Direct solid sample analysis of low-cost jewelry using spectroanalytical techniques: exploratory chemical data evaluation and metals migration with synthetic sweat

Thaila Lorena de Araújo[a], Fabiola Manhas Verbi Pereira[b] and Edenir Rodrigues Pereira-Filho[a]*

[a]*Group of Applied Instrumental Analysis, Chemistry Department, Federal University of São Carlos, 13565-905 São Carlos, São Paulo State, Brazil.*
[b]*Group of Alternative Analytical Approaches (GAAA), Bioenergy Research Institute (IPBEN), Institute of Chemistry, São Paulo State University (UNESP), Araraquara, São Paulo 14800-060, Brazil.*
Corresponding author: Edenir R. Pereira-Filho (erpf@ufscar.br)

Supplementary material

Fig 1SM: Sample S1 image before and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.	LIBS emission spectrum
Before LIBS data acquisition.	
After LIBS data acquisition in the rear part of the sample.	XRF spectrum
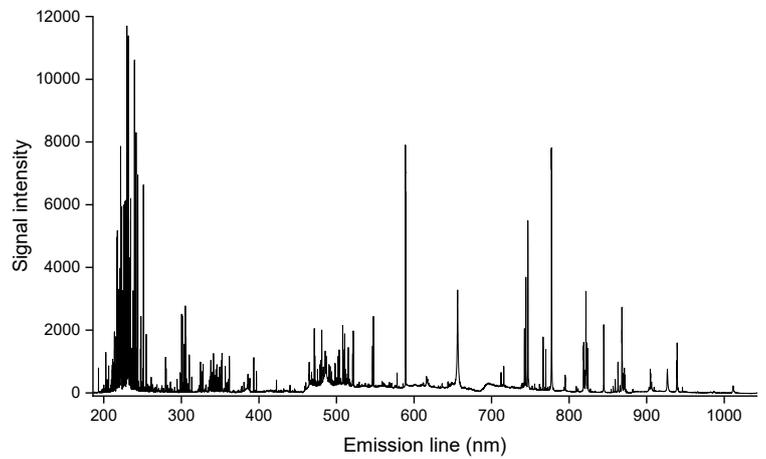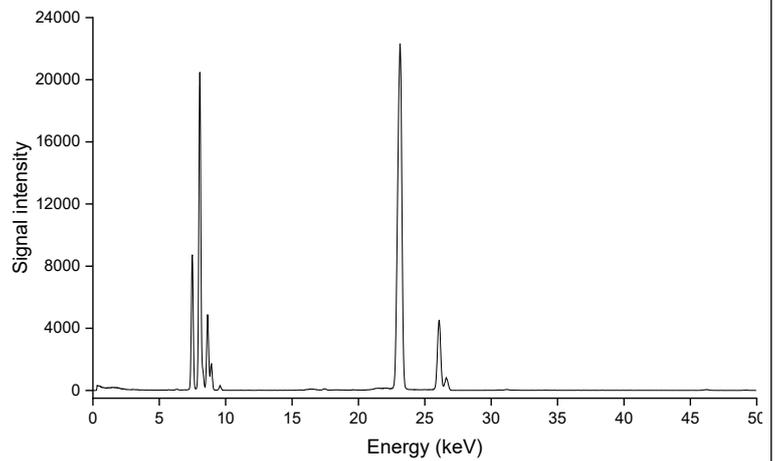
	LIBS emission spectrum
Fig 2SM: Sample S2 image before and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.	
Before LIBS data acquisition **After LIBS data acquisition** 	XRF spectrum
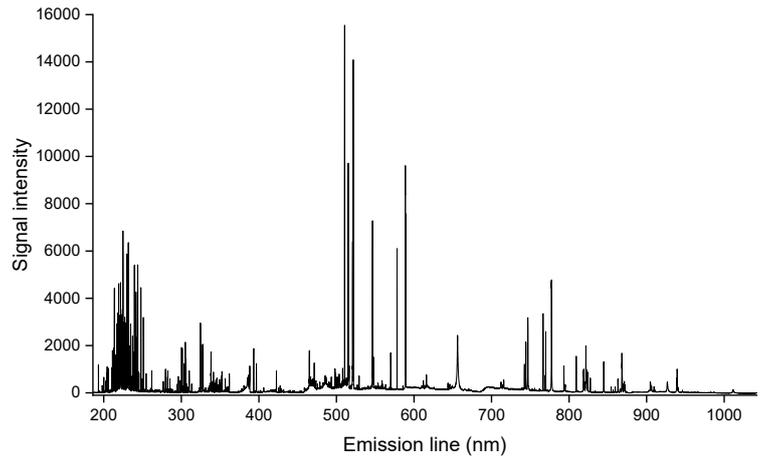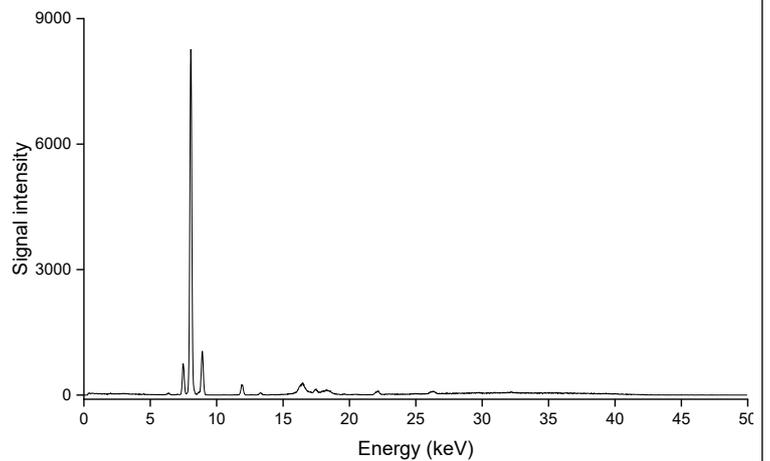
	LIBS emission spectrum
Fig 3SM: Sample S3 image before and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.	
Before LIBS data acquisition 	
After LIBS data acquisition (The sample was analyzed twice using LIBS, to optimize the region of the data acquisition.) 	**XRF spectrum**
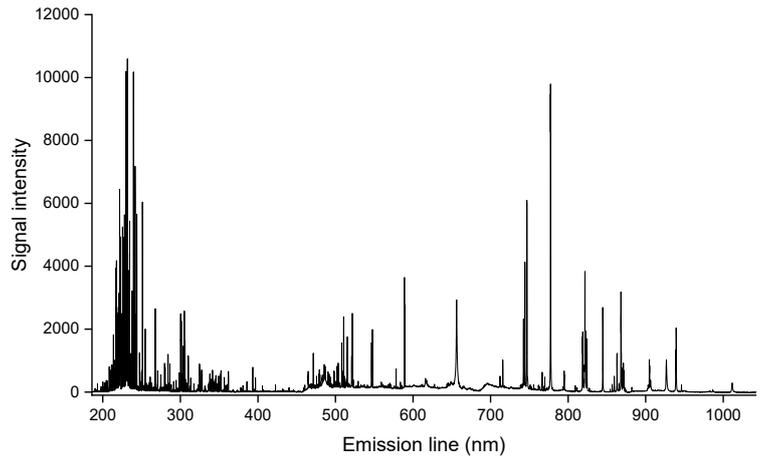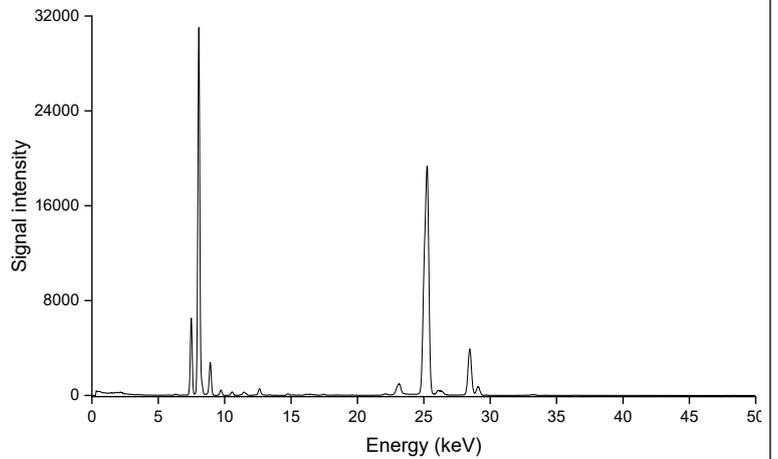
	LIBS emission spectrum
Fig 4SM: Sample S4 image before and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.	
Before LIBS data acquisition 	
	XRF spectrum
After LIBS data acquisition (The sample was analyzed twice using LIBS, to optimize the region of the data acquisition.) Data used in the study discussion	
Fig 5SM: Sample S5 image before and	LIBS emission spectrum
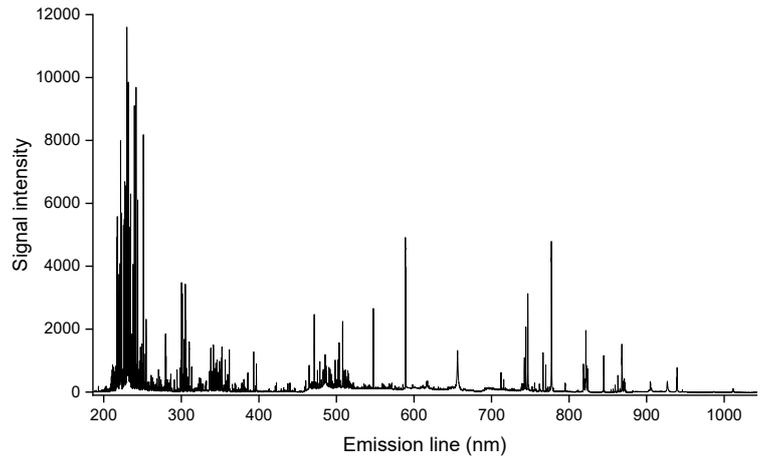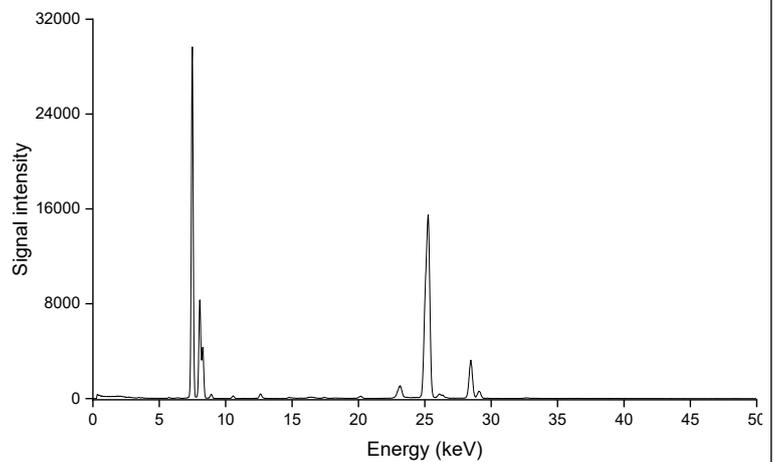
after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.
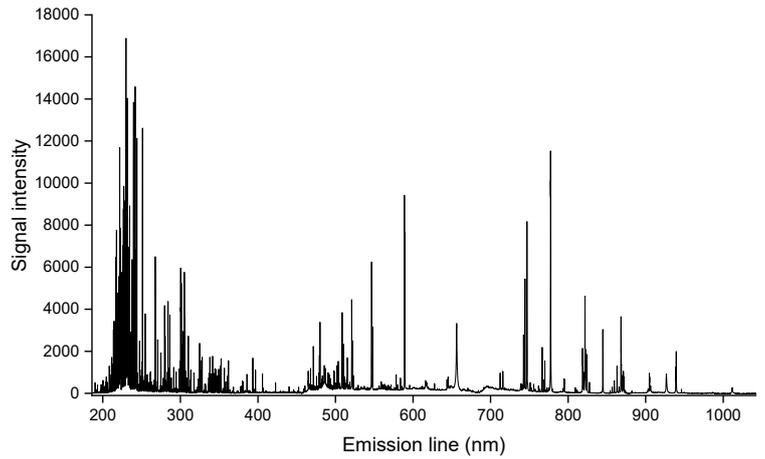
Before LIBS data acquisition

