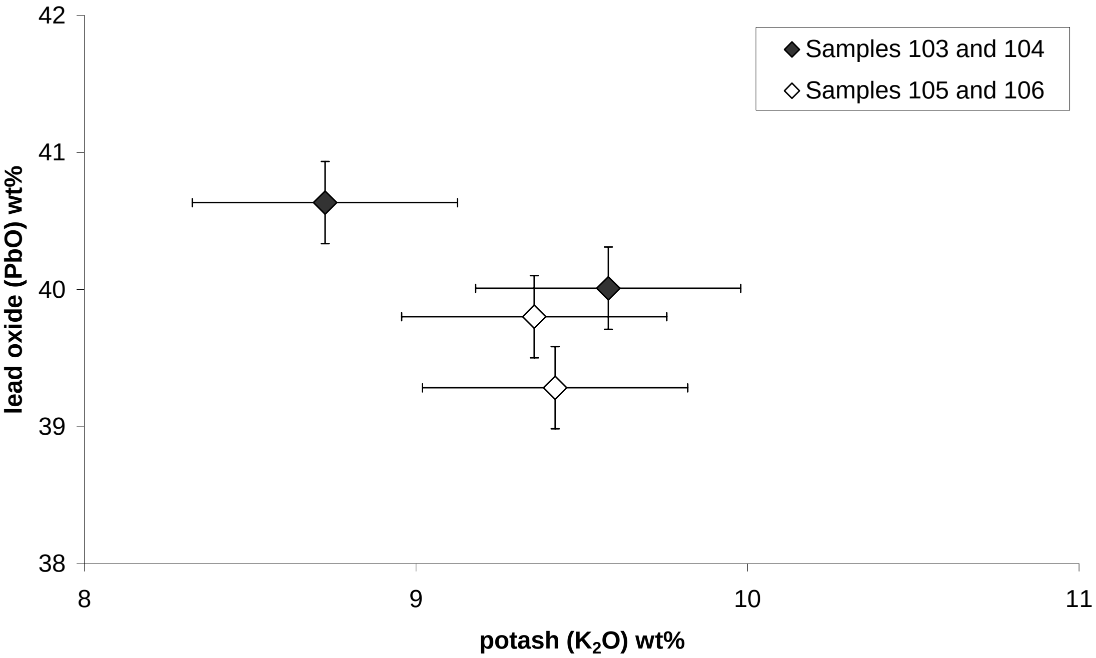

Figure 5. Potash and lead oxide contents of four samples taken from two vessels. The error bars show a single standard deviation (i.e. 68% probability).

The linescans provide information about the chemical heterogeneity across the samples but the samples are an order of magnitude or two smaller than the whole vessels. An investigation of variation in chemical composition across whole vessels was possible for five vessels, each of which was sampled twice (foot and bowl). In three cases, the two samples were within a single standard deviation (68% probability) and in two cases the two samples were within two standard deviations (95% probability). Therefore, the small samples taken are representative of the vessels as a whole.

Results

Introduction

Of the 52 vessels sampled, 13 are alkali glasses and 39 are lead glasses. The alkali glasses occasionally contain small amounts of lead oxide but usually in such small proportions that it can have had no significant effect on the properties of the glass. The lead glasses are composed almost entirely of silica, potash and lead oxide with very low levels of the oxides commonly found at low levels in alkali glasses (soda, magnesia, lime, phosphorus oxide, etc).

The alkali glasses

The alkali glasses contain varying levels of soda (Na_2O) and potash (K_2O) (figure 6). Some of the samples with high levels of soda have compositions that are similar to Venetian *cristallo* (Verità 1985) while others have compositions that are similar to *façon de Venise* glasses produced in the Low Countries (de Raedt *et al*. 1997) or England (Mortimer 1993). A few of the alkali glasses contain as much (or more) potash as soda and are similar to mixed alkali glasses known to have been produced in England during the 17th century (e.g. Dungworth 2003, Dungworth & Mortimer 2005).

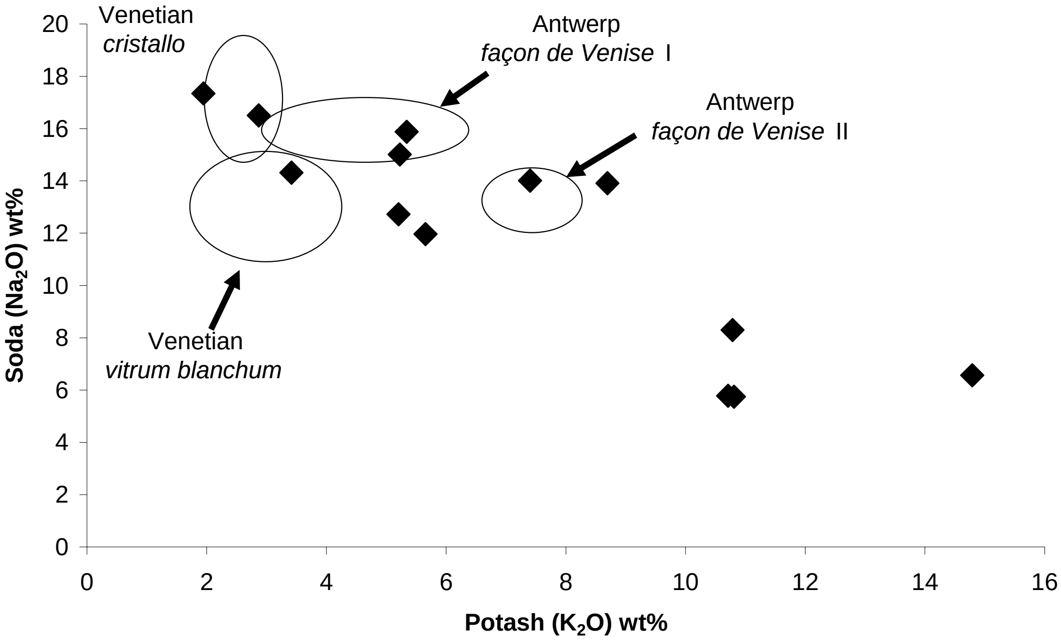

Figure 6. Plot of soda against potash. The ellipses show the compositional limits of Venetian glass (after Verità 1985) and Antwerp façon de Venise *glass (after de Raedt* et al*. 1997).*

The alkali source used for these glasses is likely to have been marine plants rich in soda and potash. Neri (Cable 2001) and other contemporary sources describe the use of *barilla*, that is the ash of salworts such as *Salicornia*, as the alkali source for the finest crystal glasses. Published analyses of *barilla* or *Salicornia* ash (Ashtor & Cevidalli 1983; Brill 1999: Table XXIV C; Wedepohl 2003: table 2A) show soda to potash ratios of between 1:1 and 10:1. An alternative source of alkali was kelp or seaweed ash (Cable 2001: 321–2) which can contain lower soda to potash ratios (e.g. Brill 1999: Table XXIV C; Muspratt 1860: 918) and could give rise to mixed alkali glasses. The degree to which sodium and potassium in an ash would be incorporated into a glass depends on the amount of chlorine and sulphate present. Sodium and potassium oxides and carbonates will quickly react with silica to form a glass, however, alkali chlorides and sulphates tend not to react with silica to form glass. When glass is manufactured from alkalis containing high levels of chlorine and sulphate, an immiscible liquid rich in alkali chlorides and sulphates (called sandever) forms on top of the glass. The sandever had to be scraped off the top before the glass underneath could be used.

The proportion of soda and potash from the alkali that is incorporated into the glass will also vary depending on how the alkali was purified. Alkalis could be purified by washing or they could be burnt. Neri stresses the importance of purifying *barilla*, by washing, before it was used in glassmaking (Cable 2001). The ash was dissolved in water, insoluble material settled to the bottom of the vessel, while the water (containing the soluble fraction from the ash) was decanted and then dried. Experiments with the purification of ashes shows that a wide range of impurities such as magnesium, phosphorus, calcium, aluminium and iron are largely removed (Brill 1999: Table XXIC C; Stern & Gerber 2004). Evidence for the washing of marine plant ashes often can be seen in the iron oxide contents of ashes and Ventian *cristallo* and *façon de Venise* glass; the proportion of iron in the best alkali glasses of the period is much lower than that of the ashes (figure 7). Plant ashes could also be purified by burning which would tend to convert sulphates (and possibly chlorides) into carbonates or oxides. The temperature at which the plants were burned would have a significant affect on the form of the alkalis (chlorides, sulphates, carbonates, oxides, etc) and so influence the degree to which they would react with silica and become incorporated into the glass. Little experimental investigation has been carried out to determine the extent to which soda and potash in ashes (whether purified or not) such as *barilla* or kelp are incorporated into glass.

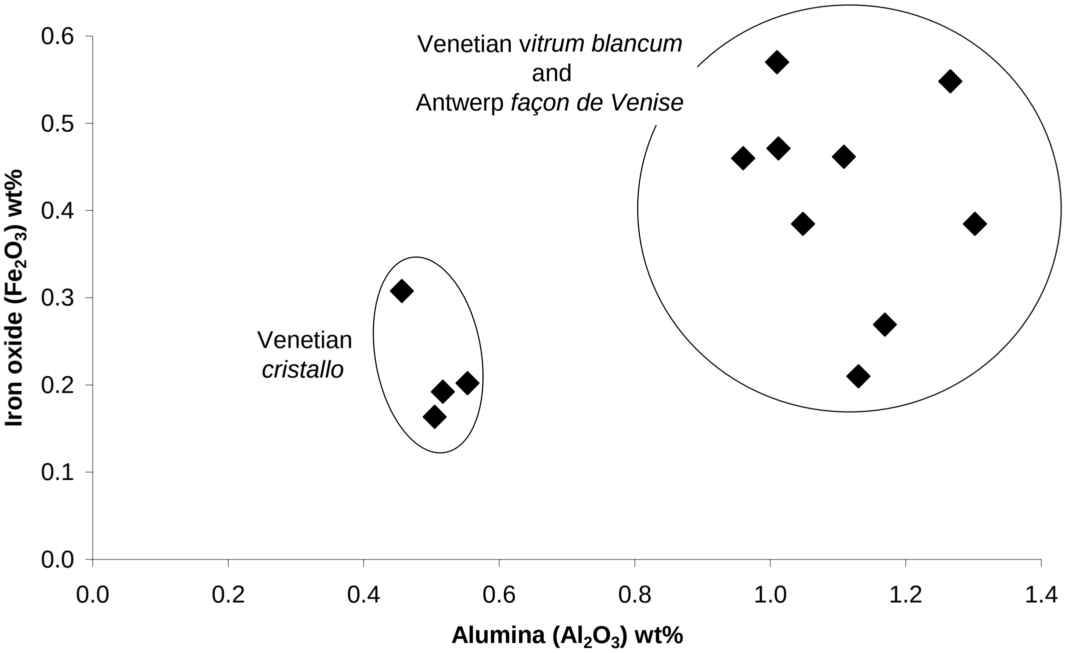

Figure 7. Plot of alumina against iron oxide for the alkali glasses. The ellipses show the compositional limits of Venetian glass (after Verità 1985) and Antwerp façon de Venise *glass (after de Raedt* et al*. 1997)*

The analysed alkali glasses contain varying levels of alumina and iron oxide (figure 7). Four samples contain low levels of these impurities, comparable with the best Venetian *cristallo*, while others have relatively high levels (although still much lower than contemporary ‘green glass’, cf. Dungworth 2003). The distinction between these two groups almost certainly reflects differences in the quality of the alkali and the way in which it was purified.

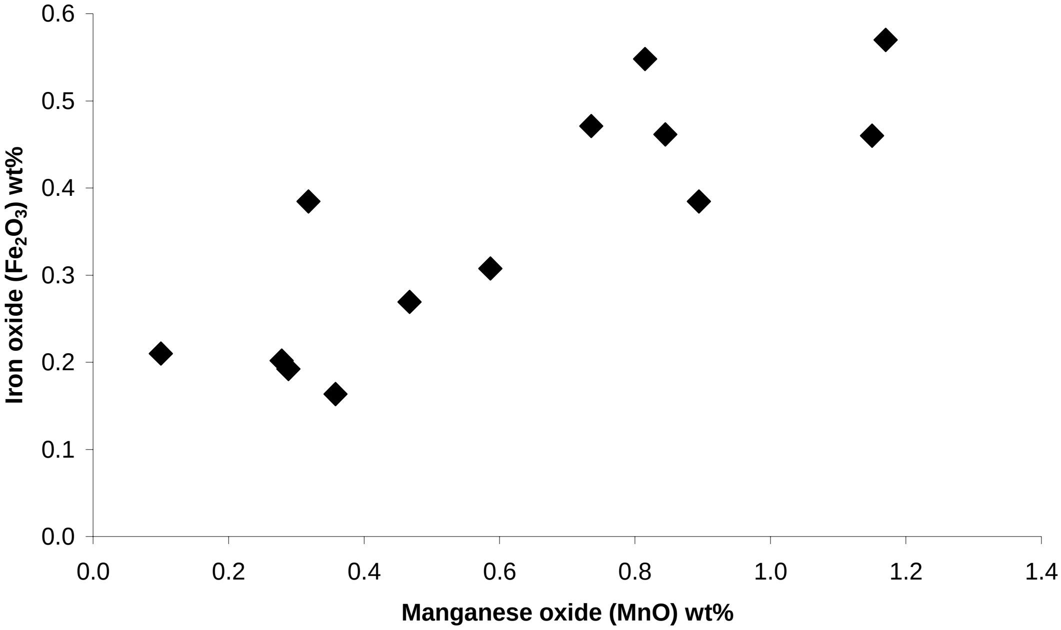

Figure 8. Plot of manganese oxide against iron oxide for the alkali glasses

All of the alkali glasses contain manganese oxide (in the range 0.1–1.2%, see figure 8). Manganese oxide is a minor component in many terrestrial plant ashes (e.g. Sanderson & Hunter 1981) and when found in ‘forest glass’ it is usually assumed to be an ‘impurity’ (cf. Stern & Gerber 2004). However, by at least the 16th century manganese was being used to deliberately de-colourise some glass (Smith & Gnudi 1990: 312). Even where glassmakers used high quality and carefully processed raw materials, these would often contain small proportions of iron oxide which would give the glass a pale green or blue-green colour. Small amounts of manganese oxide make glass pink which would cancel the green/blue-green colour caused by the iron. As long as the glassmakers added the right proportion of manganese, the result would be a colourless glass with slightly reduced transparency. The thirteen alkali glass samples analysed show a strong correlation between iron oxide and manganese oxide ($r^2 = 0.712$) while the other oxides (in particular the alkalis) show no correlation with manganese oxide ($r^2 < 0.3$). Figure 8 shows that the manganese oxide to iron oxide ratio was maintained at around 1.7.

