

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Analyses of Selected Ceramics and Glass Artefacts

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Abstract

With the close co-operation of the Dolenjska Museum in Novo Mesto, Slovenia, a systematic chemical analysis of excavated pottery (dated to the Early Iron Age, 8-4 century B.C.E.) and glass objects (most probably from the same historic era) was initiated. In-house instrumental facilities at the National Institute of Chemistry, Ljubljana, enabled a systematic approach to the analysis (preparation of laboratory standards, selection of sample ablation procedures, inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) analysis), while the preliminary laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses were realised with close co-operation with the Laboratory for Analytical Chemistry (Eidgenössische Technische Hochschule – ETH) in Zürich. In this paper, some preliminary results will be presented and some future work described.

Introduction

Archaeological investigations have become more and more dependent on the appropriate chemical analysis of excavated artefacts. Numerous modern analytical techniques exist for this

purpose, with each technique becoming increasingly more efficient with regard to sensitivity and selectivity. Moreover, many of these techniques are non-destructive and permit the simultaneous determination of a large number of macro- and micro-components.

Results obtained using these methods should fulfil at least two major requirements –they should be as accurate as possible and they should be repeatable in the long-term.

Greater accuracy can be achieved by using reference materials. Long-term reproducibility with comparability of results using different analytical methods obtained initially in different laboratories can only be assured through the analysis of certified reference materials. These materials should have a chemical composition closely resembling that of the analysed archaeological artefacts.

To improve the inter-comparison of the obtained results, a laboratory reference material was prepared in such a way that approximately three kilogram of pieces of archaeological pottery found in different graves were collected. These fragments, dating from different historic periods were classified as waste material after the restoration process was completed. The pieces were thoroughly cleaned with water, dried and ground in a tungsten carbide grinding mill. After grinding, the samples were collected in a plastic container, where they were thoroughly homogenised by shaking for one day. The homogenised sample was split into four fractions, equipped and was appropriately labelled and sealed. One fraction was used for systematic analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) systems.

The production of pottery in ancient Slovenia was most probably organised locally since transportation costs were very high, the technology was simple and well known, and the raw material – clay – was available locally in large quantities. Only a small number of items may have been imported from other European regions, based on the characteristic shape of some of the items.

The first glass objects found in Slovenia date to the Late Bronze Age (1300-700 B.C.E.). Because of the unknown source of the beads, they were classified by association with the other items with which they were found in burial contexts. These are small ring shaped glass beads ranging in diameter from two to five millimetres. Mostly the glass is transparent with various tints of blue colour. The beads were found in grave urns filled with ashes mixed with burned bones. Glass beads have only been found in excavations conducted in the last twenty years. Prior to this time the grave soil was not subjected to flotation and the tiny beads were not recovered. The majority of glass beads found in Slovenia date to the Early Iron Age (8-4 century B.C.E.) and were excavated on Kapiteljska Njiva and Mestne Njive in Novo Mesto. Based on the number of glass beads found at these locations, the Novo Mesto archaeological site is one of the richest in Europe.

In contrast to the ceramic items, the origin of prehistoric glass objects found in Slovenia is still unknown. There are two major questions still to be answered: where was(were) the production site(s) of the raw glass and where was(were) the production site(s) of the finished objects.

In this paper, some preliminary results obtained by LA-ICP-MS analysis of powdered samples of pottery and of the selected glass objects, are presented and compared to those obtained by ICP-OES and ICP-MS (after the appropriate sample decomposition – fusion decomposition or fuming decomposition by hydrofluoric acid (HF)). The results of LA-ICP-MS analysis of selected

glass samples will be presented as well with special emphasis on the procedures to be developed in order to begin to generate a high quality data base which can be used later to locate the sources of the raw materials.

Experimental

Measuring Conditions:

Samples were analysed sequentially using ICP-AES (Thermo Jarrell-Ash AtomScan 25), ICP-MS (Agilent Technologies, 4500 plus) and LA-ICP-MS (Perkin Elmer Sciex Elan 6100 DRC; Perkin Elmer, Norwalk, CT, U.S.A), 193 nm excimer laser (MicroLas GeoLas; MicroLas, Göttingen, Germany).

