

## Post-medieval glass from the Castle of Cosenza, Italy: chemical characterization by LA-ICP-MS and SEM-EDS

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**ABSTRACT.** – This work reports results of the chemical characterization of twenty-six samples of variously coloured post-medieval glass fragments found during excavations near the Castle of Cosenza (Calabria, Southern Italy). All the glass fragments are currently housed in the City Museum of Cosenza. They were studied by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) for major elements and Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICP-MS) for trace elements and REE concentrations. Information on the provenance of each find and the technology of glass-making was obtained.

**RIASSUNTO.** – Nel presente lavoro vengono illustrati i risultati di una caratterizzazione geochemica di ventisei frammenti di vetri post-Medievali, da incolore a variamente colorati, rinvenuti durante l'attività di pulizia lungo le strutture perimetrali del Castello Svevo di Cosenza (Calabria, Italia). L'intero materiale archeologico attualmente è custodito all'interno del Museo Civico di Cosenza.

Al fine di determinare la concentrazione degli elementi maggiori e in tracce, i frammenti vitrei sono stati analizzati utilizzando due diverse metodologie: la microscopia elettronica con associata la microanalisi (SEM-EDS) e la tecnica analitica LA-ICP-MS

Obiettivo principale del presente studio è stato

quello di caratterizzare geochimicamente i diversi reperti vitrei al fine di risalire, dalle proprietà geochemiche alla possibile provenienza del materiale sorgente ed alle diverse tecniche di produzione del vetro.

**KEY WORDS:** *Vitreous finds, Castle of Cosenza, SEM-EDS, LA-ICP-MS.*

### INTRODUCTION

The methodological approach used in this work is that of morphological analysis of 26 post-medieval glass fragments, combined with their geochemical characterization. Correct determination of the chemical composition of a glass, in terms of both major and trace elements, is very important not only for archaeometric aims, but also because, in some cases, it can indicate the techniques used and thus the period in which the glass was made (Shortland and Tite, 2000; Shortland and Eremim, 2006).

The first geochemical studies on archeological findings for archaeometric purposes were carried out by Cann and Renfrew in 1964, on obsidian, a natural glass widely used as a raw material in prehistoric times. Since then, many studies have been carried out, on both natural and synthetic glass, applying analytical methods with two

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main aims: i) to analyse the elements which may be discriminating as regards classification of materials; ii) to identify the best analytical non-destructive technique supplying geochemical data on major, trace and ultra-trace elements.

Over the years, several destructive (XRF, ICP-MS) and non-destructive (PIXE, INAA, SEM-EDS) methods have been variously applied in archaeometric studies (Acquafredda *et al.*, 1999; De Francesco *et al.*, 2008, and references therein). The LA-ICP-MS technique has recently been introduced, combining the typical advantages of ICP-MS (precision, reproducibility, rapidity of analysis, high number of analysable elements) with its micro-destructive feature. The hole produced during laser ablation has a diameter of about 50 microns and is thus practically invisible to the naked eye. This method, thanks to its particular features, can resolve micro-analytical problems not only of heterogeneous materials but also of homogeneous ones, such as natural (Gratuze, 1999; James *et al.*, 2005; Carter *et al.*, 2006; Barca *et al.*, 2007, 2008) and synthetic glass (Vincenzi *et al.*, 2002; Silvestri *et al.*, 2005; Wagner *et al.*, 2007), revealing total chemical composition.

The main component of synthetic glass is silica, called a vitrifier. It is widely used because, in suitable cooling conditions, it spontaneously produces glassy masses. However, its high melting point (about 1700° C) limits its use in the pure state. The vitrifying mixture must be combined with substances called fluxes, which lower its melting point. The fluxes frequently used in ancient glass production were alkaline substances, in particular the compounds of sodium and potassium.

Although fluxes facilitate glass production, they do form weak bonds, giving rise to easily alterable glass, so that “stabilizers” such as alkaline-earth oxides are added to reduce this effect. The most commonly used stabilizers in ancient glass-making are calcium oxide (CaO), magnesium oxide (MgO), and lead oxide (PbO),

since historic sources until the end of the XVIII century refer to only two raw materials (vitrifier and flux), their introduction into ancient glass may appear to have been casual, except for lead oxide, the addition of which is always intentional (Fiori *et al.*, 2004).

In the course of centuries, changes were made in the basic compositions of glass, although the main raw material remained silica. Until the VIII century A.D., the principal added compounds were sodium, introduced by means of “natron” (Shortland and Tite, 2000; Silvestri *et al.*, 2005), and stabilizers such as CaO (sodic-calcic glass). Later, sodic ash from beech plants was also used, leading to the production of glass which also contained small percentages of potassium and magnesium, producing intermediate “mixed-alkali” glasses (Fiori *et al.*, 2004).

In northern Europe during medieval times, the most frequently used flux was potassium, added to the glass paste in the form of potassic ash from continental plants (mainly beech), yielding “potassic-calcic-magnesian” glass, unfortunately very easily alterable (Fiori *et al.*, 2004).

However, although the composition of major elements is highly discriminating as regards age of production and materials used, accessory elements, such as iron, copper, cobalt, manganese, antimony and tin, added in very small percentages, have a considerable influence on the colors of ancient glass.

#### TYPE-MORPHOLOGICAL ANALYSIS OF VITREOUS ARTIFACTS (D. DE PRESBITERIS)

During the reorganization of the collection of the Archaeological Museum of Cosenza, after the transfer of the museum from the local Cosenza’s Public Library to the monumental complex of St. Augustine, a large number of heterogeneous objects of various kinds were found, coming from excavations near the castle overlooking the city.

The presence of these materials in the

museum is due to “recovery” that took place probably in the first five years of two thousand, during cleaning activities carried out along the walls of the fortress. The preliminary and macroscopic examination of the potteries allowed us to classify them chronologically between XV and XIX; in addition to the furnishings pottery we found also twenty-six glass fragments characterized by a rich variety of morphology and typology.

Among these there are also two pieces of window plates (CSV25 and CSV26). The vitreous body of artifacts is almost always colorless. From the qualitative viewpoint, the glass surfaces show alterations in iridescence and also several impurities and small air bubbles, indicating the imperfect quality of the production.

