

Energy-Dispersive X-Ray Fluorescence Analysis of Celtic Glasses

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Celtic glasses of different colors, opaque or transparent, in the form of beautiful ornaments were characterized according to elemental composition by energy-dispersive x-ray fluorescence analysis. This analytical technique is nearly non-destructive and was the method of choice for this project. The Celtic glasses were loaned for the time of analysis by museums and private collections under the guarantee that no harm would be done to the objects. The main goal was to establish a reliable analytical method to achieve qualitative and quantitative results within acceptable errors. The historical and physical background is given and describes the motivation for this task. Preliminary tests carried out before the series measurements started are described and show that within a certain error range good results can be expected from samples of different shapes, with uneven or rough surfaces. Experimental conditions for the determination of light elements and subsequent extension to medium- and high-Z elements are described. The results from the test studies and for selected samples with various colors and shapes are presented. Copyright © 2000 John Wiley & Sons, Ltd.

HISTORICAL BACKGROUND

The origin of the people called by the Greeks *Κελτοί* and by the Romans *Celtæ* or *Gallii* is still not known and remains very controversial. The oldest ancient written sources mention the Celts somewhere in the region of the Upper Danube. However, it is certain that the Celts belonged to the large family of peoples speaking Indo-European languages.

Corresponding to the historical Celts, the La Tène Culture (ca 500–0 BC) was composed of a distinct and homogeneous cultural complex covering large areas of Europe (Fig. 1). However, many Celtic tribes settled in different lands out of the range of the La Tène Culture.

Through their close connections with the Mediterranean civilization, the Celts adopted many of the technological advances of the other cultures. The Celtic artists created a characteristic decorative style, making works of art in almost every class of manufactured article. During the late La Tène period, under the influences of Roman civilization, Celtic society displayed a strong social differentiation and probably was on the verge of transformation into a formal class structure and statehood.

Celtic domination in Europe ended soon after Caesar's conquest. Concurrent with the defeat by the Roman Empire, the Celts lost power not only to the Dacians in the Lower Danube region but also to the Germans in the area of Middle and Upper Danube and east of the Rhine. However, the total annihilation of the Celts never occurred. The Gauls (Celts) lasted longer in Britain and Ireland. Those

regions have never been Romanized enough to destroy the Celtic culture, which still exists to this day.

CELTIC GLASS

The Celtic La Tène Culture, as the first one in Europe out of the Mediterranean region, achieved highly specialized glass manufacture. The specific Celtic forms of bracelets and ring-beads made of glass came into common use at the beginning of the Middle La Tène (LT C) period. The art of glass working in eastern *Celtica* was certainly one of the components of a general trend in which the eastern Celtic tribes adopted new technologies during the second half of the third century BC. This cultural development was an aftermath of the retreat movements of the historical Celtic raids on Macedonia, Thrace and Greece.

Glass jewelry was a common product in the Celtic world and it seems that it was manufactured in many workshops in different places in the large area of the La Tène Culture. Identification of glass workshops is not an easy matter for archeologists, and scholars making a thorough study of the subject still do not agree as to whether the Celts produced the basic glass or whether they imported raw glass from Mediterranean sources. The Celtic craftsmen, who possessed a high degree of technical knowledge in metal-working, were certainly able to produce glass.

The artifacts studied here represent Celtic glass-work from the Middle and Late La Tène periods (LT C–D, i.e. ca 250–50 BC). This collection resulted from a stay of Celtic tribes in the present area of Austria. The glasses have been collected from many archeological sites of the La Tène Culture in NE Austria. The tested collection