ICP-AES:

- RF Power: 1350 W;
- Nebuliser: pneumatic (cross-flow);
- Gas flow-rates: plasma gas 1.0 l/min, carrier gas 0.9 l/min and coolant gas 14 l/min;
- Observation height: 15 mm;
- Sample flow-rate: 1.7 ml/min.

ICP-MS:

- RF power: 1250 W;
- Nebuliser: Babington type;
- Gas flow-rates: plasma gas 0.93 l/min, carrier gas 0.93 l/min and coolant gas 14 l/min;
- Sample flow-rate: 0.5 ml/min.

LA-ICP-MS:

- 193 nm ArF excimer laser (MicroLas GeoLas; MicroLas, Göttingen, Germany) coupled to a Sciex Elan 6100 DRC ICP-MS (Perkin Elmer, Norwalk, USA);
- Laser: 120 μm , 5 Hz, 12 J/cm²;
- ICP-MS: 1400 W, 0.7 l/min argon (mixing gas) and 1.0 l/min helium used as carrier gas;
- Data acquisition: 30 seconds background, 1 minute ablation time, data evaluation according to Longerich et al. (1996).

Sample preparation

For LA-ICPMS, the glass beads were not specially prepared. The surface was cleaned with ultrapure water (purified using Millipore Milli-Q[®] Element Ultrapure Water System) and dried. Subsequently, the glass bead was fixed on a stainless steel rod and put into the ablation cell (Figure 1). Each colour was analysed individually using a laser beam of eighty microns in diameter. At each sampling spot more than forty elements were measured. The calibration was carried out using glass reference standards from the National Institute of Standards and Technology (NIST 610). The percentages of the trace elements were calculated based on the normalisation to 100 weight percent of the major element oxides.

For the analysis of powdered pottery, the samples were prepared in two ways – by fusion decomposition with lithium metaborate (LiBO_2) and by fuming decomposition with hydrofluoric acid.

One hundred milligrams of well-pulverised and homogenised sample (or about 100 mg of certified reference material National Bureau of Standards (NBS), SRM 99a sodium feldspar), together with 500 milligrams of lithium metaborate, was weighed into a platinum crucible. The mixture was melted for thirty minutes and after cooling the content was dissolved in 200 millilitres of five percent (v/v) nitric acid (HNO_3). The sample was then transferred into a 200



Figure 1. Glass bead installed on the stainless steel rod. The ablation site is marked with a red ellipse.

millilitre volumetric flask and diluted to the mark. The concentration of individual elements was determined by using the appropriate calibration curves.

Fuming decomposition started by adding of 500 milligrams of pulverized sample (or about 500 mg of certified reference material NBS, SRM 99a sodium feldspar) to a 100 millilitre polytetrafluoroethylene (Teflon[®]) crucible and wetting with water. One millilitre of 65 percent perchloric acid (HClO_4) and 15 millilitres of 40 percent hydrofluoric acid were added and the mixture was heated to dryness. The whole procedure was repeated. The dry residue was dissolved (at a temperature below the boiling point) with 10 millilitres of 32 percent hydrochloric acid (HCl). The dissolved residue was transferred into 50 millilitre volumetric flasks and diluted to the mark with Milli-Q[®] water.

Approximately two grams of powdered sample was pressed in tablets (1 cm i.d. 5 mm thick). No additives were added to the sample. The applied pressure was 10 Kp/cm², internal standard silicon dioxide (SiO_2) (44.3 percent, Si = 207087 ppm), and Al_2O_3 (18.4 percent, Al = 97381 ppm).

Results

Two sample dissolution techniques were used in order to assure a higher quality of data which are to be used as reference values in later analysis. An independent experiment was carried out in which the powdered pottery sample was pressed in tablets and analysed by LA-ICP-MS. The results of these experiments are summarised in Table 1 (matrix components) and in Table 2 (trace elements).