The most represented are the bottles of which there are many pieces of necks or portions of

funds (Fig. 1-2). Of particular interest, from the morphological viewpoint, is the bottle fragment CSV11 characterized by a thickened edge brimmed, a cylindrical neck slightly tapered in its central part and a surface decorated with long vertical grooves. Two bottlenecks (CSV7 and CSV8) also tapered but diversified in the edge can be dated to XV-XVI centuries. The first shows an edge flared and squared (Gasparetto, 1986, p. 207, no. 235; Vannini, 1987, p. 625, no. 3461, Table p. 640), the second differs for the rounded edge (Gasparetto, 1986, p. 127, no. 1). The fragments CSV9 and CSV10 are comparable to a bottle attested in the XVI century (Vannini, 1987, p. 643, no. 3565; Coscarella, 1992, p. 159, Fig. 76, nos. 1-2). Three other bottle bottoms (CSV2, CSV3, CSV4) can be attributed to the same historical period. They are three pedestals characterized by a pronounced conoid belonging to a bottles with



Fig. 1 – Bottle neck of finds CSV7, CSV8, CSV9, CSV10, and CSV11.

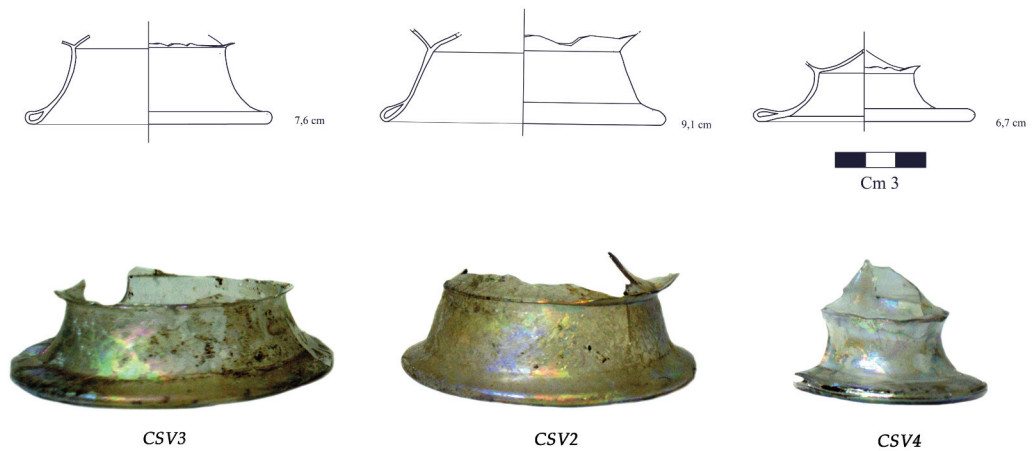


Fig. 2 – Funds of the bottle CSV2, CSV3 and CSV4.

globular or pear-shaped border and long and narrow necks (Barrera, 1991, p. 349, Fig. 2, no. 48, p. 354, Fig. 5, 9). The diffusion of morphologically similar bottle is already documented in the XV century, as is testified in the fresco of the Nativity of Paolo Uccello in the Cathedral of Prato (Ciappi, 1991, p. 302, Fig. 23) and the fresco of the Birth of the Baptist realized by Ghirlandaio in church of S. Maria Novella in Florence (Stiaffini, 1991, p. 255, Fig. 2). Similar types are also certified in stratigraphic contexts of the XV century in northern and central areas of the Italian peninsula (Gasparetto, 1986; Curina, 1987; De Vetis and Di Mella, 1987; Luzi, 1988; Stiaffini, 1991). Instead, at a later age (centuries XVI-XVII) is dated a third bottle (CSV10) characterized by a vertical edge square, a short cylindrical neck and a sky-blue coloration.

A portion of an umbonate fund (CSV12) could document the presence of a flask or a big bottle (Vannini, 1987, p. 632, no. 3447) dating to the XVII-XVIII centuries.

Between the vitreous material are also found two fragments (CSV16 and CSV17) that suggest the presence of an inkwell (Cuteri and De Natale,

2007, p. 152, Fig. 5). The extreme fragmentation of the article makes it impossible to identify precise typological comparisons and to determine the exact chronology, however, the object was made between the XVII and XIX centuries. On the other hand, it might belong to the small apod fund with pronounced conoid (CSV14) in dark green glass. Along with the bottles, some funds associated to different types of glasses were found. One is a glass cup belongs to the truncated conic foot (CSV1). The single foot, although intact, does not allow speculation either on the shape or on the history of the artifact, as similar cups have been documented since the XVI century and their production continues until the XVII-XVIII centuries (Cini, 1985 p. 542, no. 945, Table LXXXVII; Barrera, 1991, p. 352, Fig. 8, 30).

Another type of object is the glass CSV13 characterized by a marked conoid bottom. Similar specimens, very common on the tables of XVI and XVII centuries, located not only in pictorial representations but also in stratigraphic contexts in the central-northern and southern parts of the Italian peninsula (Andronico, 2003, p. 98, no. 289, Table XXXVII).

At a salt shaker (CSV15), yellow-orange in color, belongs the little knob in the shape of a pine cone, this is all that remains of two small circular dishes (Stiaffini, 2004, p. 31). The object, devoid of the second cup and partially fragmented in the first, for manufacture, degree of purity and thickness of glass, typical of industrial production, can be chronologically classified in the XIX century.

The sample collection also contains other glass fragments, (CSV6, CSV18, CSV20, CSV22, CSV23) which are so small that they cannot, at present, be attributed to any type of artifact.

#### ANALYTICAL TECHNIQUES

Geochemical studies were carried out at the Department of Earth Sciences, University of Calabria (Italy), by means of two different methods: SEM-EDS (model FEI Quanta 200) for analysis of major elements, and LA-ICP-MS, in which an Elan DRCe-Perkin Elmer/SCIEX plasma mass spectrometer was coupled with a model UP213, Nd-YAG laser (New Wave) to determine trace elements and REE.

A small piece of about 5 x 5 mm was sampled from each glass finding, and cleaned in an ultrasound bath with Millipore water to remove all traces of soil. Samples were then fixed on slides, with the fresh side facing upward. Due to their small size, three or four samples could be positioned on each slide.

LA-ICP-MS analyses were carried out before SEM-EDS. Each analytical run was carried out on one slide at a time, associated with the glass reference material NIST 612-50 ppm (Pearce *et al.* 1997), used for external calibration of the instrument (Barca *et al.*, 2007). Every sample under analysis was visualized by a PC-controlled CCD camera.