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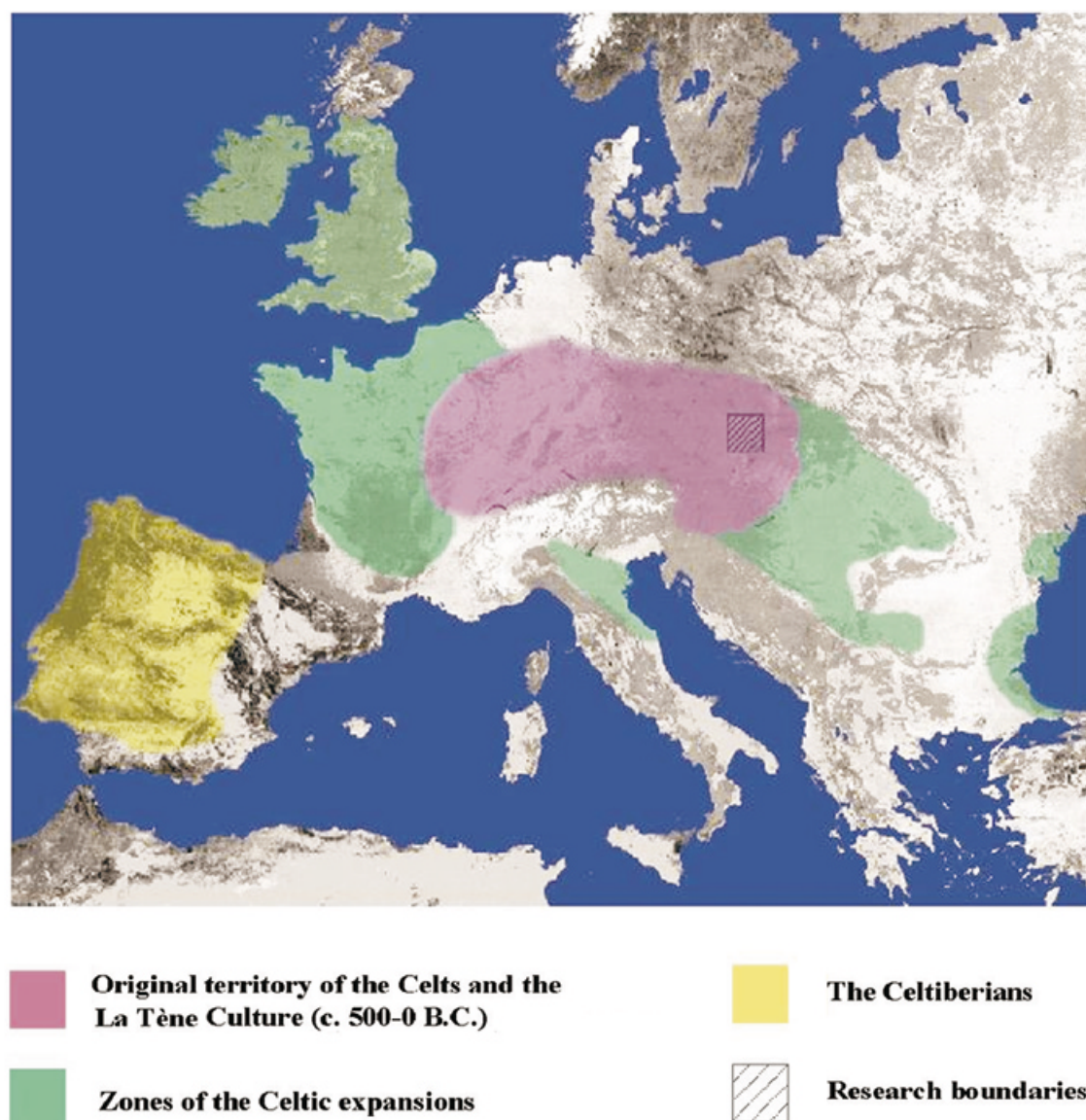


Figure 1. Map of Europe with Celtic territory in 500–0 bc and the location of the research site.

consists already of more than 100 pieces, mostly bracelets and ring-beads, represented in the greater part only by small fragments.

The knowledge about the presence of specific chemical elements which suggest the use of specific combinations of raw materials in ancient glass helps answer archeological and technological questions in different areas of research: identification and location of the raw materials; investigation of the ways in which glass quality (coloration, transparency, etc.) can be modified; chemical characterization of glass products at presumed centers of glass production; reconstruction of the paths of distribution of finished glass products from the glass production centers to the areas of glass ‘consumption;’ comparison of the presence of the components in Celtic glass with the composition of other ancient glass, to be able to place them into an overall technological context.

The fact that it is possible to carry out non-destructive analyses opens up new possibilities for the study of objects of archeological importance.

PHYSICAL BACKGROUND

The unique beauty and value of Celtic glasses require an absolutely non-destructive analytical method for their elemental analysis, and several analytical techniques have already been applied.¹ Energy-dispersive x-ray fluorescence (EDXRF) analysis is the method of choice in this work.^{2–4} The properties of this technique, viz. a large dynamic range in concentration, detectable elements from Na to U, simultaneous multi-element capacity and short measuring time from 100 to 1000 s, are well suited to solve the analytical task. The elemental composition of the colored glasses, the patterns on it and the opaque or transparent parts can be correlated with the elements present. This has been done for glasses from other cultures also.^{5–8} The homogeneity of the samples, the surface quality and the geometric shape of the individual artifacts were considered and methods were tested to establish whether the results from the measurements would be sufficiently accurate to be interpreted. After a serious

testing period of the method using standard reference glasses which were investigated in a variety of positions and with slight geometric changes⁹ so as to resemble true artifacts, the observed error was accepted to give data ready for further interpretation by statistical procedures and historical understanding.

The experiments were separated into two sections, mainly using the optimized excitation conditions on the one hand for the light elements using the Rh L-line series to excite elements from Na to S and the continuum up to 15 keV to excite with sufficient accuracy elements up to Ti. The other set was subjected to a 35 kV excitation voltage to quantify metals, earth metals, plus Cd, Sn and Sb. The samples were measured in conventional geometry with a 45° incidence angle to the sample surface and a 45° emission angle to the detector at four positions across the surfaces with a narrow 1 mm collimated beam to avoid the influence of the geometric form of the surface. With the software package QXAS¹⁰ developed under the auspices of the IAEA the net peak areas were calculated and using the fundamental parameter program the conversion of measured intensities into concentrations of the elements was performed. All the data were used to obtain averages and standard deviations. Most of these data were used as the primary information on composition and correlation with the colors of the bulk glass or ornaments. Statistical interpretation will be necessary to obtain answers to the many historical questions mentioned in the historical introduction.

EXPERIMENTAL AND RESULTS

The analyzer used was a Spectrace 5000 instrument manufactured by Tracor Northern. This spectrometer is an automated EDXRF analyzer used for non-destructive elemental analysis of solids and liquids. The system includes the features and flexibilities necessary for solving a wide range of analytical problems, and can be configured to accommodate a variety of sample geometries.