After LIBS data acquisition
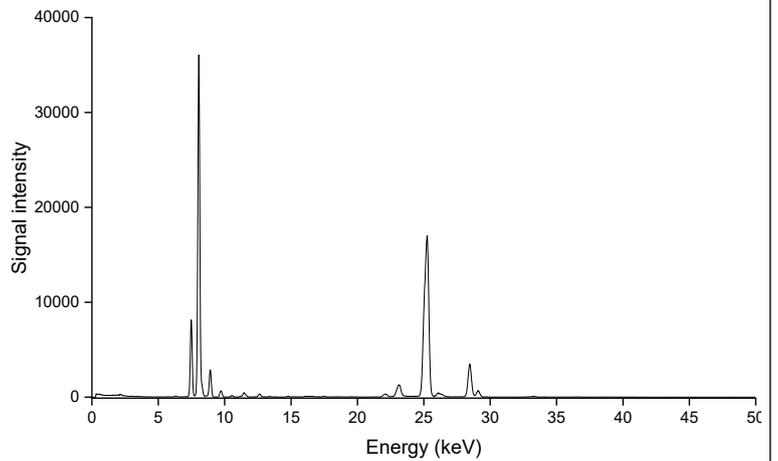
XRF spectrum

Fig 6SM: Sample S6 image before and

LIBS emission spectrum

after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.

