

DIRECT SOLID ANALYSIS OF LA TÈNE BRONZE FIBULAS OF DIFFERENT ORIGIN BY MEANS OF LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (LA-ICP-MS)

Siegfried Swoboda
Gerhard Stingeder
Thomas Prohaska¹

Introduction

Elemental pattern are widely applied for the characterization of metallic artefacts in order to prove authentication of alloys and to provide useful archaeometalurgical information on the production process and provenance.^{2,3,4,5} Most methods require tedious sample preparation and include digestion of a significant amount of material, which is not always applicable especially if considering precious artefacts. Therefore, investigations require a method which allows destruction free analysis without sample contamination in combination with high spatial resolution, non-interfered assessment of elemental and isotopic information with high sensitivity and a high sample throughput for statistically relevant population studies.

Over the last years, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become a mature and versatile tool for direct solid analysis of multi-element pattern. The method combines the benefits of a laser ablation system with high lateral resolution (from 5 to several hundreds μm) and the simultaneous multi-element and isotopic analysis capabilities at low concentration levels of the ICP-MS. The benefits of this combined method are well reported in review

articles.^{6,7} Several studies have shown that this technique can be applied for the trace element analysis concentrations in various matrices such as glass^{8,9,10}, fluorite¹¹, soil¹², tooth¹³ and even gemstones^{14,15,16}.

Authentication of antique silver objects using LA-ICP-MS showed good precision of 10% RSD for the signal repeatability of the analyte and the possibility of dating artefacts before and after 1850.¹⁷ Moreover, fingerprinting of ores of Muslim coinages (8th – 11th Century) and of ancient gold coins (approx. 300 BC) was helpful in solving questions on the provenance of archaeological gold.^{18,19} Archaeological iron samples were analyzed in order to determine their origin and enabled good classification using matrix-matched standard reference material for quantification.²⁰

One of the major problem ablating alloys by using a laser is the observation of selective volatilization caused by the different melting temperatures of the components of the alloy. Melting temperatures are 232°C for Sn, 420°C for Zn and 1083°C for Cu, which are the main components of bronze. Several studies showed that wavelength and fluence of the laser

¹ University of Natural Resources and Applied Life Sciences, Department of Chemistry, Division of Analytical Chemistry – VIRIS Laboratory, Muthgasse 18, A-1190 Vienna, Austria; corresponding author: thomas.prohaska@boku.ac.at.

² OUTRIDGE 1997.

³ GAGEAN 1998.

⁴ DEVOS 2000.

⁵ DE WANNEMACKER 2000.

⁶ GÜNTHER 1998.

⁷ BECKER 2003.

⁸ FLEM 2002.

⁹ GÜNTHER 1996.

¹⁰ GÜNTHER 1999.

¹¹ KOCH 2002a.

¹² LEE 2003.

¹³ URYU 2003.

¹⁴ GUILLONG 2001.

¹⁵ RESANO 2003.

¹⁶ GUILLONG 2003.

¹⁷ DEVOS 1999.

¹⁸ GUERRA 1999.

¹⁹ JUNK 2001.

²⁰ DEVOS 2000.

have an important influence on the melting temperature and fractionation.^{21,22,23,24} Fractionation will occur after evaporation as well if one or more elements diffuse in the gaseous phase to the transport-tubing or if large particles are transported to the plasma less efficiently than small particles. Significant differences in the composition of samples and standards may result in systematic calibration errors.²⁵ Recently, a model for congruent and non-stoichiometric vaporization was presented in order to identify optimum conditions for laser sampling.²⁶ As a consequence, the method of choice for calibration is external calibration and internal standardisation via an element with known concentration using a matrix-matched solid reference material in order to correct for variations of the ablation efficiency.^{27,28}

Within this work, LA-ICP-MS was applied for the analysis of bronze fibulas from different origin of the La Tène period in order to study the potential to assess the provenance via the alloy composition.

Experimental

Samples

The investigated fibulas were provided by museums from France, Switzerland, Czech Republic and Austria (Table 1). All fibulas were made of bronze and showed differently pronounced surface corrosion (this effect is described in more detail later in this work).

Country	Origin	Periode (Lt B1 – 375-325 BC)	Number of samples
France	Villeseneux		1
	St. Memmie		3
	Grandes Loges		2
	Trouans 7 (Cha.)		1
	Lenharrée (Cha.)		1
	Bucy-le-Long		2
	Dommartin-L.		3
	Meulson		1
	Monte Troté		2
Czech Republic	Duchcov		10
	Holubice		1
	Tikovice		1
	Rousinov		1
Austria	Pottenbrunn		1
	Mannersdorf		2
Switzerland	Andelfingen		2
	Bern		2
	Büren		3
	Leukerbad		1
	Meinisberg		2
	Mirchel		1
	Münsingen-Rain		8
	Stettlen-Deisswil		3
	St. Sulpice		12
	Müns.Trägermatten		1
	Vevey		10
Zürich-Altstetten		3	

Table 1: List of investigated finds.

²¹ IIDA 1990.

²² GEERTSEN 1994.

²³ CROMWELL 1995.

²⁴ GAGEAN 1998.

²⁵ AESCHLIMAN 2003.

²⁶ HERGENRÖDER 2006.

²⁷ TIBI 2003.

²⁸ KOCH 2002b.

A solid Cu-based standard reference material (IARM 91B, ARMI, USA) with known trace element composition was used for assessing quantitative data. The measurements were validated using a copper reference material (BCR 075, Brussels, Belgium) added with low amounts of Ni, Zn, As, Sn, Sb, Pb and Bi. (Table 2)

Element	IARM-91 (mg kg ⁻¹)	CRM075 (mg kg ⁻¹)
P	120	n.c.
Ni	5600	1.45
Cu	820000	999000
Zn	34900	3.47
As	10	3.74
Sn	65700	1.09
Sb	1900	2.56
Pb	71500	3.27
Te	1.5	1.52
Bi	n.c.	1.44
Fe	560	9

Table 2: Copper reference material.

Instrumentation

Analysis was performed by using LA-ICP-MS. The fibulas were fixed with plasticine on a glass slide and placed into the ablation cell without prior preparation. The laser beam was focused on the surface of the samples by adjusting the ablation cell in x-, y- and z-axis. A high-energetic beam created from the laser impinges on the sample surface leading to evaporation of a small amount of sample from the surface. This dry aerosol is transported by means of a He carrier gas through plastic tubing to the plasma of the ICP-MS. Ablation was performed under 100% Helium atmosphere due to the smaller particle size distribution and reduced laser-induced fractionation^{28,29,30}. Furthermore, the deposition of visible particles around the ablation pit is significantly decreased when He is used instead of Ar¹⁰.

