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ARCHAEOMETRICAL ANALYSIS OF GLASS BEADS: POTENTIAL, LIMITATIONS, AND RESULTS

Adelphine Bonneau, Jean-François Moreau, Ron G.V. Hancock, and Karlis Karklins

Over the past few decades, several new analytical techniques have been used to determine the composition and the likely production centers of glass beads found at archaeological sites around the world. Made since antiquity, glass beads are important artifacts which can provide much more information than their small size suggests. This article reviews the most common analytical techniques used to study glass beads – optical microscopy, scanning electron microscopy (SEM), x-ray fluorescence (XRF), instrumental neutron activation analysis (INAA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and Raman spectroscopy – and discusses their potential, limitations, and what results may be expected.

INTRODUCTION

Glass beads are found around the world in many different cultures and societies from antiquity to the present day. Their study is very important and can provide technical and cultural information regarding their manufacturers and users. Most of the analytical techniques utilized are the same as those applied to glass in general. Recently, Janssens (2013) compiled a review of a large range of techniques for analyzing glass. Previous studies include Pollard and Heron (1996:149-193) and Bertolotti et al. (2013). It is, however, sometimes difficult to apply the same techniques to glass beads because of their size and the limited possibilities of sampling. Based on a workshop conducted by the authors in January 2014 at the annual meeting of the Society for Historical Archaeology, this article summarizes the various analytical techniques, indicating what is involved and what the results might reveal. Technical details have been kept to a minimum so the descriptions will be understandable by everyone. For more detailed information on each process, see Janssens (2013).

ANALYTICAL TECHNIQUES

There are two extreme positions in archaeometry regarding analytical techniques: the intensive use of them without a real archaeological question behind the analysis and, the opposite, the rejection of their use. Luckily, more and more studies adopt a middle ground.

Years ago, archaeometry was seen as a very peculiar science, the preserve of physicists and chemists who carried out analyses that could only be understood by them and who did not necessarily understand the problems and needs of archaeologists. This attitude has changed significantly in the last decades thanks to large-scale diffusion of information and the training of scientists in archaeological sciences. Still, relatively few studies are being conducted with good collaboration between scientists and archaeologists. It is extremely important to know when and where to consult an archaeological scientist (Pollard and Bray 2007).

Where does one find an archaeological scientist? Well-known museums such as the British Museum, the Louvre, and the Smithsonian have their own laboratories with such scientists but they generally only work on their museum's collections or on collections from other collaborative museums. Other archaeological scientists are situated in dedicated laboratories such as the Research Laboratory for Archaeology and the History of Art at the University of Oxford and the Canadian Conservation Institute in Ottawa, Ontario. Most archaeological scientists, however, are situated in non-archaeometrical/archaeological laboratories (mainly in universities), in departments such as geology, chemistry, physics, or material sciences, and thus are not too easy to find by someone who is not in the field of archaeometry. A good way to find one is to consult recent publications where their details are provided; *see* the Archaeometric Analysis section of the Researching the World's Beads Bibliography (http://www.beadresearch.org/Pages/Archaeometric%20Analysis.pdf) or Janssens (2013).

Most of the time, archaeologists and other researchers come to archaeological scientists when they have heard of a new technique that they want to apply to their artifacts, or when they have many artifacts and do not know what to do with them. In such cases, analysis tends to give unusable

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results and wastes time and money. Before analysis is undertaken, the archaeologist must pose specific questions to the archaeological scientist that need to be addressed in the analysis and will determine the appropriate technology that is required. Generally, questions about specimen sampling, time, and costs will be the center of initial discussions. A research plan can then be created, keeping in mind that analytical techniques should always be used coupled with typology and other historical and archaeological methods. Before any kind of analysis, beads should be well cleaned (ultrasonification may be needed) to avoid contaminating the results.

The most common techniques used to analyze glass beads are optical microscopy, scanning electron microscopy (SEM), x-ray fluorescence (XRF), instrumental neutron activation analysis (INAA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and Raman spectroscopy. These instruments are not specifically dedicated to the analysis of glass and glass beads, and unless they are in a specific laboratory dedicated to archaeometrical studies, they are rarely used for this purpose. They were initially developed for the fields of chemistry, biology, materials sciences, and geology. Interdisciplinary studies subsequently brought scientists and archaeologists together and new protocols and sometimes new components were created to allow the various techniques to be applied to archaeological materials. It is thus extremely important to have a technician who can correctly prepare samples and apply the correct protocol to get good results.

Optical Microscopy

Macro- and microscopic observation of beads is often ignored as a first step in bead analysis but is a very important step of any study. Indeed many questions regarding manufacturing techniques and use of the artifacts can be answered by visual examination.

For instance, bubbles in drawn glass beads and striae on the surface are elongated while those in wound beads tend to be round (Figure 1). Wound beads also exhibit wind marks that encircle the diameter. In the case of blown beads, the presence of elongated bubbles reveals that they were blown in heated drawn tubes rather than free blown.

Drawn beads were sometimes flashed in clear glass to prevent discoloration and make them shinier. This thin layer may sometimes only be visible under magnification (Figure 2). Some specimens exhibit crackled surfaces (Figure 3), probably the result of thermal shock due to improper annealing.

Information regarding bead use may also be observed using the microscope. An examination of the ends of a bead may reveal battering suggesting their use in necklaces or bracelets. There may also be thread wear on the edges of the perforation.

Finally, microscopic observation reveals the state of degradation of the glass. Most of the analytical techniques detailed below perform surface analysis, so they give results from the first micrometers of the glass. If the glass is altered, the results will not reveal the true composition of the glass. Degraded glass results from the chemical reaction between it and the molecules present in its environment, whether archaeological or ethnological. This results in changes to the glass structure and the chemical composition.

Chemically altered glass has a very particular texture which can be easily identified under the microscope: one can see holes with a texture like honeycombs and sometimes iridescence is present as well (Figure 4A). On the other hand, mechanically altered glass is characterized by elongated holes on the surface (Figure 4B). These are caused by usage and/or soil conditions.