The levels of lime (and magnesia) in the alkali glasses vary across a wide range (figure 9). Lime and magnesia are strongly correlated with each other, and both are positively correlated with strontium oxide, so it is possible that a magnesian limestone was added to the glass. However, the first recorded deliberate addition of lime to glass occurs in the mid 18th century (Cable 2003). Alternatively, these oxides may derive from the raw materials (ash and sand) used. The careful purification of raw materials would tend to remove lime and magnesia and some of the glasses contain very low levels of these oxides.

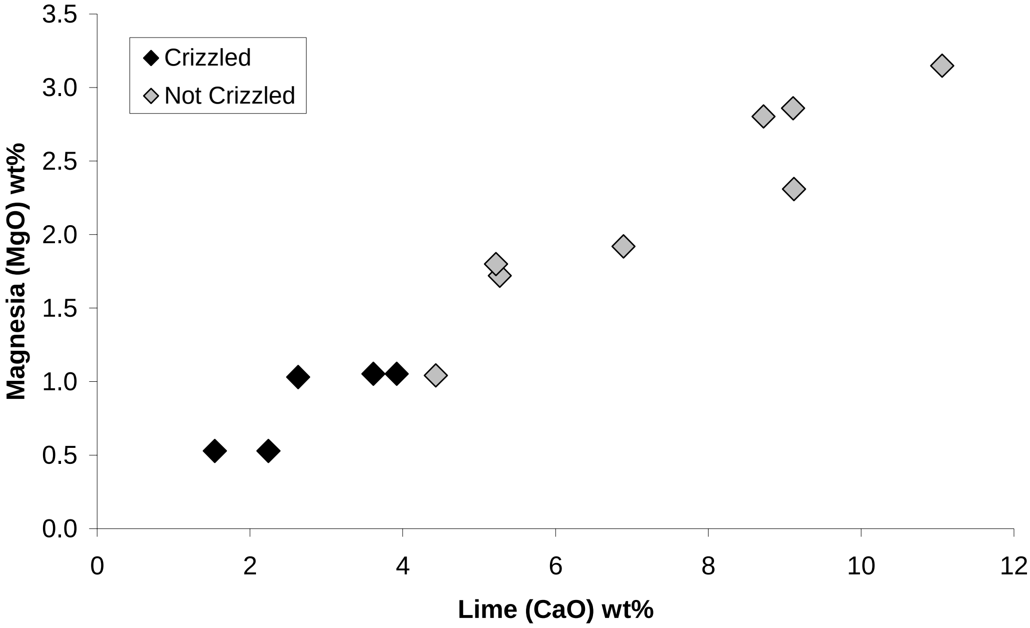

Figure 9. Plot of magnesia against lime for the alkali glass samples

Five of the thirteen alkali glasses analysed here had suffered from the surface corrosion known as crizzling. It is not certain when this became noticeable; whether during the late 17th century or during the centuries since. All of the crizzled glasses contain low levels of magnesia and lime (<5wt% of both combined). The crizzling process and the role of network stabilisers such as lime and magnesia are discussed in more detail below.

Lead oxide was detected in six of the alkali glasses (0.8–10wt% PbO). However, these glass are not lead glasses like those described below: they contain a wide range of elements normally associated with alkali glasses (sodium, magnesium, alumina, chlorine, iron, manganese, etc). In many cases the lead may have been unintentionally incorporated into the alkali glasses due to the use of lead glass cullet. However, one alkali glass vessel sampled (number 40) dates to before Ravenscroft's patent and yet contains 1.6wt% PbO. This is similar to the results for one of the 'white glasses' manufactured at Silkstone prior to the introduction of lead glass (Dungworth 2003). A 'white glass' was manufactured at Silkstone in the 1660s which contained roughly equal parts of soda and potash (a mixed alkali glass), and an average of 1.4wt% PbO. Such a small amount of lead oxide would have had relatively little effect on the physical properties of these glasses. However, it can hardly be accidental in such glasses as a batch (typically 100kg) would have to include 1.5kg of lead oxide.

Four of the alkali glasses have seals, including two with raven's head seals (samples 25 and 30), one boar/bear (sample 4) and one 'bow and lily' (sample 27). The application of seals is mostly strongly associated with Ravenscroft's glass but was also used by other glassmakers from 1676 to *c*.1681. If the raven's head seals are genuine then they show that for at least part of this period, Ravenscroft was producing an alkali glass. It is also possible that some of Ravenscroft's rivals used raven's head seals in an attempt to pass their glass off as Ravenscroft's (Thorpe 1929: 123; 1949: 158).

The analysis of late 17th century drinking glasses reported here contributes to the long-standing problem of distinguishing between Venetian glass and the products of different northern European glassmaking areas. Some of the finest Venetian glass (*cristallo* Verità 1985) is chemically indistinguishable from glass thought to be made in England (in particular the sealed examples as the use of makers seals appears to be restricted to England). The history of glassmaking in northern Europe in the 16th and 17th centuries contains numerous references to the migration of skilled glassmakers from northern Italy to northern Europe. By the seventeenth century crystal glassmakers in northern Europe were using the same raw materials as those in northern Italy (Cable 2001: 308–313; Godfrey 1975: 159). The analysis of the alkali glasses confirms that by the late 17th century English crystal was of a composition that is indistinguishable from the slightly earlier Venetian *cristallo*. In addition, Verità (1985) draws a distinction between *cristallo* and *vitrum blanchum*, the latter contains less soda and higher levels of minor and trace elements. In fact, the composition of *vitrum blanchum* is almost indistinguishable from *façon de Venise* glasses produced in northern Europe. It cannot be assumed that 17th century glasses with chemical compositions comparable with Venetian *cristallo* were necessarily made in Venice.

The lead glasses

A total of 52 of the analysed samples (comprising 8 samples of glassworking waste from Dublin and 44 samples from 39 different vessels) are lead glasses. They are composed almost entirely of the oxides of lead, silicon and potassium (these oxides typically make up 98% of the glass). The minor oxides which are usually present in alkali glasses (e.g. magnesia, phosphorus oxide and lime) are either absent or present at very low levels. The chemical composition of these lead glasses probably reflects the use of pure ingredients: flint (or high quality sand), lead oxide and saltpetre. It is highly likely that saltpetre was the source of the potassium as saltpetre, unlike other sources of potassium, is highly oxidising and so would have prevented the well known problems of lead oxide being reduced to metallic lead and breaking out of the pots. The lead glasses can be divided into four separate groups based on the amount of potassium oxide and lead oxide present (figure 10). Each group is described separately below.

The dating evidence for vessels from each group suggests that the high potash, low lead oxide group is the earliest and that over time less potash and more lead oxide was added. The histograms showing the date ranges of the four groups of lead glasses (figure 11) were arrived at by a process similar to that used for Roman coins (cf. Brickstock 2004). This takes into account the fact that the vessels are dated to (variable) date ranges rather than single years and the number of dated vessels in each group is different. Each vessel contributes a ‘score’ of 1 (divided by its date range) to each year of its date range. The scores for each year are summed and divided by the total number of vessels in the group. This can be illustrated with an example: the group 2 lead glass includes 9 dated vessels assigned to the following dates or date ranges, 1674–1681, 1680–1685, 1680, 1680–1687 (2 vessels), 1682–1692, 1685–1692, 1683–1690, 1676–1690. The first vessel contributes 0.125 (1/8) to each of the years from 1674 to 1681, the second vessel contributes 0.1667 (1/6) to each of the years from 1680 to 1685, the third vessel contributes 1 (1/1) to 1680, etc. The scores for each year for the compositional group (in this case group 2) are summed. The summed scores for each year are divided by the total number of dated vessels (in this case 9) to make comparisons between compositional groups easier.

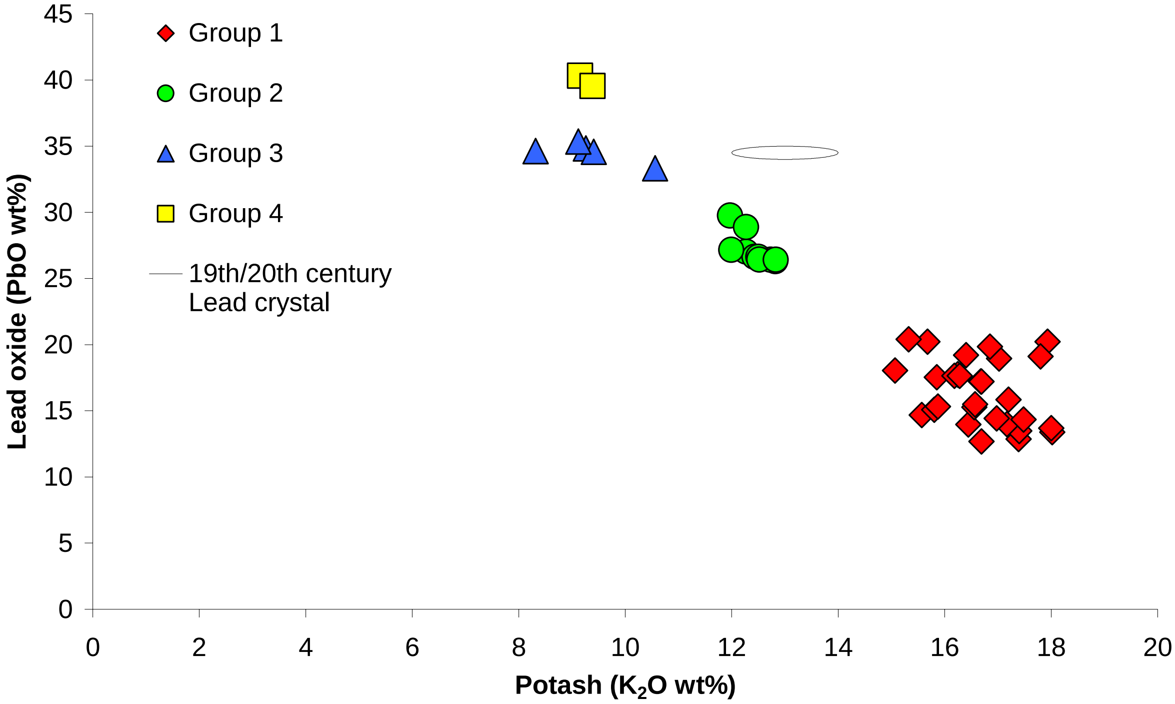

Figure 10. Potash and lead oxide contents of the lead glasses showing the four groups and the range of compositions for 19th and 20th century lead crystal for comparison

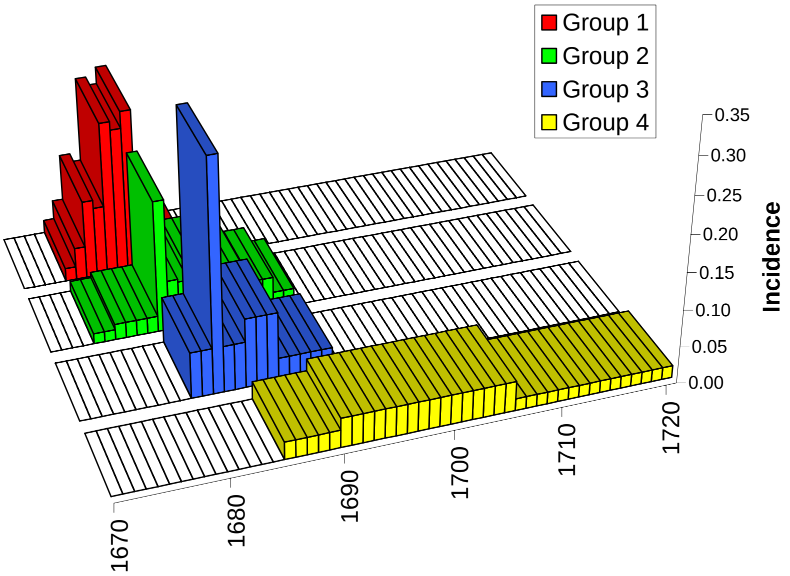

Figure 11. Date range for the four groups of lead glasses

The Group 1 lead glasses

A total of 33 samples of lead glass (comprising 8 samples of glassworking waste from Dublin and 25 samples from 22 vessels) belong to group 1. This compositional group has the lowest levels of lead oxide (12–20% PbO) and the highest levels of potash (15–18% K_2O) of all the lead glass groups (table 8). Thirty of the glasses analysed had group 1 compositions. Previous work on lead glasses shows that a few have lead contents comparable with the group 1 lead glasses analysed here. Watts (1975) estimated that two out of the seven vessels examined had 12.5–14.5% PbO, while Emeleus (1960) determined the lead oxide content of four of the vessels studied as 13–18%. It is possible that two sub-groups of lead glass can be recognised: the first with 12–16% PbO and the second with 17–20% PbO. Unfortunately there is no correlation between lead oxide content and the trace/minor elements discussed below.