The tubing empties directly to the torch of the ICP and the aerosol is atomized and ionized on the way through the different heating zones of the plasma. The degree of ionization is more than 90% for most components. The positively charged ions are extracted from the plasma through an interface into the high vacuum area of the mass spectrometer where they are

separated according to their mass/charge ratio and finally detected by a secondary electron multiplier (SEM). (Fig. 1)

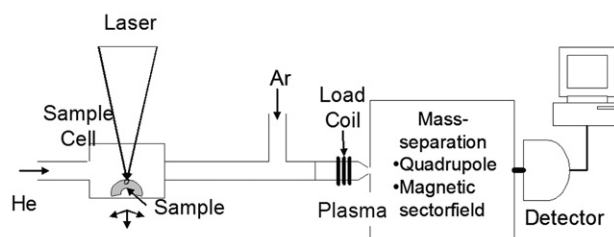


Fig.1: Schematic figure of a mass-spectrometer with secondary electronic multiplex.

The laser ablation system (Ablascope Bioptic, Berlin, Germany) was equipped with a neodymium-doped yttrium aluminium garnet (Nd:YAG) laser with a wavelength of 213 nm. The laser system can also be equipped with an Nd:YAG-laser with wavelength of 266 nm, but the signal is more unstable although it shows higher initial intensity as described by Guillon et al.¹⁶. Measurements have been performed using two different types of ICP-MS: a sector field inductively coupled plasma mass spectrometer (ICP-SFMS: Finnigan MAT Element, Bremen, Germany) and a quadrupole ICP-MS (ICP-QMS: PerkinElmer SCIEX Elan DRC II, Ontario, Canada).

Both instrument lead to the same quantitative results for the major components which was proven by the analysis of certified reference materials and show mainly differences with respect to sensitivity. Sensitivity was not an issue for the main elements which were finally evaluated in this study. ICP-SF-MS allowed the analysis of additional elements such as Ni, As, S and Bi. Bronze fibulas from France, Austria and Czechia were analyzed using ICP-SFMS and the samples from Switzerland were analyzed using ICP-QMS only as a result of the availability of the instruments and the arrival of the fibulas in our laboratories. Instrumental parameters are given in table 3.

Method development and analytical protocol

Bronze refers to a broad range of copper (70%–80% Cu) alloys, usually with tin as the main additive (10% – 30% Sn). A number of elements were selected for the characterization of fibulas of different origin (Table 4). The main alloy components Cu, Zn, Sn, Sb and Pb were quantified for their elemental concentrations by external calibration. Other elements were compared with respect to their relative abundance in the single bronze samples.

²⁹ KOCH 2004.

³⁰ KOSLER 2005.

<i>Ablscope</i>	
Wavelength	213 nm
Pulse rate	10 Hz
Spot size	80 μm
Laser fluence	10 J cm^{-2}
Ablation mode	Spot scan
z-Axis adjustment	5 $\mu\text{m s}^{-1}$
Line length	800
<i>ICP-MS: ELAN 6100</i>	
Rf power	1250
Sample/skimmer cone	Ni
Sample gas flow rate – Ar	0.9 L min^{-1}
Additional gas flow rate - He	0.7 L min^{-1}
Dwell-time	50 ms
Readings/replicate	50
Sweeps/reading	1
Number of replicates	1
Scan mode	Peak hopping
<i>ICP-MS: Element MAT</i>	
Rf power	1300
Mass resolution $m/\Delta m$	3000
Sample/Skimmer cone	Ni
Sample gas flow rate (after sample cell) – Ar	1.27 L min^{-1}
Additional gas flow rate (before sample cell) - He	0.71 L min^{-1}
Runs and Passes	6 x 900
Scan duration	90 s

Table 3: Instrumental parameter.

Elements	Possible information content
Cu, Sn, Zn, Pb, As*, Sb, Ni*	Characterization of the alloy
Co, Ni*, Zn, As*, Sb, Ag, Bi*, In, Te, Hf, Bi rare earth elements (REE): Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Characterization of the source of the ore
Fe, S*	Information about the processing

Table 4: Number of elements selected for characterisation of fibulas of different origin.

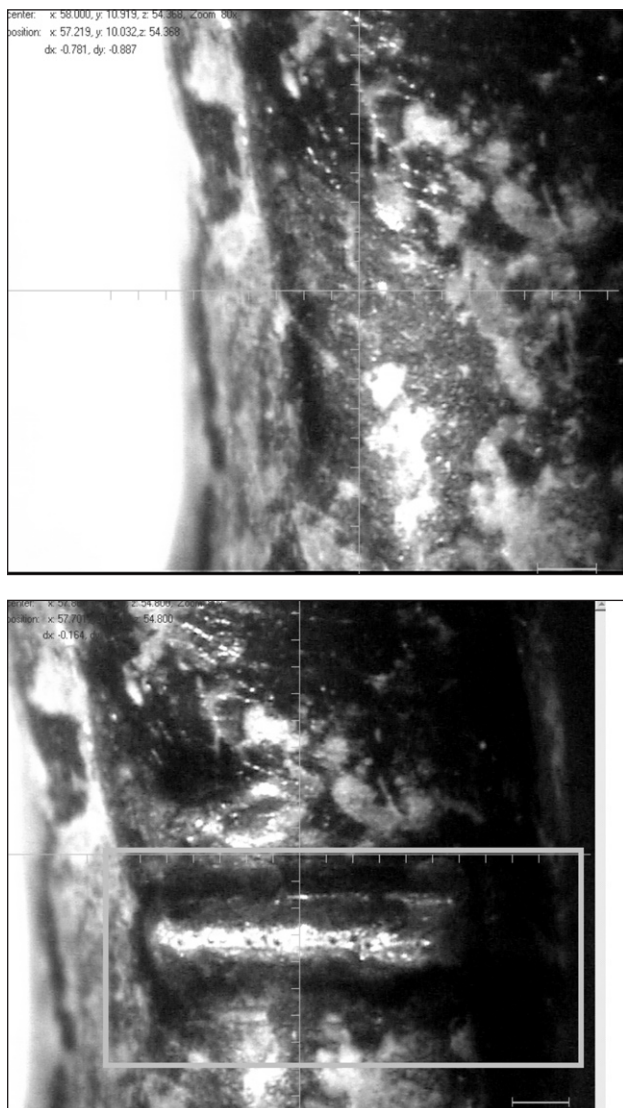


Fig. 2a, 2b: First removals of patina layer.