These features have little influence on the results but these areas should be avoided for better results as small secondarily deposited crystals may be in the holes and affect the results.

Scanning Electron Microscopy Coupled with X-ray Energy Dispersive Spectrometer

After microscopic observations, elemental analysis is often required to identify the type of glass and the colorants used and then to identify sub-groups based on the composition of the glasses. One of the methods used to obtain this information is scanning electron microscopy coupled with an x-ray energy dispersive spectrometer (SEM-EDS, sometimes designated SEM-EDRX or SEM-EDX). This technique uses an electron beam, generated by a (usually) tungsten filament, that is focused on the sample (Figure 5). The electrons interact with the sample and generate three principal rays:

1) Secondary electrons which provide a topographic image of the surface.

2) Backscattered electrons which give a chemical contrast image; i.e., parts of a sample with heavy elements will be brighter than parts with lighter elements. Newer machines, using two or more backscattered electron detectors, can product an image with topographic details as well.

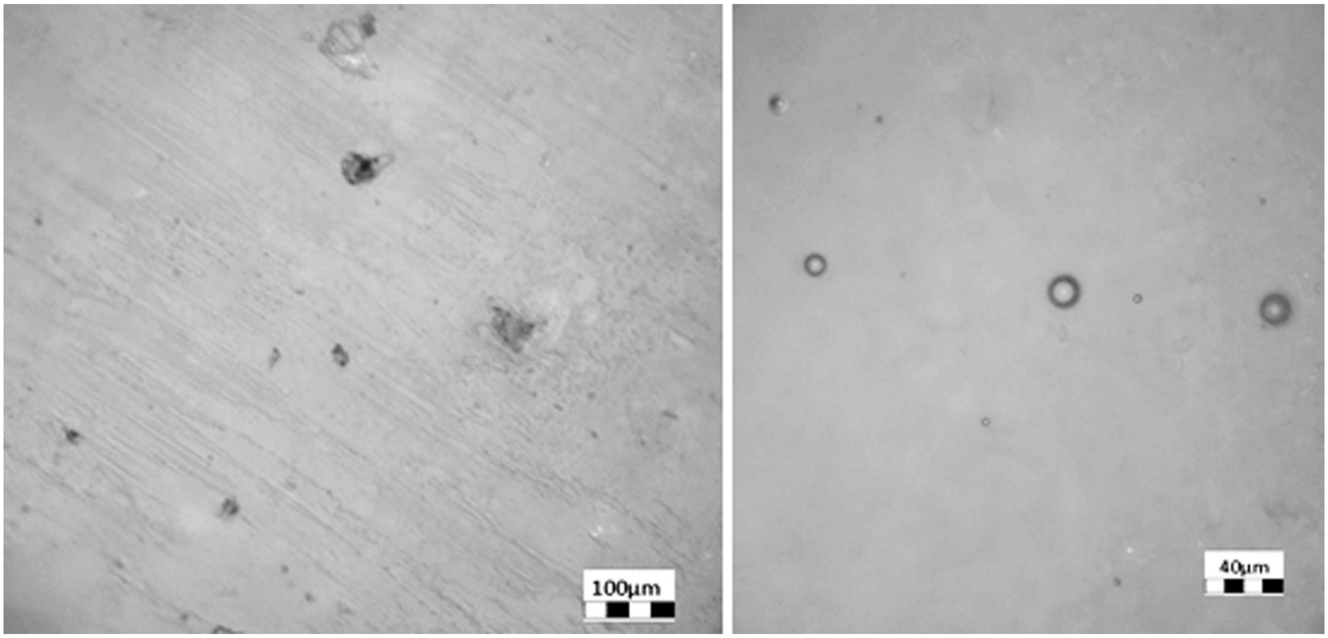

Figure 1. Microscopic view of elongated (left) and round (right) bubbles in the matrix of glass beads (all images by A. Bonneau unless otherwise specified).

3) X-rays which are characteristic of chemical elements present in the sample.

SEM-EDS thus permits both surface observation and elemental analyses. The observation function allows one to determine the nature of any alteration (Figure 6), natural or mechanical. When beads are sectioned and polished, the interaction between the layers can be investigated. Indeed, this is the area where preferential crystallization may take place and thus reveal the type of colorant/opacifier used (for an example with calcium antimony, *see* Lahlil et al. 2010).

Two kinds of systems are widely used: environmental/variable vacuum SEM and high vacuum SEM. In the first instance, no sample preparation is required. The specimen can be put directly in the chamber, but secondary electron images cannot be obtained because the secondary electrons interact with the air in the chamber before reaching the detector. In the second instance, as the chamber and sample are in a high vacuum atmosphere, electrons diffuse everywhere and create interference, called charges. To avoid this, a thin layer of carbon, gold, or another metal (called "coating") can be applied to the sample. While a carbon

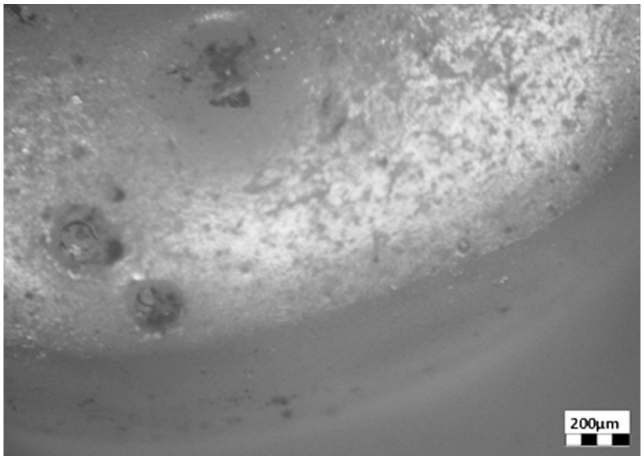

Figure 2. Bead with two layers; the core is white glass while the outer layer is transparent glass.

