Využití LIBS ve forensní a archaeomtrické analýze

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Forensní analýza

- analýza skel
- identifikace materiálů na základě prvkového složení
- analýza otisků prstů
- analýza explozivních a nebezpečných mat.
- analýza povýbuchových reziduí
- analýza kontaminantů v plastech
- nové metody identifikace materiálů !!!

Výhody

- lokální analýza
- analýza znečištěných povrchů
- analýza velmi malých množství
- málo destruktivní analýza
- velká produktivita, citlivost pro lehké prvky
- bezkontaktní analýza, terénní analýza
- nové možnosti při identifikaci
- relativně snadná kombinovatelnost s dalšími metodami (LA-ICP-MS, Raman)

Analýza skel – forensní aplikace

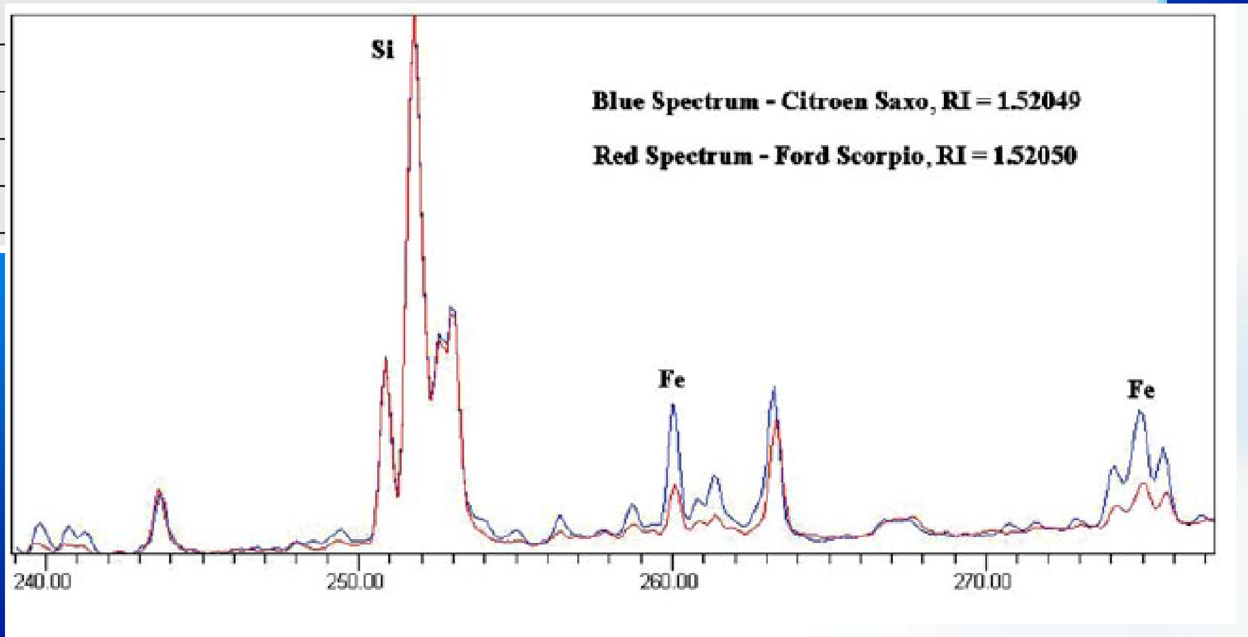
- kombinace LIBS výsledků a RI
- databáze skel pro automobily

Emission Line (nm)	Comment
Al (309.3)	Present at low concentration therefore strongest line is used.
Ba (455.4)	Present at trace levels therefore use strongest line.
Ca (442.5)	Relatively weak emission line.
Ca (527.0)	Relatively weak emission line.
Fe (275.6)	Strong emission line for this trace element.
Mg (518.4)	Weaker line chosen, as strongest line (280 nm) tends to selfabsorb.
Si (263.1)	Weakest line chosen.
Sr (407.8)	Strongest emission line for this trace element.

Ratio	
Fe (275.6) :	Si (263.1)
Mg (518.4) :	Ca (527.0)
Sr (407.8) :	Ca (442.5)
Ba (455.4) :	Ca (442.5)
Al (309.3) :	Si (263.1)