Table 8. Composition of all Group 1 glasses (averages and standard deviations)

	average	sd
Na_2O	<0.1	
MgO	<0.1	
Al_2O_3	0.3	0.3
SiO_2	65.3	2.4
P_2O_5	<0.2	
SO_3	<0.2	
Cl	<0.2	
K_2O	16.6	0.8
CaO	0.5	0.5
TiO_2	<0.1	
MnO	0.1	0.3
Fe_2O_3	0.1	0.1
As_2O_3	<0.5	
Sb_2O_5	<0.5	
PbO	16.4	2.4
Total	99.6	0.7

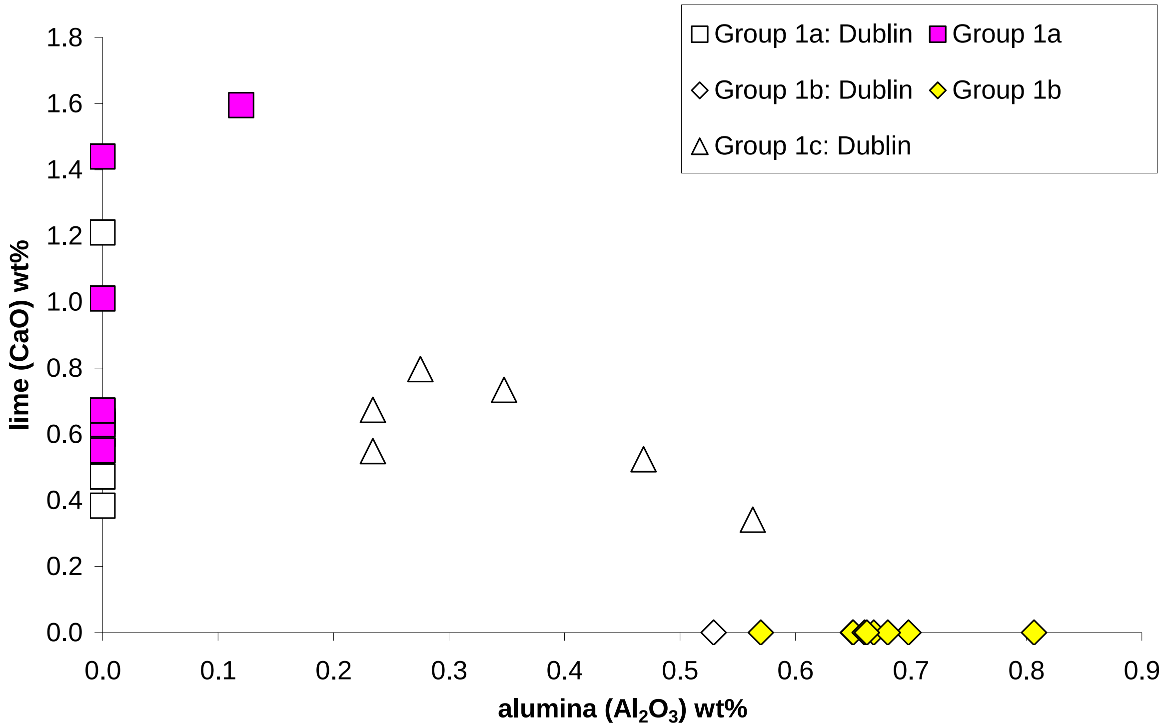

Figure 12. Plot of alumina and lime for the group 1 glasses

All of the group 1 composition glasses have suffered from crizzling (although it is not certain when this crizzling occurred). The crizzling has been caused by insufficient glass stabiliser. These glasses have very low levels of magnesia and lime, and it is only the lead oxide which can act as a glass stabiliser. Unfortunately the levels of lead oxide are too low to yield a fully stable glass.

The dating evidence for the group 1 vessels suggest that this was probably the earliest lead glass that was produced. Most of the vessels with group 1 composition can be dated to 1674 to 1681 and so are contemporary with the period of Ravenscroft’s patent. Nine of the vessels had been given a seal: two raven’s heads (samples 84 and 101/102), an S (sample 26), two plain (samples 18 and 83) and four damaged or missing (samples 19, 42/115, 43/116 and 113).

The group 1 glasses contain small amounts of impurities, in particular alumina, lime, manganese oxide and iron oxide, which allow the samples to be divided into a number of sub-groups (figure 12, table 9). Most of the group 1 glasses either have ‘high’ lime and low alumina (group 1a), or low lime and ‘high’ alumina (group 1b). The distinction between group 1a and group 1b glasses (i.e. levels of alumina and lime) may indicate the use of different sources of silica. Manganese oxide and iron oxide could not be detected in the group 1a and group 1b glasses (i.e. <0.1wt%).

Table 9. Average compositions for the group 1 sub-groups

	Group 1a	**Group 1b**	**Group 1c**
Na_2O	<0.1	0.1±0.2	0.1±0.2
MgO	<0.1	<0.1	<0.1
Al_2O_3	<0.1	0.7±0.1	0.4±0.1
SiO_2	65.1±3.0	64.4±1.6	66.9±0.9
P_2O_5	<0.2	<0.2	<0.2
SO_3	<0.2	<0.2	<0.2
Cl	<0.2	<0.2	<0.2
K_2O	17.2±0.6	16.4±0.7	16.2±0.5
CaO	0.8±0.4	<0.1	0.6±0.2
TiO_2	<0.1	<0.1	<0.1
MnO	<0.1	<0.1	0.6±0.3
Fe_2O_3	<0.1	<0.1	0.2±0.1
As_2O_3	<0.5	<0.5	<0.5
Sb_2O_5	<0.5	<0.5	<0.5
PbO	16.3±2.7	17.6±2.1	14.5±1.0
Total	99.6±0.7	99.4±0.9	99.7±0.5

Some of group 1 glasses (all from Dublin) do not fall into either group 1a or group 1b as they contain intermediate levels of both lime and alumina (figure 12). In addition, these glasses (group 1c) also contain small amounts of manganese oxide and iron oxide (Table 9). The iron oxide in these glasses probably comes from the silica and suggests the use of an inferior sand. The iron oxide and manganese oxide contents of these glasses are correlated with each other; manganese was probably added deliberately to decolourise the glass.

A single vessel does not fit into any of the group 1 sub-groups. This is a raven’s head sealed vessel (sample 84), in which alumina, lime, manganese oxide and iron oxide were undetected (<0.1wt%).

The Group 2 lead glasses

The group 2 lead glasses (10 samples from 10 vessels) have higher levels of lead oxide (26–30% PbO) and the lower levels of potash (12–13% K_2O) compared to the group 1 glasses (table 10). None of the group 2 lead glasses had suffered from crizzling, almost certainly due to the higher levels of lead oxide. Samples of lead glass examined by both Watts (1975) and Emeleus (1960) contained similar levels of lead oxide. Two of the vessels had seals: an impressed N (sample 32) and an S (sample 41). The group 2 lead glass composition has some similarities with 19th and 20th century lead crystal: the potash levels are very similar but the lead oxide levels are lower.

Table 10. Composition of all Group 2 glasses (averages and standard deviations)

	average	sd
Na_2O	<0.1	
MgO	<0.1	
Al_2O_3	0.4	0.3
SiO_2	58.8	1.2
P_2O_5	<0.2	
SO_3	<0.2	
Cl	<0.2	
K_2O	12.4	0.3
CaO	<0.1	
TiO_2	<0.1	
MnO	<0.1	
Fe_2O_3	<0.1	
As_2O_3	<0.5	
Sb_2O_5	<0.5	
PbO	27.2	1.2
Total	99.3	0.5

The available dating evidence for the vessels with group 2 composition (figure 11) suggests that they could have been made between 1674 and 1692, but are most likely to date to between 1680 and 1686. Thus it is possible that some group 2 glasses were made before Ravenscroft stopped making lead glass but most probably date to after the expiry of his patent.

The Group 3 lead glasses

The group 3 lead glasses (5 samples from 5 vessels) have higher levels of lead oxide (33–36% PbO) and lower levels of potash (8–11% K_2O) compared to the group 2 glasses (table 11). None of them had suffered from crizzling. The available dating evidence for group 3 glasses suggests that they were produced between 1680 and 1692, and definitely post date Ravenscoft's patent.

Group 3 glass has a similar composition to some of the lead glass produced at Gawber (Ashurst 1970), Bolsterstone (Ashurst 1987) and Silkstone (Dungworth 2003). Three fragments of lead glass working waste were recovered from phase 4 contexts at Silkstone (*c*.1680–1700). The average and standard deviations of the composition of this glass are given in table 11. None of the samples of lead glass analysed by Watts (1975) contained lead levels as high as those in Group 3, although several of the samples analysed by Emeleus (1960) contained similar levels of lead oxide to Group 3. The group 3 lead glass composition has some similarities with 19th and 20th century lead crystal: the lead oxide levels are very similar but the potash levels are lower.

Table 11. Composition of Group 3 glasses and three samples of Silkstone glassworking waste (averages and standard deviations)

	Group 3	**Silkstone**
Na_2O	<0.1	<0.1
MgO	<0.1	<0.1
Al_2O_3	0.4±0.3	0.8±0.2
SiO_2	55.4±0.5	53.5±0.3
P_2O_5	<0.2	<0.2
SO_3	<0.2	<0.2
Cl	<0.2	0.3±0.1
K_2O	9.3±0.8	9.0±0.6
CaO	<0.1	0.4±0.3
TiO_2	<0.1	<0.1
MnO	<0.1	<0.1
Fe_2O_3	<0.1	0.3±0.2
As_2O_3	<0.5	<0.5
Sb_2O_5	<0.5	<0.5
PbO	34.5±0.7	34.1±0.7
Total	100.0±0.7	98.9±0.1

The Group 4 lead glasses

Table 12. Composition of Group 4 glasses and 3 samples of Silkstone glassworking waste (averages and standard deviations)

	Group 4	**Silkstone**
Na_2O	<0.1	<0.1
MgO	<0.1	<0.2
Al_2O_3	0.5±0.1	0.7±0.0
SiO_2	49.5±0.4	50.3±0.4
P_2O_5	<0.2	<0.2
SO_3	<0.2	<0.2
Cl	<0.2	0.2±0.0
K_2O	9.3±0.2	9.0±0.2
CaO	<0.1	<0.1
TiO_2	<0.1	<0.1
MnO	<0.1	<0.1
Fe_2O_3	<0.1	<0.1
As_2O_3	<0.5	<0.5
Sb_2O_5	<0.5	<0.5
PbO	39.9±0.6	38.7±0.3
Total	99.5±0.2	99.5±0.1

Group 4 lead glass (4 samples from 2 vessels) has a composition that is distinct from the other groups; the potash content remains the same as group 3 (*c*.9%) but the lead oxide content is higher (*c*.40% PbO) than the other groups. The Group 4 composition is also seen in samples of glassworking waste from Silkstone (Table 12) and Bolsterstone. The dating evidence for the group 4 glasses suggest that they were probably made in the 1690s. None of the group 4 glasses had suffered from crizzling. The group 4 lead glasses are the only ones which consistently contain a higher proportion of lead oxide than 19th and 20th century lead crystal glass.

Melting characteristics

Pohlmann (1976) has investigated the melting characteristics of potash-lead glasses by measuring the viscosity of 11 different glasses (each at 900, 1200 and 1400°C). This data was then used to plot viscosity contours for each temperature; figure 13 shows the viscosity contours for 1200°C. At 1200°C, lead glasses of groups 1, 2 and 3 share similar viscosities values, while group 4 glass has a distinctly lower viscosity. These differences in viscosities are more pronounced at 900°C but are negligible at 1400°C (see table 13). At any given temperature, the main influence on the viscosity of these glasses is the molar fraction of silica: the lower the proportion of silica the less viscous the glass. Increasing the proportion of either potash or lead oxide will produce a lower viscosity but, in the compositional region shown in figure 13, lead oxide content has more influence than potash content.

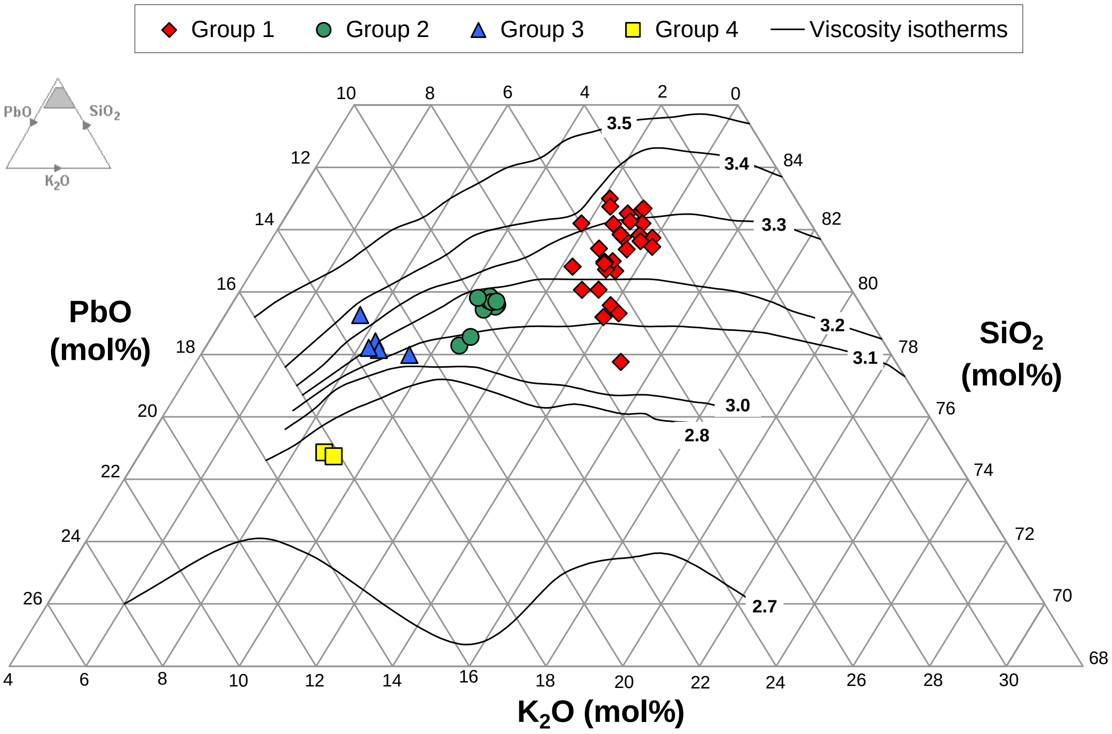

Figure 13. Viscosity contours (log[n]) for lead-potash-silica glasses at 1200°C (after Pohlmann 1976)

Lead glasses of compositional groups 1–3 would have required almost identical conditions for melting (*c*.1250°C), forming (*c*.1000–1050°C) and annealing (*c*.640–740°C), while group 4 would have required lower temperatures (*c*.1160, *c*.930 and *c*.540°C, respectively).