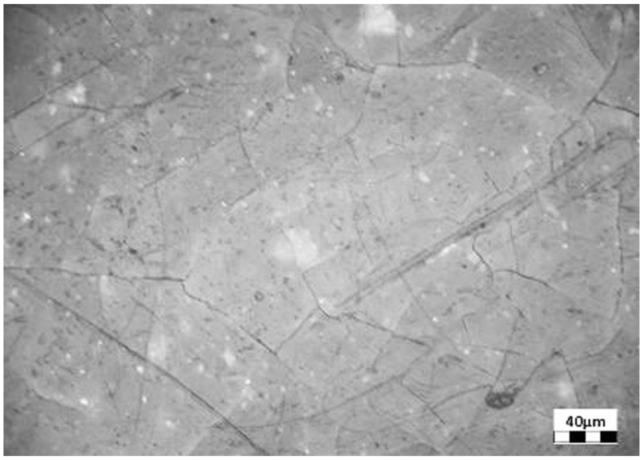

Figure 3. The crackled surface of a glass bead viewed under the microscope.

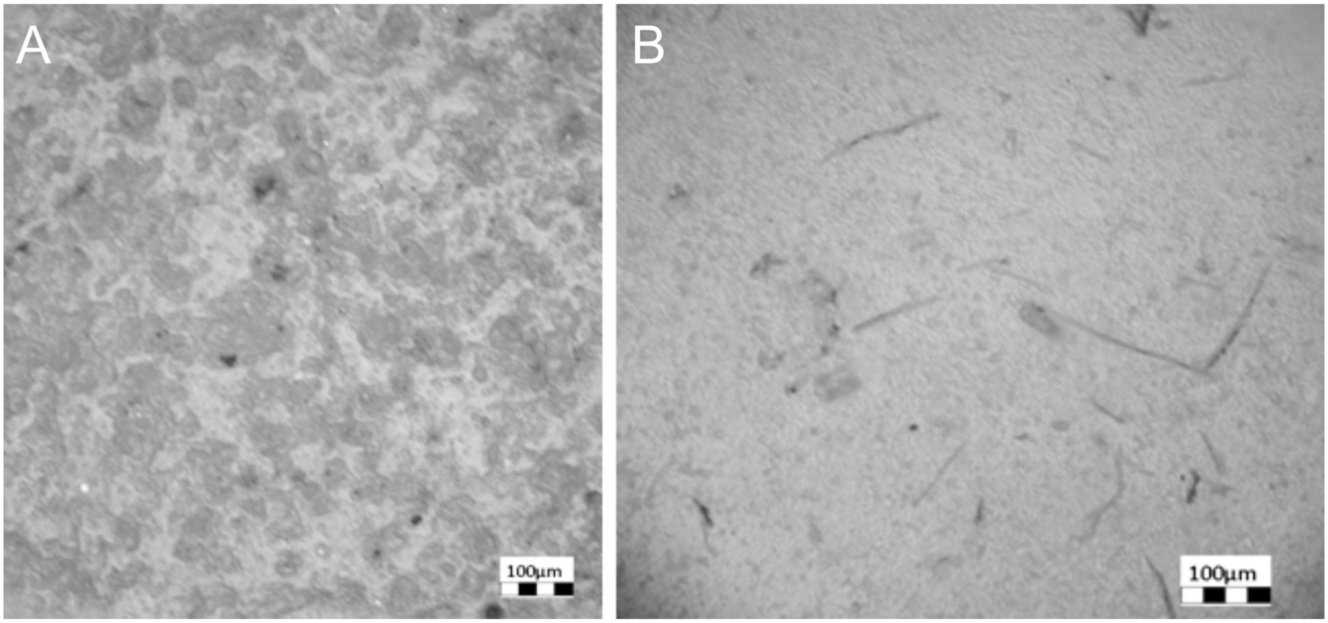

Figure 4. Chemically altered glass (A) and mechanically degraded glass (B).

layer can be removed after analysis if the bead has a smooth surface, gold and other metal layers cannot.

Elemental analysis is also possible with SEM-EDS. Using the energy of the x-rays emitted by the sample, it is possible to determine which chemical elements are present. Unfortunately, as the electron beam has limited power, it is not possible to detect all the chemical elements in the periodic table and their detection depends on the amount in the sample. Chemical elements can be detected from boron to lead, with differences depending on the instrument used. Moreover, they need to be present in amounts greater than 1-2% oxide weight to be detected.

Using these qualitative elemental results, it is possible to identify the type of glass (alkali, lead, etc.) and the colorants and opacifiers used (Figure 7). Semi-quantitative analysis, which allows the identification of glass sub-groups, is also possible but the samples need to have flat, polished faces. This requires that the beads be embedded in epoxy resin, sectioned, and polished (Figure 8). In this case, it is not possible to recover the bead after analysis. Moreover, as

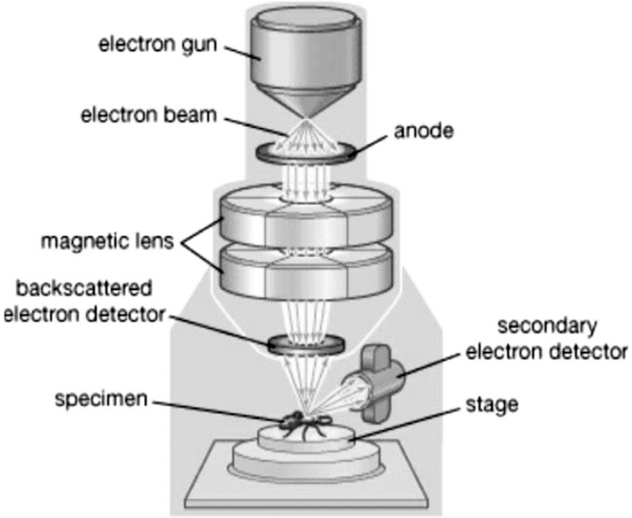

Figure 5. Schema of the SEM-EDS apparatus (*Encyclopedia Britannica*).