Before LIBS data acquisition
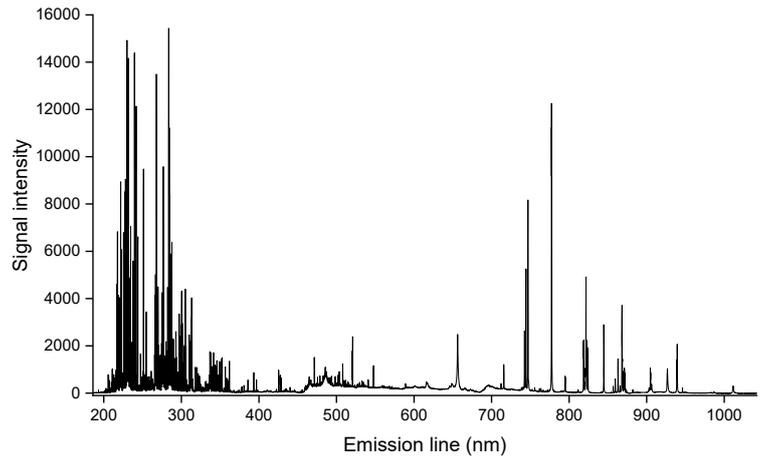
After LIBS data acquisition

XRF spectrum
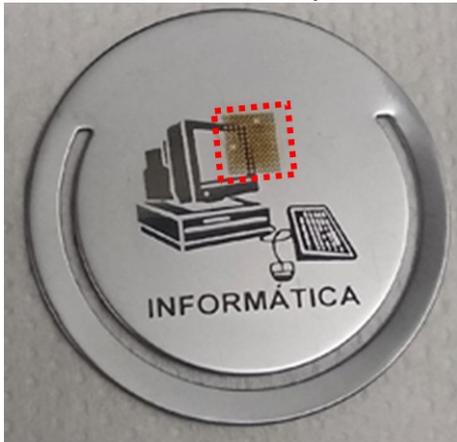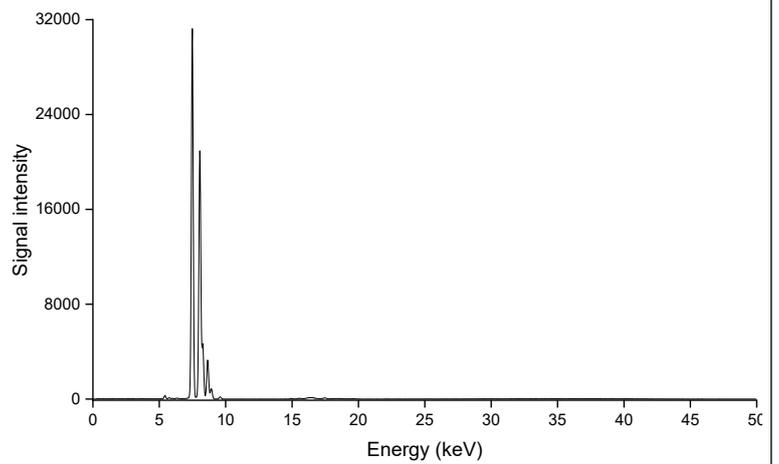
	LIBS emission spectrum
Fig 7SM: Sample S7 image before and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.	
Before LIBS data acquisition	
After LIBS data acquisition	**XRF spectrum**
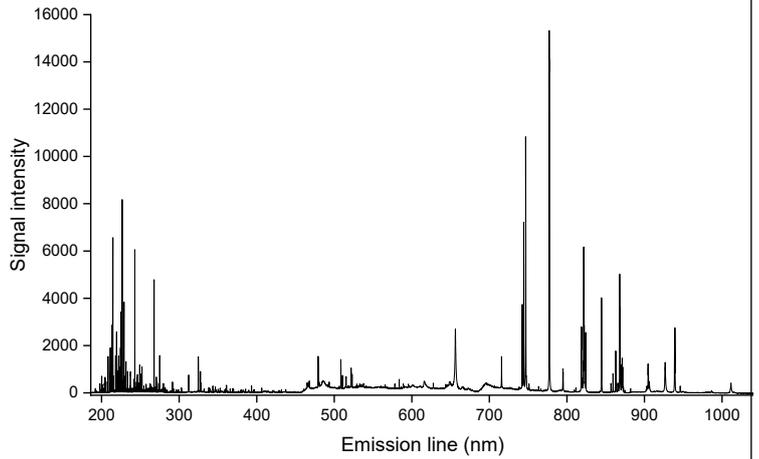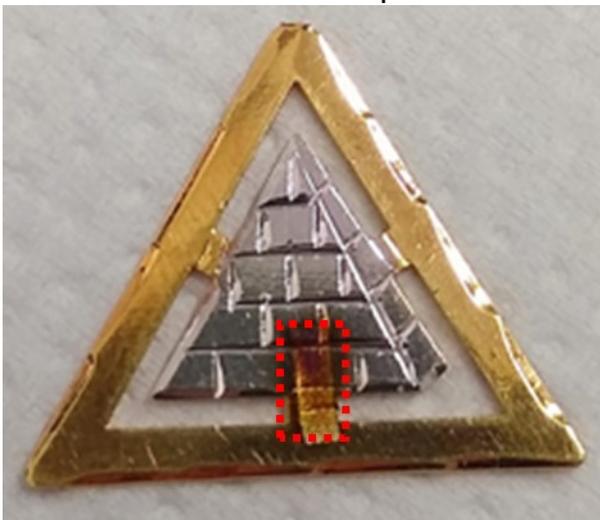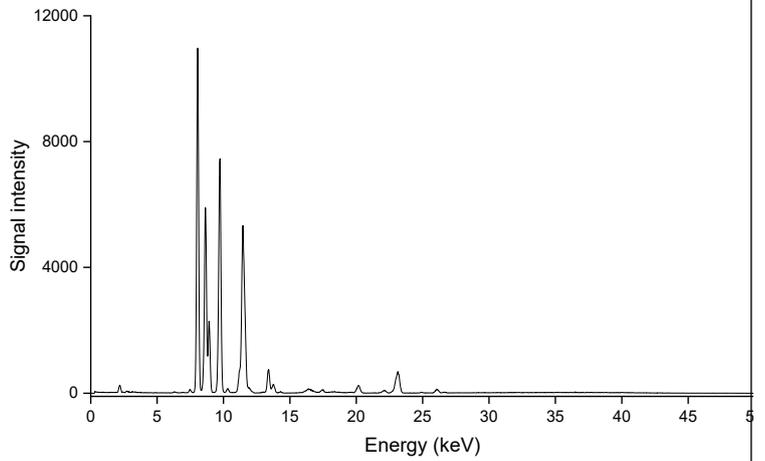
	LIBS emission spectrum
Fig 8SM: Sample S8 image before and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.	
Before LIBS data acquisition	
	XRF spectrum
After LIBS data acquisition (The sample was analyzed twice using LIBS, to optimize the region of the data acquisition.) Data used in the study discussion	
Fig 9SM: Sample S9 image before and	LIBS emission spectrum

after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.
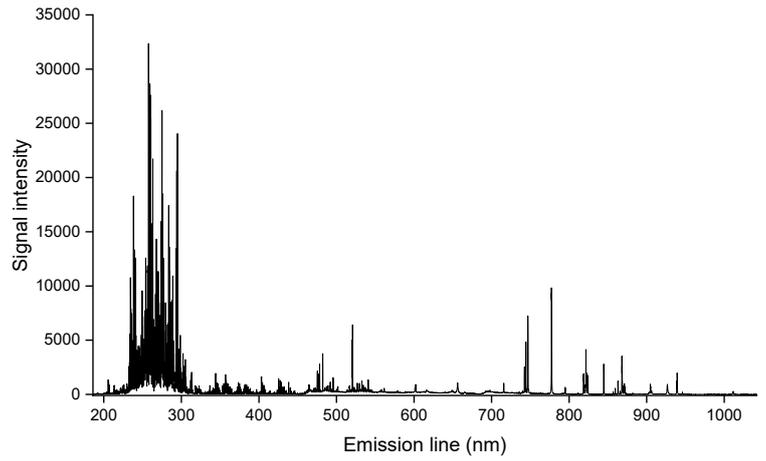
Before LIBS data acquisition