Table 13. Viscosity values (log[n]) for the four types of lead glass (after Pohlmann 1976)

Temperature	Group 1	Group 2	Group 3	Group 4
900°C	5.0–5.2	4.9–5.0	4.6–4.7	4.1–4.2
1200°C	3.0–3.4	3.1–3.2	3.0–3.4	2.7–2.8
1400°C	2.4–2.5	2.5	2.5	2.5

Weathering/Crizzling

Crizzling is a form of deterioration which has affected some of the glasses analysed here. Crizzling consists of a series of surface cracks (figure 14) which reduces transparency (Brill 1975; Newton & Davison 1989: 141). Brill noted that in the crizzled layers of glass, sodium and potassium were depleted, silicon was enriched and that calcium and lead were unchanged. Crizzling occurs due to insufficient levels of glass stabiliser. It is believed that the oxide of any divalent cation (e.g. magnesia, lime, lead oxide, often summed as RO) can act as a glass stabiliser (Newton & Davison 1989: 143). In alkali glasses it is primarily lime that stabilises the glass and in many cases this was a naturally occurring impurity in the raw materials used. During the 17th and 18th centuries glassmakers were able to purify their raw materials to such an extent that they virtually removed lime and some glass of this period has suffered from crizzling as a result. By the mid 18th century the necessity of adding lime had been realised (Cable 2003).

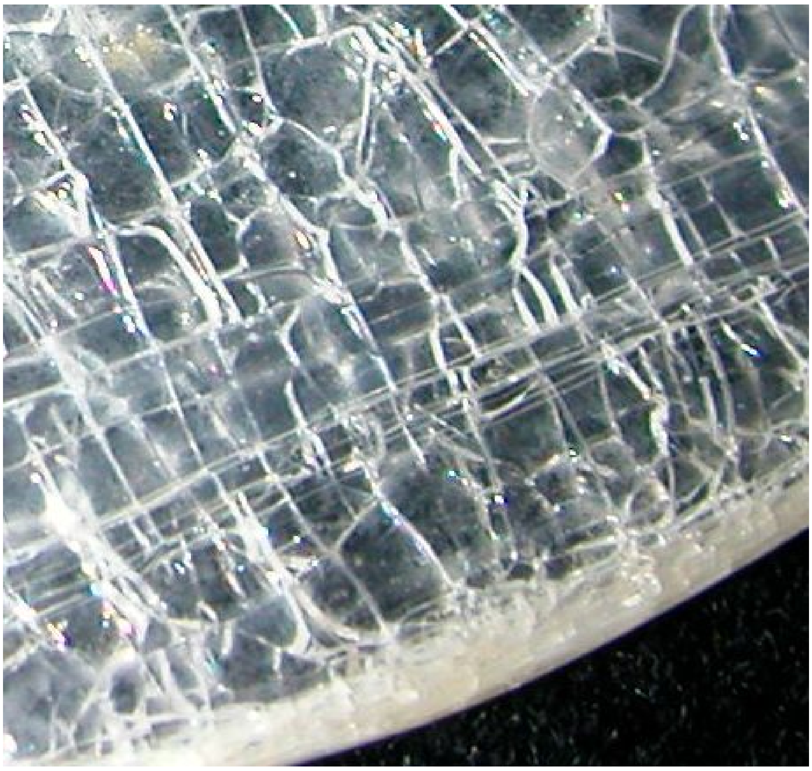

Figure 14. Photograph of crizzled vessel from Wells (sample nos. 43 & 116)

Of the 13 alkali glasses analysed here, the 5 with the lowest levels of lime had all suffered from crizzling (2.6–6.1mol% RO, figure 15). Most of the uncrizzled alkali glasses contain 12.2–17.8mol% RO. One alkali glass (sample 25) which does not appear to have suffered from crizzling has relatively low levels of network stabiliser (6.7mol% RO), however, this vessel is described as ‘thin, light metal, the surface considerably eroded’ (Charleston 1968: 166) so a crizzled surface may have been lost.

Of the 45 lead glasses analysed, all of group 1 composition (4.3–9.2mol% RO) had suffered from crizzling, while all the remaining glasses (9.4–16.3mol% RO) were uncrizzled (figure 15). The dating evidence for the crizzled lead glasses analysed shows that all were made prior to 1686, and most prior to 1681.

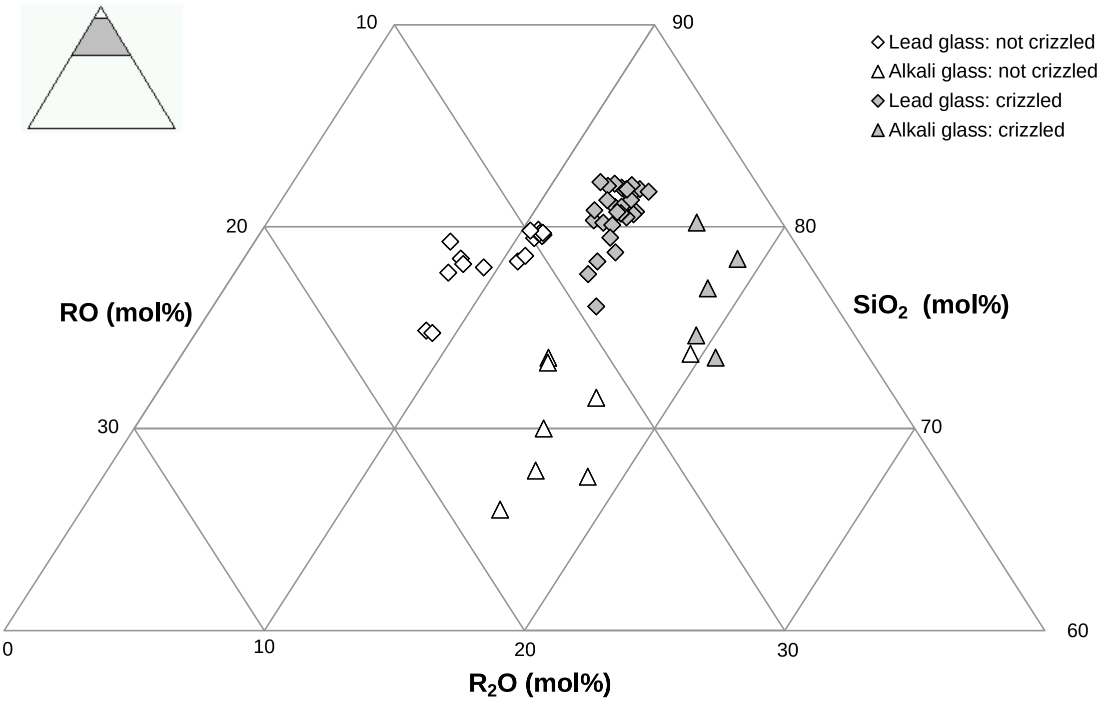

Figure 15. Ternary plot of the major components (SiO_2, R_2O and RO) in molar% showing the low RO values for the crizzled glasses

Five samples of crizzled glass were investigated in detail to examine the nature and extent of the corroded surface layers. The samples included alkali and lead glasses and crizzled and uncrizzled examples. Examination of the samples with the SEM showed that the uncrizzled examples were homogenous with no distinct surface layers (figures 16 and 18). The crizzled examples on the other hand all have surface layers that are darker (back scattered electron detector) compared to the core (uncorroded) glass (figures 20, 22 and 24). These crizzled surfaces are 40–140microns thick.

A series of analyses were carried out on each of the samples at 20micron intervals starting at the outer surface of the sample and continuing 200–300microns into the glass. The uncrizzled alkali glass (sample 22, figures 16 and 17) and the uncrizzled lead glass (sample 32, figures 18 and 19) show no depletion or enrichment of any oxides near the surface.

The crizzled alkali glass (sample 4, figures 20 and 21) has a distinct surface layer 40microns thick. In this layer the alkali content (Na_2O and K_2O, often summed as R_2O) declines quickly as the outer surface of the layer is approached while the level of stabilisers (RO) remains near constant. The two crizzled lead glasses (sample 81, figures 22 and 23 and sample 64, figures 24 and 25) have crizzled surfaces 80–140microns thick. In both cases the levels of lead oxide remain fairly constant through the crizzled layer while the potash shows a dramatic fall (from 16–18% to 5–6% K_2O) at the interface of the unaffected/crizzled glass. The potash then continues to decline more slowly through the thickness of the crizzled layer; reaching *c.*2% K_2O at the outer surface.

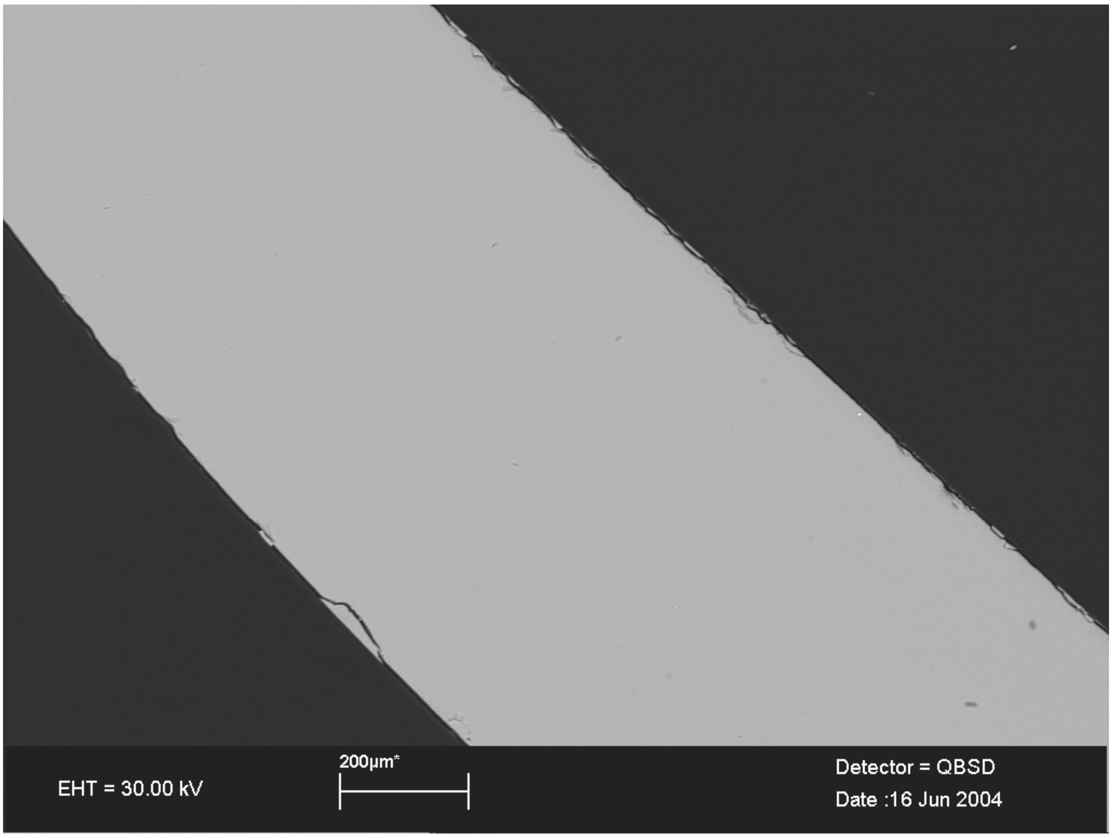

Figure 16. SEM image (back scattered electron detector) of an uncrizzled alkali glass (sample 22)

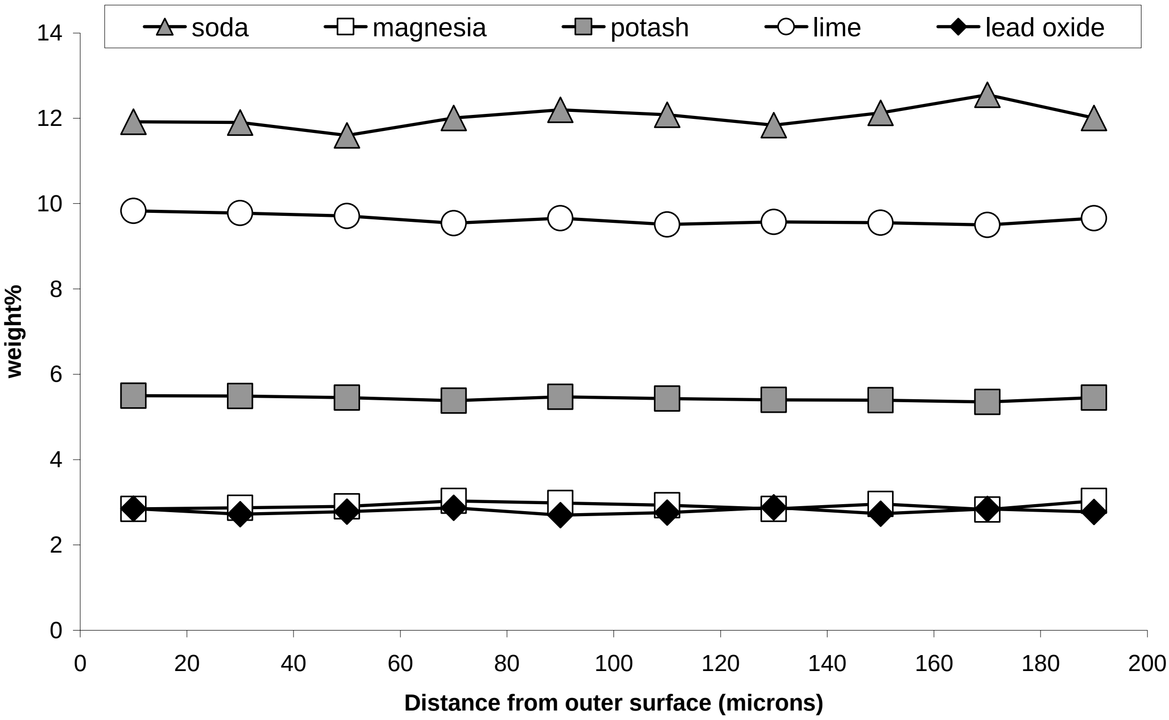

Figure 17. Linescan through the outer 200microns of an alkali glass (sample 22). The glass is homogenous with no change in composition as the surface is approached