During each run, between 25 and 30 analyses were carried out, of which 15-20 were done on unknown samples (five point analyses per fragment), two for quality control on a standard

sample analysed as “unknown”, and eight on the standard sample at the beginning and end of the runs, in order to calibrate the instrument. Laser ablation of samples was carried out in the ablation cell with a beam creating a crater of about 50 microns, and the vaporized material was transported by a helium-argon flow to the ICP, where it was quantified (Gunther and Heinrich, 1999).

Calibration was carried out on standard glass NIST SRM 612 (50 ppm) produced by the National Institute of Standards and Technology, also to check the quality of the analyses the standard glass NIST SRM 610 (500 ppm) was analysed as “unknown”. Lastly, the concentration of SiO<sub>2</sub> for each glass fragment determined by SEM-EDS was used, for internal standardization.

To assess the accuracy of the analytical data, the mean value of analyses on standard NIST 610, used for quality control, was compared with those reported in the literature (Pearce *et al.*, 1997; Dulski, 2001; Gao *et al.*, 2002). Accuracies expressed as percent differences between measured and certified values were always less than 10%, and most plotted in the range +/-5%.

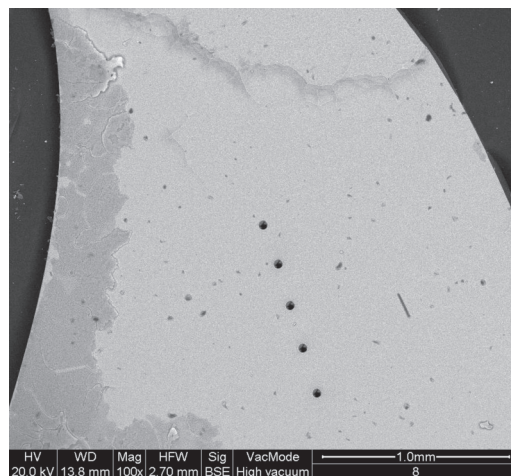


Fig. 3 – BSE image of sample CSV8 after LA-ICP-MS analysis, clearly showing 5 spots due to laser ablation.

After LA-ICP-MS analyses, the surface of each sample was covered with a layer of graphite and analysed by SEM-EDS. Attempts were made to carry out the analyses as close as possible to the ablation craters (Fig. 3). All signals recorded during the ICP runs were then processed by a PC with the GLITTER program. Lastly, in order to assess the homogeneity of the glass fragments, mean values and standard deviations were calculated for each sample.

#### RESULTS OF GEOCHEMICAL ANALYSES and DISCUSSION

The samples turned out to contain high concentrations of  $\text{SiO}_2$  (62-81%),  $\text{Na}_2\text{O}$  (5-17%) and  $\text{CaO}$  (6-14.4%), the results are listed in TABLE 1.

Potassium was the element which varied most greatly. Most samples had concentrations ranging between 2-5% (in weight), whereas CSV11 and CSV14 had very low (0.3% and 0.9% respectively) and CSV7 and CSV15 very high ones (7.5% and 9% respectively).

TABLE 1  
*Concentrations of major elements, expressed as % weight oxides by SEM-EDS.*

Sample	$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{K}_2\text{O}$	$\text{CaO}$
CSV1	15.21	3.56	1.89	66.62	3.06	6.81
CSV2	12.45	1.87	2.25	68.16	3.39	7.60
CSV3	17.26	3.47	4.22	61.85	5.11	5.90
CSV4	4.72	2.15	1.41	81.00	3.02	5.79
CSV5	12.19	3.83	1.99	65.6	3.53	10.78
CSV6	14.57	3.44	1.48	69.05	1.83	7.60
CSV7	11.96	2.42	3.63	62.02	7.45	9.29
CSV8	9.30	1.93	3.13	72.71	2.78	6.38
CSV9	10.32	4.37	2.16	67.72	2.47	10.21
CSV10	16.95	2.51	2.31	65.06	3.31	7.44
CSV11	12.49	2.76	2.56	72.63	0.32	8.11
CSV12	14.00	2.14	2.56	68.15	2.87	6.50
CSV13	8.89	3.77	1.95	69.08	2.77	10.79
CSV14	9.06	5.68	2.74	64.67	0.88	14.42
CSV15	7.64	0.55	0.90	71.89	8.93	9.15
CSV16	12.76	3.47	2.38	67.39	1.59	9.65
CSV17	10.64	2.99	2.17	68.50	1.81	11.58
CSV18	16.80	5.83	1.57	64.14	2.05	8.27
CSV19	10.27	4.30	2.33	67.56	2.54	10.26
CSV20	10.86	3.56	2.67	64.69	4.84	9.85
CSV21	10.50	3.09	2.49	62.65	5.41	10.56
CSV22	14.50	2.14	1.81	68.80	4.03	5.92
CSV23	10.67	3.35	2.89	66.06	4.23	9.70
CSV24	12.40	3.78	2.79	63.97	4.53	8.50
CSV25	10.93	3.74	2.82	65.21	4.38	9.62
CSV26	9.42	2.80	2.59	67.87	4.63	9.68

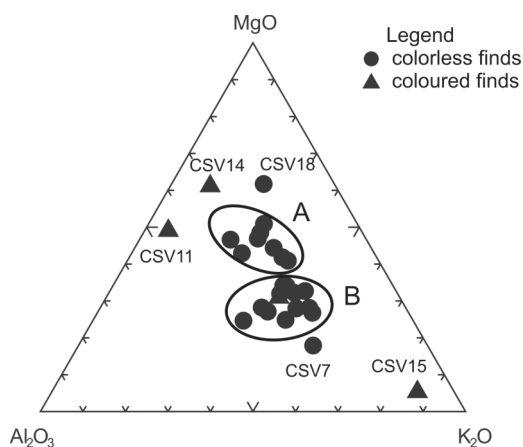


Fig. 4 –  $\text{Al}_2\text{O}_3$ - $\text{MgO}$ - $\text{K}_2\text{O}$  triangular diagram. The ellipses enclose two different group of glasses.

The ( $\text{Al}_2\text{O}_3$ - $\text{MgO}$ - $\text{K}_2\text{O}$ ) triangular diagram (Fig. 4) identifies two compositional groups: the  $\text{MgO}$ -rich group A, and the  $\text{K}_2\text{O}$ -rich group B; some samples were geochemical outliers. Group A contains samples CSV1, CSV5, CSV6, CSV9, CSV13, CSV16, CSV17, and CSV19, and group B CSV2, CSV3, CSV4, CSV8, CSV10, CSV12, CSV20, CSV21, CSV22, CSV23, CSV24, CSV25, and CSV26. Samples CSV7, CSV11, CSV14, CSV15, and CSV18 are outliers.