After LIBS data acquisition
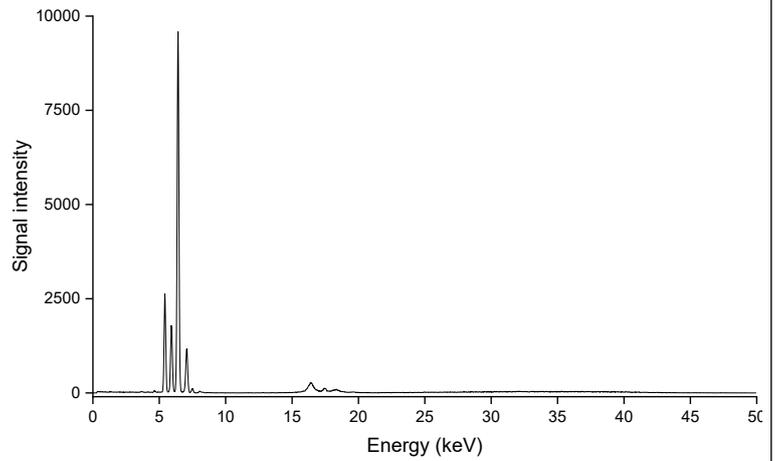
XRF spectrum

Fig 10SM: Sample S10 image before and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.

LIBS emission spectrum
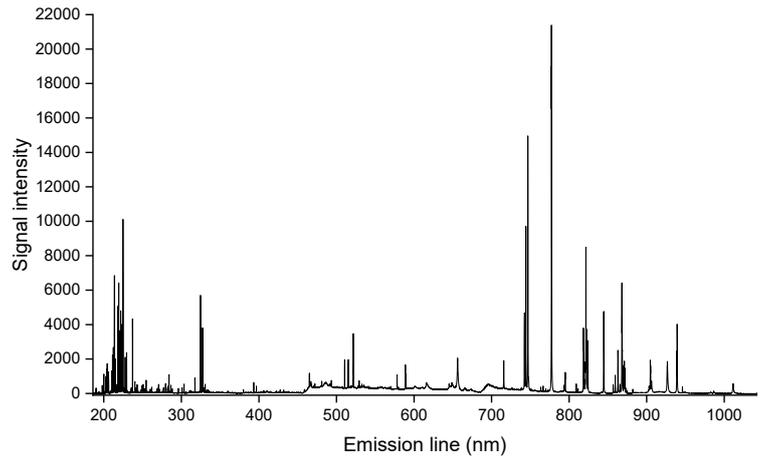
Before LIBS data acquisition

After LIBS data acquisition (The sample was analyzed twice using LIBS, to optimize the region of the data acquisition.)

Data used in the study discussion

XRF spectrum
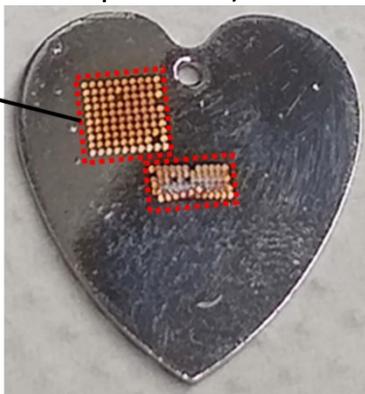
LIBS emission spectrum
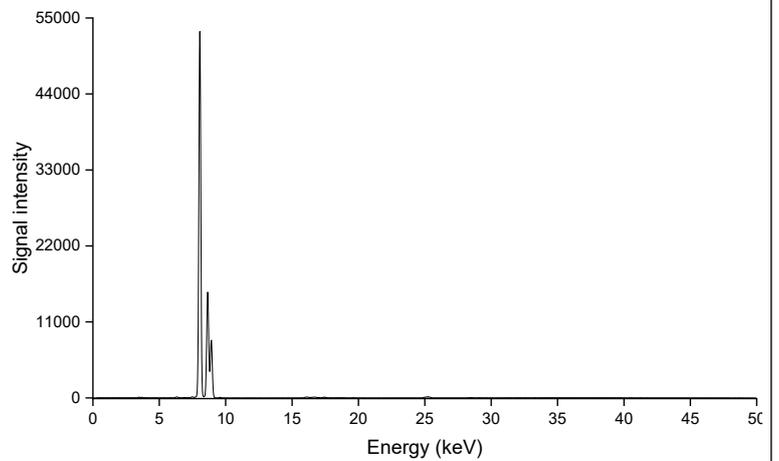
Fig 11SM: Sample S11 image before and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.

Signal intensity vs Emission line (nm)