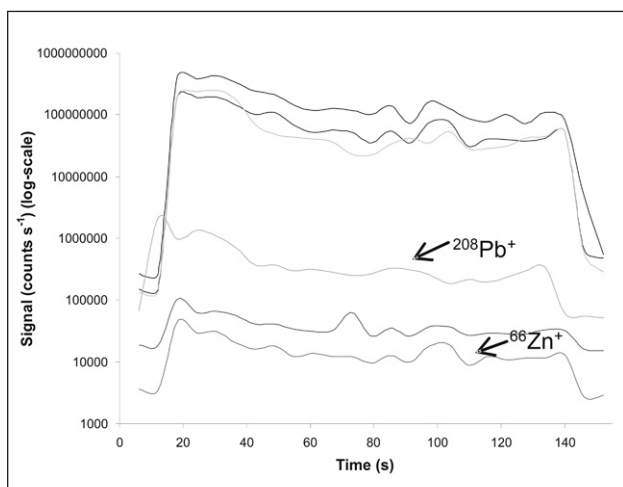
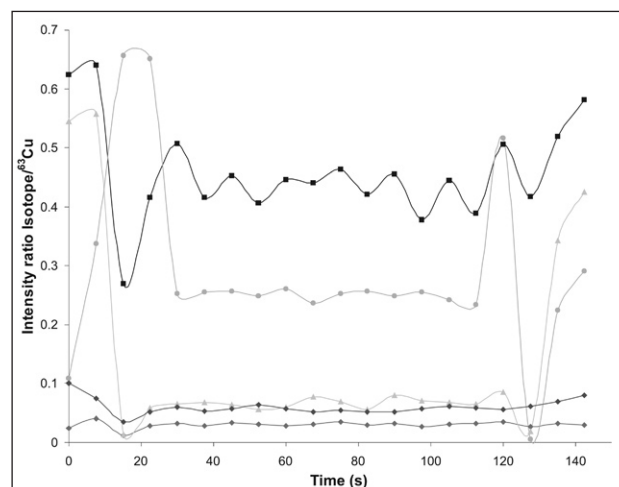


Fig. 3a: Stable ablation identified by monitoring the main alloy components.

Most samples were extensively corroded and some fibulas showed a thick patina layer on the surface. Corrosion may lead to a modification of the element concentration in the surface area of the fibulas. Thus, the surface was scanned 3 times with a 200 μm diameter spot along a line of 800 μm length to remove the patina layer to obtain a shiny alloy surface (Figures 2a and 2b). The laser fluence at the spot size of 200 μm was adjusted to 3.5 J cm^{-2} .

Three specific positions on the pre-ablated surface were subsequently analyzed using a spot-size of 80 μm . Ablation was performed using a repetition rate of 10 Hz and a laser-fluence of 10 J cm^{-2} . It is important that the focus of the laser beam (with the highest energy density) is always on the sample surface. Ablation is incomplete and the signal decreases abruptly when the focus gets lost. Therefore, the z-axis had to be adjusted to stabilize the signal as possible. In the present study, a z-axis movement of 5 $\mu\text{m s}^{-1}$ was provided for an ideal correlation between the signal intensity and signal-stability. The signal intensity vs. ablation time was monitored for all investigated isotopes. A plateau of stable ablation was identified by monitoring the main alloy components (Fig. 3a). The signals at this plateau were averaged and referenced to the ^{63}Cu signal (Fig. 3b). Since Cu is not always present in the same concentration, the absolute amounts were finally corrected to obtain composition of 100% in total.

During method development, a continuous signal-loss of the ablated reference material was observed. The signal of e.g. ^{63}Cu decreased within 1 day from 6×10^5 counts s^{-1} (cps) to 2×10^5 cps whereas the isotope / ^{63}Cu ratios varied only with a RSD of below 5%. One of the reasons is material deposition on the sampler and the skimmer cone in the interface area of the ICP-MS. In addition to Cu we applied Sn as internal

Fig. 3b: Signals averaged and referenced to the ^{63}Cu signal.

standard. Both elements led to precisions for the concentrations in the range of 1% to 3% RSD for the homogeneously distributed elements after internal standardisation.

Quantification was performed using a solid Cu-based standard reference material (IARM 91B, ARMI, USA) with known trace element composition which was analyzed under the same conditions as the bronze fibulas. This procedure was validated using the copper reference material BCR 075 (Brussels, Belgium). Recovery rates between 92% and 112% could be found for elements measured on different days. RSD of the results are below 10% for $n = 10$ measurements. The standards IARM-91B and BCR-075 were measured at the beginning, after every fifth sample and as final sample. The obtained intensities of the samples were corrected with a factor which was determined from the variation of the signal of the reference material before and after a series of samples.

Ten replicate analyses of the blank were made for the determination of the limits of detection (LOD) and are presented as concentration equivalent of three times standard deviation in table 5.

Element	LOD (mg kg ⁻¹)
P	103
Ni	16
Cu	64
Zn	5.8
As	0.9
Sn	66
Sb	2.5
Pb	56
Te	1.4
Bi	1.3
Fe	19

Table 5: Concentration equivalent of the three times standard deviation

Results and discussion

The signals of the pre-ablation of the corroded surface were recorded and quantified since different element concentrations in the patina compared to the alloy were expected. The complete ablation of the patina surface is crucial to prevent that erratic values are used for further interpretation. Due to the long repository time in soil, corrosion led to a significant displacement of the element concentration in the alloy (Figures 4a and 4b). The patina surface shows enrichment in Sn, Zn, Pb and Fe compared to depletion in Cu. Other elements show an inhomogeneous distribution in the patina. The final abla-

tion for the quantification of the elements in the alloy was performed when the ratio of Sn vs. Cu of the pre-ablation (patina) changed to a constant proportion (alloy) which is inverse compared to the ratio in the patina surface. Table 6 shows the results of selected line-scans of two samples and the change of concentration of the elements Cu, Sn, Zn, Pb and Fe. The removal of patina using pre-ablation worked satisfyingly for all samples except for two fibulas from Switzerland (one from Mirchel and one from Büren). Complete removal of the patina layer was unsuccessful for these samples even after eight line-scans on each of the two samples. Mechanical removal of the patina was not considered, since it would have led to a greater damage of the artefacts and reproducible pre-treatment of the samples was requested.

