ICPS : A MULTI-ELEMENT APPROACH TO GLASS ANALYSIS

Michael Heyworth *

Before the 1960's the analytical techniques used for the analyses of early glass were either wet cheminal methods or involved optical emission spectroscopy which yielded qualitative an semi-quantitative résults. The majority of analyses were carried out using a very small number of samples an looked at a very restricted range of elements.

Since then, x-ray fluorescence, neutron activation analysis and atomic absorption techniques have been more widely used to analyse early glass and it has been possible to produce quantitative results for a wider range of elements with greater accuracy.

In the analysis of glass it is important to obtain data for a comprehensive range of elements from a large number of geographically and chronologically distributed samples before more general patterns can be expected to emerge. Recent research at the University of Bradford in the UK has investigated the potential of the relatively new analytical technique of inductively coupled plasma spectrometry (ICPS) for the analysis of glass materials. ICPS has been available for several years but its impact on archaeology has been negligible.

ICPS combines the advantages of optical emission spectroscopy and atomic absorption. In addition it overcomes many of the interelement interference effects that occur so often with techniques such as atomic absorption. Plasma spectrometry offers the prospect of good accuracy and high precision for major and minor elements in glass and good precision for many trace elements down to the 1ppm level. Major and minor elements can be analysed to as least as good a precision by conventional wavelength dispersive x-ray fluorescence but the advantage of the plasma spectrometer by comparison, lies in the relative ease of handling smaller samples an in greater numbers, both of which are often critical factors with regard to archaeological materials. It is even possible to detect a number of the rare earth elements and if an enrichment procedure is followed in the preparation of the sample then it is possible to analyse nearly all the rare earth elements. In the analysis of glasses the correlations between major and trace elements are fundamental to the determination of raw material types and associated impurities, and to date have been derived from two separate techniques, XRF and NAA, each with differing systematic errors.

Typically, ICP spectrometry requires a sample of 100 mg (0.1g) of glass to be ground up and dissolved in acid. The sample preparation method used removes silica in the dissolution procedure, but all the other major and minor elements, and many trace elements, can be determined in this more concentrated solution. Each complete analysis requires only 1-2 minutes (excluding sample preparation time) and the résults can be output on a computer as concentrations using calibration data stored in the computer memory. The silica content of the glass can be calculated by difference.

With a multi-element approach it is possible to consider the suite of elements/oxides in terms of (i) those major oxides necesary to produce a working glass, usually soda, lime and silica ; (ii) those minor oxides present as impurities in likely raw materials ; (iii) those trace elements which are associated with the major and minor elements ; and (iv) those elements which were added deliberately to the glass batch and which reflect technological differences between the glass groups. The groupings of the elements used in this step-process allow a fuller understanding of the compositional differences in the groups of glass. It often requires a comprehensive range of elements to draw distinctions between groups of glass samples. This indicates the value of a multi-element approach such as is possible by ICPS but is not so readily achieved by some other methods or combinations of methods.

It is also important to have a detailed knowledge of the archaeological context from which the glass came or it is very difficult to build up a picture of the nature of the glass industry which produced the glass. Archaeological evidence can be used to reconstruct the social and economic environment in which the glass was produced. It may be that there was a group of glassworkers who, through patronage, could rely on continued supplies of raw materials and who produced and melted glass in the area. or the glass may reflect a reworking process that took place with cakes or even cullet being transported especially for the purpose. These questions cannot be answered from chemical analysis alone. We do not often find any physical evidence of the sort of industry which is portrayed in Medieval documents. However the archaeological evidence, coupled with comprehensive analytical data, can go a long way to help us understand the nature of the ancient glass industries.

The multi-element approach, adopted here using inductively coupled plasma spectrometry, together with a detailed study of the archaeological contexts, will significantly increase our understanding of the glass industry in the past. This is now being applied to large groups of middle Saxon glass from England from which it is hoped to gain a more detailed knowledge of the glass industry at this time.

* School of Physics, University of Bradford, England.