Before LIBS data acquisition

After LIBS data acquisition

XRF spectrum

Signal intensity vs Energy (keV)
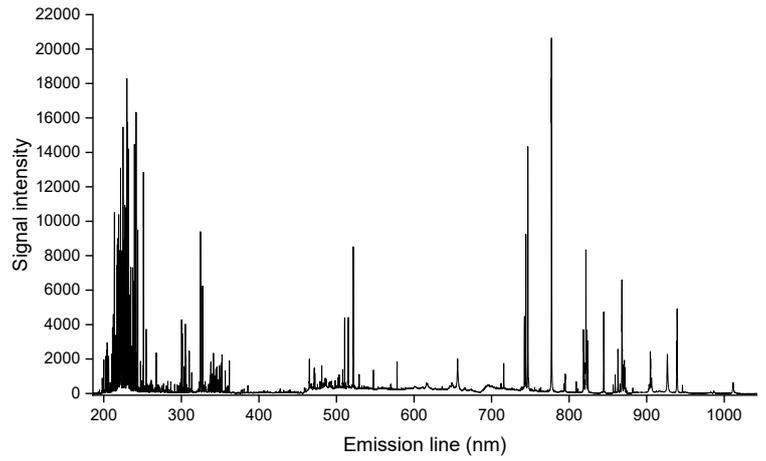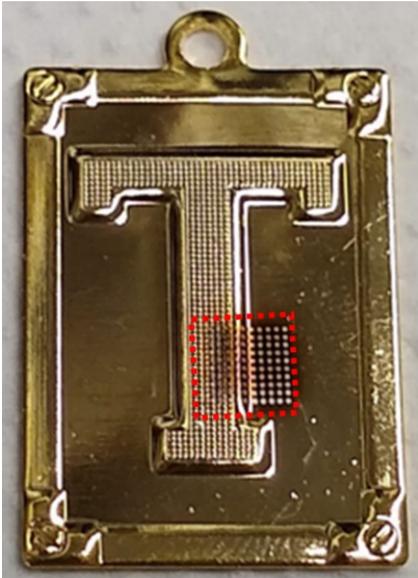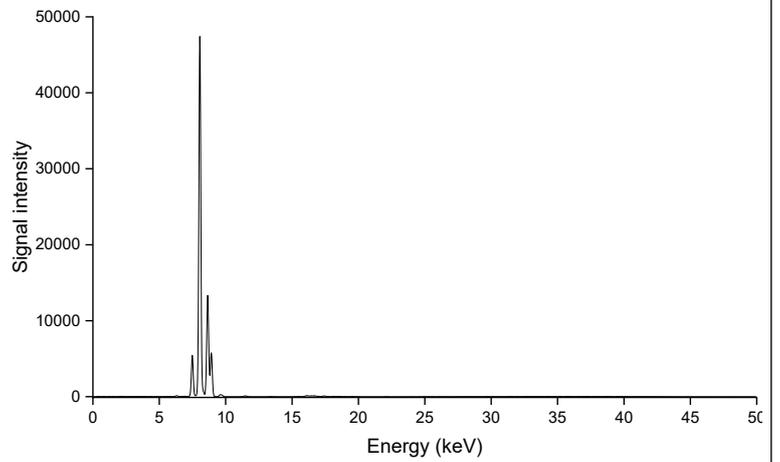
Fig 12SM: Sample S12 image before and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.	**LIBS emission spectrum**
Before LIBS data acquisition **After LIBS data acquisition**	**XRF spectrum**
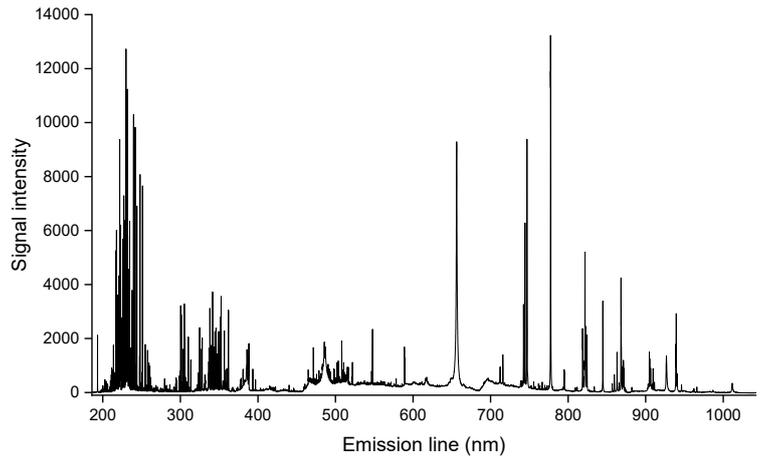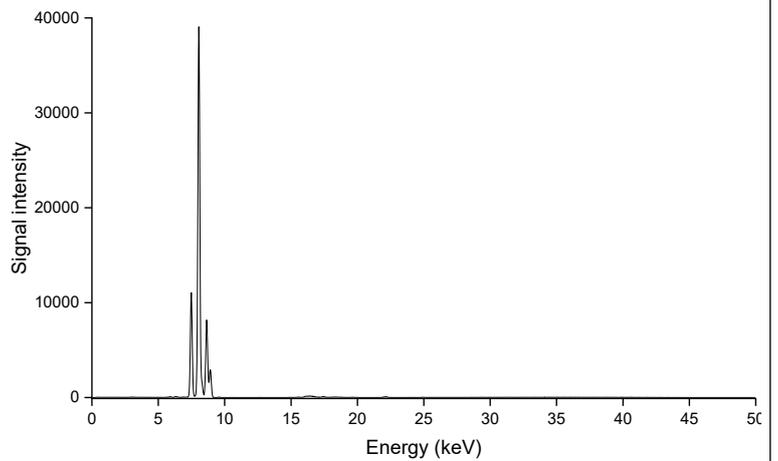
	LIBS emission spectrum
Fig 13SM: Sample S13 image before and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.	
Before LIBS data acquisition	
After LIBS data acquisition	XRF spectrum
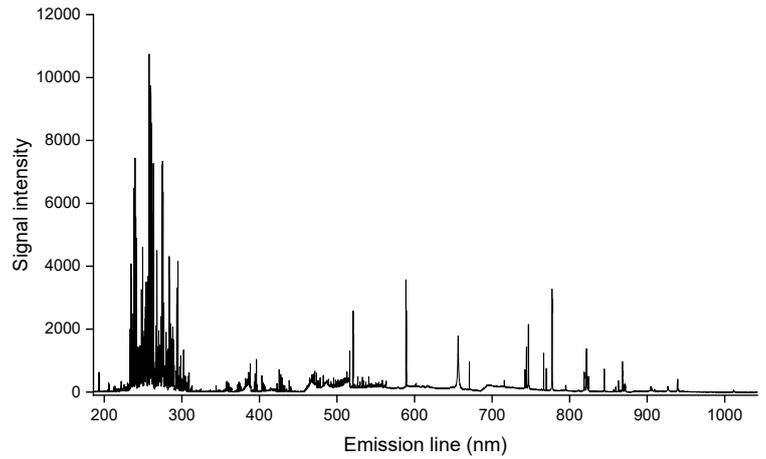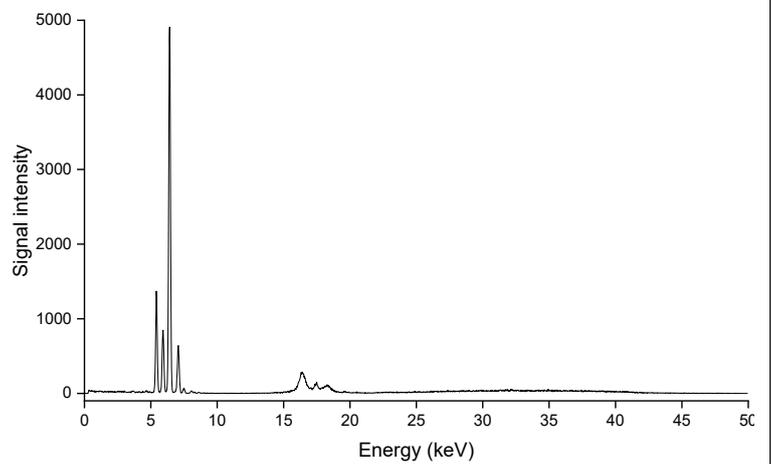