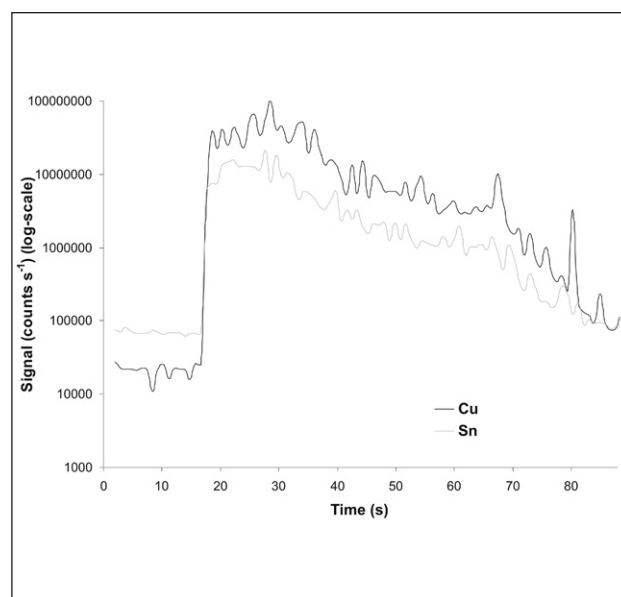
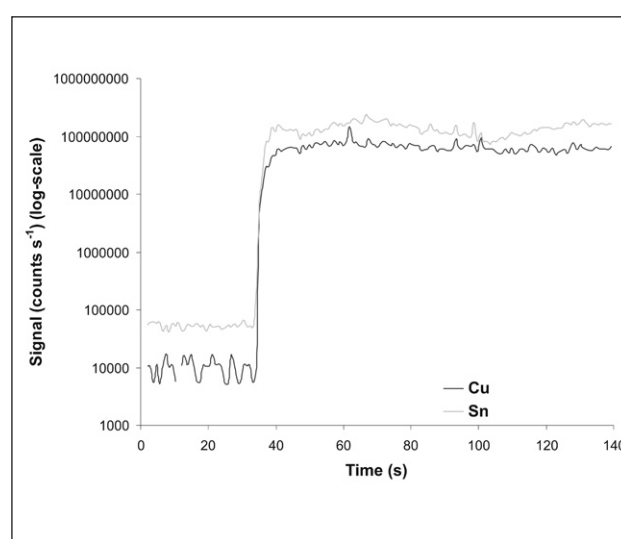


Fig. 4a, 4b: Significant displacement of the element concentration in the alloy because of long repository time in soil.

Line-scan	Cu [mg kg ⁻¹]	Zn [mg kg ⁻¹]	Sn [mg kg ⁻¹]	Pb [mg kg ⁻¹]	Fe [mg kg ⁻¹]
Dux18963 1.	431088	316	562058	5386	758
Dux18963 3.	864072	32	134945	542	n.d.
Dux18986 1.	478408	1312	493745	25179	354
Dux18986 3.	889630	52	106749	3047	n.d.
Dux18986 4.	911662	19	85961	2099	n.d.

Table 6: Result of selected line-scans of 2 samples and change of concentration of Cu, Zn, Sn, Pb and Fe.

Tables 7a and 7b show the concentrations of the main components of the investigated fibulas. After statistical evaluation a classification in two groups is possible. Nonetheless, these groups could not be allocated explicitly to the finding sites. The clas-

sification depends on the concentration of Cu and Sn, as seen in figure 5. Samples marked in grey have higher concentration of Sn in the range of 200 g kg⁻¹ to 400 g kg⁻¹ whereas samples marked in black have Sn-concentration below 200 g kg⁻¹.