A schematic arrangement of an EDXRF measurement is shown in Fig. 2. Sample excitation is effected with the direct or direct filtered primary beam from a low-power x-ray tube (17.5 W maximum rating). This technique provides efficient excitation across the full analytical range of the instrument, from sodium to uranium. The simplicity of the x-ray optics provides a high degree of sensitivity, reproducibility and reliability.

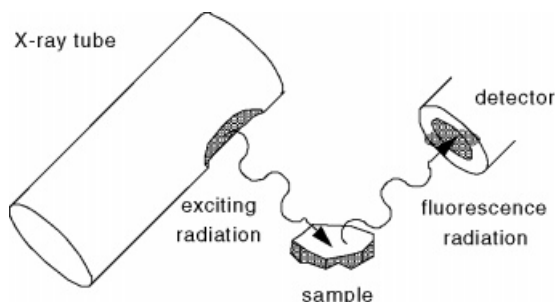


Figure 2. Scheme of a typical EDXRF experimental set-up used for taking the analytical data.

The direct mode is selected in cases where a collimated beam is required or the sample is low in mass or for analysis of low atomic number elements.

Filtering of the primary beam provides optimum peak-to-background ratios for a particular element range. Filtering effectively eliminates the background by transmitting only x-ray energies above the spectral range of interest. Sensitivity is optimized by selecting a filter that passes only radiation near, but above, the element absorption edge.

X-rays emitted by the sample are detected by a cryogenically cooled, lithium-drifted silicon [Si(Li)] detector. This high resolution (155 eV/5.9 keV) solid-state device provides the technology that is the basis for the wide applicability of EDXRF.

The Spectrace 5000 has a 10-position tray for 31 mm diameter samples or sample cups. Atmosphere selection allows three choices: air, helium or vacuum. Air is the most common mode of operation, allowing analyses for all elements having emission lines above 4.5 keV (or atomic number above 22, Ti).

Excitation is effected by an air-cooled x-ray tube with an Rh anode and 125 µm Be window. This extremely thin tube exit window allows the emission of low-energy continuum and also the intense Rh L-line series efficiently excites the light elements. The x-ray generator provides voltages from 5 to 50 kV in 1 kV increments and a current range from 0 to 0.35 mA in 0.01 mA increments. A six-position filter wheel facilitates optimum filter adjustment. It includes Al, cellulose, Cu, two Pd positions and a position with no filter. Collimators can vary in diameter between 1 and 10 mm. During the experiments with Celtic glasses a 1 mm collimator was used to minimize sample geometry effects.

The x-ray detector system includes an Si(Li) detector (30 mm² area, 155 eV resolution for 5.9 keV) with a Be window of 12 µm thickness, well suited for the detection of light elements.

The experimental parameters for the measurements were chosen as follows:

Voltage:	15 kV	35 kV
Current:	0.35 mA	0.35 mA
Atmosphere:	Vacuum	Air
Livetime:	1000 s	1000 s
Filter:	No filter	Al filter

The first set-up with 15 kV provides excellent K-line detection and analysis of elements from sodium to titanium. The second opens up the possibility, because of the good excitation conditions, of examining K-lines up to Sn. Elements with higher excitation energies for K-lines are analyzed with the help of L- and M-lines.

Sample holder

In order to be able to analyze the Celtic artifacts, a technical problem had to be solved, namely how to mount specimens of different shapes and sizes. A further complication was the fact that for the measurement of the breaking surface the small area represents an unstable base on which stand the samples. A spectrocup made of plastic had the best structure. The bottom side of the spectrocup was removed, so that a cylindrical plastic tube remained.

The bottom side was replaced with a number of pieces of fishing line (diameter 0.2 mm), which formed a grid structure. To hold the samples in a fixed position, four threads were cut through the wall of the container, which were perpendicular to each other. With screws it was possible to fix each sample from four sides in such a way that the desired surface was irradiated by the x-rays. To establish the best position, several test measurements for 10 s were made.

The plastic of the spectrocup also met expectations and supplied an excellent blank spectrum. A set of eight of these special holders were produced to allow automatic measurements with the sample changer.

Homogeneity

In order to have a better overview for the homogeneity of the Celtic glasses, a series of measurements of 21 randomly chosen samples from a museum were made. Some of these samples were partly very corroded or

generally in a state rather unfavorable for the EDXRF measuring method, so test measurements were performed.

The technical parameters were always the same: voltage, 35 kV; current, 0.35 mA; atmosphere, air; filter, aluminum; and livetime, 100 s.

Generally the samples were pieces of broken glasses with a slightly curved shape and some of the most beautiful ones are shown in Fig. 3. On the exterior were sometimes ornaments, partially or full colored. The colored ornamentations were from a yellow substance. The lower surfaces were smooth, although one could discover unevenness with the help of a microscope.

Points on the upper and lower surface and on the breaking surfaces were measured in order to obtain full information about the state of the sample. First was the measurement of points on the side without ornamentation, the second the ornament itself and third at a location on the breaking surface.

The comparison of the different sides showed some inhomogeneities, probably produced due to environmental



Figure 3. Fragments of Celtic glass bracelets. Top row left, blue fragment with ornament, No. 18; top row middle and right, front and side views of green–blue fragment, No. 19; bottom row left and right, blue fragment with white ornament, No. 39; bottom row middle, knobbed bead, presumed to be imported from the Black Sea area, No. 72.

influences. Analyzing the two breaking points gave much better results since (1) these parts were changed much less by the environmental influences and (2) they show a smoother surface.