	LIBS emission spectrum
Fig 14SM: Sample S14 image before and after LIBS data acqusion (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.	
Before LIBS data acquisition 	
	XRF spectrum
After LIBS data acquisition (The sample was analyzed twice using LIBS, to optimize the region of the data acquisition.) Data used in the study discussion → 	
Fig 15SM: Sample S15 image before	LIBS emission spectrum
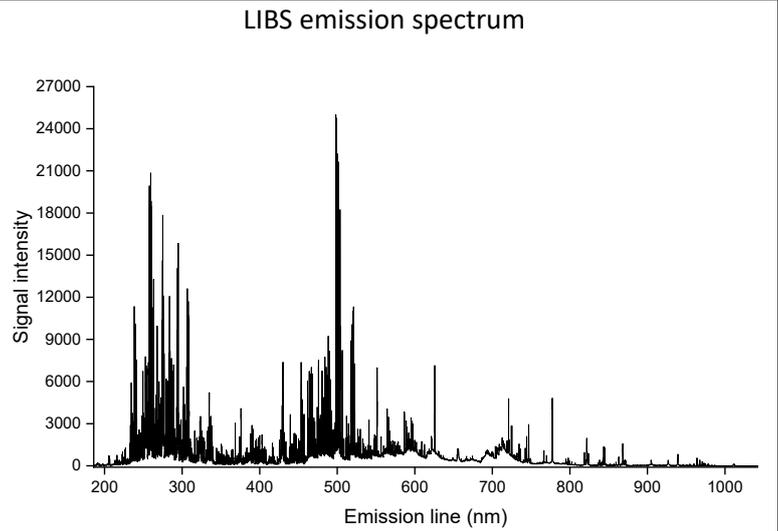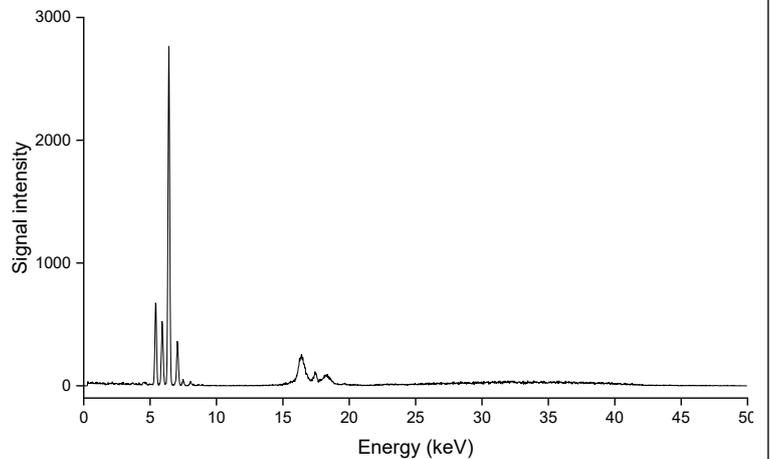
and after LIBS data acquision (see red dotted retangule). LIBS emission spectrum (right and upper part) and XRF fluorescence spectrum (right and below part). Both data were recorded in the same surface region.
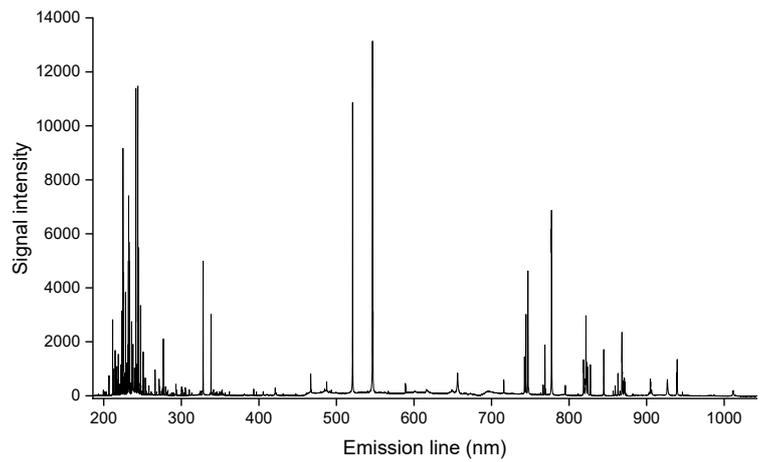
Before LIBS data acquisition