As  $\text{K}_2\text{O}$  and  $\text{MgO}$  were almost never added accidentally to the glass, the compositional differences between the two groups and the outliers reflect the differing methods used to produce them.

The  $\text{MgO}$ - $\text{K}_2\text{O}$  diagram (Fig. 5), generally used to classify ancient glass samples (Shortland and Tite, 2000; Polla *et al.* 2008; Angelini *et al.*, 2008), provided useful indications on source materials. Particularly the high values of potassium and magnesium, found in all samples, excluded the use of natron compounds as sources of alkaline-earth elements (Turner, 1956; Henderson, 1985; Lilyquist & Brill, 1993;

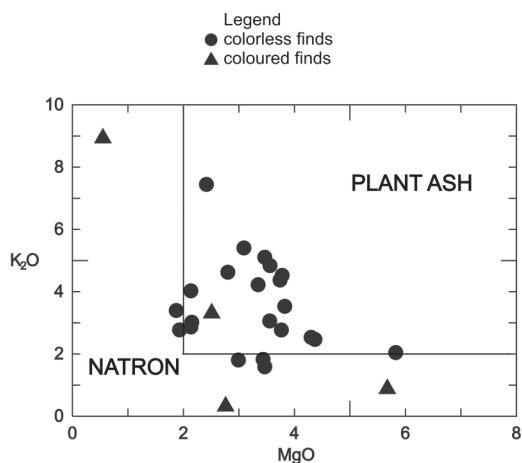


Fig. 5 –  $\text{MgO}$ - $\text{K}_2\text{O}$  diagram. Areas within rectangles show compositional ranges typical of glass produced with natron (lower left) and plant ash (top right). All samples plot in the area typical of High Magnesium Glasses (HMG).

Shortland and Eremin, 2006) and indicated the use of plant ash for almost all samples. Almost all of them, in both groups A and B, plot in the HMG (High Magnesium Glasses) compositional interval, according to Polla *et al.* (2008) and Angelini *et al.* (2008).

As regards trace elements and REE, 42 elements were analysed in all samples (TABLE 2).

Trace element concentrations identified samples which, with very similar chemical compositions, may be fragments of the same object. Examples are CSV9 and CSV19; CSV16 and CSV17; and CSV21 and CSV24; the spider diagram (Fig. 6) of trace elements clearly highlighted the overlap of these samples, in particular the elements Co, Cu, Ni, As, Sn, Sb and Pb are extremely discriminating and show the perfect chemical similarity of the different fragments.

CSV16 and CSV17 contain more lead ( $\text{Pb} = 3125$ - $3174$  ppm) and antimony ( $\text{Sb} = 352$ - $364$  ppm), as clearly seen in Fig. 7. The presence of lead in the glass is not accidental, since this element was already exploited in very ancient

TABLE 2  
*Concentrations of trace and rare earth elements expressed in ppm, obtained by LA-ICP-MS analyses. Mean values of five analyses for each finding.*  
 $\sigma$  = standard deviation.