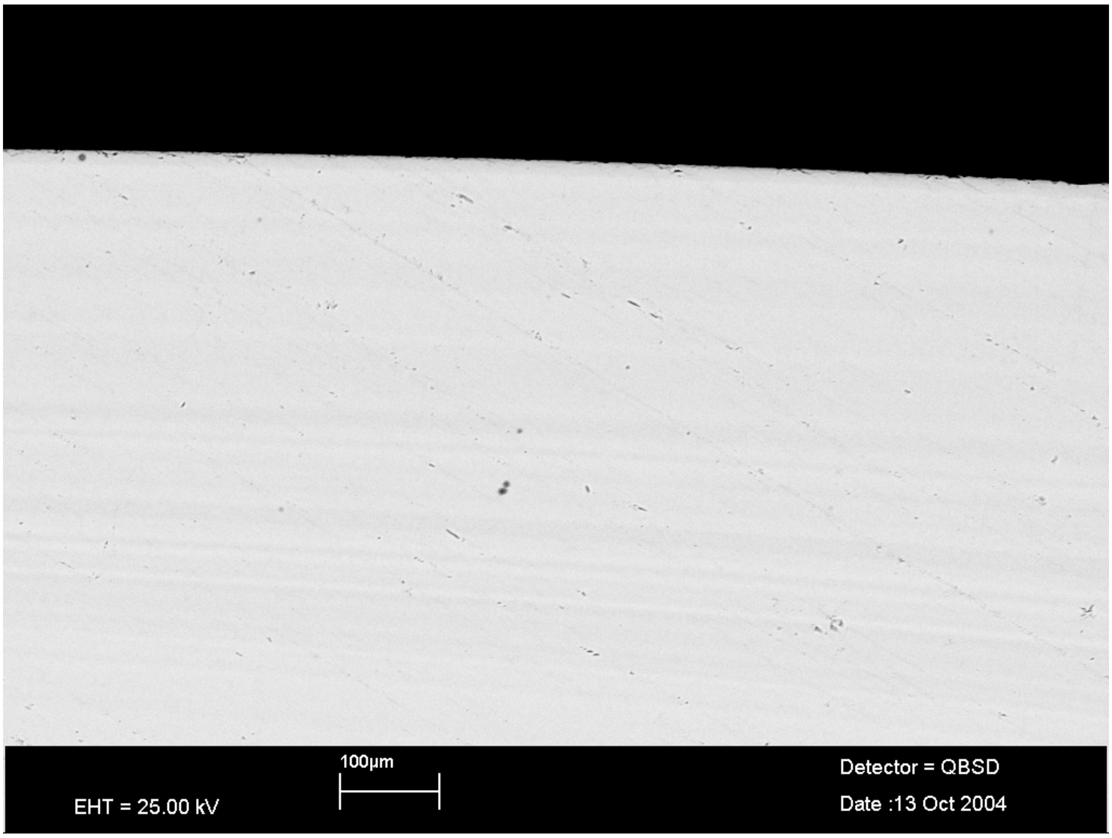

Figure 18. SEM image (back scattered electron detector) of an uncrizzled group 2 lead glass (sample 32)

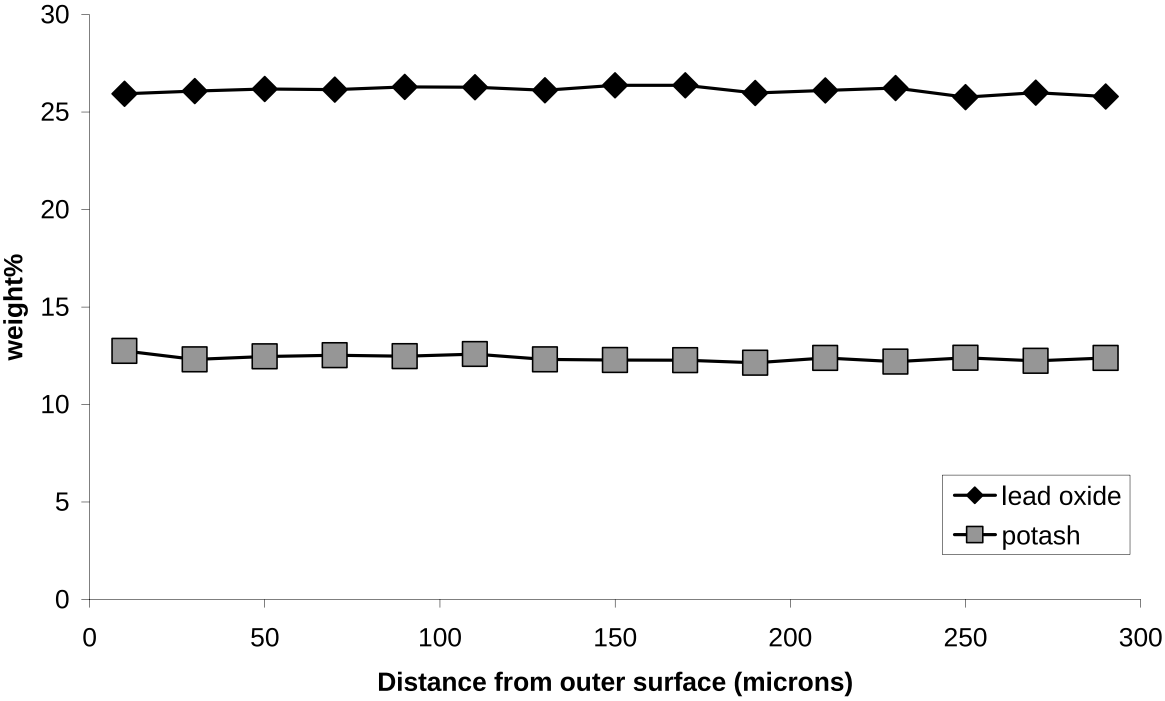

Figure 19. Linescan through the outer 300microns of a group 2 lead glass (sample 32). The glass is homogenous with no change in composition as the surface is approached

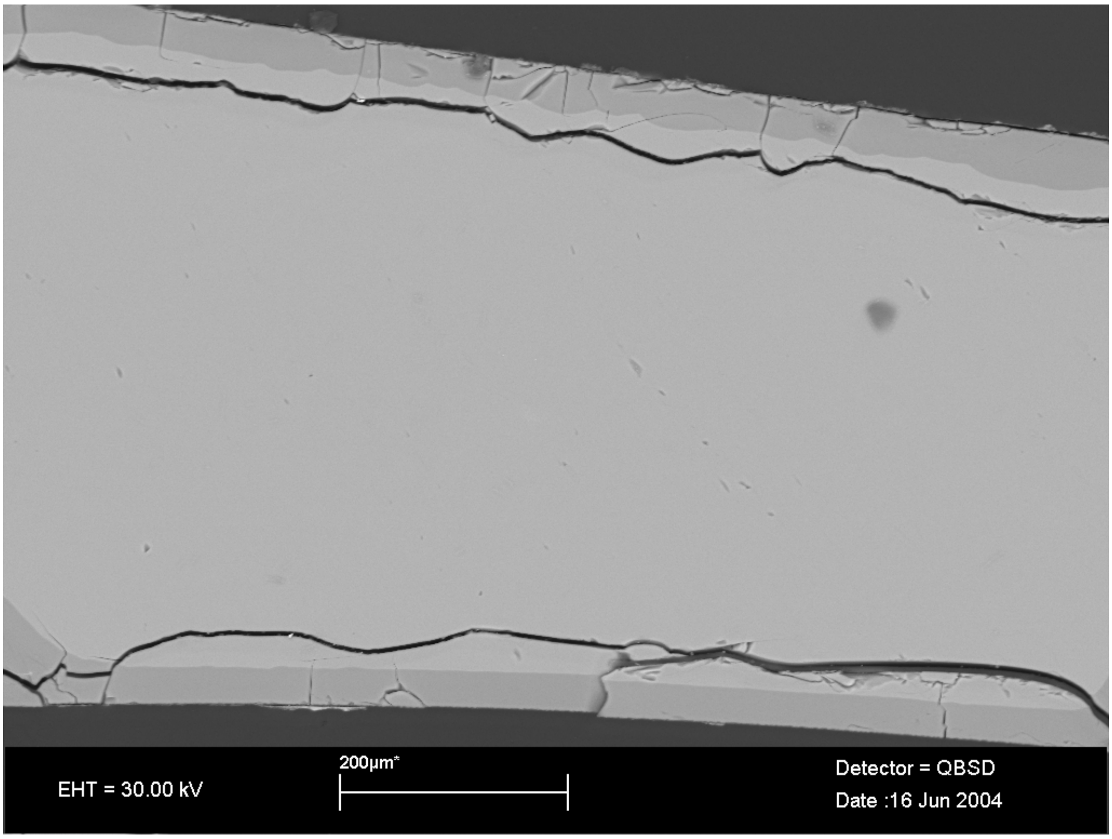

Figure 20. SEM image (back scattered electron detector) of crizzled alkali glass (sample 4)

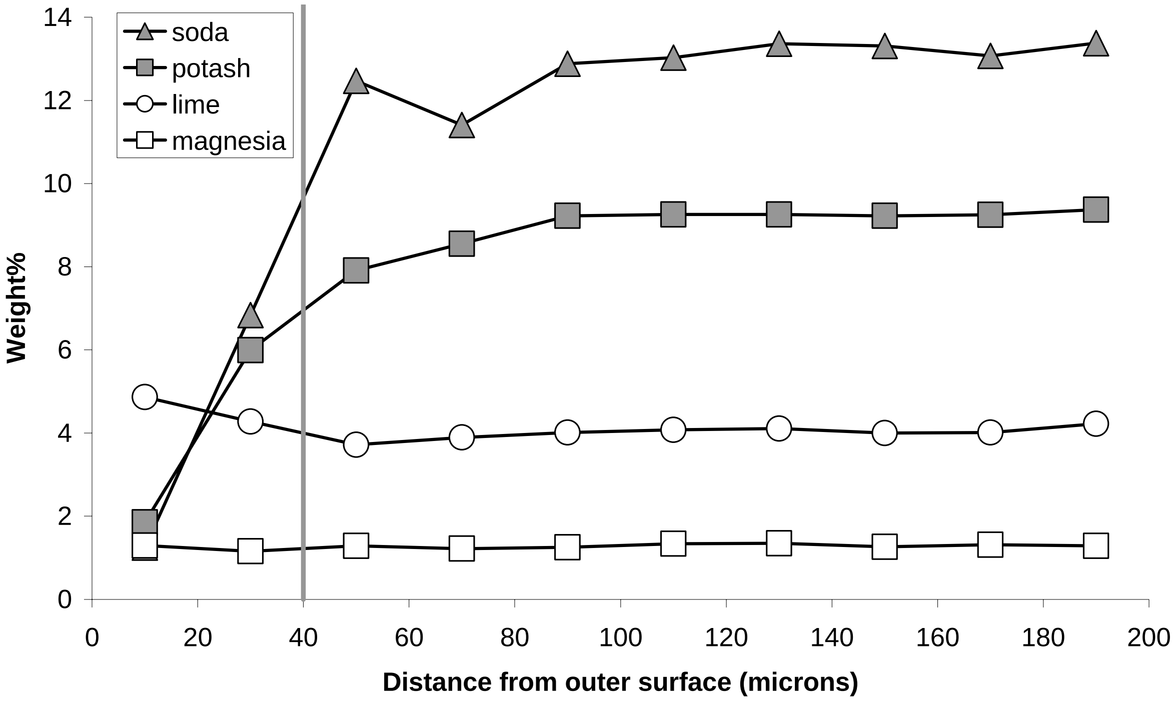

Figure 21. Linescan through the outer 200microns of an alkali glass (sample 4). Within the crizzled surface soda and potash are depleted while the levels of the lime and magnesia remain unchanged. The vertical grey line shows the limit of the surface crizzling observed with the SEM (cf. figure 20)

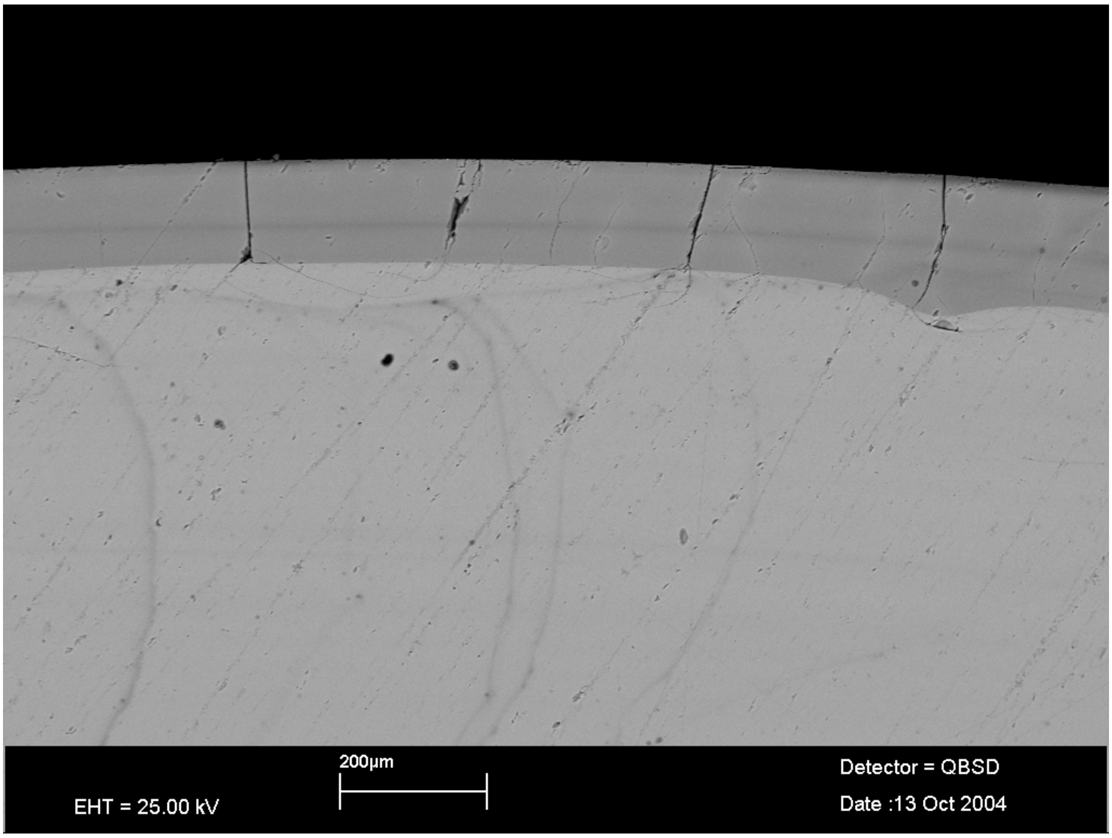

Figure 22. SEM image (back scattered electron detector) of a crizzled Group 1 lead glass (sample 81). Note the crizzled surface layer is clearly visible as the darker grey layer at the top and contains prominent cracks