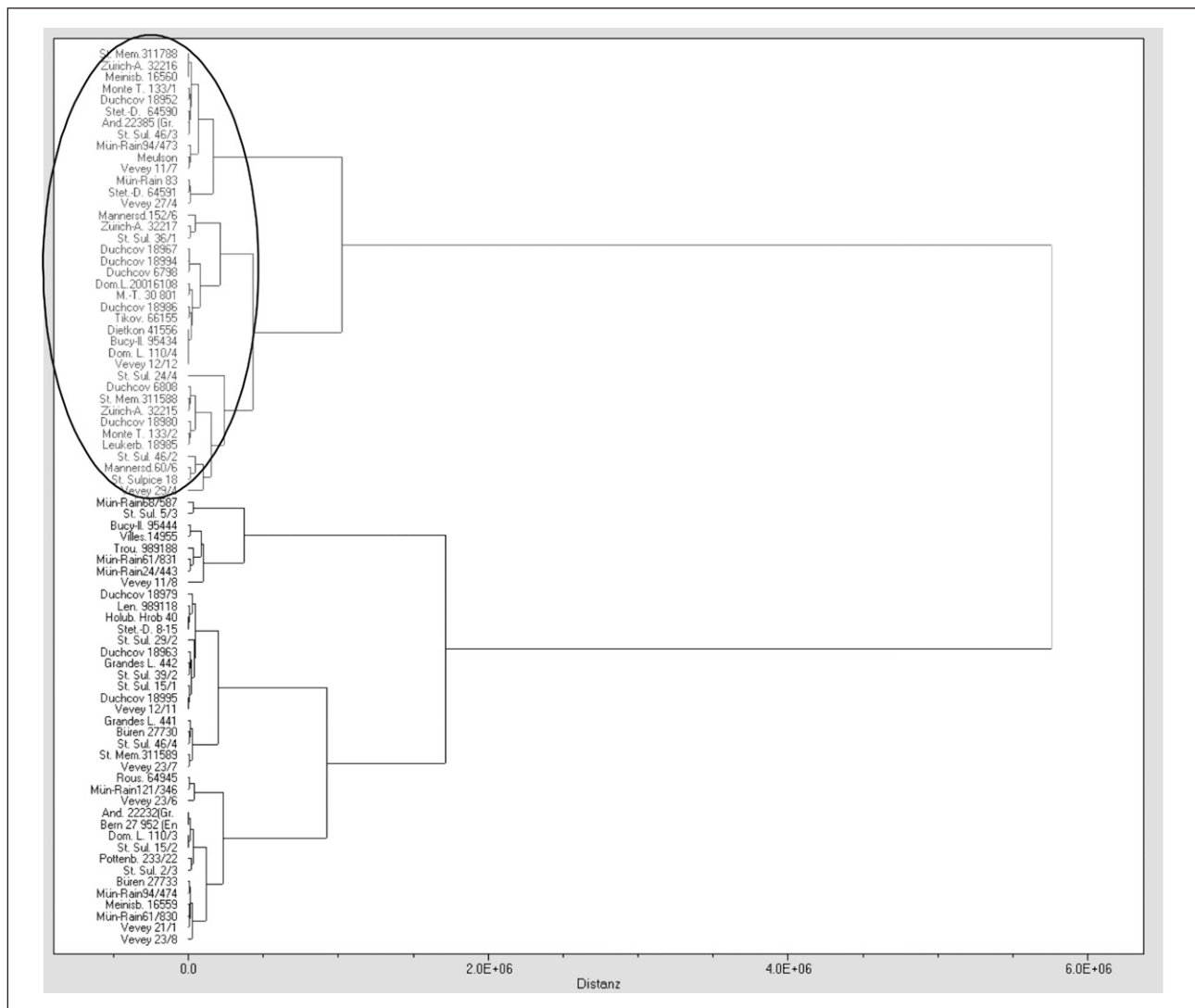


Fig. 5: Concentration of Cu and Sn.

Sample	Cu [g kg ⁻¹]	Sn [g kg ⁻¹]	Zn [mg kg ⁻¹]	Sb [mg kg ⁻¹]	Pb [mg kg ⁻¹]
Pottenbrunn 233/22	710 ± 30	280 ± 25	n.d.	840 ± 44	15 000 ± 3 000
Zürich-Altstetten 32215	860 ± 10	145 ± 10	n.d.	510 ± 63	601 ± 67
Zürich-Altstetten 32216	850 ± 3	160 ± 3	n.d.	n.d.	430 ± 31
Zürich-Altstetten 32217	920 ± 12	83 ± 12	n.d.	300 ± 16	610 ± 180
Dietkon-Gigerpeter 41556	890 ± 6	110 ± 6	1560 ± 600	320 ± 24	478 ± 83
Andelfingen 22232 (Gr. 6)	750 ± 20	253 ± 21	1490 ± 1100	700 ± 60	800 ± 91
Andelfingen 22385 (Gr. 29)	850 ± 15	155 ± 15	n.d.	202 ± 7	n.d.
Bern 27 952 (Enzingerstr.)	740 ± 30	260 ± 30	n.d.	210 ± 37	165 ± 30
Bern 39997 (Bümplitz)	780 ± 31	200 ± 35	n.d.	1 100 ± 190	2 500 ± 500
Büren 27730	760 ± 40	240 ± 38	n.d.	260 ± 31	1600 ± 770
Büren 27733	750 ± 60	250 ± 55	140 ± 74	430 ± 57	3150 ± 950
Leukerbad 18985	870 ± 10	130 ± 8	n.d.	180 ± 5	n.d.
Meinisberg 16559	720 ± 75	280 ± 70	n.d.	260 ± 50	270 ± 62
Meinisberg 16560	840 ± 16	160 ± 16	n.d.	160 ± 55	n.d.
Münsingen-Rain 61/831	650 ± 60	350 ± 53	220 ± 30	670 ± 160	1 000 ± 290
Münsingen-Rain 83	820 ± 20	180 ± 17	n.d.	670 ± 72	690 ± 71
Münsingen-Rain 94/473	815 ± 40	180 ± 30	210 ± 56	2 600 ± 570	6 300 ± 1100
Münsingen-Rain 94/474	730 ± 31	270 ± 30	340 ± 280	4 700 ± 340	660 ± 90
Münsingen-Rain 61/830	720 ± 20	270 ± 15	500 ± 270	520 ± 20	2 300 ± 580
Münsingen-Rain 68/587	560 ± 37	430 ± 40	750 ± 280	290 ± 50	870 ± 250
Münsingen-Rain 121/346	630 ± 40	370 ± 45	n.d.	410 ± 85	690 ± 59
Münsingen-Rain 24/443	650 ± 100	350 ± 100	230 ± 30	480 ± 180	350 ± 90
Stettlen-Deiswil 8-15	790 ± 40	200 ± 38	350 ± 130	430 ± 75	600 ± 220
Stettlen-Deiswil 64590	850 ± 20	150 ± 19	n.d.	300 ± 6	n.d.
Stettlen-Deiswil 64591	820 ± 9	180 ± 8	n.d.	320 ± 64	n.d.
St. Sulpice 15/1	790 ± 22	200 ± 21	2 700 ± 1 200	600 ± 85	2 200 ± 450
St. Sulpice 15/2	730 ± 32	260 ± 33	9 700 ± 1 200	94 ± 5	290 ± 80
St. Sulpice 29/2	760 ± 6	220 ± 7	330 ± 80	2 200 ± 170	17 000 ± 3 000
St. Sulpice 36/1	920 ± 5	73 ± 0.5	n.d.	700 ± 43	11 000 ± 5 000
St. Sulpice 39/2	780 ± 40	220 ± 37	5 400 ± 2000	670 ± 140	1 300 ± 350
St. Sulpice 46/2	900 ± 45	99 ± 3	n.d.	72 ± 5	190 ± 22
St. Sulpice 46/3	830 ± 23	160 ± 22	1 700 ± 400	650 ± 150	1 500 ± 340
St. Sulpice 46/4	750 ± 46	240 ± 43	5 300 ± 2 200	630 ± 87	2 800 ± 940
St. Sulpice 24/4	770 ± 43	13 ± 2.4	180 000 ± 33 000	500 ± 71	43 000 ± 13 000
St. Sulpice 2/3	730 ± 40	240 ± 36	20 000 ± 2 300	170 ± 39	900 ± 140
St. Sulpice 5/3	540 ± 11	460 ± 12	n.d.	960 ± 1100	n.d.
St. Sulpice 18	880 ± 8	100 ± 6	2 900 ± 700	490 ± 10	20 000 ± 3 300
M.-Tägermatten 30 801	890 ± 12	110 ± 11	n.d.	350 ± 40	300 ± 39
Vevey 21/1	720 ± 11	280 ± 11	350 ± 5	370 ± 23	280 ± 13
Vevey 11/7	840 ± 20	160 ± 16	890 ± 100	400 ± 64	1 200 ± 700
Vevey 11/8	630 ± 39	320 ± 52	240 ± 42	2 100 ± 680	49 000 ± 15 000
Vevey 12/11	750 ± 38	240 ± 40	720 ± 420	470 ± 110	1 900 ± 840
Vevey 12/12	880 ± 13	120 ± 5	n.d.	590 ± 25	580 ± 85
Vevey 23/6	700 ± 31	280 ± 29	n.d.	1800 ± 350	19 000 ± 2 000
Vevey 23/7	760 ± 24	230 ± 24	n.d.	1 400 ± 120	1 700 ± 100
Vevey 23/8	720 ± 19	270 ± 18	n.d.	1 700 ± 210	18 000 ± 280
Vevey 27/4	810 ± 18	190 ± 19	550 ± 130	830 ± 110	1 200 ± 120
Vevey 29/4	820 ± 6	100 ± 6	n.d.	10 000 ± 160	66 000 ± 370

Table 7a, 7b: Main components of the investigated fibulas.