Analýza skel – forensní aplikace

Description	Mg(518.4)/Ca (527.0)	Fe (259.7)/Si (263.1)	Sr (407.8)/Ca (442.5)	Ba (455.4)/Ca (442.54)	Al (309.3)/Si (263.1)
Peugeot 405	1.907 +/- .087 (4.5 %)	.828 +/- .036 (4.4 %)	1.015 +/- .134 (13.2 %)	1.607 +/- .183 (11.4 %)	.188 +/- .025 (13.6 %)
Ford Escort	2.227 +/- .081 (3.6 %)	.097 +/- .023 (24 %)	.882 +/- .075 (8.5 %)	1.247 +/- .108 (8.7 %)	.392 +/- .026 (6.6 %)
Hyundi Accent	1.806 +/- .099 (5.5 %)	.443 +/- .051 (11.4 %)	.811 +/- .15 (18.4 %)	.339 +/- .073 (21.6 %)	.362 +/- .074 (20.4 %)
Vauxhall Astra	2.236 +/- .105 (4.7 %)	.379 +/- .033 (8.6 %)	.451 +/- .06 (13.2 %)	.386 +/- .052 (13.6 %)	.287 +/- .038 (13.3 %)
Peugeot 205	2.151 +/- .085 (4 %)	.467 +/- .021 (4.6 %)	1.878 +/- .197 (10.5 %)	.68 +/- .063 (9.3 %)	.243 +/- .025 (10.2 %)
Peugeot 405	2.12 +/- .083 (3.9 %)	.48 +/- .063 (13 %)	1.158 +/- .253 (21.9 %)	.807 +/- .129 (16 %)	.257 +/- .039 (15.3 %)
Rover 216	2.383 +/- .09 (3.8 %)	.366 +/- .026 (7.2 %)	.627 +/- .072 (11.4 %)	.37 +/- .037 (10 %)	.26 +/- .016 (6 %)
VW Golf	2.255 +/- .104 (4.6 %)				
Citroen Saxo	2.049 +/- .073 (3.6 %)				
Maestro	2.171 +/- .122 (5.6 %)				
Daewoo Leganza	2.323 +/- .055 (2.4 %)				
VW Polo	2.787 +/- .068 (2.4 %)				



Analýza plochých automobilových skel – kombinace LIBS, LA-ICP-MS a RI

- 23 vzorků skel
- LIBS – poměry intenzit, LA – poměry konc.
- LIBS – určení 83% skel s 99% conf. Int.
- LIBS/RI – 96 – 99%
- LIBS/RI/LA-ICP-MS – 100%

Bridge CM et.al.:APPLIED SPECTROSCOPY **Volume:** 60 **Issue:** 10 **Pages:** 1181-1187 **Published:** OCT 2006

Analýza papírů a inkoustů

• analýza papírů – potahované X nepotahované, hloubkové profily u potahovaných papírů

H. H¨akk¨anen, J. Houni, S. Kaski, J.E.I. Korppi-Tommola: Spectrochimica Acta Part B (2001) 737

• analýza pigmentů

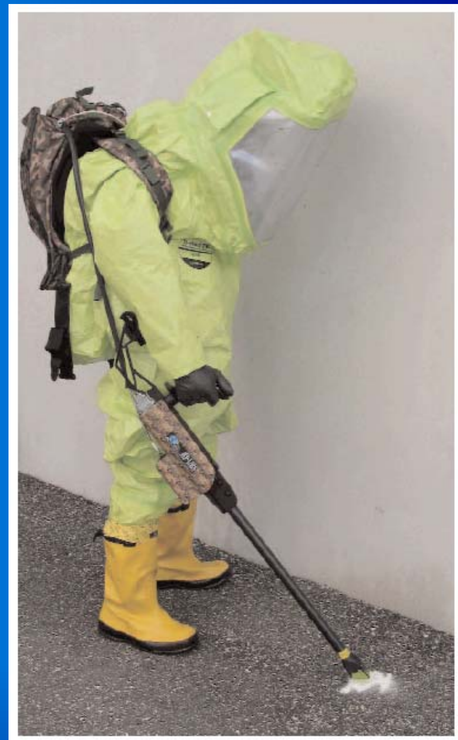
• identifikace plnidel

Bezpečnostní – forensní aplikace

US ARMY RESEARCH LABORATORY OVERVIEW OF LIBS FOR DEFENSE AND SECURITY APPLICATIONS

Frank C. De Lucia, US Army Research Laboratory, Amsrd-Arl-Wm-Bd, Aberdeen Proving Ground, MD 21005, Russell S. Hamron, Andrzej W. Miziolek, Chase A. Munson

Researchers at the US Army Research Laboratory have applied Laser Induced Breakdown Spectroscopy to a variety of defense and security related applications. These applications range from using a man portable system for potential bioagent identification to standoff experiments of explosive residues. The versatility of the LIBS technology is one of its attractive features for future use in the field. At ARL, LIBS experiments have been performed for potential chemical and bio warfare agent detection, landmine casing identification, and explosive residue detection and discrimination. We will present a synopsis of the various LIBS applications currently being pursued at ARL.



Bezpečnostní – forensní aplikace

Test of a stand-off laser-induced breakdown spectroscopy sensor for the detection of explosive residues on solid surfaces