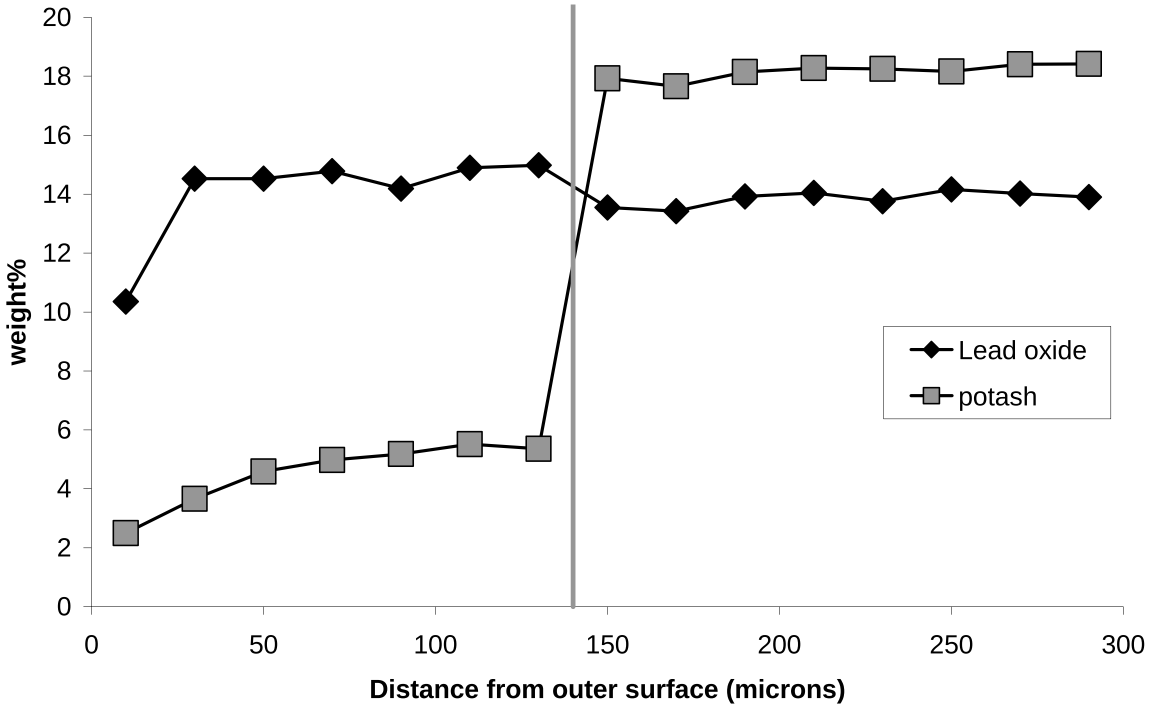

Figure 23. Linescan through the outer 300microns of crizzled surface of a crizzled group 1 lead glass (sample 81). The vertical grey line shows the limit of the surface crizzling observed with the SEM (cf. figure 22)

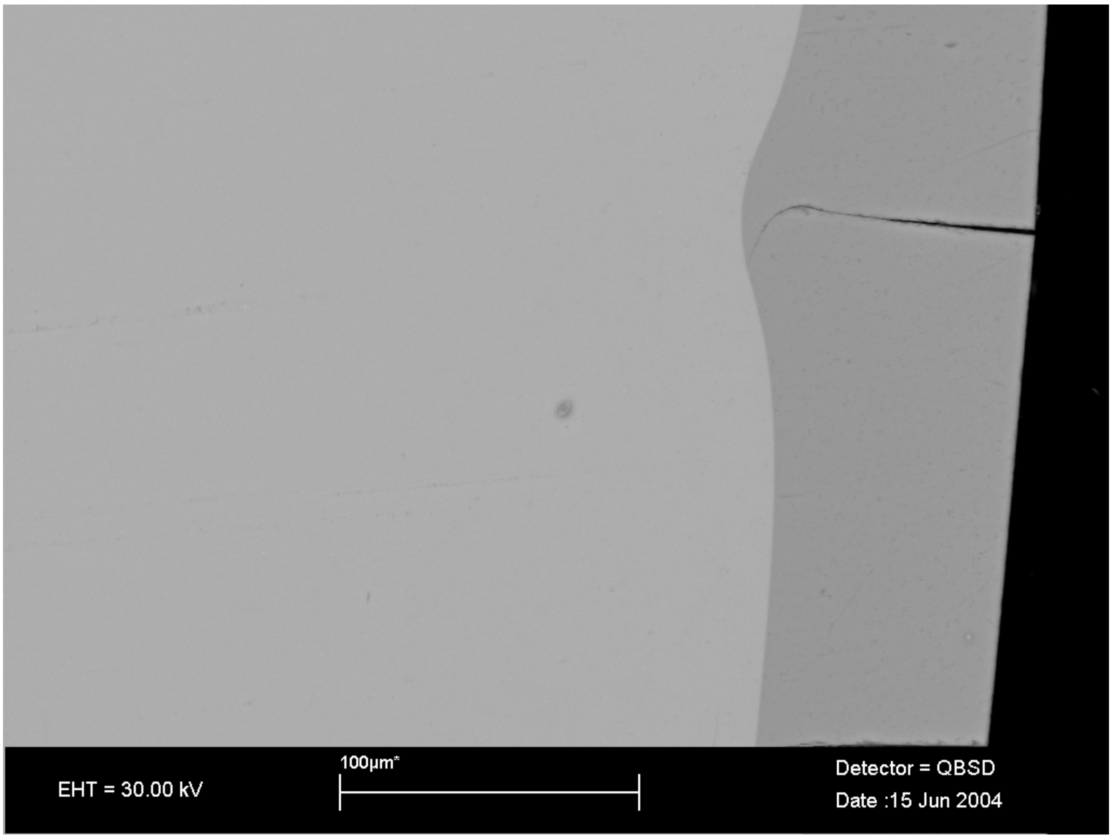

Figure 24. SEM image (back scattered electron detector) of a crizzled Group 1 lead glass (sample 64). Note the crizzled surface layer is clearly visible as the darker grey layer to the right and contains a prominent crack

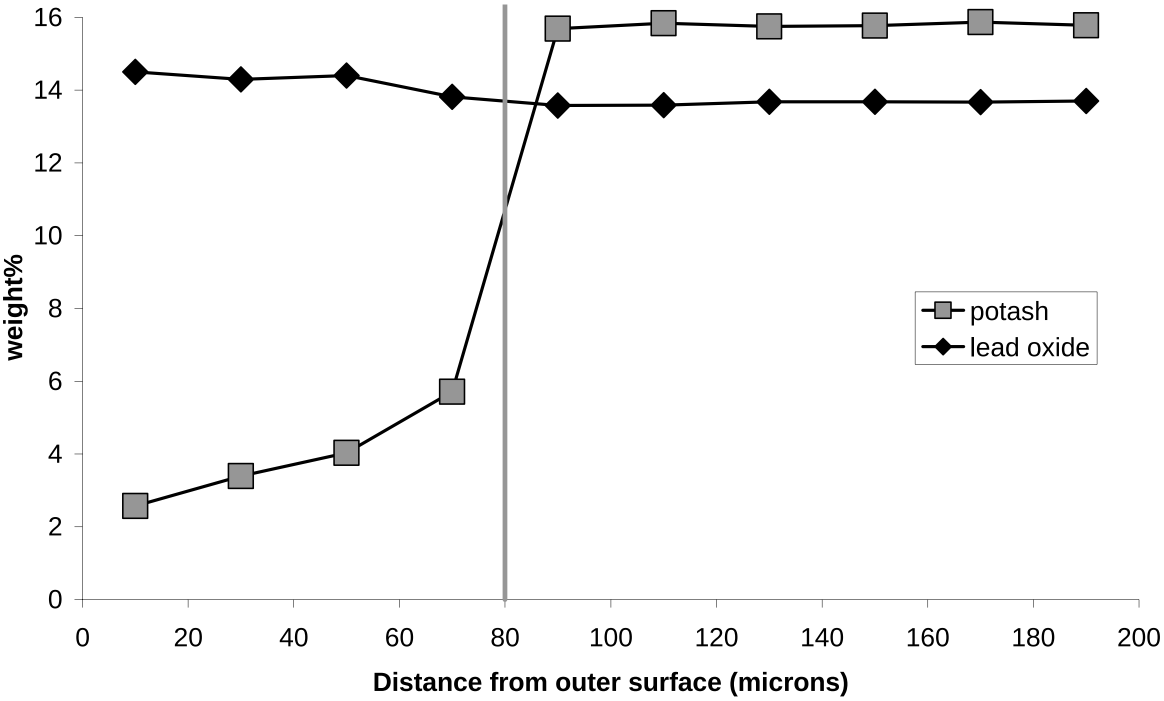

Figure 25. Linescan through the outer 200microns of crizzled surface of a crizzled group 1 lead glass (sample 64). The vertical grey line shows the limit of the surface crizzling observed with the SEM (cf. figure 24)

Discussion of Results

Summary of findings

The analysed glass samples show a wide variety of chemical compositions: some are alkali glasses while others are lead glasses. The alkali glasses include examples made before, during and after the Ravenscroft patent. Two of the alkali glasses have raven's head seals but it is not certain whether these were made by Ravenscroft as a stop-gap during the period when crizzling was seen as a problem or whether they were made illicitly by another glassmaker.

The lead glass samples can be divided into four groups based on the levels of potash and lead oxide present. The four groups show a chronological trend; group 1 is the earliest and contains the lowest levels of lead oxide, later groups contain higher levels of lead oxide (table 14).

Table 14. Summary of chemical composition (wt%) and date ranges for the four groups of lead glasses. Date range gives the earliest and latest dates for all the vessels in the group. The 80% date range covers the median 80% date range (based on the data shown in figure 11).

Group	SiO_2	K_2O	PbO	date range	80% date range
1	65.3±2.4	16.6±0.8	16.4±2.4	1674–1685	1676–1680
2	58.8±1.2	12.4±0.3	27.2±1.2	1674–1692	1680–1689
3	55.4±0.5	9.3±0.8	34.5±0.7	1680–1689	1681–1688
4	49.5±0.4	9.3±0.2	39.9±0.6	1685–1720	1686–1709

Group 1 is contemporary with the period of Ravenscoft's patent but probably only includes glass made after the crizzling problem was declared to be solved (1676). All of the group 1 glasses had suffered from crizzling due to low levels of glass stabiliser present. It is not certain when these samples suffered from crizzling but it is likely that it did not occur in the late 17th century. Groups 2 and 3 are chemically distinct from each other but are almost chronologically indistinguishable from each other. The production of these glasses probably starts at the end of Ravenscroft's patent and demonstrate that lead glassmakers continued to experiment with the proportions of raw materials. The trend is completed by the group 4 glasses which are the latest and have the highest levels of lead oxide.

Sealed vessels

The practice of adding a maker's seal to vessels is most famously identified with George Ravenscroft, although there is some evidence that seals were used perhaps a year before the first record of a Ravenscroft seal. The earliest Ravenscroft seal was advertised in October 1676 but the raven's head seal was not specified until May 1677. The practice of sealing appears to have been restricted to British glassmakers and was abandoned soon after Ravenscroft left the business in 1681 (Charleston 1984: 124–5).

The fifteen vessels with seals are made of alkali glass or lead glass of group 1 or group 2 composition; none of the vessels made using group 3 or group 4 lead glass had seals (table 15). The raven's head seals have the potential to shed most light on the nature of the glass manufactured by Ravenscroft. Of the four vessels with raven's head seals that were analysed, two are lead glasses but two are alkali glasses. The two alkali glasses could have been made by Ravenscroft but there is the suspicion that these two sealed vessels were contemporary forgeries. Unfortunately the raven's head sealed vessels still do not provide definite information about the composition of the glass for which Ravenscroft obtained a patent in 1674, as they were produced at least 2 years after the patent was granted.

Table 15. Sealed vessels

Seal	Alkali	Group 1	Group 2
Raven's head	2	2	
S		1	1
N			1
Boar/Bear	1		
Bow & Lilly	1		
Plain	1	1	
broken, missing, unidentified		4	
Totals	**5**	**8**	**2**

Lead glass-making materials

The lead glasses of groups 1–4 appear to only use a narrow range of glass-making materials. Documentary evidence suggests that the source of silica was originally calcined flint and that this gradually changed to white sand over the last quarter of the seventeenth century. Too little is known about the range of trace elements present in the flint and sand that was used to positively confirm this, but nothing in the analysis is inconsistent with this trend. Indications are that the iron content of flint was lower than that of sand, so the iron oxide content of the flint glasses may be a guide to the source of silica used.

The analyses show that plant ashes could not have been the main source of alkali for the lead glasses. They also show no sign of any significant use of borax. Although the measurement techniques used in this study were not suitable for detecting boron, the term borax is usually taken to mean sodium borate. The very low levels of sodium present in these lead glasses mean that the borax content would, at most, have been less than one percent — insufficient to make a significant impact on the properties of the glass. However, borax could well be present in trace amounts as a result of the use of cullet containing borax. The most likely source for the alkali is saltpetre (nitre), for the first time available in bulk at a reasonable price due to the ending of the royal monopoly. It is possible that calcined tartar was used alongside saltpetre as a source of potassium oxide for the glass. However, it is very unlikely that uncalcined tartar would have been used in a glass mixture containing lead oxide, since it is a powerful reducing agent and quickly reduces the lead oxide to metallic lead, with disastrous results for the pots. Tartar contains a reasonable amount of calcium oxide, particularly if it is from red wine, so only glasses with reasonably high levels of calcium oxide are likely candidates for the use of tartar as a partial source of alkali. The major source of lead oxide is likely to have been red lead, although litharge and white lead (lead carbonate) are possible alternatives. It is possible that lead was actually introduced into the batch as a lead silicate (a high-lead glass), called at the time *vitrum saturni* (Brain 2002).

Arsenic is present in few of the glasses, but always at low levels. In particular it is present in the two 'S' sealed glasses. The 'S' sealed glasses both have very low levels of impurities, suggesting a lot of care went into their manufacture and that the addition of the arsenic was deliberate. The traditional attribution of 'S' sealed glasses is to the Savoy glasshouse under Hawley Bishop. Similarly a number of the glasses analysed display low levels of antimony, which may have been deliberate additions, or may have resulted from the use of opaque white glass as cullet.