Sample	Cu [g kg ⁻¹]	Sn [g kg ⁻¹]	Zn [mg kg ⁻¹]	Sb [mg kg ⁻¹]	Pb [mg kg ⁻¹]
Bucy-le-long 9 54 34	880 ± 8.5	110 ± 9	n.d.	80 ± 20	170 ± 16
Bucy-le-long 9 54 44	670 ± 33	330 ± 33	50 ± 30	400 ± 100	440 ± 18
Lenharrée (Ch) 989118	790 ± 22	210 ± 21	60 ± 20	180 ± 30	200 ± 20
Trouans 7 (Ch) 989188	660 ± 17	340 ± 16	1700 ± 1500	280 ± 80	180 ± 60
Dom.-Lettré (Ch) 20016108	890 ± 33	110 ± 10	50 ± 20	70 ± 40	50 ± 20
Dommartin Lettré 110/3	720 ± 28	280 ± 30	2000 ± 900	600 ± 200	500 ± 50
Dommartin Lettré 110/4	880 ± 10	120 ± 10	120 ± 30	130 ± 20	230 ± 10
Grandes Loges 441	750 ± 29	250 ± 30	70 ± 20	230 ± 70	250 ± 60
Grandes Loges 442	830 ± 66	170 ± 16	350 ± 20	700 ± 40	500 ± 70
Meulson 99-XXII-0085	870 ± 20	130 ± 20	20 ± 3	90 ± 7	60 ± 20
Monte Troté 133/1	850 ± 26	150 ± 26	n.d.	230 ± 20	630 ± 150
Monte Troté 133/2	870 ± 12	130 ± 6.3	15 ± 1	260 ± 90	650 ± 6
St. Memmie 311588	860 ± 35	140 ± 35	30 ± 2	340 ± 30	210 ± 60
St. Memmie 311589	870 ± 13	130 ± 8.5	110 ± 30	600 ± 100	200 ± 25
St. Memmie 311788	850 ± 14	150 ± 14	100 ± 40	350 ± 50	290 ± 70
Villeseneux 14955	670 ± 14	330 ± 50	60 ± 10	530 ± 10	360 ± 50
Duchcov 18952	870 ± 46	130 ± 8.5	180 ± 100	700 ± 100	200 ± 40
Duchcov 18963	750 ± 47	240 ± 47	200 ± 100	1 000 ± 160	1 300 ± 500
Duchcov 18967	900 ± 16	95 ± 3.8	50 ± 40	160 ± 20	700 ± 200
Duchcov 18979	810 ± 12	170 ± 17	1000 ± 200	600 ± 120	3 200 ± 600
Duchcov 18980	860 ± 10	120 ± 1.6	160 ± 80	210 ± 30	1 000 ± 300
Duchcov 18986	880 ± 13	120 ± 3.2	150 ± 60	240 ± 30	3 600 ± 1 300
Duchcov 18994	900 ± 20	100 ± 1.2	130 ± 20	350 ± 60	330 ± 60
Duchcov 18995	870 ± 130	130 ± 17	160 ± 40	130 ± 80	270 ± 50
Duchcov 6798	890 ± 4	100 ± 4	300 ± 200	450 ± 50	900 ± 300
Duchcov 6808	880 ± 12	110 ± 9	50 ± 30	370 ± 30	500 ± 300
Holubice Hrob 40	770 ± 28	220 ± 30	60 ± 30	5 300 ± 2 300	700 ± 140
Rousinov 64945	680 ± 20	320 ± 20	10 ± 3	220 ± 2	1 300 ± 80
Tikovice 66155	880 ± 12	120 ± 2	1 600 ± 100	320 ± 7	200 ± 20
Mannersdorf 152/6	940 ± 7	45 ± 4	60 ± 30	3 000 ± 370	12 200 ± 1 300
Mannersdorf 60/6	870 ± 24	100 ± 10	70 ± 50	1 400 ± 170	23 000 ± 9 000

Table 7a, 7b: Main components of the investigated fibulas.

All fibulas measured were bronze alloys and Cu and Sn are the main components except for one fibula (St. Sulpice 24/4) which had Zn as second main component. The other samples showed large variations in their Zn content up to two orders of magnitude.

The fibulas from Mannersdorf and Pottenbrunn in Lower Austria showed high concentration of lead in the range from 10 000 to 25 000 mg kg⁻¹. Only four fibulas from Vevey (11/8, 23/6, 23/8 and 29/8) and four from St. Sulpice (29/2, 36/1, 24/4 and 18) showed this high amount, as well. Statistical evaluation using Cu, Sn and Pb as main components showed that these samples could be classified into 1 group (Figs. 6 and 7). Especially the samples from Mannersdorf show elevated levels of Bi, which are higher by a factor 5 to 10 compared to the other samples, which were analyzed

for Bi. As and Sb showed large inhomogeneities both within one sample and between different samples. The contents have no statistical correlation with other elements. Sulphur could only be analyzed in a selected number of samples using ICP-SF-MS. Nonetheless, it is obvious that especially the samples originating from Duchcov show high sulphur levels in the range of 1000 to 8000 mg kg⁻¹. The sulphur in these samples is inhomogeneously distributed within the alloy as reflected by the high RSD of the results. REE (rare earth element) distribution (congruent pattern) is generally an excellent tool to determine the origin of samples. Unfortunately the REE levels were below LOD in all samples and could therefore not be used for sample authentication. The same is true for other elements which were under investigation (Co, Ag, In, Te and Hf).