Cristina Lo´ pez-Moreno, J. Anal. At. Spectrom., 2006, 21, 55–60

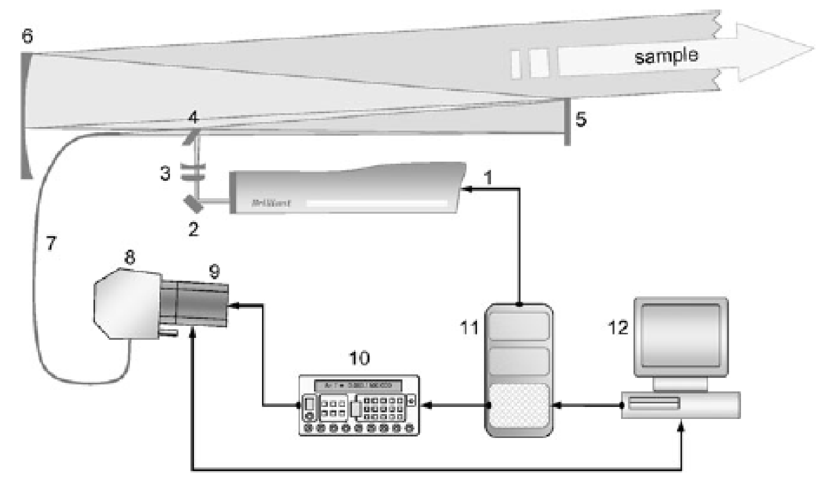


Fig. 1 Experimental setup. 1, Laser source. 2, Folding mirror. 3, Lenses. 4, Dichroic mirror. 5, Flat aluminium mirror. 6, Parabolic aluminium mirror. 7, Fiber optic cable. 8, Spectrograph. 9, iCCD. 10, Pulse and delay generator. 11, Power laser supply. 12, Computer.

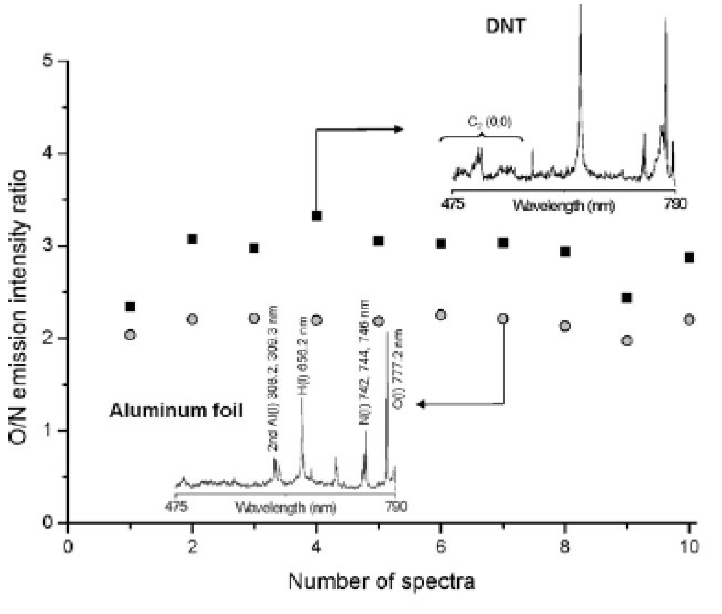


Fig. 3 O(I) 777.2 nm to N(I) 746.8 nm peak intensity ratio for 10 single shots spectra at a 45 m distance from an aluminium foil (■) and a DNT solution deposited on the same aluminum foil (○). The inset show DNT (top) and aluminium (bottom) spectra.

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Fig. 4 Snapshot of the system during a field test of the stand-off LIBS sensor featuring C. López-Moreno.

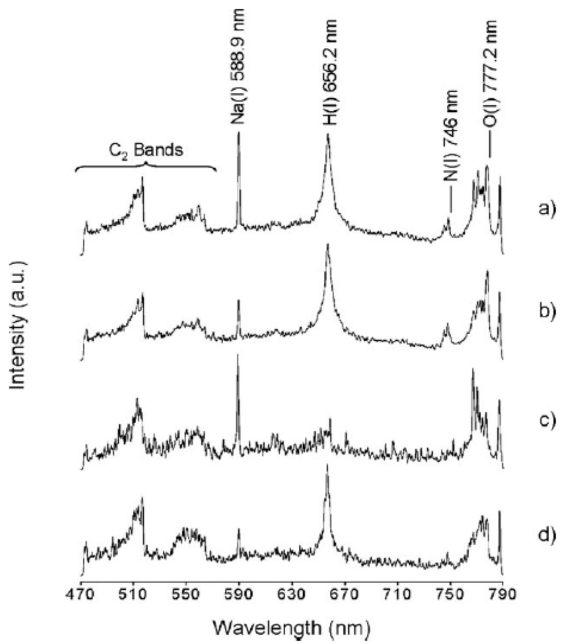


Fig. 5 Single shot stand-off LIBS spectra of four of the known samples at a 30 m distance. (a) 100 ppm TNT solution, (b) C4 fingerprint, (c) car paint, (d) oil fingerprint.

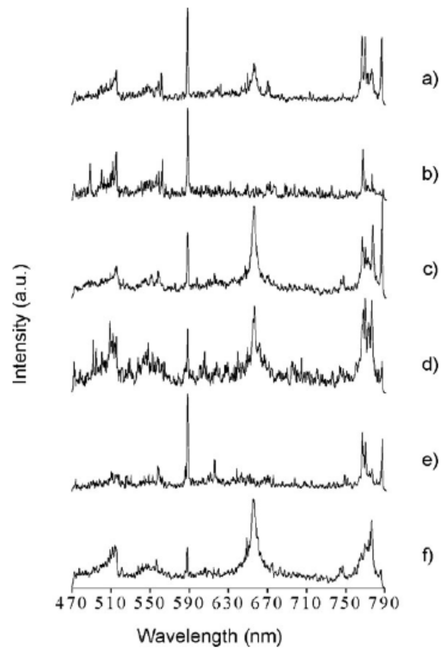


Fig. 6 Single shot stand-off LIBS spectra of the blind-test samples at a 30 m distance. (a) Acetone, (b) human fingerprint, (c) 100 ppm TNT solution, (d) TNT fingerprint, (e) no sample and (f) C4 fingerprint.