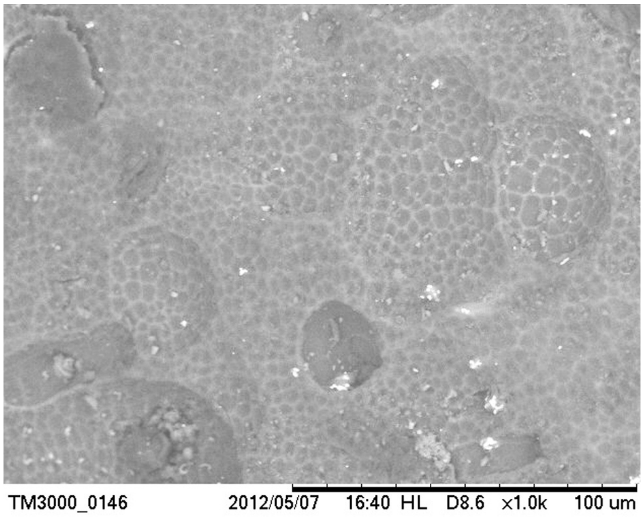

Figure 6. Backscattered electron image of a chemically altered glass.

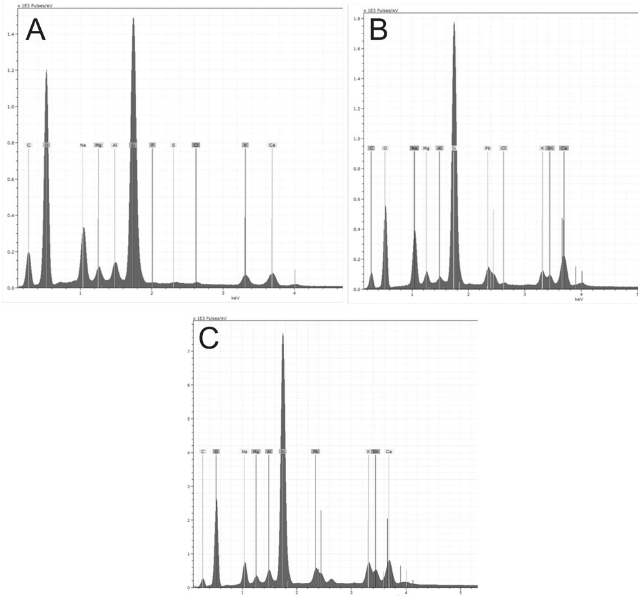

Figure 7. Examples of EDS spectra (x: x-ray energy in keV; y: counts). A, alkaline glass; B, lead-glass; C, glass opacified with tin.

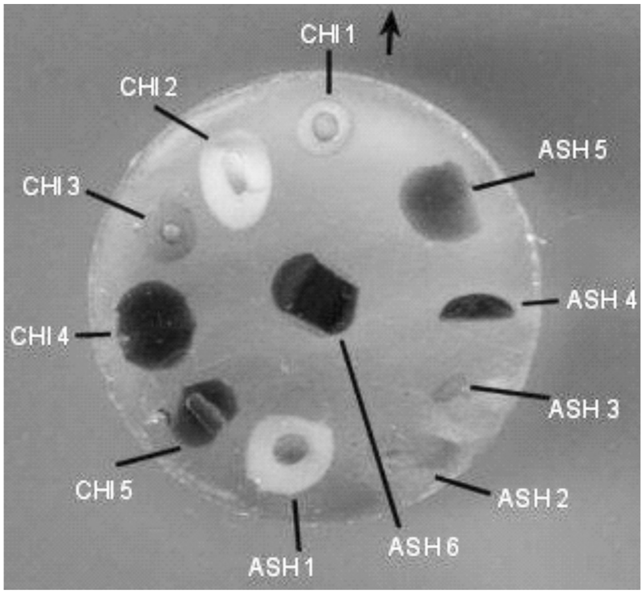

Figure 8. Glass beads prepared for semi-quantitative analysis with SEM-EDS.

detailed earlier, a layer of carbon or metal may be applied to it. The kind of coating used needs to be carefully chosen to avoid skewing the results. These are expressed in oxide weight or elemental weight with a relative error of 2-10%. Researchers need to remember that each percentage comes with an error, not always provided by the machine. To reduce the error, use glass standards and take readings at different points on the specimen to assess the homogeneity of the glass.

A useful technique for both observation and elemental analysis, SEM-EDS has been widely used to study glass beads; e.g., Garcia-Heras et al. (2005), Heck and Hoffmann (2002), and Shugar and O'Connor (2008). It is easy to find a lab and the cost is relatively low. If more detailed results are desired (e.g., trace elements, heavy elements, or more precise quantification), x-ray fluorescence (XRF) should be considered. SEM-EDS and XRF are often used together (the three cited articles are good examples).

X-ray Fluorescence

X-ray fluorescence (XRF) is very similar to SEM-EDS but observation is not possible. In this process, x-rays are focused on the sample which is excited and generates new x-rays which characterize the chemical elements. The results are expressed as spectra, as for the SEM-EDS.

As x-rays are more powerful than electrons, XRF can detect chemical elements from sodium to, theoretically, the end of the periodic table, and the rays go deeper into the sample (ca. 1µm for SEM-EDS; ca. 10-100 µm for XRF). As for SEM-EDS, the limits of detection (LOD) depend on the chemical elements. To simplify, the LOD is about 0.2-1% oxide weight for light elements and about 3 ppm to 20 ppm oxide weight for the heavy elements. These limits are provided as indications only and differ from one machine to another.

As in the case of SEM-EDS, XRF analysis cannot be quantitative without a prepared plane surface. Depending on the machine used, samples need to be in a powder form or polished in an epoxy resin (micro-XRF). Moreover, this technique requires the use of standards that have the same texture and density as the samples. Glass standards, such as NIST 610 or NIST 612, are well known but need to be in the same form as the samples; i.e, as a powder if the sample is in that form or polished if the sample was prepared that way. Furthermore, quantitative analysis for elements lighter than aluminum and silicon are not recommended even with prepared samples and using standards. This is a limitation for glass analysis in general.