Geometry study

In order to establish the effects of geometry influences on measurements, a series of experiments were performed, divided into four sections: (1) $4 \times 90^\circ$ rotation test in the reference plane; (2) angle dependence vs reference plane; (3) height dependence vs reference plane; and (4) surface roughness dependence.

A possible loss of intensity is expected in all four cases. To study all cases, a flat glass reference standard with dimensions $35 \times 35 \times 3$ mm was selected, in this case NIST SEM 1412, Multielement Glass (National Institute of Standards and Technology, Gaithersburg, MD USA). This standard was used throughout the entire measuring procedure, including the partial surface destruction. The measurements were made with two different excitation energies, (i) 15 kV, 0.35 mA, no filter, in vacuum and (ii) 35 kV, 0.1 mA, aluminum filter, in air.

Rotation test. First the square-shaped SRM was placed on the sample tray and the fluorescence intensity was measured in the four positions achieved by a rotation through 90° in the reference plane. The reference plane is defined by the plane of the sample tray. Table 1 shows the results obtained from measurements at 15 kV. The data shown are the mean value of the net counts collected with operating conditions 15 kV, 0.35 mA, 1000 s, of the four positions for all detected elements. The maximum deviation in one of the positions from the mean value is given in counts and percentages of the mean value.

Angle dependence of fluorescence intensities. The angle dependence of the fluorescence intensities was measured, the sample being inclined with respect to the reference plane, as shown in Fig. 4. This was performed by supporting one edge of the selected standard with small Al plates of 0.5 mm thickness on one side to bring the sample up to 2 mm inclined above the sample tray. The inclined sample was rotated four times through 90° degrees as described in the rotation test.

Table 1. Rotation test on SRM in the reference plane ($4 \times 90^\circ$) with operating conditions 15 kV, 0.35 mA (counts in 1000 s)

Element	Mean value	Max. total deviation	Max. deviation (%)
Na	2161	153	7
Mg	6739	284	4
Al	34688	448	1
Si	429379	4013	<1
K	105494	778	<1
Ca	126365	937	<1
Fe	3050	177	6
Zn	386053	2779	<1
Cd	34087	657	2
Ba	68984	787	1
Pb	35596	257	<1

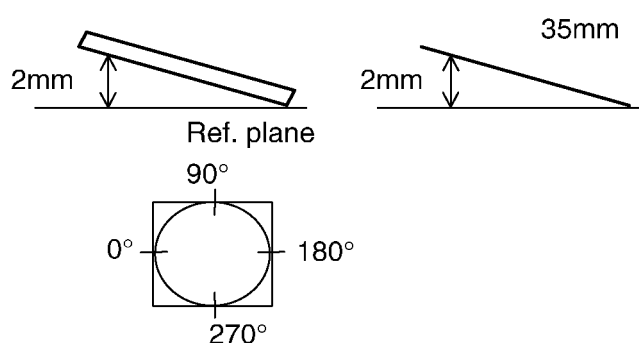


Figure 4. Sketch of the arrangement to measure the inclined 35×35 mm square sample of an SRM in the four different positions for the rotation study.

Table 2 shows results from 15 and 35 kV measurements. The maximum deviation calculated is given in column 2 for 15 kV and in column 3 for 35 kV. The results were achieved as the absolute value of the difference between a measured point and an in-plane point taken for the maximum of the deviation and divided by the in-plane point value times 100 to give a percentage.

Height dependence. In this test the offset from the reference plane and its influence on the fluorescence intensities of each element in the sample were observed. The measurements started at the plane of the sample tray ($H = 0$ mm), then the sample was lifted parallel to the reference plane in steps of 0.5 mm with Al plates up to $H = 2$ mm. The results are presented in Fig. 5 from measurements with an applied voltage of 15 kV and in Fig. 6 for 35 kV. In particular in Fig. 6 'El' means elastic scattering (Rayleigh) and 'Inel' means inelastic scattering (Compton). The x -axis (H) represents the distance between the reference plane and the sample. The percentage value on

Table 2. Rotation test on SRM inclined at about 3° to the reference plane ($4 \times 90^\circ$) with operating conditions 15 kV, 0.35 mA (counts in 1000 s)

Element	Max. deviation between reference plane position and inclined sample position (%)	
	15 kV, 0.35 mA, 1000 s	35 kV, 0.1 mA, 1000 s
Na	3	
Mg	18	
Al	9	
Si	9	
K	8	15
Ca	9	14
Ti		9
Fe	18	
Cu		18
Zn	9	11
Sr		10
Zr		7
Inelastic scatter peak (35 kV)		7
Elastic scatter peak (35 kV)		10
Cd	10	10
Sb		17
Ba	10	
Pb	9	11