Bezpečnostní – forensní aplikace

Test of a stand-off laser-induced breakdown spectroscopy sensor for the detection of explosive residues on solid surfaces

Cristina Lo´ pez-Moreno, J. Anal. At. Spectrom., 2006, 21, 55–60

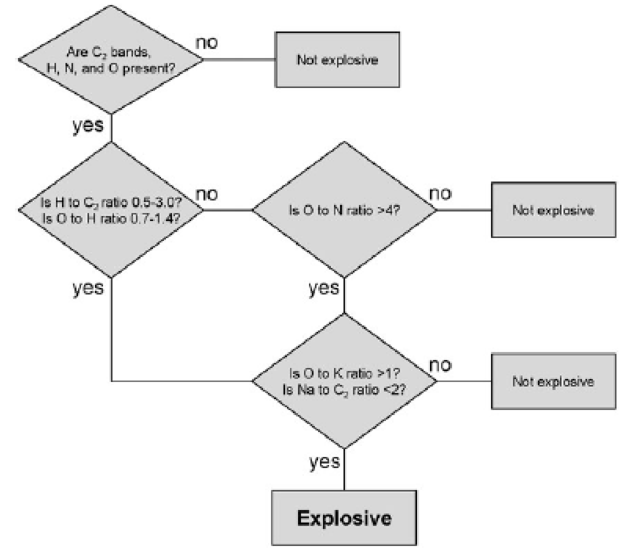


Fig. 7 Representative decision making strategy for stand-off LIB spectral analysis of energetic materials.

Table 2 Results of the test with known samples as obtained with the flowchart in Fig. 7

Actual	Presence C_2, H, N	O/H_2 ratio	O/H ratio	O/K ratio	O/N ratio	Na/C_2 ratio	Flow chart result	Correct
TNT fingerprint	Yes	0.75 [Yes]	1.07 [Yes]	1.46 [Yes]	—	0.52 [Yes]	Explosive	✓
Diesel fuel fingerprint	Yes	5.07 [No]	0.42 [No]	—	3.77 [No]	—	Non-explosive	✓
RDX 100 ppm	Yes	0.60 [Yes]	0.72 [Yes]	1.40 [Yes]	—	0.52 [Yes]	Explosive	✓
Acetone	No	—	—	—	—	—	Non-explosive	✓
C4 fingerprint	Yes	1.82 [Yes]	0.75 [Yes]	1.90 [Yes]	—	0.89 [Yes]	Explosive	✓
Tape residue	Yes	1.13 [Yes[	1 [Yes[	1.19 [Yes[	—	0.84 [Yes[	Explosive	X false positive
TNT 100 ppm	Yes	1.60 [Yes]	0.72 [Yes]	1.21 [Yes]	—	1.62 [Yes]	Explosive	✓
Beef fingerprint	Yes	3.40 [No]	0.55 [No]	—	2.55 [No]	—	Non-explosive	✓
CompB 100 ppm	Yes	0.71 [Yes]	1.14 [Yes]	1.36 [Yes]	—	0.69 [Yes]	Explosive	✓
Cheese fingerprint	Yes	1.24 [Yes]	0.67 [No]	0.63 [No]	5.26 [Yes]	3.11 [No]	Non-explosive	✓
PETN 100 ppm	No	—	—	—	—	—	Non-explosive	X false negative
Grease fingerprint	Yes	4.82 [No]	0.48 [No]	—	2.35 [No]	—	Non-explosive	✓
Paint	Yes	0.73 [Yes]	1.55 [No]	—	3.39 [No]	—	Non-explosive	✓
Oil fingerprint	Yes	1.48 [yes]	0.46 [No]	—	3.35 [No]	—	Non-explosive	✓
Ink	Yes	2.65 [Yes]	0.60 [No]	—	2.65 [No]	—	Non-explosive	✓

Bezpečnostní – forensní aplikace

Nové přístupy k identifikaci – skla, identifikace biologických a chemických zbraní, identifikace rezidui …

- různé výkony laseru
- chemometrické zpracování celého spektra
    - normalizace spektra
    - detrendování spektra
    - PCA, PCR, Neural Network, ….
    - diskriminační analýza
- velké nároky na výpočetní výkon
- kombinované techniky

Archaeometrické aplikace

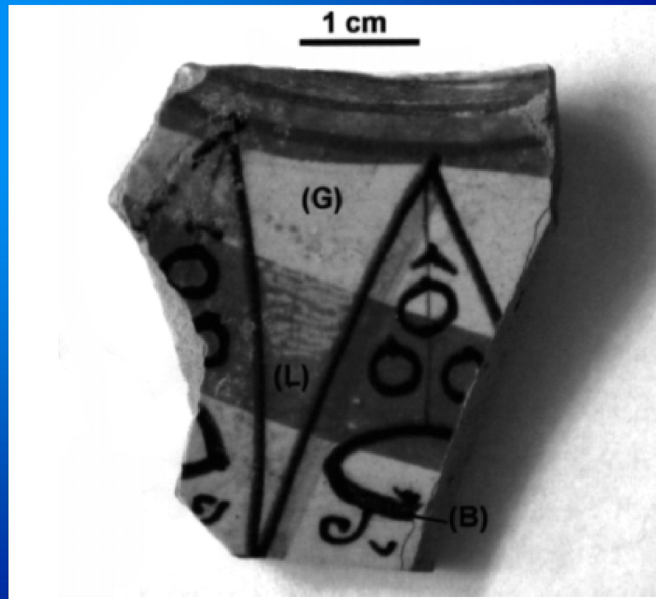
• analýza nádob, šperků a kovových úlomků z Kréty