After LIBS data acquision

XRF spectrum
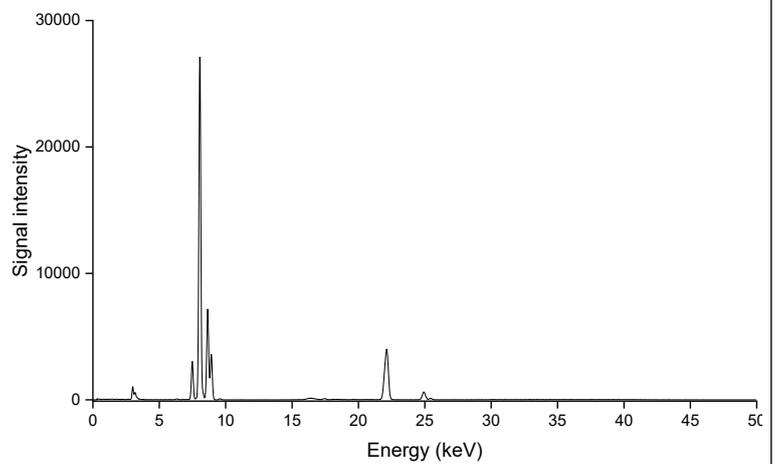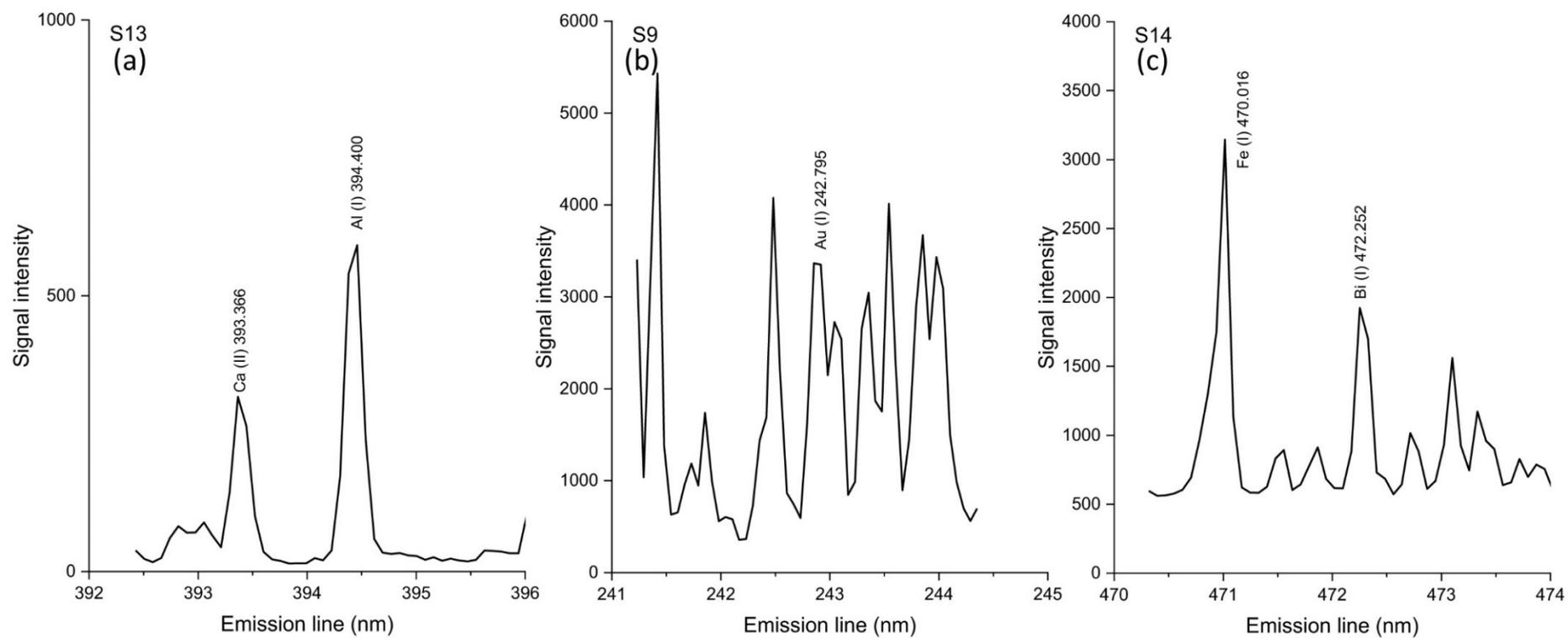
Fig 16SM. Observed emission lines (nm) from the LIBS recorded spectra for samples S13 (a), S9 (b), and S14 (c), part 1.
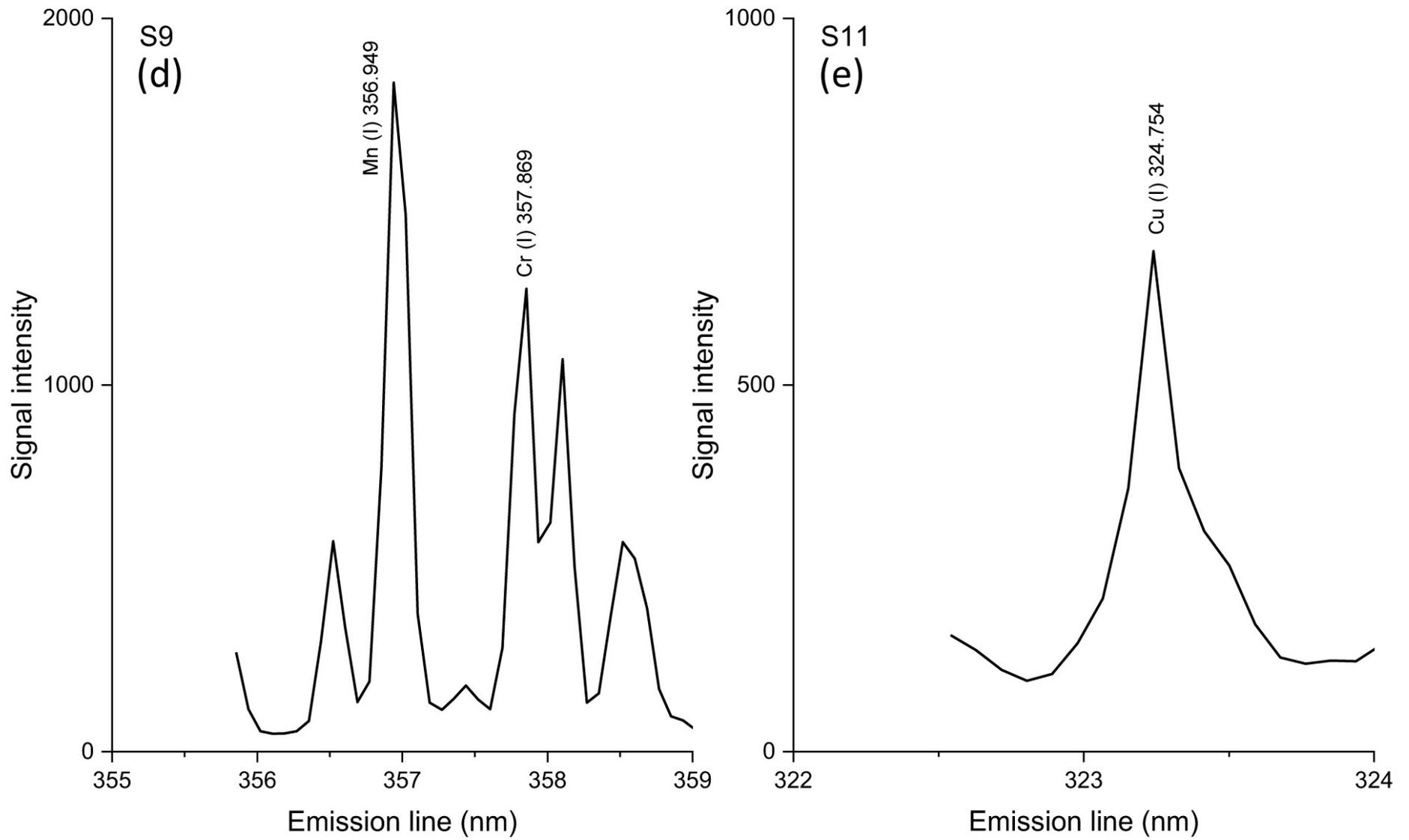
Fig 16SM. Observed emission lines (nm) from the LIBS recorded spectra for samples S9 (d) and S11 (e), part 2.
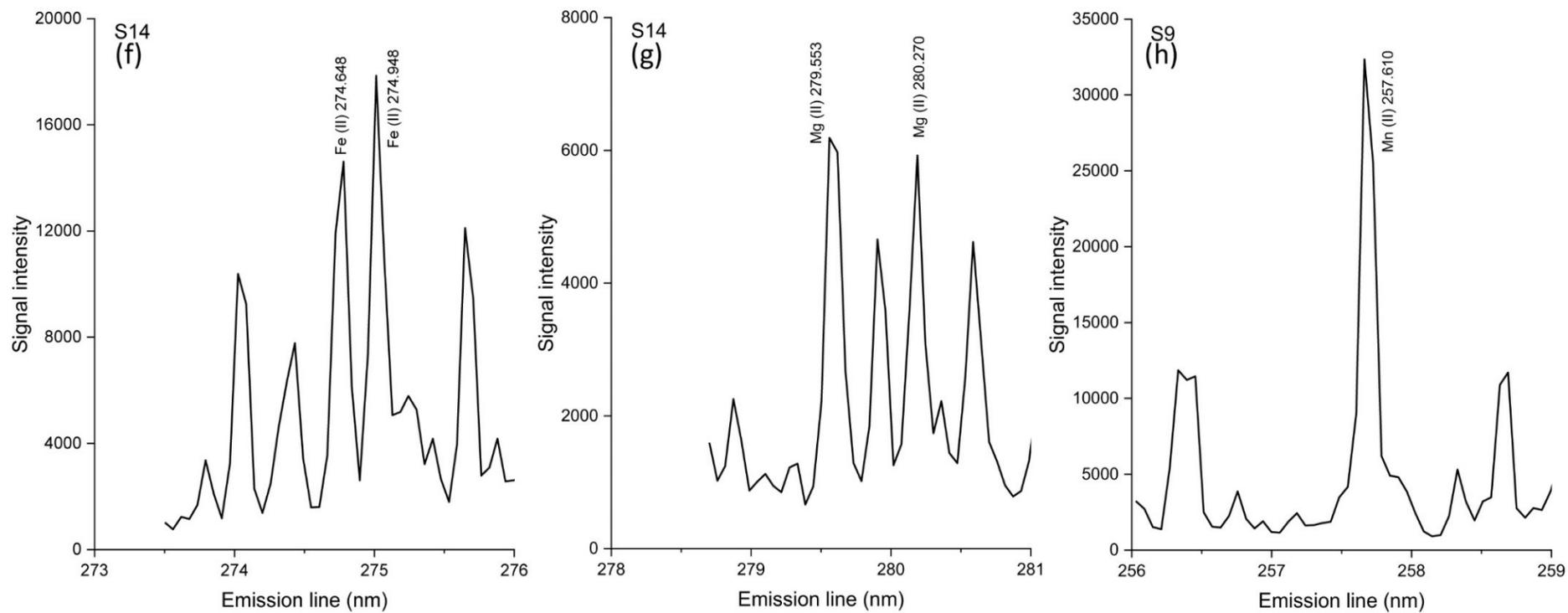
Fig 16SM. Observed emission lines (nm) from the LIBS recorded spectra for samples S14 (f and g), and S9 (h), part 3.