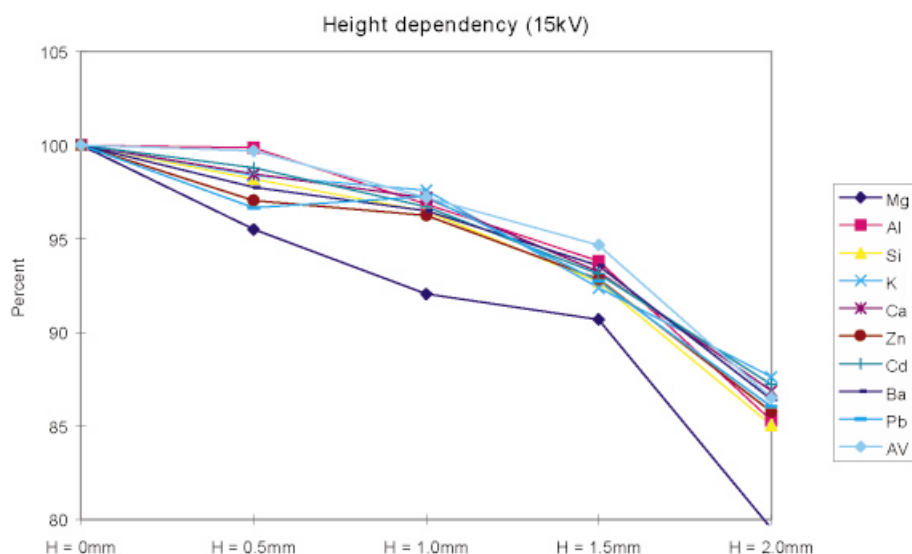


Figure 5. Results from a study of SRM height offset from the reference plane in steps of 0.5 mm from 0 to 2 mm. The percentage data given are the ratios $[N(H)/N(0)] \times 100$ where N is counts of the respective elemental fluorescence radiation and H is the position measured with 15 kV excitation.

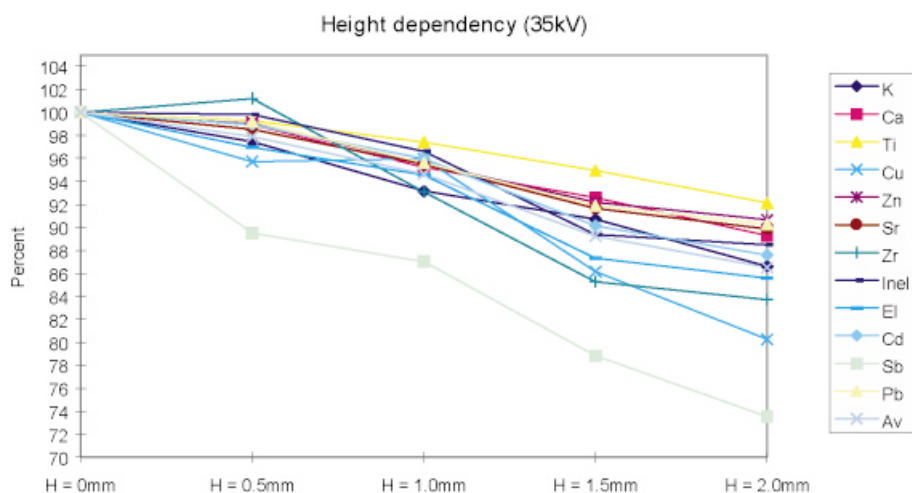


Figure 6. As Fig. 5 but with 35 kV excitation.

the y-axis is calculated as $[N(H)/N(0)] \times 100$, where N is the counts of the respective elemental fluorescence line after a 1000 s collection time.

Surface roughness dependence. To find out the effect of a rough surface on the measured results, the standard glass was scratched manually on the surface with a sharp steel screwdriver to obtain a rough surface, which had a status comparable to the rough Celtic samples. Results of these measurements are given in Table 3 for the excitation at 15 and 35 kV. In the second and third columns the ratios between the rough and smooth surface of the measured fluorescence counts of the elements at the two different voltages are given.

Conclusions of test experiments.

Rotation test. As can easily be seen, the average errors were below 2%. Exceptions were those elements with the smallest peak areas, which was not unexpected.

Angle dependence of fluorescence intensities. The inclined sample at a rotation of 180° shows the largest

Table 3. Comparison of ratio of fluorescence counts of elements from scratched and smooth surfaces

Element	Ratio $[N(\text{scratched})/N(\text{smooth})] \times 100$ (%)	
	15 kV, 0.35 mA, 1000 s	35 kV, 0.1 mA, 1000 s
Na	94.8	
Mg	77.6	
Al	74.6	
Si	72.4	
K	73.4	85.2
Ca	77.3	87.1
Ti		89.5
Cu		94.2
Zn	83.3	90.7
Sr		94.3
Zr		87.4
Cd	76.8	93.9
Sb		85.1
Ba	77.1	
Pb	88.2	93.9
Mean	79.6	90.1

deviation from the in-plane values that are presented in Table 2. This can be understood by the geometry of the incident primary beam and the detector position. The data for the other three cases (0, 90 and 270°) show a deviation below 10%.

From these results, it can be concluded that the analysis of Celtic glasses will be possible even for naturally inclined samples or those having a breaking surface with similar inclination. By the design of the sample holder, the best possible geometry conditions can be adjusted.

Height dependence. The variations of the height with respect to the reference plane shown in Figs 5 and 6 gives the errors caused of inexact adjustment. At a maximum of 2 mm above the reference plane a maximum deviation of about 20% was observed. The deviation at a level of 1.5 mm shows a loss of 5.3% for this position. If the sample is lifted more, this error will rapidly increase. From the real measurements on Celtic samples done so far, it could be seen that this condition was easily fulfilled. Surface deviations were approximately within the range of 1 mm.