• analýza vícevrstvé keramiky – semikvantitativní a kvantitativní analýza – výhoda málo destruktivní

Table 3
Estimated glaze composition in (%) of weight

Sample	Al_2O_3	CaO	Cu	FeO	MgO	Na_2O	PbO	SiO_2	SnO_2
D1	2.9	2.3	0.044	0.43	0.53	0.14	14	67	5.3
D16	4.6	2.3	0.021	0.43	0.93	0.27	6.1	78	1.4
D22	7.2	–	0.042	0.11	–	0.044	6.0	76	5.3
			0.081[a]						
D24	4.2	5.5	0.036	0.19	0.64	0.08	18	65	0.61
D29	7.2	–	0.081	0.16	1.1	–	29	47	2.6
D31	2.5	1.4	0.016	0.45	0.64	0.29	12	74	2.6
			0.038[a]						
D40	3.0	–	0.083	–	0.64	0.29	23	66	2.0
D42	3.0	2.7	0.045	0.38	0.91	0.14	14	73	0.68
D48	3.9	2.2	0.033	0.17	0.41	0.14	15	70	–
			0.03[a]						
G2	5.6	4.2	0.02	0.65	–	0.49	8.7	77	1.4
	2.6[b]	3.9[b]		2.4[b]			16.0[b]	61.5[b]	5.0[b]
D4	9.1[b]	1.6[b]	–	0.2[b]	0.7[b]	2.7[b]	28.1[b]	50.1[b]	5.0[b]
D46	4.7[b]	4.6[b]	–	0.9[b]	–	–	29.1[b]	50.7[b]	1.1[b]

[a] Measured by ICP.
[b] Semi-quantitative analysis with SEM-EDX [28].



F. Colao et al. / Spectrochimica Acta Part B 57 (2002) 1219–1234

Archaeometrické aplikace

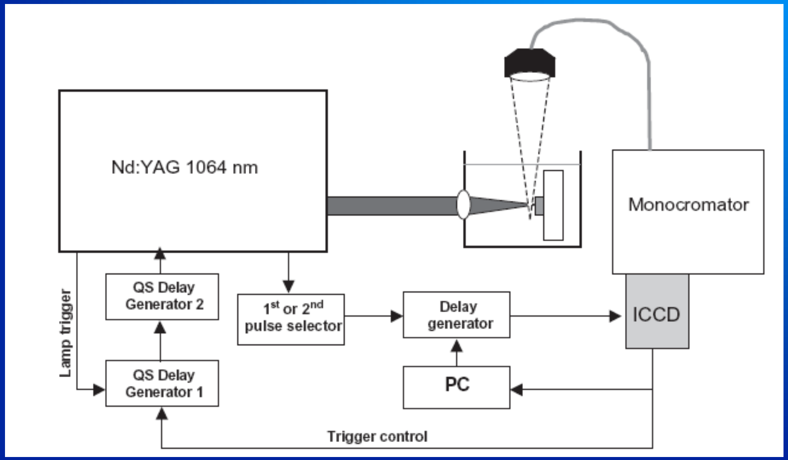
• identifikace pigmentů – kombinace LIBS a Raman Burgio L. et.al.: APPLIED SPECTROSCOPY Volume: 54 Issue: 4 Pages: 463-469 Published: APR 2000

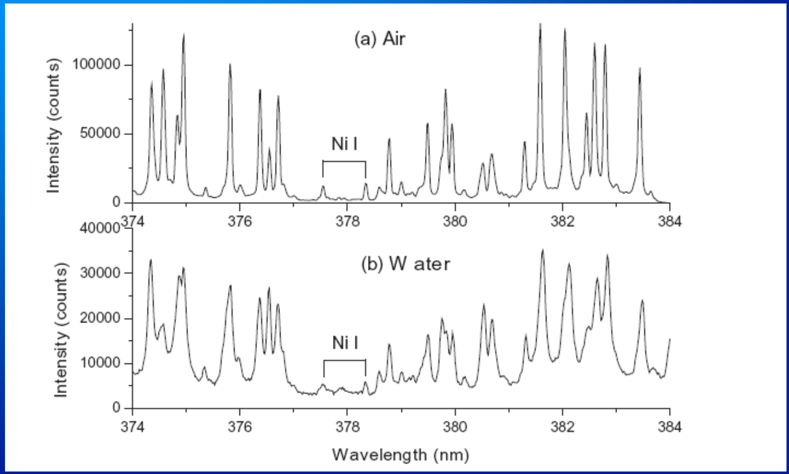
Dva lasery, identifikace nepůvodních pigmentů