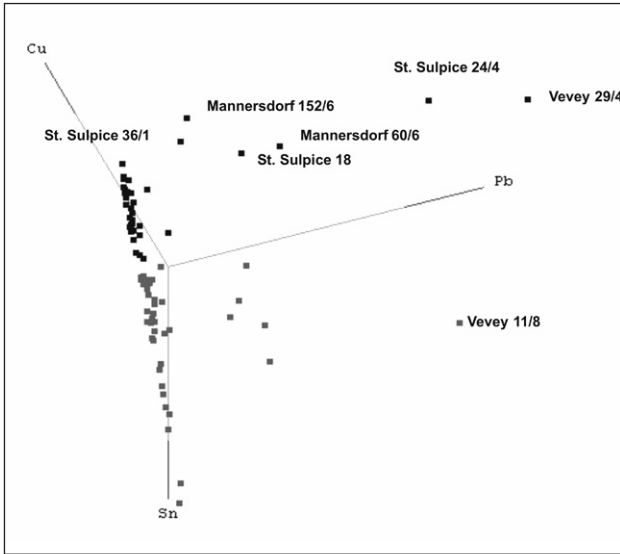


Fig. 6: Statistical evaluation of group 1.

Conclusion

LA-ICP-MS was applied as versatile quasi non destructive method for the direct analysis of a large number of bronze artefacts. Quantification by using matrix matched standards lead to accurate results. We could show that corrosion of the surface layer leads to a significant alteration of the alloy composition and shows in general depletion in Cu. Possible sources of e.g. Pb (alloy vs. soil) in the corroded surface can be assessed by applying isotope ratio measurements on cross sections in future work.

The main components could be used in order to classify groups of the fibulas whereby a direct allocation of the alloy to a finding site could not be performed. These observations reflect the possible fact that alloys do not necessarily originate from the same source when found at the same site. Transfer of goods and re-melting of objects can allude to the significantly different composition of the used and partially recycled materials. Additional archaeological information in combination with the chemical analysis can be used to identify the production site of the samples in the future. The assessment of isotopic composition is a potential tool in future works for the allocation of single elements (e.g. Pb) to the provenance of the metal, as well.

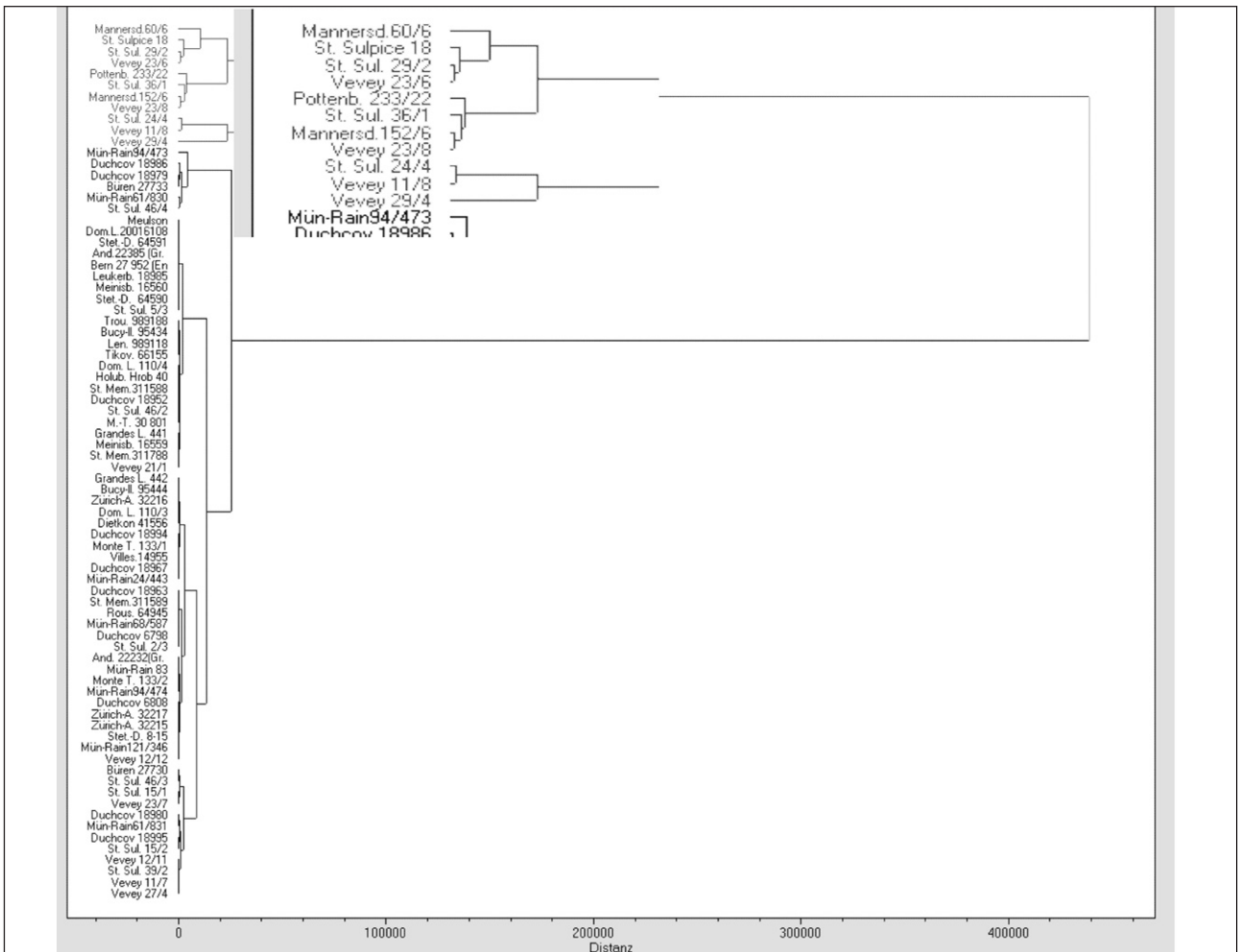


Fig. 7: Statistical evaluation of group 1.