	CSV1	CSV2	CSV2	CSV3	CSV3	CSV4	CSV4	CSV5	CSV5	CSV6	CSV6	CSV7	CSV7	CSV8	CSV8	CSV9	CSV9	CSV9
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Li	14.73	5.98	16.76	6.81	21.43	4.68	7.40	15.16	15.72	7.25	11.47	5.25	26.32	7.74	19.32	8.97	12.39	4.05
B	39.78	8.62	63.10	11.39	49.83	8.13	56.63	5.36	19.79	2.50	55.21	3.16	57.91	9.45	60.37	7.03	37.46	6.66
P	n.d.	-	1895	3.04	n.d.	-	820	4.63	1043	4.51	14454	0.01	1539	4.99	n.d.	-	n.d.	-
Sc	1.59	1.78	2.61	8.13	1.50	1.42	1.48	7.20	2.14	11.94	1.09	3.89	1.34	7.38	2.76	0.63	4.07	7.22
Ti	785	6.38	813	0.64	622	2.52	228	5.74	799	2.25	247	4.73	546	2.12	1004	2.43	1491	2.83
V	9.63	3.50	12.75	4.47	6.55	3.68	7.54	2.39	11.73	3.70	5.44	2.34	5.98	7.71	16.84	4.12	20.18	2.85
Cr	6.98	1.32	11.56	6.30	7.67	7.19	10.28	5.99	11.37	5.91	13.03	5.32	4.66	0.91	12.33	6.29	24.63	9.10
Mn	9100	5.09	11435	2.10	3604	1.09	1777	2.26	4948	3.93	1923	1.21	3293	1.65	14423	1.29	10262	2.39
Fe	2479	4.78	4914	3.74	2502	1.36	1914	3.73	3489	3.20	2079	5.05	2359	2.68	4596	1.37	5296	4.51
Co	29.94	4.79	13.11	5.09	10.59	4.79	2.41	4.15	34.56	7.98	13.95	4.38	10.29	2.86	16.20	3.80	21.23	1.76
Cu	15.99	0.85	20.36	5.48	11.51	4.79	102	5.80	16.75	4.15	15.66	2.55	10.41	4.95	23.22	3.82	42.93	1.10
Ni	18.82	1.95	14.32	5.54	17.34	4.04	5.84	9.18	13.57	6.81	10.17	6.05	7.49	4.61	15.48	8.40	13.88	2.97
Zn	48.16	5.76	102	4.32	31.54	6.37	24.67	9.78	32.68	4.20	38.95	4.40	25.12	1.70	114	2.36	61.05	1.89
As	36.20	7.51	3.83	10.71	23.91	5.59	2.83	8.00	35.57	4.04	22.93	5.47	22.86	5.84	5.28	8.35	4.85	1.90
Rb	15.60	5.48	13.42	3.92	56.92	3.77	17.20	3.12	19.20	5.00	12.94	5.36	53.05	3.31	16.09	2.76	21.61	6.96
Sr	542	3.74	232	2.77	465	1.96	273	4.37	707	2.95	661	2.00	443	2.88	280	1.56	704	4.00
Y	3.32	3.62	5.98	3.77	14.99	2.45	1.64	5.67	5.32	5.09	2.30	9.08	13.00	3.96	6.96	5.48	7.17	4.34
Zr	152	6.86	94	1.40	163	1.32	9.63	6.43	151	2.41	9.85	5.44	149	3.74	107	1.43	336	2.94
Nb	2.49	3.41	2.71	2.40	3.24	0.90	10.43	2.61	3.27	0.83	6.46	3.02	7.21	3.31	8.77	4.39	2.17	8.39
Sn	5.20	3.86	3.21	4.25	1.70	8.32	24.21	2.60	4.82	6.54	150	2.77	1.58	5.37	4.64	3.35	5.73	8.39
Sb	0.45	7.95	0.81	4.39	0.52	7.20	4.70	6.14	n.d.	-	0.50	6.75	n.d.	-	0.68	8.32	0.92	3.07
Cs	0.38	8.34	0.35	1.18	0.80	6.10	0.14	6.15	0.32	6.10	0.18	8.46	0.86	6.28	0.39	8.76	0.47	12.61
Ba	417	4.75	478	0.96	301	1.68	60.94	4.95	305	4.93	145	3.50	306	4.39	494	2.44	197	4.66
La	6.62	4.59	8.18	1.24	11.07	4.92	1.71	3.47	6.76	2.70	2.27	8.21	10.75	5.96	8.92	3.08	8.71	6.10
Ce	12.07	7.04	16.13	1.13	20.57	2.63	2.95	4.08	13.30	2.54	3.48	0.95	19.64	3.04	17.33	3.56	16.75	0.93
Pr	1.47	5.93	1.76	2.15	2.48	4.85	0.34	5.79	1.57	2.17	0.55	6.91	2.39	5.15	1.95	7.23	1.96	8.96
Nd	6.10	2.05	7.81	7.52	9.20	5.87	1.06	1.33	6.29	4.48	2.40	3.02	8.75	2.21	7.88	5.66	7.60	7.63
Sm	1.04	4.02	1.43	6.92	1.98	8.95	0.38	4.07	0.92	3.86	0.46	2.17	1.54	10.14	1.52	7.89	1.88	5.34
Eu	0.13	8.00	0.28	3.51	0.23	9.11	n.d.	-	0.13	2.77	0.10	9.98	0.16	1.77	0.28	11.58	0.31	10.52
Gd	0.95	9.69	n.d.	-	1.82	0.78	0.57	9.74	0.93	10.88	0.21	9.03	1.52	2.01	1.44	8.65	0.97	9.83
Tb	0.14	1.47	0.22	3.27	0.28	5.73	n.d.	-	0.15	7.64	0.07	12.59	0.31	2.31	0.16	0.91	0.22	1.59
Dy	1.16	3.66	0.84	0.76	2.30	0.92	n.d.	-	0.79	10.54	n.d.	-	2.18	4.54	1.02	1.39	1.06	7.71
Ho	0.17	5.17	0.21	7.69	0.51	2.92	n.d.	-	0.18	1.94	n.d.	-	0.49	0.29	0.29	2.86	0.31	0.23
Er	0.52	1.37	n.d.	-	1.86	5.32	0.13	9.28	0.47	6.89	0.18	2.79	1.21	5.84	0.64	9.47	0.62	11.47
Tm	0.08	9.30	n.d.	-	0.28	7.73	n.d.	-	n.d.	-	n.d.	-	0.26	3.58	n.d.	-	n.d.	-
Yb	0.65	4.35	n.d.	-	1.18	8.39	n.d.	-	0.40	8.95	n.d.	-	1.68	10.10	0.60	5.94	0.86	0.83
Lu	n.d.	-	0.07	6.43	0.32	1.96	n.d.	-	n.d.	-	0.02	3.48	0.28	7.99	0.12	9.53	0.11	4.52
Hf	3.35	1.69	2.43	4.99	3.51	3.89	0.25	1.11	3.62	6.15	0.30	5.15	3.13	4.96	2.61	4.35	8.73	1.54
Ta	0.20	7.66	0.22	10.43	0.26	9.60	0.10	9.90	0.24	10.21	0.16	5.00	n.d.	-	0.20	7.55	0.34	0.62
Pb	12.48	6.06	15.51	2.46	12.50	0.45	72.92	1.24	9.60	5.24	1.45	3.32	11.72	5.84	17.55	4.90	34.60	3.78
Th	1.65	8.17	2.16	6.05	4.43	1.70	0.45	8.55	1.69	5.46	0.47	5.00	4.31	4.78	2.39	6.04	2.34	6.04
U	0.52	4.88	0.59	0.96	1.80	5.17	0.27	4.16	0.65	9.13	n.d.	-	1.70	8.15	0.66	7.54	0.92	5.09



TABLE 2  
Continued...