In the case of portable XRF, only qualitative analysis should be performed. This instrument is a great tool for pre-selecting beads to be analyzed using laboratory techniques. Keep in mind, however, that x-rays can have very similar readings for different chemical elements; lead and antimony are great examples. This requires a good understanding of the machine and the ability to interpret automatic identifications made either by laboratory or portable instruments. This applies to both SEM-EDS and XRF analysis.

As for SEM-EDS, many researchers have used XRF to analyze glass beads. The articles cited in the SEM-EDS section are good examples and show the differences and similarities of the two techniques. Researchers should bear in mind that portable XRF should be used only for qualitative analysis and not for quantitative analysis.

XRF analysis is relatively inexpensive and very useful in quantifying chemical elements in glass, even in small proportions, and to define glass sub-groups which may be linked to production sites. For provenance studies, however, XRF is sometimes not precise enough and instrumental neutron activation analysis (INAA) or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) may be better suited for this purpose.

Instrumental Neutron Activation Analysis

INAA is based on the irradiation of a sample by neutrons in a nuclear reactor. A minute portion of the sample is turned into radioactive isotopes representing the chemical elements present in it. When they return to their stable state, they release gamma-rays which, recorded by a gamma spectrometer, can be related to an atom. As for SEM-EDS and XRF, each level of gamma-ray energy is linked to a specific element in the periodic table. This technique identifies the elements present in the sample and their quantity. As for XRF, it requires standards for quantification. One of the great advantages of INAA is that no sampling is generally required for beads. Beads of a mass of 5-10 mg are placed in plastic tubes that go directly into the irradiation site of the nuclear reactor. On the other hand, if a bead is composed of more than one layer of glass, the results will reflect the composition of the entire bead with no distinction between the layers. If the two glasses are very different in composition, the results will not reveal this.

Intensive chemical analysis of glass trade beads excavated in North America has been performed since the 1990s using INAA (e.g., Hancock et al. 1996, 1997; Moreau et al. 2002, 2006; Moreau and Hancock 2010). More than 30,000 beads have been analyzed, resulting in a very important database maintained by R.G.V. Hancock of McMaster University, Toronto, Ontario. Unfortunately, to be able to return beads to their owners, only short-life elements have been studied: aluminum, calcium, chloride, magnesium, potassium, sodium, tin, antimony, cobalt, copper, manganese, vanadium, arsenic, and gold. INAA is able to quantify almost all the elements in the periodic table but then samples need to be irradiated for a long time and thus they stay radioactive for decades, precluding their return.

Using the INAA database, attempts have been made to date beads using elemental composition comparison and a pattern of the use of opacifiers in white beads from the 17th century onward has been established (Figure 9) (Moreau et al. 2006; Moreau and Hancock 2010; Sempowski et al. 2000). The database is so significant that it was used in studies of trade glass beads found in Europe (Karklins et al. 2002) and in South Africa (Prinsloo and Colomban 2008).

A recent pilot study conducted by Bonneau et al. (2014) investigated the influence of INAA on the matrix of glass beads. Ten beads were analyzed and no important changes were recorded. Nevertheless, if Raman analysis is planned, it is recommended that it be carried out before INAA analysis. To be able to quantify other elements for provenance studies, for example, LA-ICP-MS is one of the possibilities.

The main limitation of INAA is that it turns a minute part of the sample into radioactive isotopes, thus limiting analysis to elements with short half lives unless one is willing to sacrifice the samples. Another limitation is that INAA is more expensive than the previous techniques.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry

LA-ICP-MS is a combination of three apparatus: a laser which ablates (pulverizes) a minute part of the sample, a plasma source which ionizes the ablated material, and a mass spectrometer which sorts the elements depending on their mass and charge (Figure 10). The sample is placed inside a vacuum chamber and a laser is focused on the point to be sampled. This point, depending on the laser and the machine, is about 100 μm which cannot be seen with the naked eye. The ablated material is then transported to the plasma source in a gas where it is ionized; i.e., each atom is separated and positive or negative charges are attached to it. The mass spectrometer then separates and quantifies the ions. The results are presented in the form of a chromatogram (Figure 11). There are two methods to undertake the initial ablation: spot or line. Using the spot method, the laser goes deeper and deeper into the bead. This is useful when the bead is composed of several layers as the constituents of each layer can be determined. In line analysis, the laser moves across the surface.

The LA-ICP-MS technique requires knowing the amount of one of the chemical elements in the sample (an "internal standard") before it is analyzed. For beads, silicon is often the chosen element. Another way to obtain quantification has been developed by Gratuze (*see* Janssen 2013:201-234) which does not require quantifying an element before analysis. Almost all of the elements in the periodic table can be recorded, but interference may occur