Surface roughness dependence. It is shown that the mean value of the ratio as a percentage depends on the excitation energy. The mean value for 15 kV was 79.6%, but for 35 kV it was 90.1%.

Generally, it follows that the deviations which result from bad positioning and rough surface of the SRMs affect the measured values within the above values. Therefore, it can be assumed that based on these results the quantification of the elements in the Celtic samples will be possible despite their shape within a maximum error of 20%.

Quantitative analysis of glass standards

The use of standard reference materials (SRMs) is a common method to check the results of one's own measurements. The quantification procedure includes the same steps as for unknowns and the SRMs are treated in the same way as the sample. The following steps are undertaken for the quantification procedure in a sample: collection of XRF spectra, spectrum evaluation as peak deconvolution and net peak counts of the elements, and quantification using the fundamental parameter technique. On the experimental side this requires the determination of the instrumental geometry factor, a measurement which is done on one ultra-pure single-element sample. If it can be proved that the chosen experimental conditions and the data evaluation procedure for the standards fits the quantification of unknowns is not a problem.

Therefore, two NIST standards: (1) Soda Lime Container Glass (SRM 621) and (2) Multicomponent Glass (SRM 1412), were measured and analyzed. The technical parameters were the same as intended for the unknown samples: voltage, 15 kV; current, 0.35 mA; filter, none; atmosphere, vacuum; and livetime, 1000 s. With these operating conditions, three Soda Lime standards and eight Multicomponent Glass standards were analyzed. The calibration of the system, for the determination of the instrumental constant required in the software package AXIL Fundamental Parameters, was executed with a piece of pure aluminum. Owing to the position of aluminum in the Periodic Table, good quantification results are expected for energy region up to

Table 4. Comparison of certified and measured data from NIST Soda Lime Container Glass (SRM 621)

Component	Certified value (%)	Mean value (measured) (%)	100 × (mean – certified)/certified (%)
Na ₂ O	12.74	7.9	–38
MgO	0.27	0.24	–12
Al ₂ O ₃	2.76	2.29	–17
SiO ₂	71.13	60.25	–15
SO ₃	0.13	0.23	+74
K ₂ O	2.01	1.56	–23
CaO	10.71	9.71	–9
TiO ₂	0.014	0.016	+14
BaO	0.12	0.11	–6

Table 5. Comparison of certified and measured data from NIST Multicomponent Glass (SRM 1412)

Component	Certified value (%)	Mean value (measured) (%)	100 × (mean – certified)/certified (%)
Na ₂ O	4.69	5.36	+14
MgO	4.69	2.94	–37
Al ₂ O ₃	7.52	6.82	–9
SiO ₂	42.38	47.11	+11
K ₂ O	4.14	3.65	–12
CaO	4.53	4.27	–6
BaO	4.67	6.11	+30

Ti K α or for the low-Z elements. It is also suitable for Ba and Cd, because their L-lines are in the calibrated region.

Results are presented in Tables 4 and 5 and show the mean concentration values as a percentage for $n = 3$ and 8, respectively. The deviations as a percentage from measured and certified values are given in the last column.

In conclusion, one can see that for the light elements the errors are in the region of 20%, within the expected uncertainty. The results for elements such as Na and S are still under investigation. There are several reasons for such deviations. The sample is thick, corrections for self-absorption have to be considered based on theoretical fundamental parameters and the x-ray tube spectrum in this energy range is strongly dependent on the real tube in use but was taken from theoretical calculations. Also, the detector efficiency is calculated based on theoretical data and technical data on the thickness of the Si dead layer and Au contact layers were taken from manufacturers' information, which has the greatest influence on the Na results. Some of the elements Mg, Ti and Ba are present in the higher $\mu\text{g g}^{-1}$ (ppm) range, so errors up to 20% have to be accepted.

Qualitative and quantitative analysis of Celtic glasses

EDXRF has the capacity to give qualitative and quantitative results for sample analysis. Before the quantification procedure it is worth presenting the results of qualitative analysis to establish how often certain elements are found in the examined sample. Especially for archeological pieces, sometimes just the existence of a certain element shows clearly the origin or location of manufacture of a sample. With the help of qualitative analysis, normally a trend can be seen.

In the case of Celtic glasses, so far 30 artifacts have been measured and the results of qualitative analysis are available. In Fig. 7 the rate of occurrence is given which defines the existence of individual elements in the samples considered ($n = 30$).

The existence of some of the elements such as Na, Si and Ca is expected. The presence of Co in all of the samples agrees with other publications,^{2,4} in which analysis of blue Celtic glasses was described. The concentration of Pb varies; in some of the samples it is low, whereas in others it is much higher. It is difficult to detect Cl, since during the excitation with an Rh tube the Rh L-lines overlap Cl $K\alpha$.

As an example, the results of the quantitative analysis of two samples shown in Fig. 3 are presented in Tables 6 and 7. In Fig. 3 the top row (middle and right) shows a green–blue fragment of a Celtic glass bracelet with a yellow ornament (No. 19) in front and side view. The blue glass part looks blackish in the photograph but with illumination by light becomes a blue color. Two analysis points were chosen in the blue area, three in the green

area and two on the ornament. The colorants of blue and green were subjected to further investigations of higher Z elements. In the ornament the main colorant element is lead. Sample 72, which is a knobbed bead, can be seen in Fig. 3 in the middle of the bottom row. Again the yellow ornament has a high lead concentration, whereas the white ring shows no lead.