Archaeometrické aplikace

- **Identifikace archeologických vzorků pod hladinou moře – dvoupulzní technika, 1064 nm, 10 Hz, 8 ns, 320 mJ (suma pro oba pulzy) – rozlišení různých slitin kovů, dřeva, analýza sedimentů na objektech**

V. Lazic et. al: Spectrochimica Acta Part B 60 (2005) 1014 – 1024





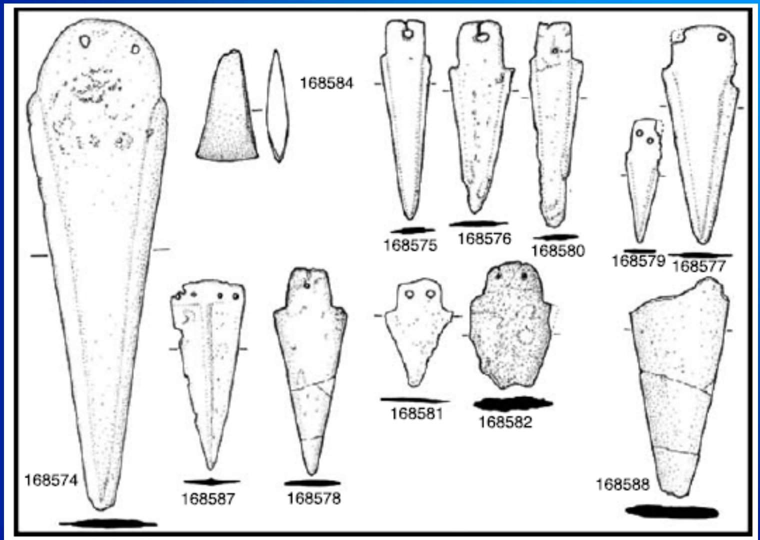
Archaeometrické aplikace

Archaeometrické aplikace

• **Diskriminační analýza prehistorickcých bronzí**

- CF LIBS (Calibration Free) a následná diskriminace s využitím hlavních komponent

Michela **Corsi et. al.: Microchim Acta 152, 105–111 (2005)**



Archaeometrické aplikace

- CF LIBS výsledky

Table 1. Samples composition (in %) obtained with CF-LIBS analysis

Campione	Cu	Ca	Al	Na	Mg	Si	Ag	Pb	As	Fe	Sb
168578	97.50	0.11	0	0.01	0.10	1.53	0	0	0.75	0	0
168577	92.23	1.34	0.71	0.44	0.49	3.99	0.17	0	0.63	0	0
168576	96.78	0.19	0.03	0.49	<0.01	1.98	0.02	0	0.53	0	0.29
168574	98.73	<0.01	0	0.01	<0.01	0.25	0.11	0	0.14	0	0
168588	92.19	2.40	0.04	0.70	0.27	0.85	0.01	0.12	3.40	0	0
168584	96.29	1.50	0	0.32	1.34	0	0.36	0	0.09	0	0
168582bis	95.37	1.06	0.09	0.40	0.22	2.14	0.01	0	0.71	0	0
168582	95.34	0.05	0	0.1	0.01	0.06	0.52	1.12	1.41	1.41	0
168581	98.27	<0.01	0	0.01	0.08	1.05	0.08	0	0.50	0	0
168580	93.71	0.50	0.01	0.02	0.06	4.63	0	0	1.07	0	0
168579	96.92	0.20	0.04	1.60	0.01	0	0.53	0	0	0	0.08
168575	93.44	3.90	0.42	0	0.38	0.87	0	0	0.99	0	0
168587	98.25	<0.01	0	0	0.08	0	0.06	0.10	0.40	1.11	0