Lead glass recipes

There is very little overlap in the composition of the four lead glass groups and it appears that changes in the recipe occurred in a series of discrete steps rather than as a gradual progression. From this analysis it appears likely that all the British lead glass industry was using virtually the same recipe and that all shifted to the next recipe within a short space of time. In particular the group 1 recipe used in Dublin is virtually indistinguishable from that used in England. However, as discussed above, less than six years elapsed between the introduction of group 1 glass and that of group 3. It is impractical to expect to use archaeological or stylistic dating to resolve to better than plus or minus one year. Thus, there is no prospect that analysis of excavated glass will provide evidence of where the changes in recipe were initiated or of how the use of the new recipes spread. The most likely mechanism for spreading information about developments in glass-making recipes was by communication between those glassmakers in England who came from Altare (in particular Da Costa and Odaccio). Whatever the mechanism by which the information was spread, the evidence of the glass composition suggests that glassmakers were not overly secretive about their methods. It seems unlikely, therefore, that Ravenscroft's move to Henley on Thames was motivated by a need for secrecy.

The changes in composition between groups 1 and 4 did not occur simply as the result of increasing the lead oxide content. As the proportion of lead oxide added to the batch was increased, the proportion of potash was decreased. The changes in chemical composition between groups 1 and 3 (Figure 26) contrasts with their similar melting characteristics (Figure 13 and Table 13). It is possible that these three lead glass recipes were arrived at by maintaining a constant furnace temperature and altering the proportions of the three ingredients until a satisfactory glass was formed.

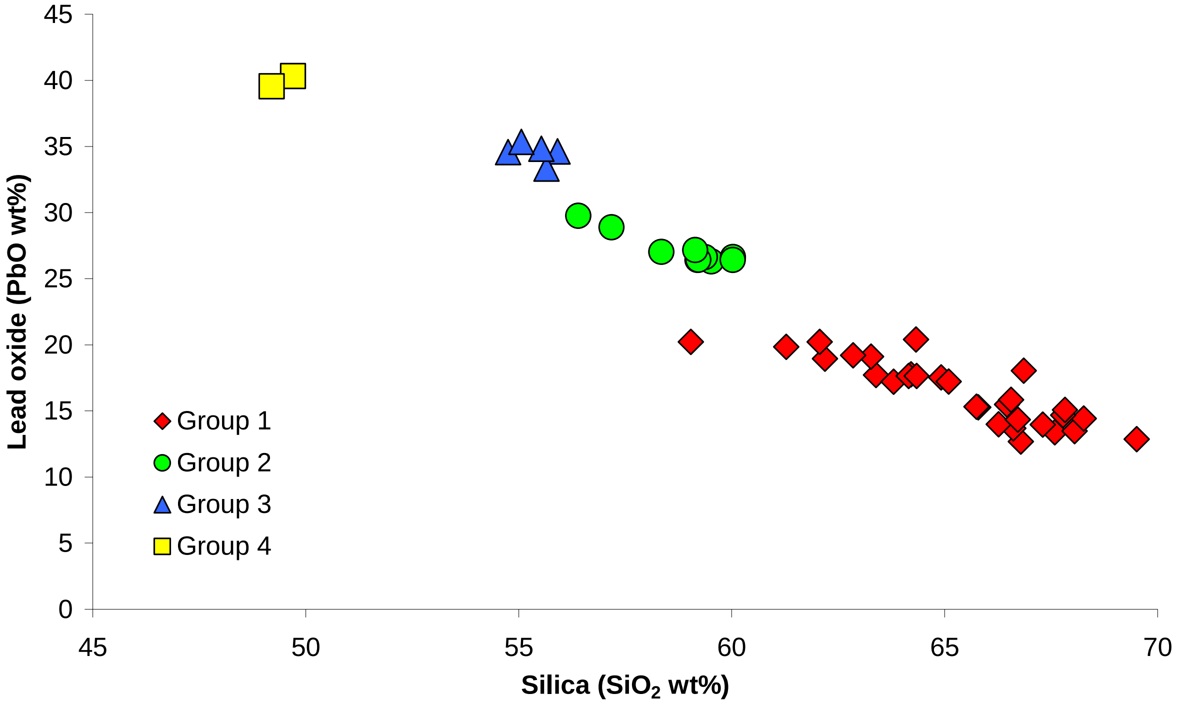

Figure 26. silica and lead oxide contents of the analysed lead glasses

The introduction of group 1 and group 2 recipes may both have been triggered by a desire to overcome the problem of crizzling, but that cannot be said of groups 3 and 4. These must have been driven by a desire for weight and the refractive quality of the metal. However, the group 4 recipe did not persist; glassmakers soon lowered the lead oxide content to that of the earlier group 3 glass as the basis for the enduring ‘full-lead crystal’. The high lead content of group 4 may have caused a number of problems. Firstly, without correction from added decolourisers the lead would give a yellow tint to the glass (Marson 1918: 33). Secondly, the high lead to saltpetre ratio makes it much more likely that a reducing atmosphere in the furnace would create metallic lead in the pots with potentially disastrous results. This is probably why the alkali content was not reduced when moving from group 3 to group 4 (see figure 10), as it had been for the other transitions. Thirdly, the working range of the metal is reduced compared to the metal of group 3.

Lead glass melting
The recipe for group 1 glasses would have been about 28 pounds of red lead and 56 pounds of saltpetre to one hundred weight (112 pounds) of calcined flint or sand. This would have required a temperature of around 1250°C for melting. As the amount of lead in the mixture was increased (up to group 3 levels), the melting temperature remained constant due to the lowering of the potash/saltpetre content. The group 4 lead glass would have melted at a lower temperature (*c*.1160°C) as the increase in lead content was not accompanied this time by a decrease in the proportion of potash/saltpetre.

There has been considerable discussion in the past about the use of closed or open pots for melting lead glasses. A closed pot separates the atmosphere above the molten glass from the products of combustion in the furnace. The earliest evidence of the use of closed pots in England comes from the excavation at the site of the Bolsterstone glasshouse and these pots are thought to date from the very end of the 17th or the beginning of the 18th century (Ashurst 1987). There is no known documentary evidence for the use of closed pots earlier than this, yet glass historians have postulated that they would have been essential in order to melt lead glass. This seems to have been on the basis of an assumption that the crystal glass furnaces were coal-fired, but this is clearly not universally true (see above page 7). The only glasses analysed that had measurable sulphur content were the mixed alkali glasses, suggesting that this may have been due to the presence of sulphates in the plant ashes, rather than contamination from the products of coal combustion. From the Smithfield site in Dublin there is only evidence for the use of open pots and no evidence at all for coal firing. We also know from documentary sources that the Savoy glasshouse was wood fired and that wood was still used in glassmaking in 1695. However, the Silkstone site was definitely producing lead glass *c*.1680–1700 and was coal-fired. Thus further work is required to try to quantify the contamination introduced with coal and wood-firing and the effect that covering the pots has on the melting of the glass batch.

The invention of ‘flint’ glass
The review of the documentary evidence shows that Ravenscroft obtained a patent in 1674 for glass manufacture and that his glass was made using a new recipe and/or ingredients. None of the lead glasses analysed for this project can be shown to have been produced during the period of Ravenscroft’s patent *and* pre-date the adverts

claiming that the crizzling had been solved and the introduction of seals (i.e. 1674–1676).

Hooke's description of glass made at the Savoy in 1673–4 and Plot's description of glass made by Ravenscroft at Henley 1674–6 both list the same ingredients: flint, tartar, borax and nitre (saltpetre). If both the tartar and the borax were calcined before use, the resultant glass would have been viable for melting in a 17th century furnace. However, such a glass would contain virtually no stabilisers and would tend to suffer from crizzling, although it is not certain how long it would take for such corrosion to become noticeable. None of the glasses analysed for this project have compositions which correspond to the Hooke/Plot descriptions. It is possible that glass vessels produced in the period 1673–6, using the Hooke/Plot ingredients, ultimately suffered from catastrophic crizzling and have not survived in museum collections. It is possible that fragments of this glass would survive in archaeological contexts but they have not yet been recognised.

If it is accepted that Ravenscroft's earliest glass was made to the recipe given by Hooke and Plot, then his patent was not for a lead glass. It also follows that the crizzling problem involved the fairly radical solution of replacing borax with lead oxide; a sequence of events which has been rejected by Moody (1988; 1989) and Watts (1975).

There are several possible hypotheses about how the group 1 glass recipe was 'invented':

1. The recipe was developed under Ravenscroft's direction at the Savoy and Da Costa's contribution was to bring practical knowledge of furnace and refractory technologies to enable it to be put into regular production at Henley and the Savoy.
2. The recipe had been developed in Nijmegen and Odaccio and Da Costa simply bought it over to England and Ireland.
3. The recipe was 'invented' in Henley or the Savoy and Odaccio knew quite rapidly what Da Costa was doing and copied it.
4. The recipe was 'invented' in Dublin and Da Costa knew what Odaccio was doing and copied it.
5. Some mixture of the other hypotheses involving multiple inventive steps or simultaneous invention.

Conclusions

Documentary evidence suggests that the glass for which Ravenscroft obtained a patent was a borate-soda-potash-silica glass (see table 1 for the range of possible compositions). This glass was found to suffer from crizzling and the borax was replaced by lead oxide. It is far from clear who was responsible for the initial use of lead in 'flint glass'. The analysis of 52 samples of lead glass vessels and working waste shows that none of these were borate-soda-potash-silica glasses. The analysed glasses fall into 2 major groups: alkali glasses and lead glasses.

The alkali glasses occasionally contained some lead oxide but it was soda and potash which acted as fluxes and lime and magnesia which acted as stabilisers. The soda to potash ratios in the alkali glasses vary across a wide range and indicate that alkalis were obtained from several different sources. The low alumina, titania and iron oxide contents of the alkali glasses shows that they were manufactured from carefully selected and perhaps purified raw materials. In some cases, the purification of the raw materials had the unwelcome effect of removing magnesia and/or lime which left the glass unstable and subject to crizzling. Manganese was deliberately added to most of the glasses to decolourise them.

The lead glasses are composed almost exclusively of silica, potash and lead oxide; the range of impurities seen in most alkali glasses are virtually absent (magnesia, alumina, phosphorus oxide, titania, iron oxide, etc). The lead glasses were made from high-purity ingredients, probably saltpetre, litharge and flint or white sand. The lead glasses can be divided into four sub-groups based on the proportions of potash and lead oxide. The earliest, group 1, has the highest potash and lowest lead oxide content and was produced during the period after it was claimed that the crizzling problem had been solved (1676–1681). There is no evidence that lead glasses were produced before 1676. All of the group 1 glasses have suffered from crizzling. There is no certainty about when this occurred, but it is probably that it did not occur in the 17th century. The succeeding groups, which were largely produced after the expiry of Ravenscroft’s patent, show a decline in potash and an increase in lead oxide content.

Recommendations for future work

Future research could usefully examine further samples of glass and attempt to reproduce glass recipes of the period. Analysis of glass should be concentrated on vessels likely to date to the crucial period (1674–76), both in Britain and Europe (in particular the Netherlands), and debris from production sites (in particular the Savoy, Henley, Dublin and Nijmegen). Experimental glass batches should be prepared to reproduce the Plot/Hooke glass as well as the group 1 compositions. This will provide information about the melting characteristics of these glasses as well as their propensity to crizzle.

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Appendix 1

Details of provenance, etc of samples

Ref	Site	Reference	type	class	seal	Date	Colour	Crizzle	Area
3	London, Lloyd's Lime Street	GM96 ER87	cigar	2A	none	1666–1668	Pinkish	Yes	
4	Guildford, Tunn Inn	Catalogue 37	Greene		boar/bear	1674	Pinkish	Yes	
7	Hull	61/74/69	Greene	5D(ac)	none	1670–1675	Pinkish	No	
11	London	A26067	Roemer		none	1682	Clear	No	
12	London, Long Alley, Moorfields	Box 17B 16948	Roemer		none		Clear	No	
13	London, Southwark	GM21890	Roemer		none		Pale green	No	
14	London	A27637	Roemer		none		Clear	Yes	
17	London, Nonsuch	1-13	knopped		none	1665–1675	Clear	No	
18	London, Billingsgate	BIG82 309 1004	taper	6A(a)	plain	1674–1681	Pale green	Yes	
19	Oxford	1915 99d	taper	6A(c)iiip	unidentified	1674–1681	Clear	Yes	
21	London	NRF88 468 780	taper	6B(a)	none	1680	Clear	Yes	
22	London, Pindar/Clifton Street	GM15629	taper	6B(c)iiip	none	1674–1676	Pale green	No	
25	London, Aldersgate	GM14630	taper	6C(c)iiip	ravens head	1677–1681	Pinkish	No	
26	London	V&A c589-1925	taper	6C(c)iii	S	1674–1681	Clear	Yes	
27	Northampton		taper	6C(c)iii	“bow & lily”	1674–1681	Pinkish	Yes	
30	London, Westminster	A889	taper	6C(c)iv	ravens head	1677–1681	Pinkish	Yes	
32	London, Billingsgate	BIG82 570 915	taper	6D(c)iiif	N impressed	1674–1681	Clear	No	
35	Jamestown	NN40/7AT	bowl		none	1665–1675	Pinkish	Yes	
36	Port Royal	PR89 599	taper	6D(a)	none	1680–1685	Clear	Yes	
37	Port Royal	PR87 556-7	knopped		none	1675–1685	Clear	Yes	
38	Port Royal	PR90 9012–0	4-foil knop		none	1680–1685	Clear	Yes	Bowl
39	Port Royal	PR87 632 0	4-foil knop		none	1680–1685	Clear	No	Bowl
40	Port Royal	PR89 764-4	Greene		none	1670–1674	Pale green	No	Bowl
41	Port Royal	PR90 2074–14	taper	6C(c)	S	1680	Clear	No	
42	Wells	2/1009	taper		missing	1676	Clear	Yes	
43	Wells	2/1095	taper		broken	1674–1681	Clear	Yes	Bowl
48	London, Moorfields	GM1649	4-foil		none	1680–1687	Clear	No	
50	Port Royal	PR87 531	4-foil		none	1680–1687	Clear	No	
52	Port Royal	PR87 533–3	4-foil		none	1680–1687	?	No	
54	Port Royal	PR87–591	Baluster		none	1685–1692	Clear	No	
55	Port Royal	PR87 574–2	Baluster		none	1680–1687	Clear	No	