The overall error varies from element to element and reaches a maximum of 20%.

Archeological interpretation

The studied artifacts resulted from a stay of the Celtic tribes in the present area of eastern Austria. The majority the finds studied represent Celtic glass-work from the Middle and Late La Tène periods (glass bracelets and ring-beads) and were found on the open Celtic settlements. The other group of findings comes from the late Hallstatt and early La Tène graves (small beads of various types), and their Celtic origin is still not clear. The artifacts were collected from different archeological

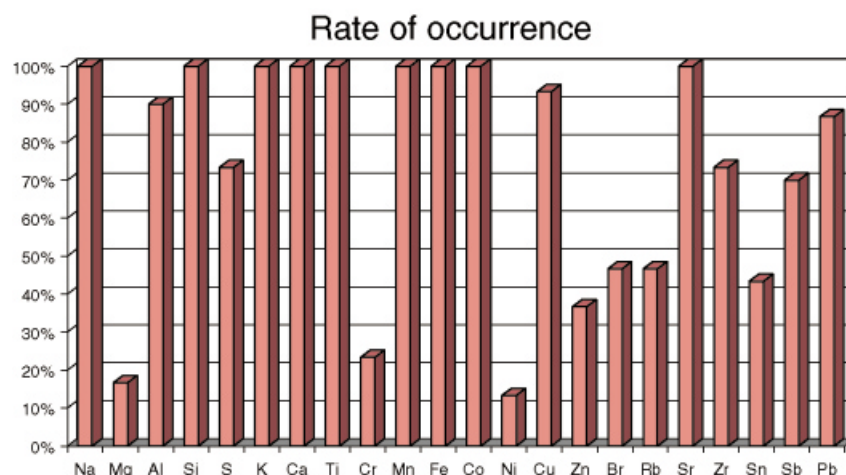


Figure 7. Rate of occurrence of chemical elements in the set of 30 artifacts.

Table 6. Analytical results for sample 19, in particular three different colors of the artifact (top row, middle and right in Fig. 3)

Component	Blue			Green		Ornament (yellow)	
	Position 1 ($\mu\text{g g}^{-1}$)	Position 2 ($\mu\text{g g}^{-1}$)	Position 1 ($\mu\text{g g}^{-1}$)	Position 2 ($\mu\text{g g}^{-1}$)	Position 3 ($\mu\text{g g}^{-1}$)	Position 1 ($\mu\text{g g}^{-1}$)	Position 2 ($\mu\text{g g}^{-1}$)
Na	27100 \pm 2200	18900 \pm 1940	8418 \pm 1464	11600 \pm 1560	14300 \pm 1720	<DL	23600 \pm 2480
Na ₂ O	73061 \pm 2970	50954 \pm 2610	22692 \pm 1970	31270 \pm 2100	38548 \pm 2310	<DL	63617 \pm 3350
Mg	<DL	1432 \pm 383	<DL	1293 \pm 334	<DL	3256 \pm 597	1570 \pm 486
MgO	<DL	2374 \pm 635	<DL	2145 \pm 554	<DL	5399 \pm 990	2604 \pm 807
Al	3881 \pm 254	6798 \pm 278	2985 \pm 209	3003 \pm 216	2804 \pm 231	2804 \pm 231	6707 \pm 323
Al ₂ O ₃	7333 \pm 480	12800 \pm 530	5642 \pm 395	5676 \pm 409	5300 \pm 437	5300 \pm 437	12700 \pm 610
Si	182800 \pm 400	176000 \pm 410	155400 \pm 350	163100 \pm 370	198500 \pm 400	225600 \pm 540	221900 \pm 500
SiO ₂	391100 \pm 860	376500 \pm 870	332300 \pm 760	349000 \pm 780	424500 \pm 850	482600 \pm 1160	474600 \pm 1060
S	794 \pm 82	949 \pm 84	310 \pm 68	399 \pm 70	256 \pm 70	7440 \pm 228	2114 \pm 131
SO ₃	1982 \pm 207	2370 \pm 210	774 \pm 171	997 \pm 176	639 \pm 176	639 \pm 176	5278 \pm 327
K	2562 \pm 50	3507 \pm 54	1782 \pm 44	2118 \pm 45	1915 \pm 45	6729 \pm 111	4925 \pm 85
K ₂ O	3086 \pm 60	4224 \pm 65	2146 \pm 53	2551 \pm 55	2306 \pm 55	8106 \pm 134	5932 \pm 102
Ca	37800 \pm 100	36300 \pm 100	28000 \pm 90	30700 \pm 90	31400 \pm 90	54600 \pm 180	56600 \pm 160
CaO	52900 \pm 140	50700 \pm 140	39100 \pm 120	43000 \pm 130	43900 \pm 130	76300 \pm 250	79100 \pm 230
Ti	565 \pm 19	845 \pm 20	449 \pm 18	513 \pm 18	416 \pm 17	1329 \pm 38	1172 \pm 32
TiO ₂	943 \pm 32	1409 \pm 34	750 \pm 30	855 \pm 31	695 \pm 28	2218 \pm 64	1956 \pm 53
Pb	Low	Low	No	No	No	High	High

Table 7. Analytical results for sample 72, in particular three different colors of the artifact (bottom row, middle in Fig. 3)