Different sample decomposition procedures resulted in different samples, which were later analysed by the selected analytical technique (ICP-OES and/or ICP-MS). After fusion decomposition by lithium metaborate, the samples contained very high concentrations of matrix originating from the lithium metaborate. Because of that contamination, this set of samples was not analysed by ICP-MS. The other set of samples were decomposed by fuming with hydrofluoric

acid. The remaining hydrofluoric acid was removed after the dissolution was finished, and consequently no additional matrix component was added to these samples. In these samples, the elemental analysis was performed by using ICP-OES and ICP-MS.

| Matrix comp. (%) | FSD-ICP-OES | r.s.d., % (n=23) | FMD-ICP-OES | r.s.d., % (n=27) | FMD-ICP-MS | r.s.d., % (n=27) | LA-ICP-MS* | r.s.d., % | LA-ICP-MS** | r.s.d., % |
|--------------------------------|-------------|------------------|-------------|------------------|------------|------------------|------------|-----------|-------------|-----------|
| SiO ₂ | 44.3 | 3.3 | / | / | / | / | 44.9 | 4.76 | 44.3 | / |
| Al ₂ O ₃ | 19.1 | 3.2 | 21.9 | 2.0 | 18.4 | 4.8 | 18.4 | / | 18.2 | 4.8 |
| Fe ₂ O ₃ | 5.3 | 3.5 | 6.1 | 1.8 | 6.1 | 2.7 | 0.36 | 9.8 | 0.35 | 8.8 |
| MgO | 0.76 | 5.5 | 0.78 | 2.5 | 0.76 | 3.7 | 0.46 | 3.5 | 0.45 | 4.5 |
| TiO ₂ | 1.16 | 83.0 | 1.03 | 5.6 | 1.17 | 8.0 | 0.57 | 14.1 | 0.55 | 13.6 |
| CaO | 0.70 | 31.3 | 0.61 | 5.7 | 0.65 | 8.2 | 0.42 | 2.0 | 0.42 | 4.8 |
| K ₂ O | 1.0 | 18.0 | 1.2 | 4.2 | 1.2 | 3.7 | 0.31 | 14.4 | 0.30 | 12.4 |
| P ₂ O ₅ | 1.08 | 4.2 | 1.19 | 2.3 | / | / | 0.30 | 12.7 | 0.29 | 11.0 |
| MnO ₂ | 0.059 | 4.4 | 0.068 | 2.5 | 0.065 | 2.7 | 0.045 | 11.5 | 0.044 | 10.3 |

FSD-Fusion Decomposition, FMD, Fuming Decomposition (HF) *int. standard Al₂O₃, **int. Standard SiO₂

Table 1. Determination of Matrix Component and Traces Elements in Archaeological Pottery, by ICP-MS, ICP-OES and LA-ICP-MS

| Traces (%*10 ⁻⁴) | LA-ICP-MS* | r.s.d. (%*10 ³) | LA-ICP-MS** | r.s.d. (%,*10 ³) | FMD - ICP-MS | r.s.d. (%*10 ³) |
|------------------------------|------------|-----------------------------|-------------|------------------------------|--------------|-----------------------------|
| Li | 49.3 | 7.7 | 48.5 | 3.8 | 80 | 19 |
| B | 54.1 | 17.7 | 53.5 | 20.4 | 100 | 174 |
| Na | 824.3 | 10.9 | 812.4 | 9.5 | 850 | 5 |
| V | 142.9 | 6.5 | 140.6 | 4.8 | 180 | 3 |
| Cr | 128.7 | 15.0 | 125.5 | 11.8 | 200 | 4 |
| Co | 21.7 | 9.8 | 21.4 | 4.3 | 26 | 10 |
| Ni | 118.6 | 8.0 | 116.8 | 6.7 | 136 | 3 |
| Cu | 76.9 | 8.3 | 75.7 | 7.0 | 90 | 24 |
| Zn | 154.7 | 7.7 | 152.0 | 5.9 | 190 | 14 |
| As | 23.2 | 6.0 | 22.9 | 4.8 | 30 | 90 |
| Rb | 90.4 | 7.5 | 89.0 | 5.5 | 94 | 4 |
| Sr | 34.4 | 6.1 | 34.0 | 8.4 | 54 | 5 |
| Cd | 1.6 | 11.9 | 1.5 | 12.3 | 2 | 113 |
| Sn | 6.3 | 10.1 | 6.2 | 7.8 | 5 | 10 |
| Ba | 256.6 | 1.7 | 253.2 | 3.8 | 500 | 81 |
| Pb | 42.8 | 6.3 | 42.2 | 5.5 | 20 | 73 |
| U | 4.3 | 17.1 | 4.2 | 16.2 | 0.5 | 41 |