	CSV10	CSV10	CSV10	CSV11	CSV11	CSV11	CSV12	CSV12	CSV12	CSV13	CSV13	CSV13	CSV14	CSV14	CSV15	CSV15	CSV16	CSV16	CSV17	CSV17	CSV18	CSV18
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Li	26.01	1.36	7.57	6.99	14.79	0.14	15.78	8.87	19.49	4.58	17.19	6.84	15.27	5.84	16.79	8.63	10.50	10.10				
P	93.52	6.34	25.62	3.04	114	0.09	87.01	9.84	64.06	8.51	24.39	5.03	48.06	6.65	40.68	11.96	70.14	4.17				
B	5313	11.17	43.21	7.29	1622	1.54	1550	4.96	106	11.63	388	5.93	999	3.09	1002	4.26	1271	2.86				
Sc	1.96	0.78	0.88	1.14	1.21	0.59	2.16	4.57	2.62	5.93	0.96	10.31	1.90	12.75	1.42	1.00	0.75	13.73				
Ti	1641	2.15	130	2.21	817	0.31	1209	0.99	805	2.10	1.62	3.94	699	4.82	653	1.62	264	4.48				
V	14.44	1.65	9.06	1.51	14.10	0.70	17.47	2.43	35.45	1.44	3.11	4.93	19.43	5.73	19.92	1.04	5.65	6.51				
Cr	23.99	4.54	4.12	7.53	8.85	1.60	20.87	10.40	96.18	2.13	23.16	2.24	87.67	3.68	8870	1.00	2407	0.46				
Mn	620	1.86	5526	1.28	12085	0.56	7988	5.00	96.18	1.86	240	8.12	3352	4.90	3309	1.14	2327	1.82				
Fe	3792	3.06	213	6.51	5073	1.89	5246	3.23	13567	1.86	240	8.12	3352	4.90	3309	1.14	2327	1.82				
Co	2.06	2.41	8.46	4.29	15.61	0.63	19.64	4.19	3.78	3.84	0.40	10.78	9.13	7.29	9.34	4.48	18.51	1.79				
Cu	24.95	2.57	112	4.69	22.89	0.93	44.82	5.28	19.72	5.27	8.18	7.19	78.43	1.48	80.09	3.16	12.26	8.20				
Ni	4.73	5.69	5.70	8.12	17.01	0.25	14.25	5.72	12.89	5.47	1.37	8.75	78.56	6.29	8.48	6.04	13.11	8.83				
Zn	76.82	5.15	15.10	3.77	84.62	0.87	57.03	9.14	24.34	7.37	5.60	5.50	78.56	3.00	90.08	5.76	34.12	6.84				
As	8.45	4.48	191	5.77	2.07	1.71	3.78	7.54	80.53	3.83	45.29	8.82	233	4.27	250	4.73	35.44	5.42				
Rb	22.77	3.42	0.59	7.70	16.05	0.48	22.45	2.30	26.20	1.79	136	2.86	23.05	5.64	23.78	3.25	10.65	4.00				
Sr	498	2.13	48.06	1.94	255	0.57	761	2.44	760	0.54	49.58	4.76	228	3.83	216	1.95	932	0.44				
Y	6.62	3.29	1.18	4.76	5.81	0.24	7.03	3.79	5.02	3.44	1.08	7.72	4.85	9.62	4.47	5.13	2.02	6.54				
Zr	294	0.81	109	4.00	93.74	0.62	283	1.95	82.29	1.93	11.99	2.44	125	8.11	112	1.64	10.25	3.35				
Nb	4.86	4.17	0.42	8.34	2.70	0.26	3.60	4.66	2.51	6.31	0.57	7.45	2.57	4.57	2.21	2.14	0.81	2.24				
Sn	11.42	7.76	0.55	9.45	2.70	4.46	5.61	3.05	5.06	2.24	0.78	8.88	9.20	4.88	93.88	2.50	504	5.86				
Sb	2.40	8.95	0.36	10.71	0.68	4.16	0.56	4.47	18.14	5.50	0.98	9.23	352	3.91	364	2.24	0.38	9.24				
Cs	0.12	2.40	n.d.	-	0.34	2.08	0.46	6.03	0.72	0.88	0.45	5.16	0.43	2.29	0.38	0.55	0.17	4.51				
Ba	87.75	4.31	312	2.70	438	0.65	219	1.54	137	2.75	9.47	4.65	212	5.65	205	4.16	160	0.39				
La	7.39	5.92	2.49	5.22	7.70	1.47	8.46	1.62	7.10	1.87	0.67	9.61	7.25	5.10	6.39	4.00	2.09	5.11				
Ce	15.24	2.04	1.07	5.90	15.51	1.96	15.68	2.56	12.77	1.67	1.00	6.57	12.09	6.64	11.44	3.89	3.44	6.74				
Pr	1.78	2.80	0.88	2.99	1.65	0.86	1.89	4.53	1.65	4.66	0.14	7.09	1.40	1.46	1.46	5.81	0.45	9.93				
Nd	6.64	6.74	94.91	3.91	7.40	1.82	7.58	3.73	6.50	4.02	0.30	8.50	5.41	4.18	5.53	4.18	2.21	3.84				
Sm	1.38	2.90	1.04	10.88	1.37	0.52	1.33	8.68	1.20	3.63	0.16	4.45	1.10	8.39	0.83	5.11	0.41	9.16				
Eu	n.d.	-	n.d.	-	0.16	3.05	0.30	5.13	0.29	7.65	n.d.	-	0.27	3.18	0.19	10.31	n.d.	-				
Gd	0.88	1.61	n.d.	-	0.93	3.82	1.22	7.15	1.25	3.98	0.28	16.74	1.04	2.05	0.85	2.51	0.38	5.77				
Tb	0.20	1.41	n.d.	-	0.16	0.45	0.14	0.49	0.14	2.90	n.d.	-	n.d.	-	0.15	5.85	n.d.	-				
Dy	1.12	9.15	0.31	0.08	1.38	2.57	0.96	6.66	0.85	8.32	n.d.	-	0.91	2.91	0.74	4.72	0.41	3.76				
Ho	0.22	3.84	n.d.	-	0.22	8.70	0.16	8.18	0.15	7.34	n.d.	-	0.22	3.17	0.21	4.31	n.d.	-				
Er	0.93	2.29	n.d.	-	0.45	6.73	0.67	9.57	0.43	4.77	n.d.	-	0.33	0.65	n.d.	-	0.40	3.71				
Tm	0.13	9.81	n.d.	-	0.06	2.48	n.d.	-	n.d.	-	n.d.	-	n.d.	-	0.10	8.34	n.d.	-				
Yb	0.69	8.45	n.d.	-	0.40	10.53	n.d.	-	0.57	8.76	0.21	9.66	n.d.	-	n.d.	-	n.d.	-				
Lu	0.14	10.14	n.d.	-	0.09	8.32	n.d.	-	n.d.	-	0.11	7.53	n.d.	-	n.d.	-	0.05	9.22				
Hf	6.30	0.90	2.44	9.34	2.54	6.61	4.46	4.46	1.64	0.86	0.13	3.65	2.59	3.82	2.71	4.97	0.35	11.53				
Ta	0.39	9.52	n.d.	-	0.18	0.40	0.33	4.69	0.19	8.32	n.d.	-	0.12	7.07	0.14	9.54	n.d.	-				
Pb	180	4.28	157	2.29	17.32	0.98	19.76	4.96	2.15	1.88	65.04	3.82	3125	2.18	3174	2.41	588	2.52				
Th	2.74	3.01	0.16	11.40	2.19	0.32	2.12	3.59	1.58	4.33	n.d.	-	1.96	4.58	1.70	4.99	0.54	3.44				
U	0.87	5.85	0.50	6.98	0.62	2.27	0.86	3.96	1.03	5.76	2.12	6.96	2.31	4.96	2.40	4.15	0.33	6.51				



glass-making for its double function: to create lead-based glass with special colors or opacities, and to increase the solubility of Sb, usually introduced as stibnite ( $Sb_2S_3$ ) (Fiori *et al.*, 2004). However, as the presence of antimony in CSV16 and CSV17 is associated with high lead content,

the use of bindheimite or lead antimonate [ $(Pb_2(Sb,Bi)_2O_6(O,OH))$ ] cannot be excluded.