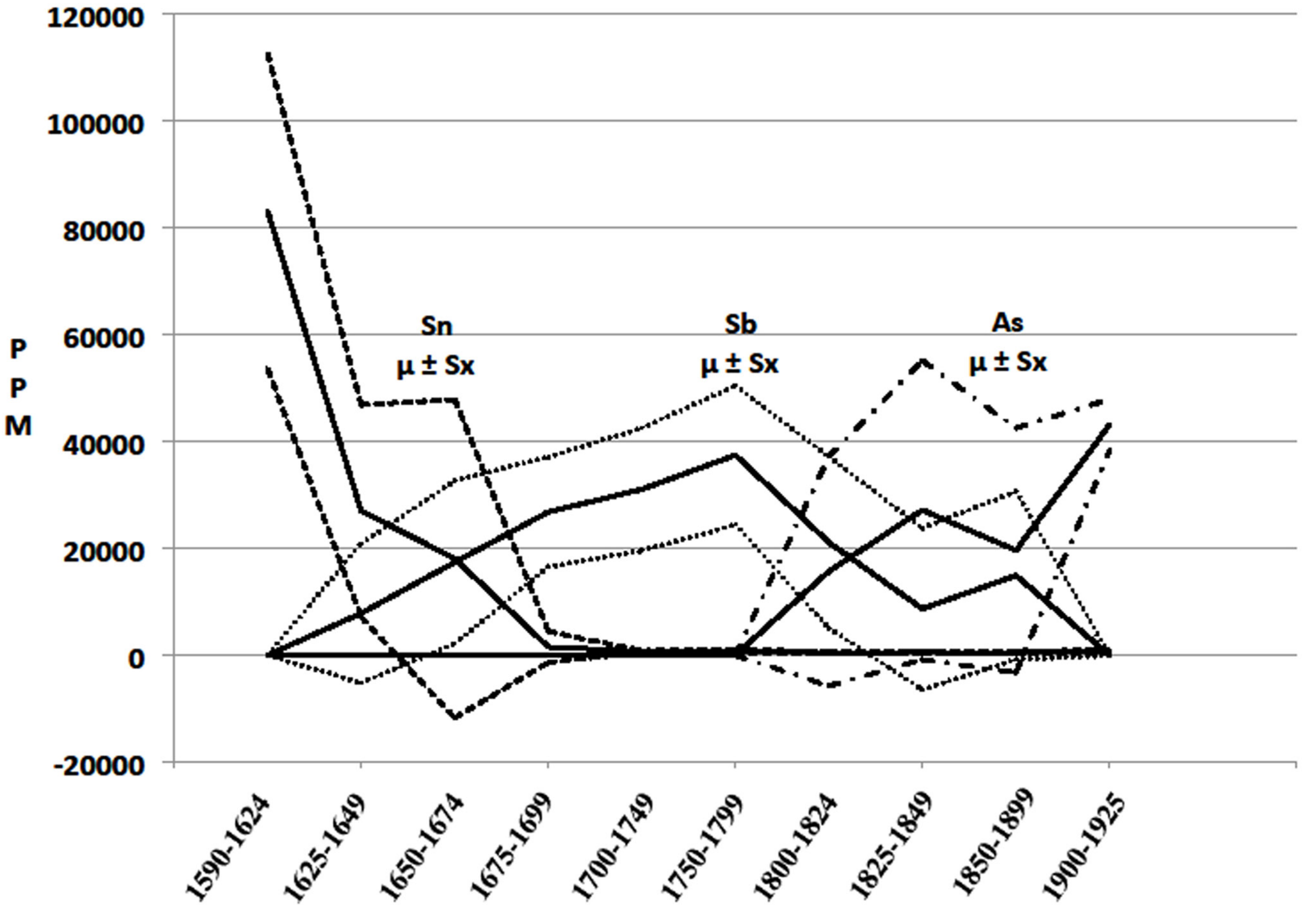

Figure 9. Pattern of the use of opacifiers in white beads over time (courtesy: J-F. Moreau).

where some ions interfere with the detection of others. To avoid any misunderstanding of the results, a careful discussion is recommended with a technician who has a thorough knowledge of the apparatus.

LA-ICP-MS and other mass-spectroscopy techniques have been used in many different studies around the world (e.g., Dussubieux 2001; Dussubieux and Gratuze 2003; Dussubieux et al. 2008, 2009; Walder 2014). This process has the great advantage that only a tiny portion of a sample is required for analysis, but the sample needs to be homogenous. Thus, replicate analysis needs to be performed at different points to avoid interference with highly crystallized spots, for example. Moreover, it is a surface technique so testing points need to be free of degradation. A quick, initial laser ablation of the spot or the line to be tested is often carried out to remove the first micrometers of glass which may be altered. For most of the other mass-spectroscopy techniques, which are not discussed here, samples have to be prepared; i.e., dissolved in acid or other chemicals before being introduce into the machine. It is, nevertheless, a requirement for isotopic analysis (*see* Janssen 2013:235-245, for more details).

LA-ICP-MS and INAA are both expensive techniques but are of great help for determining glass composition which often allows the determination of its place of manufacture.

Raman Spectroscopy

Raman spectroscopy is another analytical technique which has been developed during the last decade. This technique is still poorly known in glass studies but is cheap and can reveal a lot about glass composition. Unlike the other techniques detailed above, Raman spectroscopy analyzes molecular bonds and, thus, the matrix of the bead. It allows the determination of the "shape" of the opacifiers and colorants, and the type of glass.

In the process, a laser is focused on the sample (Figure 12). It excites molecular bonds in the sample which react