References

- AESCHLIMAN D.B., BAJIC S.J., BALDWIN D. P., HOUK R. S.
2003 Spatially-resolved analysis of solids by laser ablation-inductively coupled plasma-mass spectrometry: trace elemental quantification without matrix-matched solid standards *Journal of Analytical Atomic Spectrometry* 8, 872–877.
- BECKER J.S., DIETZE H.J.
2003 State-of-the-art in inorganic mass spectrometry for analysis of high-purity Materials, *International Journal of Mass Spectrometry*, 228 (2–3), 127–150.
- CROMWELL E. F., ARROWSMITH P.
1995 Semiquantitative analysis with laser-ablation inductively coupled plasma-mass spectrometry, *Anal. Chem.*, 67 (1), 131–138.
- DEVOS W., MOOR CH., LIENEMANN P.
1999 Determination of impurities in antique silver objects for authentication by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), *Journal of Analytical Atomic Spectrometry*, 14, 621–626.
- DEVOS W., SENN-LUDER M., MOOR C., SALTER C.
2000 Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for spatially resolved trace analysis of early-medieval archaeological iron finds, *Fresenius Journal of Analytical Chemistry*, 366, 873–880.
- FLEM B., LARSEN R.B., GRIMSTVEDT A., MANSFELD J.
2002 In situ analysis of trace elements in quartz by using laser ablation inductively coupled plasma mass spectrometry *Chem. Geol.*, 182, 237–247.
- GAGEAN M., MERMET J.M.
1998 Study of laser ablation of brass materials using inductively coupled plasma atomic emission spectrometric detection, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 53(4), 581–591.
- GEERTSEN CH., BRIAND A., CHARTIER F., LACOUR J. L., MAUCHIEN P., SJÖSTRÖM ST., MERMET J. M.
1994 Comparison between infrared and ultraviolet laser ablation at atmospheric pressure—implications for solid sampling inductively coupled plasma spectrometry, *Journal of Analytical Atomic Spectrometry*, 1, 17–22.
- GUERRA M.F., SARTHRE C.-O., GONDONNEAU A., BARRANDON J.-N.
1999 Precious metals and provenance enquiries using LA-ICP-MS *Journals of Archaeological Science*, 26 (8), 1101–1110.
- GUILLONG M., GÜNTHER D.
2001 Quasi ‘non-destructive’ laser ablation-inductively coupled plasma-mass spectrometry fingerprinting of sapphires, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 56 (7), 1219–1231.
- GÜNTHER D., LONGERICH H. P., JACKSON S. E., FORSYTHE L.
1996 Effect of sampler orifice diameter on dry plasma inductively coupled plasma mass spectrometry (ICP-MS) backgrounds, sensitivities, and limits of detection using laser ablation sample introduction, *Fresenius Journal of Analytical Chemistry*, 355, (7–8), 771–773.
- GUILLONG M., HORN I., GÜNTHER D.
2003A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd:YAG laser for laser ablation ICP-MS, *Journal of Analytical Atomic Spectrometry*, 18, 1224–1230.
- GÜNTHER D., JACKSON S.E., LONGERICH H.P.
1998 Laser ablation and arc/spark solid sample introduction into inductively coupled plasma mass spectrometers *Spectrochimica Acta Part B: Atomic Spectroscopy*, 54 (3–4), 381–409.
- GÜNTHER D., HEINRICH C. A.
1999 Enhanced sensitivity in laser ablation-ICP mass spectrometry using helium-argon mixtures as aerosol carrier, *Journal of Analytical Atomic Spectrometry*, 14, 1363–1368.
- HERGENRÖDER R.
2006 A model of non-congruent laser ablation as a source of fractionation effects in LA-ICP-MS, *Journal of Analytical Atomic Spectrometry*, 21, 505–516.
- IIDA Y.
1990 Effects of atmosphere on laser vaporization and excitation processes of solid samples *Spectrochimica Acta Part B: Atomic Spectroscopy*, 45 (12), 1353–1367.
- JUNK S.A.
2001 Ancient artefacts and modern analytical techniques – Usefulness of laser ablation ICP-MS demonstrated with ancient gold *Nuclear Instruments and Methods in Physics Research B*, 181, 723–727.
- KOCH J., FELDMANN I., HATTENDORF B., GÜNTHER D., ENGEL U., JAKUBOWSKI N., BOLSHOV M., NIEMAX K., HERGENRÖDER R.
2002 Trace element analysis of synthetic mono- and poly-

- crystalline CaF_2 by ultraviolet laser ablation inductively coupled plasma mass spectrometry at 266 and 193 nm *Spectrochimica Acta Part B: Atomic Spectroscopy*, 57(6), 1057–1070.
- KOCH J., FELDMANN I., JAKUBOWSKI N., NIEMAX K.
- 2002 Elemental composition of laser ablation aerosol particles deposited in the transport tube to an ICP, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 57(5), 975–985.
- KOCH J., VON BOHLEN A., HERGENRÖDER R., NIEMAX K.
- 2004 Particle size distributions and compositions of aerosols produced by near-IR femto- and nanosecond laser ablation of brass, *Journal of Analytical Atomic Spectrometry*, 2, 267–272.
- KOSLER J., WIEDENBECK M., WIRTH R., HOVORKA J., SYLVESTER P., MIKOVÁ J.
- 2005 Chemical and phase composition of particles produced by laser ablation of silicate glass and zircon-implications for elemental fractionation during ICP-MS analysis, *Journal of Analytical Atomic Spectrometry*, 20, 402–409.
- LEE Y. L., CHANG C. C., JIANG S. J.
- 2003 Laser ablation inductively coupled plasma mass spectrometry for the determination of trace elements in soil, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 58 (3), 523–530.
- OUTRIDGE P.M., DOHERTY W., GREGOIRE D.C.
- 1997 Determination of trace elemental signatures in placer gold by laser ablation inductively coupled plasma-mass spectrometry as a potential aid for gold exploration *Journal of Geochemical Exploration*, 60 (3), 229.
- RESANO M., VANHAECKE F., HUTSEBAUT D., DE CORTE K., MOENS L.
- 2003 Possibilities of laser ablation-inductively coupled plasma-mass spectrometry for diamond fingerprinting, *Journal of Analytical Atomic Spectrometry*, 18, 1238–1242.
- TIBI M., HEUMANN K. G.
- 2003 Isotope dilution mass spectrometry as a calibration method for the analysis of trace elements in powder samples by LA-ICP-MS, *Journal of Analytical Atomic Spectrometry*, 9, 1076–1081.
- URYU T., YOSHINAGA J., YANAGISAWA Y., ENDO M., TAKAHASHI J.
- 2003 Analysis of lead in tooth enamel by laser ablation-inductively coupled plasma-mass spectrometry, *Analytical Sciences*, 19, 1413–1416.
- DE WANNEMACKER G., VANHAECKE F., MOENS L., VAN MELE A., THOEN H.
- 2000 Lead isotopic and elemental analysis of copper alloy statuettes by double focusing sector field ICP mass spectrometry, *Journal of Analytical Atomic Spectrometry*, 15(4), 323–327.