*int. standard Al₂O₃, **int. Standard SiO₂

Table 2. Determination of Traces Elements in Archaeological Pottery, by ICP-MS, ICP-OES and LA-ICP-MS

The results of the preliminary determination of matrix components in the same sample by LA-ICP-MS show significantly different values for certain elements. Our opinion is that values obtained by LA-ICP-MS cannot be compared to those obtained by ICP-OES and/or ICP-MS yet. The main source of error could be the sample inhomogeneity. A laser beam with a diameter of 60 micrometres analyzes individual grains of a sample which could be of very specific composition. Regardless of this drawback, the direct analysis of archaeological pottery seems to be very promising if additional sample homogenisation were performed and a wider laser beam were applied

In Table 2 the results of the determination of trace elements in the same samples are shown. When the ICP-MS analytical system was applied, only samples obtained by fuming decomposition were analysed (to avoid the clogging of the cones by the very high salt content in the samples). The same set of trace elements was also determined by LA-ICP-MS. It should be pointed out that the differences in the determined concentration levels for the individual samples is even more pronounced for trace elements than for the major elements (Table 1). The reason is most probably the same inhomogeneity of the samples seen in the matrix analyses. There is most probably one additional effect, the so-called matrix effect, which was not studied in this preliminary phase. Sample composition could cause the differences in element vaporisation and other phenomena which should be studied in detail if the method is to be used in routine work. There are several potential approaches, one of which is pressing the tablets with different additives.

LA-ICP-MS is an analytical technique which is based on the evaporation of the material caused by the impact of laser beam with the sample surface. The evaporated material is transported by an inert gas into the plasma torch where atomisation and ionisation take place. The ions thus formed are separated in a mass spectrometry analyser (usually a quadrupole MS analyser). The sample is fixed in the ablation cell in such a way that it can move along the x-y axis for surface scanning. In our case the glass bead was fixed on a stainless steel rod as shown in Figure 1. The exact ablation position was fixed by observing the bead's surface through a charge-coupled device (CCD) camera. The ablation procedure was pre-programmed in such a way that the duration of the ablation procedure enabled the achievement of the steady-state signal. In Figure 2 some traces for selected elements obtained during the ablation of one site is presented.

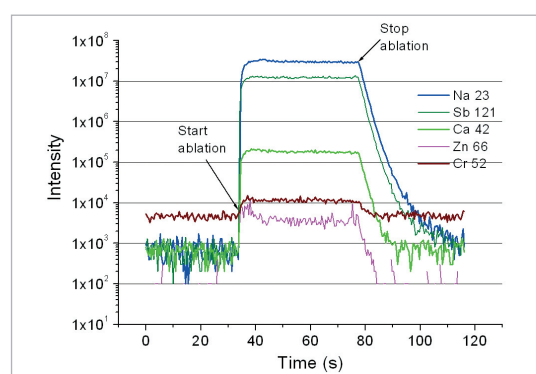


Figure 2. MS traces of selected elements, marked in the figure. Sampling start and end are marked as well. Based on the data shown in the Figure, the detector signals of very high stability demonstrate a surprisingly high homogeneity of the analysed prehistoric glass.

As already mentioned, LA-ICP-MS is a semi non-destructive analytical method. The qualification "semi" is due to the formation of craters of the diameter of the laser beam used in the process (usually 10-100 micrometres). To demonstrate the damage caused by the laser beam, the surface of a glass bead analysed by LA-ICP-MS is shown in Figure 3. The damages are really very small and can be removed completely by polishing the surface.

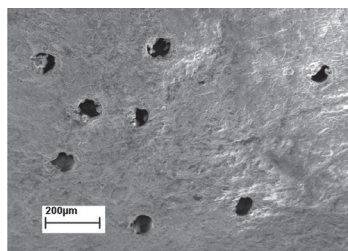


Figure 3. The textural properties of the surface of the glass bead sampled by laser beam during LA-ICP-MS analysis. (The photograph was made using field emission scanning electron microscopy (FE-SEM, Supra 35 VP, Carl Zeiss, Germany) equipped with energy dispersive spectroscopy Oxford INCA 400, Oxford Instruments Analytical, UK. Prior to the energy dispersive investigation, the sample was covered with a thin film of gold sputter deposited using a Balzers SCD 050 BAL-TEC, Germany.)