The use of antimony as a decolorizer in glass-making goes back to the VII century B.C. until almost the end of the I century B.C., when it was replaced by manganese oxide (MnO) (Fiori *et*

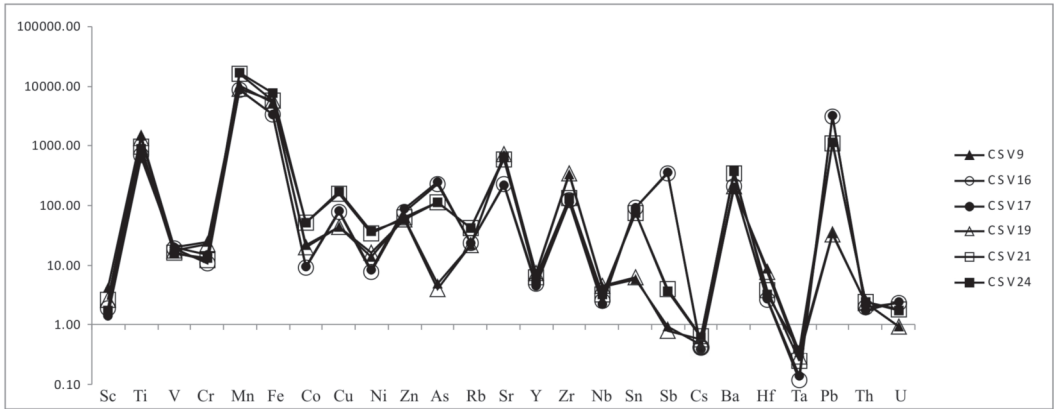


Fig. 6 – The spider diagram of trace elements analysed shows the overlap of samples CSV9 with CSV19, CSV16 with CSV17 and CSV21 with CSV24 indicating that they may be fragments of same object.

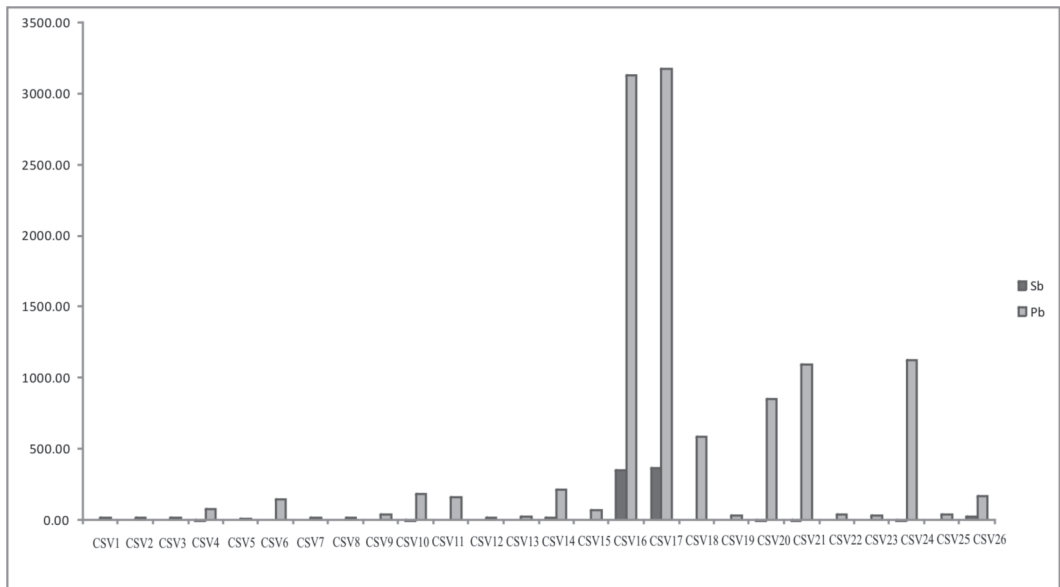


Fig. 7 – Histogram for Pb and Sb. Samples CSV16 and CSV17 are those with highest concentrations.

*al.*, 2004). The presence of antimony in CSV16 and CSV17, which are dated to the XVII-XIX centuries, permit to suppose the recycling of antimony-rich glass fragments in the frit.

As regards colors, the colorless samples have a Mn/Fe ratio between 0.85 and 3.6, and therefore occupy a clearly defined area in the Mn/Fe vs Fe and Mn/Fe vs K diagrams (Fig. 8), showing that iron and manganese played an essential role as colorizing or decolorizing agents in glass-making.

The low content of Mn in CSV10, CSV14 and CSV15 influences their color: for instance,

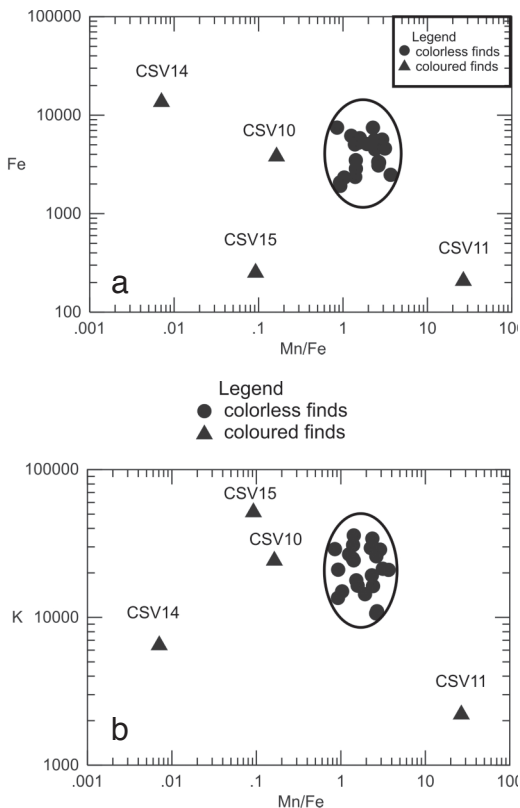


Fig. 8 – Diagrams a) Mn/Fe vs Fe; b) Mn/Fe vs K. All colorless samples have Mn/Fe ratio close to 1, and plot in a clearly defined area. Instead, colored samples have low contents of Mn, a decolorizing agent, or high contents of Fe, a colorizing agent.

CSV14, with far more iron than manganese, and with high contents of chrome (Cr) and vanadium (V), is bottle-green in color.