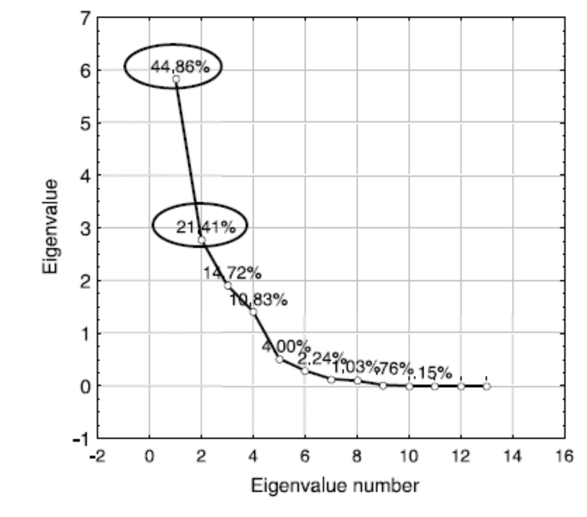


Fig. 5. Scree plot of the eigenvalues of the correlation matrix

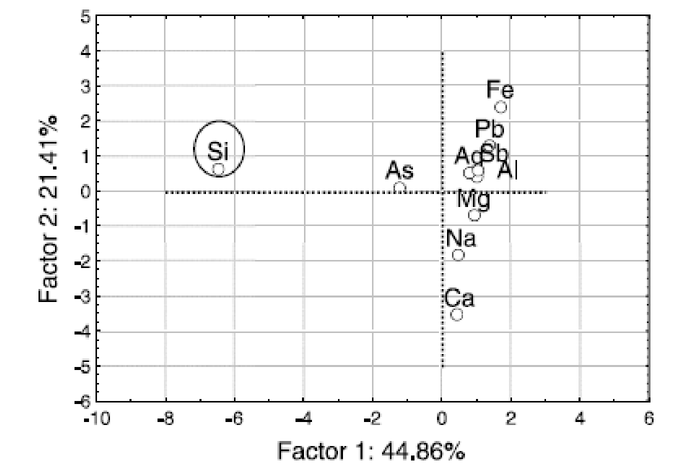


Fig. 7. Projection of the variables explaining how the elements are correlated

Archaeometrické aplikace

- vyloučení Si, Al, Ca, Mg a Na

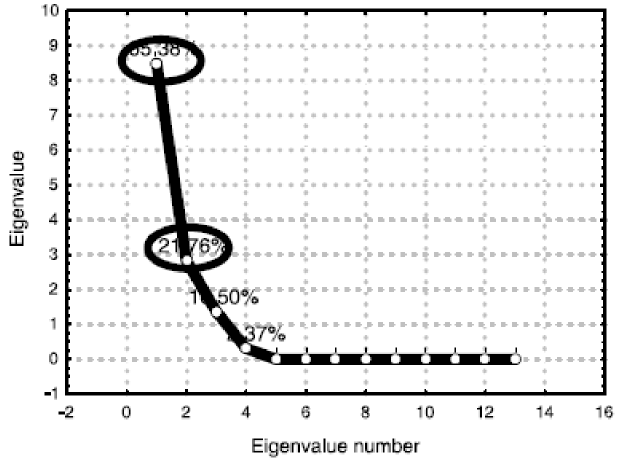


Fig. 8. Scree plot of the eigenvalues obtained without the environmental elements

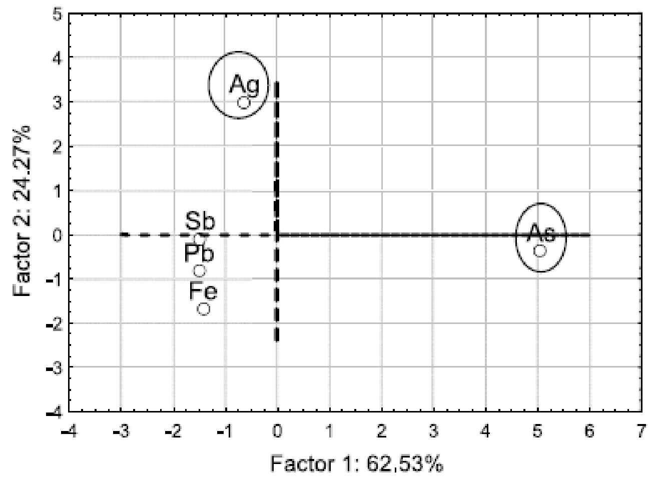


Fig. 10. Projection of the cases corresponding to the classification of the samples obtained without environmental elements

Table 2. Typological division of the samples into seven different groups

I Group	II Group	III Group	IV Group	V Group	VI Group	VII Group
168584	168574	168587	168578, 168588	168575, 168576, 168580	168577, 168579	168581, 168582