In Table 3 the results of the LA-ICP-MS determination of the elemental composition of selected fragments of glass beads found near Novo Mesto are shown. Fragments of different colours were selected in order to demonstrate the ability of the method to discriminate between the additives responsible for the colours. In the bottom row the sum of the oxides found in the individual sample is shown. It is obvious that the method gives a sum close to 100 percent. There is only one exception, Sample 3, a yellow glass which is very rich in lead oxide. The presence of lead interferes with the quantification procedure which has to be modified by using other reference standards and quantification procedures.

| Sample | Blue Glass | Sample 1, NM | Sample 2-1, NM | Sample 2-2, NM | Sample 3 Yellow glass | Green glass |
|--------------------------------|------------|--------------|----------------|----------------|-----------------------|-------------|
| Oxide | % | % | % | % | % | % |
| Na ₂ O | 15.63 | 17.71 | 17.91 | 18.28 | 18.43 | 19.33 |
| MgO | 0.699 | 0.662 | 0.497 | 0.642 | 0.484 | 0.651 |
| Al ₂ O ₃ | 2.89 | 0.461 | 0.330 | 0.359 | 2.97 | 0.357 |
| SiO ₂ | 71.50 | 71.51 | 71.51 | 71.51 | 71.51 | 71.51 |
| K ₂ O | 0.722 | 0.122 | 0.216 | 0.082 | 0.663 | 0.285 |
| CaO | 7.33 | 9.18 | 6.42 | 10.28 | 7.45 | 10.59 |
| TiO ₂ | 0.075 | 0.049 | 0.085 | 0.049 | 0.055 | 0.085 |
| V ₂ O ₅ | 0.003 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Cr ₂ O ₃ | 0.003 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 |
| MnO | 0.601 | 0.014 | 0.012 | 0.012 | 0.016 | 0.015 |
| FeO | 0.693 | 0.557 | 0.248 | 0.200 | 0.655 | 0.224 |
| CuO | 3.92 | 0.053 | 3.27 | 0.002 | 0.030 | 0.008 |
| Sb ₂ O ₃ | 0.165 | 1.62 | 0.001 | 1.33 | 3.15 | 1.43 |
| PbO | 0.650 | / | / | / | 19.75 | 0.007 |
| ΣSum (%) | 104.9 | 101.94 | 100.5 | 102.7 | 125.2 | 104.5 |

Table 3. Summarised Results of the Systematic LA-ICP-MS Analysis of Selected Glass Samples from Kapiteljska Njiva, Novo Mesto

Conclusions

LA-ICP-MS is an almost non-destructive analytical technique, offering the largest possible amount of data regarding the chemical composition of the analysed objects. It enables quantitative data for the matrix components as well as trace elements. Of special interest is the

possibility offered by LA-ICP-MS for the quantitative analysis of micro-inclusions which might be remnants of the original raw materials used in the production of the glass. The preliminary results of LA-ICP-MS analysis of prehistoric glass samples found at Kapiteljska Njiva near Novo Mesto in Slovenia demonstrated its great potential for quantitative analysis (major components as well as trace elements). The data obtained in this way will be used for the creation of a large data base, which will serve as the basis for a trans-Europe comparison of chemical compositions of similar objects, which could help determine the sources of raw glass.

Chemical composition of the in-laboratory prepared pottery reference material was determined by using different sample preparation procedures (fusion decomposition by lithium metaborate, fuming decomposition by hydrofluoric acid, pressed pellets) and by applying different analytical approaches like ICP-OES and ICP-MS and LA-ICP-MS. The results obtained by LA-ICP-MS of pressed pellets differ from those obtained by ICP-OES and ICP-MS due to relatively unknown factors which are influencing direct LA-ICP-MS analysis of powdered materials. The accuracy of the determined chemical composition of the standard should be improved by the analysis of reference materials by other available methods (neutron activation analysis, X-ray fluorescence, etc.) in order to minimise the uncertainty of the determined concentration levels of the individual oxides.

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