In general rubidium salts are used to give a violet color to glass and pottery glazes. The only violet-colored sample is CSV11; however, the low Rb (0.6 ppm) and high neodymium (Nd = 94.9 ppm), a chromophore metal belonging to the rare earth group (REE), which confers hues ranging between violet and wine-red to glass, indicates that Nd was used to color this find. The high content of Nd in the sample CSV11 is clearly highlighted in the spider diagram of REE of all finds analysed where only the glass CSV11 shows a positive peaks of neodymium (Fig. 9). Sample CSV18 differs from the others, due to a higher content of tin (Sn) (Fig. 10). Tin oxide in glass-making has a similar function to that of antimony, as an opacifier, resulting in yellow crystals in lead-based glass or white ones in glass made without lead. Thus, the lack of color of this sample is due to the relatively low content of Pb (588 ppm) (Turner and Rooksby, 1963).

## CONCLUSIONS

SEM-EDS combined with LA-ICP-MS allowed the chemical characterization of 26 glass samples found near the Castle of Cosenza (southern Italy). Two compositional groups were distinguished, and some chemically different outliers.

Most of the samples had high Mg and, together with K, indicated that plant ash was used to prepare the glasses.

Trace element concentrations revealed greater geochemical variability inside the compositional groups, identifying several fragments belonging to a single object, in which concentrations coincided. In particular, CSV9, the funnel-shaped neck of a bottle, is linked with CSV19, which is part of the elliptical section of a tubular filament applied and a decorative ribs. Confirming morphological analyses, CSV16 is

associated with CSV17, two wall fragments, perhaps of an inkwell (Cuteri and De Natale, 2007, p. 152, Fig. 5). Lastly, CSV21 is associated with CSV24, two fragments of the same object,

although its original shape cannot be conjectured, due to the tiny size of the fragments.

CSV16 and CSV17 contain high concentrations of lead and antimony. It is the

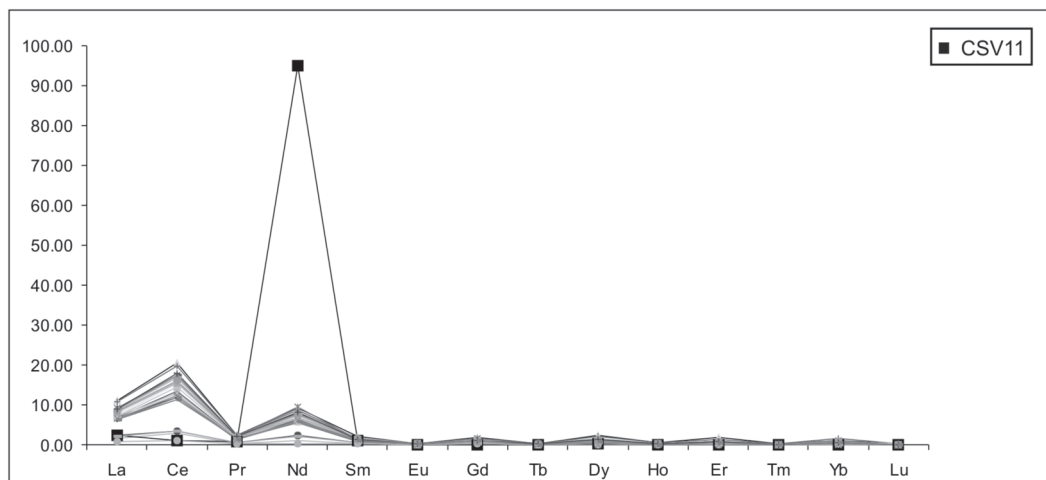


Fig. 9 – Spider diagram of Rare Earth Elements. Sample CSV11 clearly shows higher concentrations of Nd with respect to other samples.

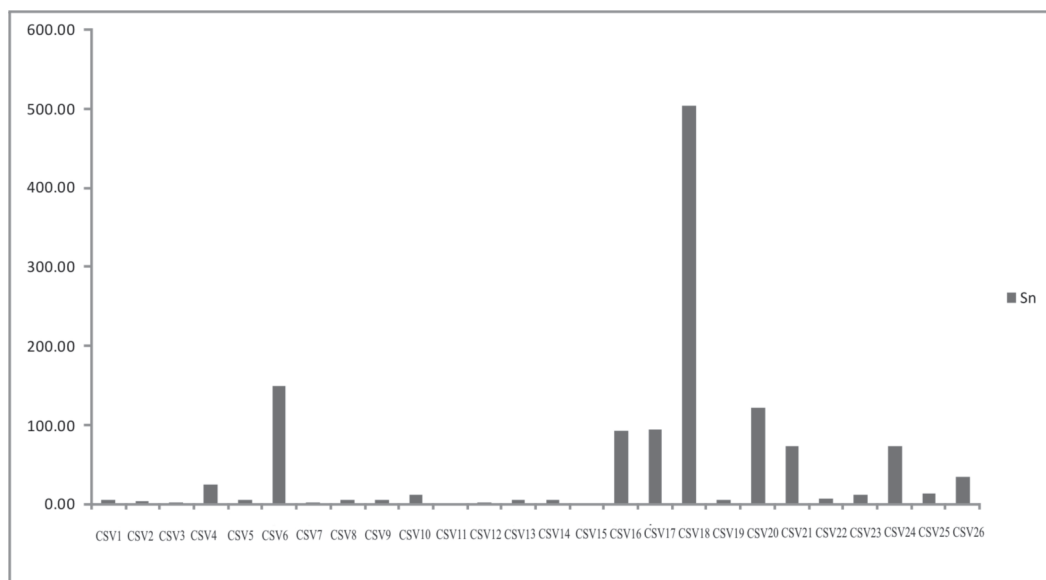


Fig. 10 – Histograms for Sn. Sample CSV18 clearly shows higher concentrations of Sn with respect to other samples.

presence of antimony in these samples which is unusual, since its use seems to have been discontinued during the I century B.C., because of the introduction of manganese oxide in glass-making (Sayre and Smith, 1967; Fiori *et al.*, 2004). Finding antimony in artifacts chronologically dated to the XVII-XIX centuries can only be explained by the custom of recycling frit (Price, 1978; Henderson and Warren, 1983; Fiori *et al.*, 2004).

Geochemical studies also identified the link between chemical composition and color. Glass colors are known to change according to a very high number of variables such as type of glass matrix, presence or one or more chromophore elements, and concentrations and ratios between various elements. It has been observed that the Mn/Fe ratio is determinant in coloring glass and that, in many cases, the presence of even only one chromophore element can be decisive in the color of the end-product. For instance, the color of sample CSV11 is interesting, and is ascribed to neodymium, an element belonging to the rare earth group, the concentration of which was determined thanks to the LA-ICP-MS analytical technique.

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