Component	Ornament (yellow)		Ornament (white)		Black	
	Position 1	Position 2	Position 1	Position 2	Position 1	Position 2
Na	<DL	<DL	6043 ± 1561	5214 ± 1511		
NaO ₂	<DL	<DL	16290 ± 2104	14055 ± 2037		
Mg	5934 ± 552	8813 ± 694	1692 ± 391	1497 ± 383	<DL	4809 ± 479
MgO	9839 ± 916	14600 ± 1150	2807 ± 648	2483 ± 636	<DL	7973 ± 794
Al	6304 ± 358	11300 ± 460	9267 ± 316	11300 ± 330	4588 ± 239	15400 ± 420
Al ₂ O ₃	11900 ± 680	21400 ± 860	17500 ± 600	21300 ± 620	8669 ± 452	29100 ± 800
Si	158200 ± 540	236100 ± 660	165800 ± 440	173800 ± 450	80300 ± 340	162400 ± 510
SiO ₂	338500 ± 1150	505000 ± 1420	354600 ± 940	371700 ± 960	171900 ± 730	347300 ± 1100
S	14300 ± 560	21900 ± 780	5027 ± 179	5518 ± 183	4804 ± 165	7847 ± 275
SO ₃	35600 ± 1390	54700 ± 1940	12600 ± 450	13800 ± 460	12000 ± 410	19600 ± 690
K	5924 ± 121	8045 ± 143	5338 ± 107	6024 ± 116	5653 ± 72	9061 ± 102
K ₂ O	7136 ± 146	9691 ± 172	6429 ± 129	7256 ± 140	6809 ± 86	10900 ± 120
Ca	47800 ± 200	54000 ± 220	67000 ± 170	66400 ± 180	48700 ± 130	59300 ± 160
CaO	66900 ± 270	75600 ± 300	93800 ± 240	92900 ± 260	68200 ± 180	82900 ± 230
Ti	780 ± 47	1307 ± 53	955 ± 34	1064 ± 35	1050 ± 31	2090 ± 44
TiO ₂	1301 ± 78	2181 ± 89	1594 ± 57	1775 ± 59	1752 ± 52	3486 ± 73
Pb	High	High	No	No	Low	Low

sites: Pottenbrunn-Ratzersdorf, Neukirchen, Niederleis, Altenburg-Umlauf, Bad Fischau, Gumping, Rosenberg, Zwingendorf, Goettlesbrunn, Oberleiserberg and Vicenice (Bohemia). The studied glass ornaments were made mostly of blue (or turquoise) and also colorless, violet, brown–yellow and green glass of different transparency. Some of them were additionally decorated with white or yellow opaque glass. The glass coloration was specified according to the Pantone color charts.

The results of the analyses obtained so far allow us to draw the following conclusions: the Celtic glass from the area of eastern Austria belongs mainly to the soda-lime type, the most common in the Ancient World; the glass colorants (e.g. cobalt, iron, copper, manganese), decolorants (antimony, manganese) and opacifying elements (lead, antimony) are strongly marked by the results of the analysis and are strongly dependent of their relative concentrations; the samples of glass studied show substantial similarities in their chemical composition and a distinctive similarity to the analogous collections from the La Tène culture; a number of other elements appear in glass probably as natural impurities.

Further conclusions concerning questions of the presumed production centers and the distribution zones and also aspects of the chronological significance of the

concentrations of different elements in the studied glasses will be possible after more data have been obtained.

CONCLUSIONS

Apart from the results of the quantification tests on the SRMs, it could be shown that fragments of Celtic glasses can be analyzed successfully. They are in most cases sufficiently homogeneous, have a sufficiently good surface quality and by using the Rh tube excited EDXRF technique a high dynamic range of concentration can be measured. Applying 15 kV the low-Z elements are measured; for medium-Z elements 35 and 50 kV are used particularly to determine Sb and Ba. A correlation among the elements causing the coloring will be obtained via statistical evaluation of all data on the elements found. Questions of archeological interest can hopefully be answered after the full data set has been interpreted.

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REFERENCES

1. J. Frana, A. Mastalka and N. Venclova, *Archaeometry* **29**, 69 (1987).
2. P. Hoffman, *Fresenius' J. Anal. Chem.* **349**, 320 (1994).
3. S. Bichlmeier, M. Heck and P. Hoffmann, in *Proceedings of the European Conference on EDXRS*, edited by J. E. Fernandez and A. Tartari, p. 311. Bologna University Press, Bologna (1999).
4. J. Braziewicz, M. Karwowski, M. Jaskola and M. Pajek, *Adv. X-Ray Anal.* **39**, 857 (1997).
5. I. C. Freestone, in *Catalogue of Mediaeval Enamels in the British Museum*, edited by N. Stratford, p. 37. British Museum Press, London (1992).
6. I. C. Freestone, in *Science and The Past*, edited by S. Bowman, p. 37. British Museum Press, London (1991).
7. M. Wegstein, H. Urban, P. Rostam-Khani, A. Wittershagen and B. O. Kolbesen, *Spectrochim. Acta, Part B* **52**, 1057 (1997).
8. G. A. Cox and A. M. Pollard, *Archaeometry* **19**, 45 (1977).
9. G. Halmetschlager, *Diplom Thesis*, Technische Universität Wien, Vienna (1998).
10. *QXAS Software Package: Quantitative X-Ray Analysis System*. IAEA Headquarters, Vienna (1995).