Archaeometrické aplikace

Chronocultural sorting of archaeological bronze objects using LIBS

F.J. Fortes, et. al. : Analytica Chimica Acta 554 (2005) 136–143

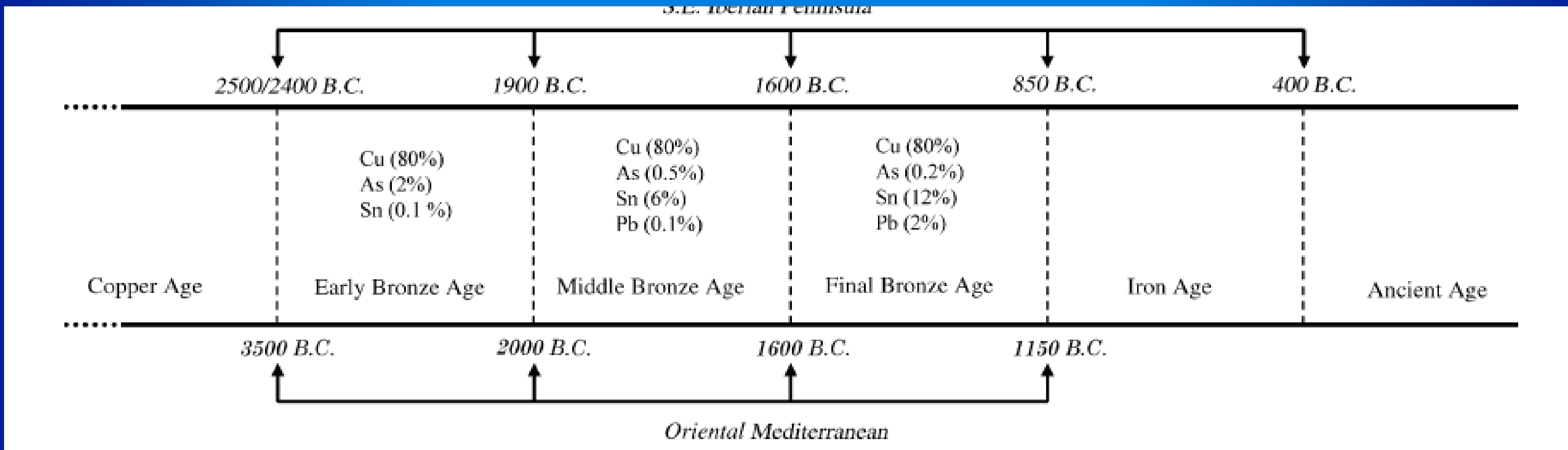


Fig. 1. Chronological classification of the Metal Ages based on the elemental constituents used for manufacture of objects in the Oriental Mediterranean and in the South East (S.E.) of the Iberian Peninsula. The compositions quoted correspond to typical alloys in the South East of the Iberian Peninsula.

Table 2
Analytical figures of merit of the LIBS method for the five elements of interest

Element	Spectral line (nm)	Correlation coefficient (R^2)	Upper limit (%)	R.S.D.[a] (%)	R.S.D.[b] (%)	C_{LOD}[c] (mg g^{-1})
Copper	244.16	0.9922	96.7	1.6	10.0	10
Arsenic	234.98	0.9987	2.9	7.6	8.0	0.20
Tin	249.57	0.9810	14.7	11.5	17.0	2.70
Lead	247.64	0.9997	11.2	18.7	12.0	0.25
Iron	234.83	0.9926	0.42	28.5	5.0	0.15

[a] Precision expressed as R.S.D. (%) of the line intensity.
[b] Precision expressed as R.S.D. (%) of the background signal either side of the spectral line at the concentration used in the C_{LOD}.
[c] Limit of detection calculated from equation: $C_{LOD} = \frac{3 \times C \times R.S.D._b}{S/B}$.

Archaeometrické aplikace

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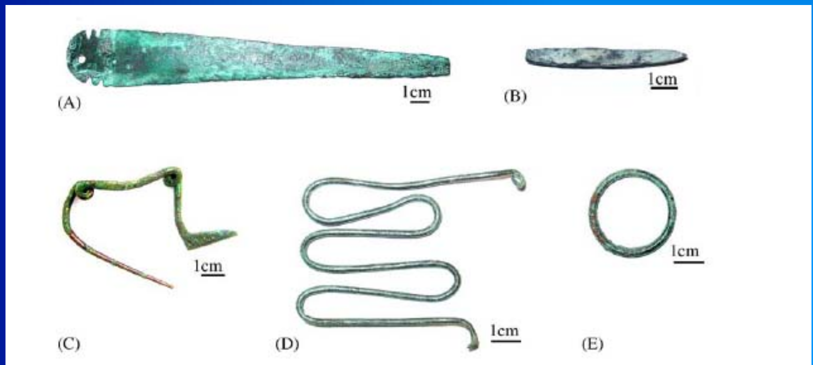

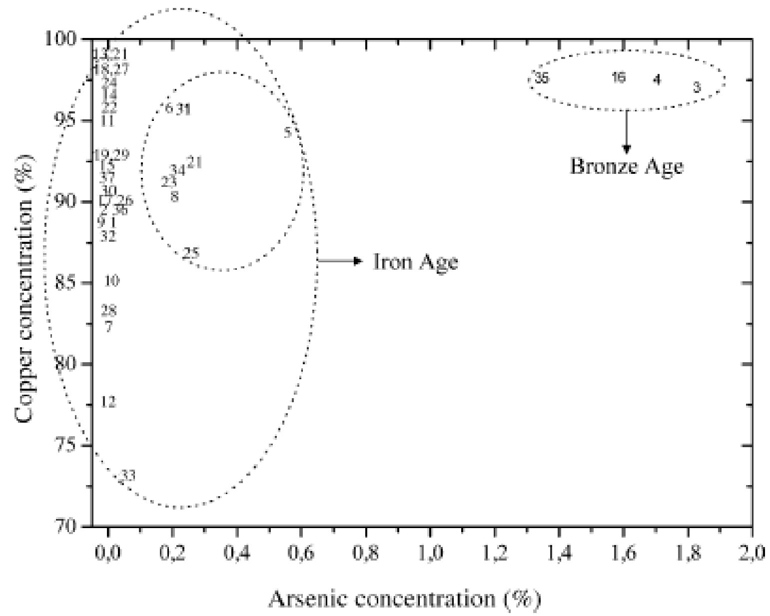

Fig. 7. Comparison of copper and arsenic concentration obtained by LIBS for the set of 37 archaeological samples.

Archaeometrické aplikace

1. Kvantitativní analýza Al v archeologicky zajímavých půdách
   Jesu´ s Anzano: Analytical Letters, 38: 1957–1965, 2005

2. Analýza pigmentů z doby bronzové a antiky
   Ann Brysbaert et.al. Journal of Archaeological Science 33 (2006) 1095-1104

3. Určení původu keramiky

4. Identifikace pigmentů v historických bibliografiích

5. Analýza starých filmů