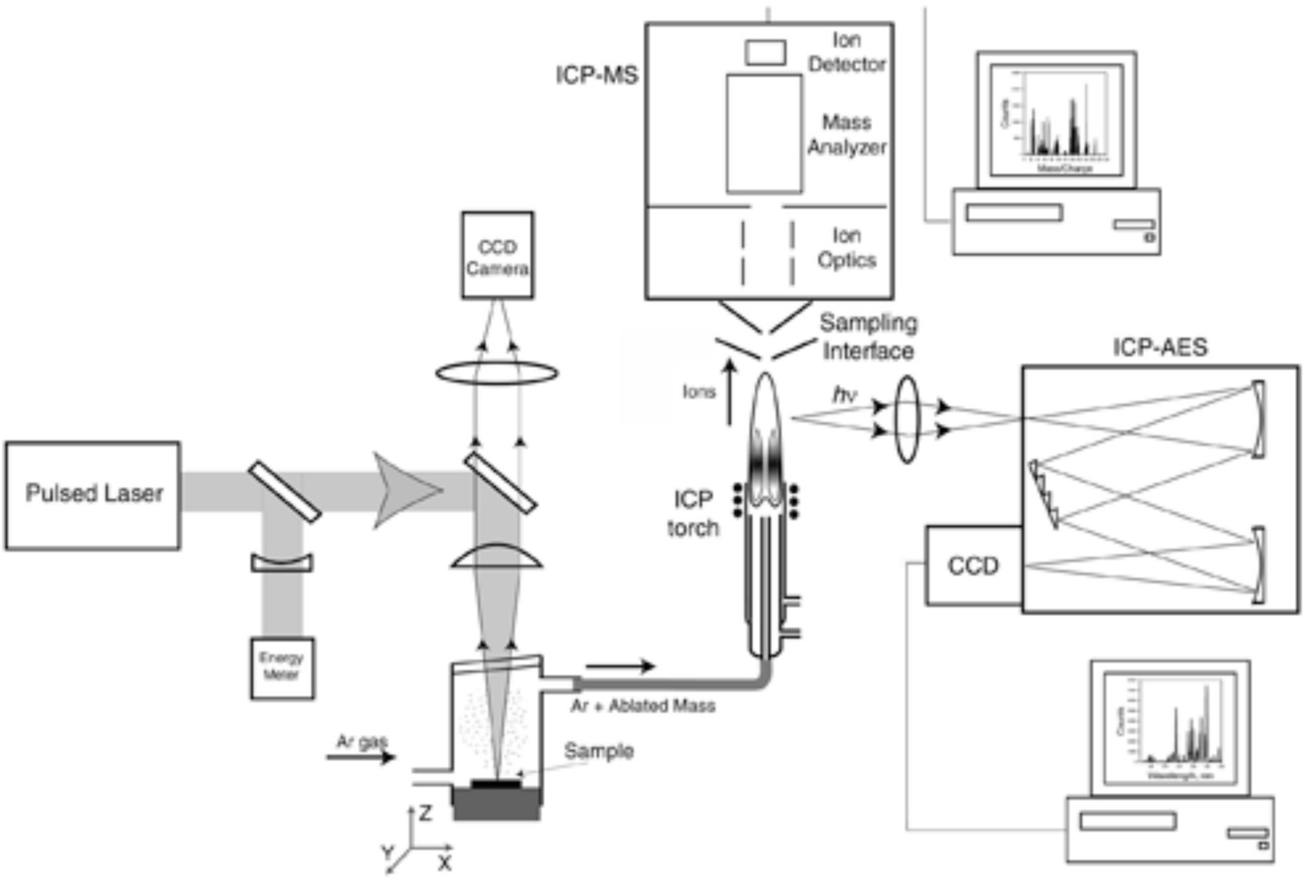

Figure 10. Schema of the LA-ICP-MS instrumentation (Energy Storage and Distributed Resources Department 2014).

by emitting three kinds of rays: Rayleigh rays which have the same wavelength as the laser, and Stokes rays and anti-Stokes rays which are characteristic of the molecule bonds that have been excited. Only the Stokes rays, which are the most intense, are recorded and the results are show as a spectrum (Figure 13). Different types of lasers are available for Raman analysis (488 nm, 514 nm, 532 nm, 633 nm, 785 nm, and 1064 nm). For glass analysis, green and red lasers (514 nm, 532 nm, and 633 nm) are the most used because they are more suitable for exciting molecular bonds in glass.

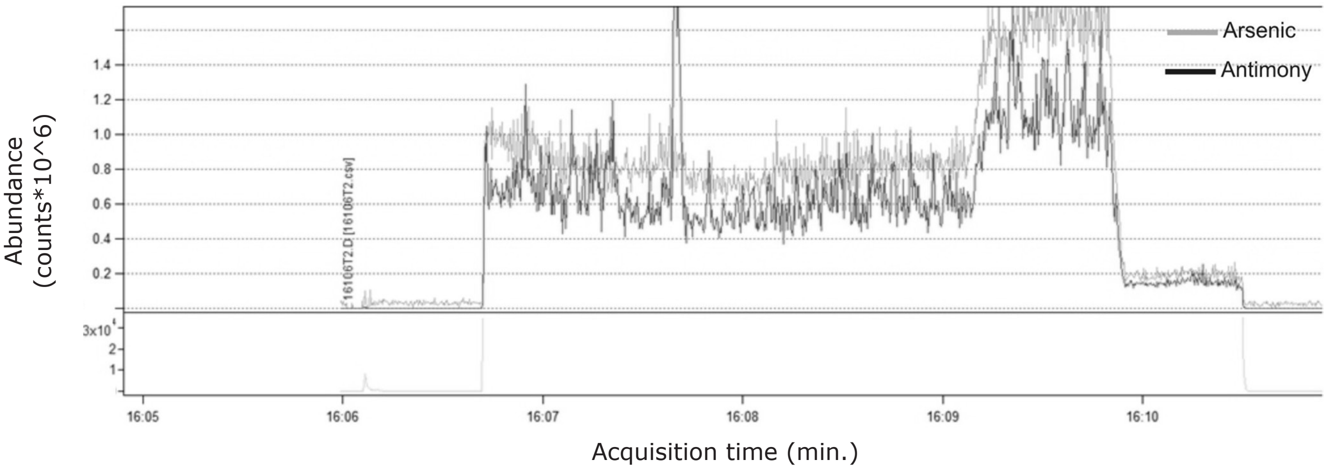

Figure 11. Example of a chromatogram from line analysis.

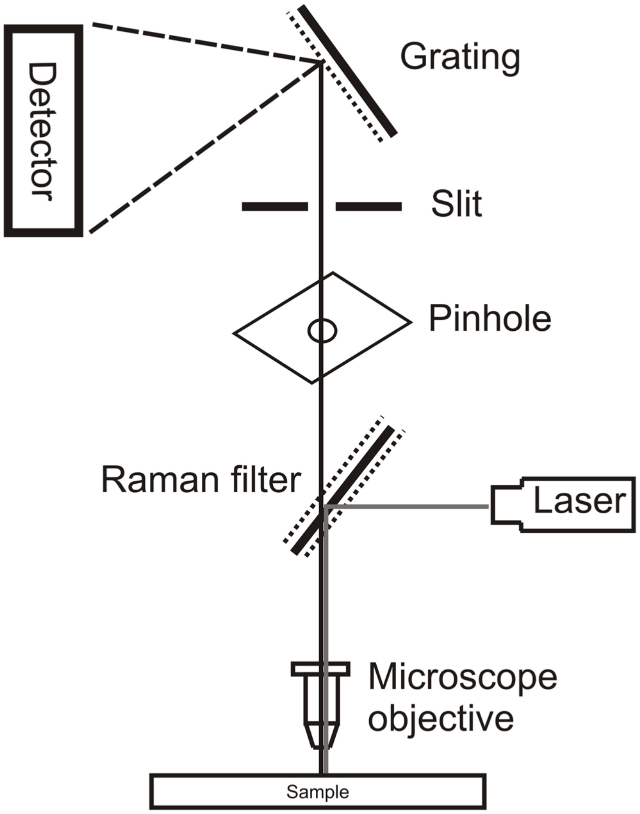

Figure 12. Schema of a Raman spectrometer.