Ref	**Site**	**Reference**	**type**	**class**	**seal**	**Date**	**Colour**	**Crizzle**	**Area**
56	Port Royal	PR87 533–4	Beaker		none	1682–1692	Clear	No	
57	Port Royal	PR87 534–2	Baluster		none	1685–1692	Clear	No	
58	Port Royal	PR87 533–4	taper		none	1683–1690	Clear	No	
60	Dublin, Smithfield	Catalogue 1	beaker		none	1678–1680	Clear	Yes	
61	Dublin, Smithfield	Catalogue 2	moil ?		none	1678–1680	Clear	Yes	
62	Dublin, Smithfield	Catalogue 3	moil		none	1678–1680	Clear	Yes	
64	Dublin, Smithfield	Catalogue 5	Working waste		none	1678–1680	Pinkish	Yes	
66	Dublin, Smithfield	Collection 7	Working waste		none	1678–1680	Pinkish	Yes	
68	Dublin, Smithfield	Collection 12	Foot		none	1678–1680	Pinkish	Yes	
70	Dublin, Smithfield	Collection 20	Working waste		none	1678–1680	Light green/blue	Yes	
71	Dublin, Smithfield	Collection 22	moil		none	1678–1680			
74	Dublin, Smithfield	F1034:10	4-foil		none	1675–1680	Clear	Yes	
80	London, Spitalfields	SSA01 88 6			none	1675–1680	Clear	Yes	
81	London, Spitalfields	SSA01 88 7	bowl		none	1674–1680	Clear	Yes	
82	London, Spitalfields	SSA01 88 8	taper		none	1675–1680	Clear	Yes	
83	London, Spitalfields	SSA01 88 9	taper		plain	1675–1678	Clear	Yes	
84	London, Spitalfields	SSA01 88 10	taper		ravens head	1677–1678	Clear	Yes	
100	Guildford, Tunn Inn	Catalogue 35	cigar		none	1676–1690	Clear	No	
101	Guildford, Tunn Inn	Catalogue 36	taper		ravens head	1677–1681	Clear	Yes	Foot
102	Guildford, Tunn Inn	Catalogue 36	taper		ravens head	1677–1681	Clear	Yes	Bowl
103	Guildford, Tunn Inn	Catalogue 38	Baluster		none	1690–1720	Clear	No	Foot
104	Guildford, Tunn Inn	Catalogue 38	Baluster		none	1690–1720	Clear	No	Bowl
105	Guildford, Tunn Inn	Catalogue 40	cigar		none	1685–1705	Clear	No	Foot
106	Guildford, Tunn Inn	Catalogue 40	cigar		none	1685–1705	Clear	No	Bowl
107	Guildford, Tunn Inn	Catalogue 46	beaker		none	1677–1690	Pale green	No	
108	Guildford, Tunn Inn	Catalogue 63	beaker		none	1677–1690	Pale green	No	
109	Guildford, Tunn Inn	Catalogue 64	beaker		none	1677–1690	Pale green	No	
110	Dublin, Smithfield	F1034: 11	taper?		none	1675–1680	Clear	Yes	
111	Dublin, Smithfield	00E0272; 947; 2	Working waste		none	1678–1680	Clear	Yes	
112	Dublin, Smithfield	00E0272; 947; 2	Working waste		none	1678–1680	Clear	Yes	
113	London, Nonsuch	19-58			damaged	1674–1681	Clear	Yes	
114	London, Nonsuch	285	taper	6A(a)iii	none	1674–1681	Clear	Yes	
115	Wells	2/1009	taper		missing	1676	Clear	Yes	
116	Wells	2/1095	taper		broken	1674–1681	Clear	Yes	Foot

Appendix 2

Chemical composition of the samples

Ref	Area	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	As_2O_3	Sb_2O_5	PbO	Total
3		17.3	1.0	0.5	74.8	0.26	<0.2	1.25	1.9	2.6	<0.1	0.29	0.19	<0.1	<0.4	<0.4	<0.4	100.2
4		13.9	1.1	1.3	68.0	0.25	0.23	0.89	8.7	3.6	<0.1	0.89	0.38	<0.1	0.45	<0.4	<0.4	99.6
7		8.3	2.8	1.0	66.4	0.42	<0.2	0.43	10.8	8.7	<0.1	0.74	0.47	<0.1	<0.4	<0.4	<0.4	100.1
11		<0.2	<0.2	0.3	55.9	<0.2	<0.2	<0.2	8.3	<0.1	<0.1	<0.1	0.16	<0.1	<0.4	<0.4	34.6	99.3
12		<0.2	<0.2	<0.2	56.4	<0.2	<0.2	<0.2	12.0	<0.1	<0.1	<0.1	<0.1	<0.1	0.80	<0.4	29.8	98.9
13		<0.2	<0.2	<0.2	55.7	<0.2	<0.2	0.22	10.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	33.3	99.8
14		<0.2	<0.2	<0.2	69.5	<0.2	<0.2	<0.2	17.4	0.6	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	12.9	100.4
17		15.0	2.3	1.0	64.9	0.32	<0.2	1.21	5.2	9.1	<0.1	0.32	0.38	<0.1	<0.4	<0.4	<0.4	99.9
18		0.3	<0.2	0.6	64.2	<0.2	<0.2	<0.2	16.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	17.6	99.0
19		0.3	<0.2	0.8	64.3	<0.2	<0.2	<0.2	16.3	<0.1	<0.1	<0.1	0.12	<0.1	<0.4	<0.4	17.6	99.5
21		<0.2	<0.2	0.7	66.5	<0.2	<0.2	<0.2	16.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	15.5	99.2
22		12.7	2.9	1.1	64.5	0.23	<0.2	0.91	5.2	9.1	<0.1	0.84	0.46	<0.1	<0.4	<0.4	3.0	101.0
25		15.9	1.0	1.2	71.0	<0.2	<0.2	1.10	5.3	4.4	<0.1	0.47	0.27	<0.1	<0.4	<0.4	0.8	101.4
26		<0.2	<0.2	<0.2	66.6	<0.2	<0.2	<0.2	17.2	0.6	<0.1	<0.1	<0.1	<0.1	0.40	<0.4	15.8	100.6
27		16.5	0.5	0.5	73.6	0.27	0.33	1.12	2.9	1.5	<0.1	0.59	0.31	<0.1	<0.4	<0.4	<0.4	98.1
30		14.0	1.1	0.5	70.8	<0.2	0.31	1.03	7.4	3.9	<0.1	0.36	0.16	<0.1	<0.4	<0.4	<0.4	99.5
32		<0.2	<0.2	0.6	59.5	<0.2	<0.2	<0.2	12.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	26.3	99.3
35		14.3	0.5	0.6	78.0	0.27	0.38	0.89	3.4	2.2	<0.1	0.28	0.20	<0.1	<0.4	<0.4	<0.4	101.0
36		<0.2	<0.2	0.7	62.9	0.42	<0.2	<0.2	16.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	19.2	99.5
37		<0.2	<0.2	0.6	64.3	<0.2	<0.2	<0.2	15.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	0.79	20.4	101.4
38		0.6	<0.2	0.7	62.1	<0.2	<0.2	<0.2	15.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	20.2	99.3
39		<0.2	<0.2	0.6	59.2	<0.2	<0.2	0.28	12.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	26.4	99.3
40		6.6	1.9	1.1	66.5	0.25	0.26	0.34	14.8	6.9	<0.1	0.10	0.21	<0.1	<0.4	<0.4	1.6	100.5
41		<0.2	<0.2	<0.2	58.4	<0.2	<0.2	<0.2	12.3	<0.1	<0.1	<0.1	0.22	<0.1	1.02	0.65	27.0	99.5
42		<0.2	<0.2	<0.2	59.1	<0.2	<0.2	<0.2	18.1	1.7	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	20.4	99.3
43	Bowl	<0.2	<0.2	0.7	61.9	<0.2	<0.2	<0.2	16.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	17.5	96.4
48		<0.2	<0.2	0.3	55.5	<0.2	<0.2	<0.2	9.3	<0.1	<0.1	<0.1	<0.1	<0.1	0.75	<0.4	34.8	100.7
50		<0.2	<0.2	0.6	59.4	<0.2	<0.2	<0.2	12.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	26.6	99.0
52		<0.2	<0.2	0.6	60.0	<0.2	<0.2	<0.2	12.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	26.6	99.8
54		<0.2	<0.2	0.6	54.8	<0.2	<0.2	<0.2	9.4	<0.1	<0.1	<0.1	0.12	<0.1	<0.4	<0.4	34.6	99.4
55		<0.2	0.3	0.9	55.1	<0.2	<0.2	<0.2	9.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	35.4	100.7

Ref	**Area**	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**CuO**	**As_2O_3**	**Sb_2O_5**	**PbO**	**Total**
56		<0.2	<0.2	<0.2	57.2	<0.2	<0.2	<0.2	12.3	<0.1	<0.1	<0.1	0.12	<0.1	0.85	<0.4	28.9	99.3
57		<0.2	<0.2	0.1	59.2	<0.2	<0.2	<0.2	12.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	26.4	98.3
58		<0.2	<0.2	0.7	60.0	<0.2	<0.2	<0.2	12.8	<0.1	<0.1	<0.1	0.15	<0.1	<0.4	<0.4	26.4	100.2
60		0.3	<0.2	0.5	67.8	<0.2	<0.2	0.20	15.6	0.5	<0.1	0.35	0.28	<0.1	<0.4	<0.4	14.7	100.4
61		<0.2	<0.2	<0.2	64.2	<0.2	<0.2	<0.2	16.2	0.7	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	17.8	99.2
62		<0.2	<0.2	0.3	65.7	<0.2	<0.2	<0.2	15.9	0.8	<0.1	0.73	0.20	<0.1	<0.4	<0.4	15.3	99.1
64		<0.2	<0.2	0.2	67.3	<0.2	<0.2	<0.2	16.4	0.5	<0.1	0.84	0.32	<0.1	<0.4	<0.4	14.0	99.8
66		<0.2	<0.2	0.2	67.8	<0.2	<0.2	<0.2	15.8	0.7	<0.1	0.24	0.10	<0.1	<0.4	<0.4	15.1	100.0
68		0.4	<0.2	0.6	66.8	<0.2	<0.2	0.25	16.7	0.3	<0.1	0.93	0.35	<0.1	<0.4	<0.4	12.7	99.2
70		<0.2	<0.2	<0.2	62.2	0.23	<0.2	<0.2	17.0	1.2	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	19.0	99.6
71		<0.2	<0.2	0.3	65.8	<0.2	<0.2	0.21	16.6	0.7	<0.1	0.45	0.12	<0.1	<0.4	<0.4	15.3	99.6
74		0.3	<0.2	<0.2	66.7	<0.2	<0.2	<0.2	17.5	0.6	<0.1	<0.1	0.12	<0.1	<0.4	0.50	14.3	100.2
80		<0.2	<0.2	<0.2	68.1	<0.2	<0.2	<0.2	17.4	0.6	<0.1	<0.1	0.12	<0.1	<0.4	<0.4	13.5	99.7
81		<0.2	<0.2	<0.2	66.6	<0.2	<0.2	0.28	18.0	0.7	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	13.7	99.2
82		<0.2	<0.2	0.7	65.1	<0.2	<0.2	<0.2	16.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	17.2	99.7
83		0.2	<0.2	0.7	63.8	<0.2	<0.2	0.25	16.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	17.2	98.8
84		<0.2	<0.2	<0.2	66.9	<0.2	<0.2	<0.2	15.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	18.0	100.0
100		<0.2	<0.2	0.6	59.1	<0.2	<0.2	<0.2	12.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	27.2	98.9
101	Foot	<0.2	<0.2	<0.2	61.0	<0.2	<0.2	<0.2	16.2	1.6	<0.1	<0.1	0.21	<0.1	<0.4	<0.4	20.2	99.2
102	Bowl	0.2	<0.2	<0.2	61.5	<0.2	<0.2	<0.2	17.5	1.3	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	19.6	100.2
103	Foot	<0.2	<0.2	0.4	49.5	<0.2	<0.2	<0.2	8.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	40.6	99.3
104	Bowl	<0.2	<0.2	0.6	49.9	<0.2	<0.2	<0.2	9.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	40.0	100.0
105	Foot	<0.2	<0.2	0.6	49.3	<0.2	<0.2	<0.2	9.4	<0.1	<0.1	<0.1	<0.1	<0.1	0.61	<0.4	39.8	99.6
106	Bowl	<0.2	<0.2	0.6	49.1	<0.2	<0.2	<0.2	9.4	<0.1	<0.1	<0.1	<0.1	<0.1	0.66	<0.4	39.3	99.1
107		12.0	3.1	1.3	62.4	0.33	<0.2	1.00	5.7	11.1	<0.1	0.81	0.55	<0.1	<0.4	<0.4	1.6	99.8
108		5.8	1.7	1.0	64.5	<0.2	<0.2	0.49	10.7	5.3	<0.1	1.15	0.46	<0.1	<0.4	<0.4	9.7	100.8
109		5.8	1.8	1.0	64.1	<0.2	<0.2	0.52	10.8	5.2	<0.1	1.17	0.57	<0.1	<0.4	<0.4	9.8	100.7
110		<0.2	<0.2	<0.2	66.3	<0.2	<0.2	<0.2	17.2	0.5	<0.1	<0.1	<0.1	<0.1	<0.2	<0.4	14.0	98.2
111		<0.2	<0.2	0.5	67.6	<0.2	<0.2	<0.2	18.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	13.4	99.5
112		<0.2	<0.2	<0.2	68.3	<0.2	<0.2	<0.2	17.0	0.4	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	14.4	100.0
113		<0.2	<0.2	<0.2	64.9	<0.2	<0.2	<0.2	15.9	1.0	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	17.5	99.3
114		<0.2	<0.2	<0.2	63.3	<0.2	<0.2	<0.2	17.8	0.6	<0.1	<0.1	<0.1	<0.1	<0.4	<0.4	19.1	100.7
115		<0.2	<0.2	0.3	59.0	<0.2	<0.2	<0.2	17.8	1.6	<0.1	<0.1	0.19	<0.1	<0.4	<0.4	20.0	98.9
116	Foot	<0.2	<0.2	0.7	64.9	<0.2	<0.2	<0.2	16.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.4	0.49	18.0	100.2