Coupled to a microscope, the instrument is called a micro-Raman spectrometer. It is then possible to focus the laser on a very small part of the bead (ca. 5 µm², depending on the microscope objective used) which permits the analysis of different layers of glass or specific inclusions. Raman spectroscopy can identify the type of glass, the kind of opacifiers and colorants used, and using spectra treatments, determine glass sub-groups. This last step requires the use of specific software such as Grams, Origin Lab, or Matlab.

The Raman spectrum of a glass is composed of two massifs (broad peaks): one centered at ca. 500 cm^{-1} (bending massif) and another at ca. 1000 cm^{-1} (stretching massif). Calculating the area under each massif and dividing them reveals the polymerization index (Ip = A500/A1000) which is related to the amount of silicon in the glass and thus following Colomban (2003, 2004), to the processing temperature of the glass. The stretching massif can be investigated using the "Qn model" which requires the identification of the different peaks composing the massif. These peaks are linked to the molecular bonds in the glass matrix and thus can reveal differences in the same glass type, due to the manufacturing processes. Combining the "Qn model" and the Ip, it may be possible to identify sub-groups of glass types (for more details, *see* Janssens 2013:275-300).

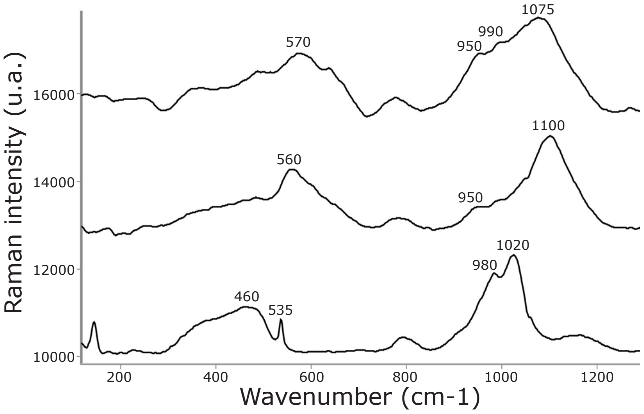

Figure 13. Example of Raman spectra of glass.

These kinds of spectra treatments require a good knowledge of the software and the mathematical processes behind the treatment.

So far, only a few studies have used Raman spectroscopy on glass beads (Bonneau et al. 2013; Prinsloo and Colomban 2008; Prinsloo et al. 2011). This technique has, however, proven its suitability and significance in other glass studies (e.g., Colomban et al. 2004, 2006; Colomban and Tournié 2007).

Raman spectroscopy is an inexpensive and quick technique to obtain information from glass beads. Its great advantage is that no preparation or sampling is required. Lasers can be powerful, however, and may burn samples if not used correctly. Raman spectroscopy suffers from fluorescence interference which is linked to sample composition and it is sometimes impossible to obtain any result. Once again, a well-trained technician is required.

CONCLUSION

This article describes six of the most commonly used and potentially useful methods to analyze glass beads. These are summarized in Table 1. Apart from INAA which examines the entire bead and portable XRF where spot analysis is ca. 1mm², all of them test a very small part of the sample (ca. 1 µµm to 100 µm). It is, therefore, necessary to test different parts (at least five) of each specimen to assess the homogeneity and reproducibility of the results. Thus, a number of results will be obtained for each object. Depending on the question asked by the researcher, one to several dozen beads will need to be analyzed.

As shown in Table 1, the cost of performing the various analytical techniques varies. SEM-EDS, XRF, and Raman analyses are generally less than $50 per hour with the help of

Table 1. Summary of Archaeometric Techniques Used to Analyze Glass Beads.

Technique	Research Potential	Sample Preparation	Relative Cost	Technician/ Training
Microscope	Observation	None or as needed	Generally none	Not required
SEM-EDS	Observation; elemental analyses (qualitative and semi-quantitative)	Coating; sections with polished surface for semi-quantitative analyses	Inexpensive	Required
XRF	Elemental analyses (qualitative and semi-quantitative)	Sections with polished surface for semi-quantitative analyses; standards required	Inexpensive	Required
INAA	Elemental analyses (qualitative and quantitative)	None	Expensive	Required
LA-ICP-MS	Elemental analyses (qualitative and quantitative); spatial repartition of chemical elements	None	Expensive	Required
Raman Spectroscopy	Observation if coupled to a microscope; molecular analysis	None	Inexpensive	Required

a technician (3-5 beads can be analyzed per hour). For INAA and LA-ICP-MS, the cost is about $70-$100 per bead. The fees charged depend on whether the researcher is a student or associated with a commercial firm, if the assistance of a technician is required, or if an agreement may be made with an institution to use their equipment.

Each technique has its merits and drawbacks, and the researcher wishing to use one or more of them should consult with an archaeological technician to determine which is the best for what information is desired. For example, it is impossible to say that SEM-EDS is better than XRF for elemental analysis as it depends on the questions asked and on the samples available to answer them. Other techniques are also available (such as x-ray diffraction or ion-beam analysis) and new ones will doubtless be developed as new requirements arise.

As most of the techniques described herein are of a complicated nature, only a brief summary of the technological aspects has been provided. The researcher should bear in mind that a well-trained person is needed to carry out the analyses detailed herein. It requires long training and a sound knowledge of each technique to be able to provide accurate results and to interpret them correctly. Moreover, more than one method is sometimes needed to answer all the questions. Thus, more than one trained person may be required to carry out the analyses.

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