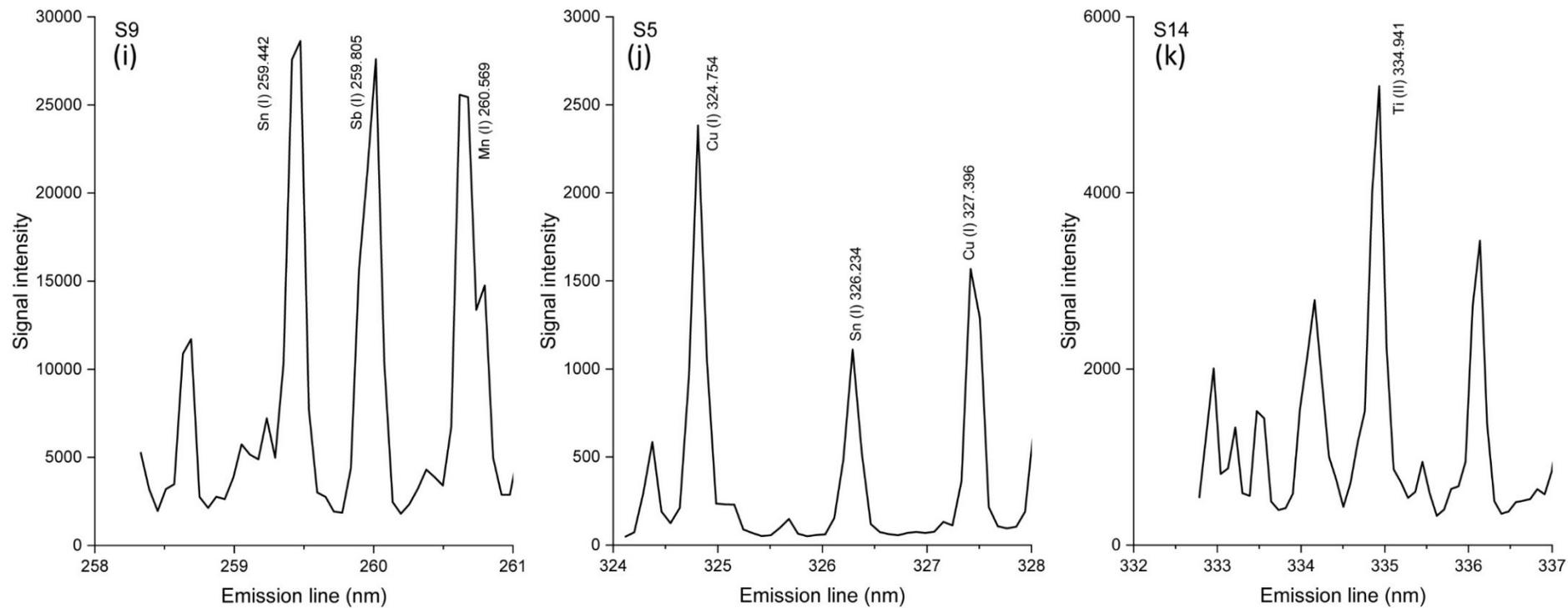
Fig 16SM. Observed emission lines (nm) from the LIBS recorded spectra for samples S9 (i), S5 (j), and S14 (k), part 4.
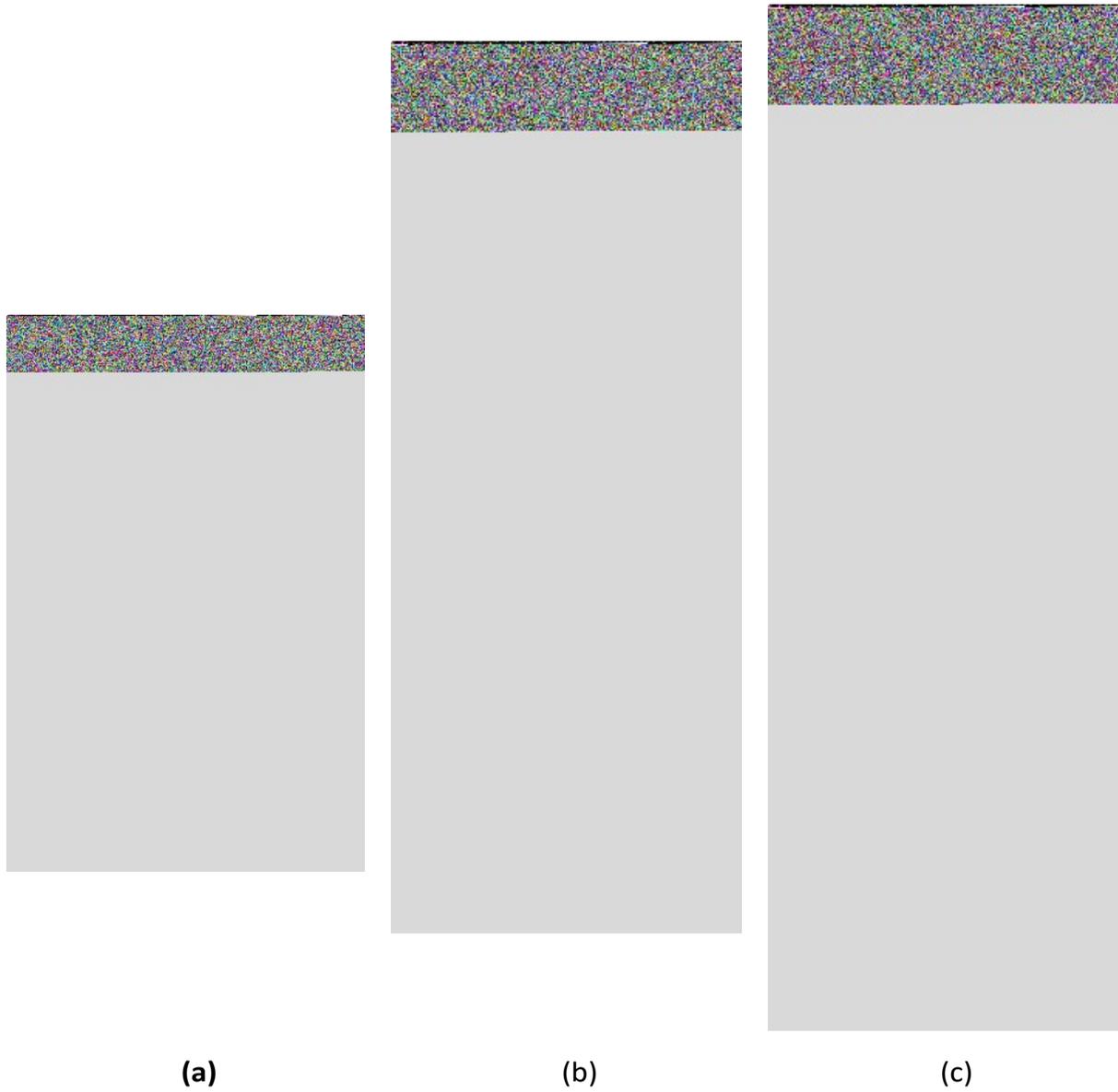
<table>
<tr><td>**(a)**</td><td>(b)</td><td>(c)</td></tr>
</table>

Fig 1. Representative samples (S) that were acquired at local stores during the experimental part: earrings (a: S1), and keychains (b: S3, and c: S5).

(d)   (e)   (f)

Fig 1. Representative samples (S) that were acquired at local stores during the experimental part: necklace pendants (d: S11, e: S13, and f: S14).
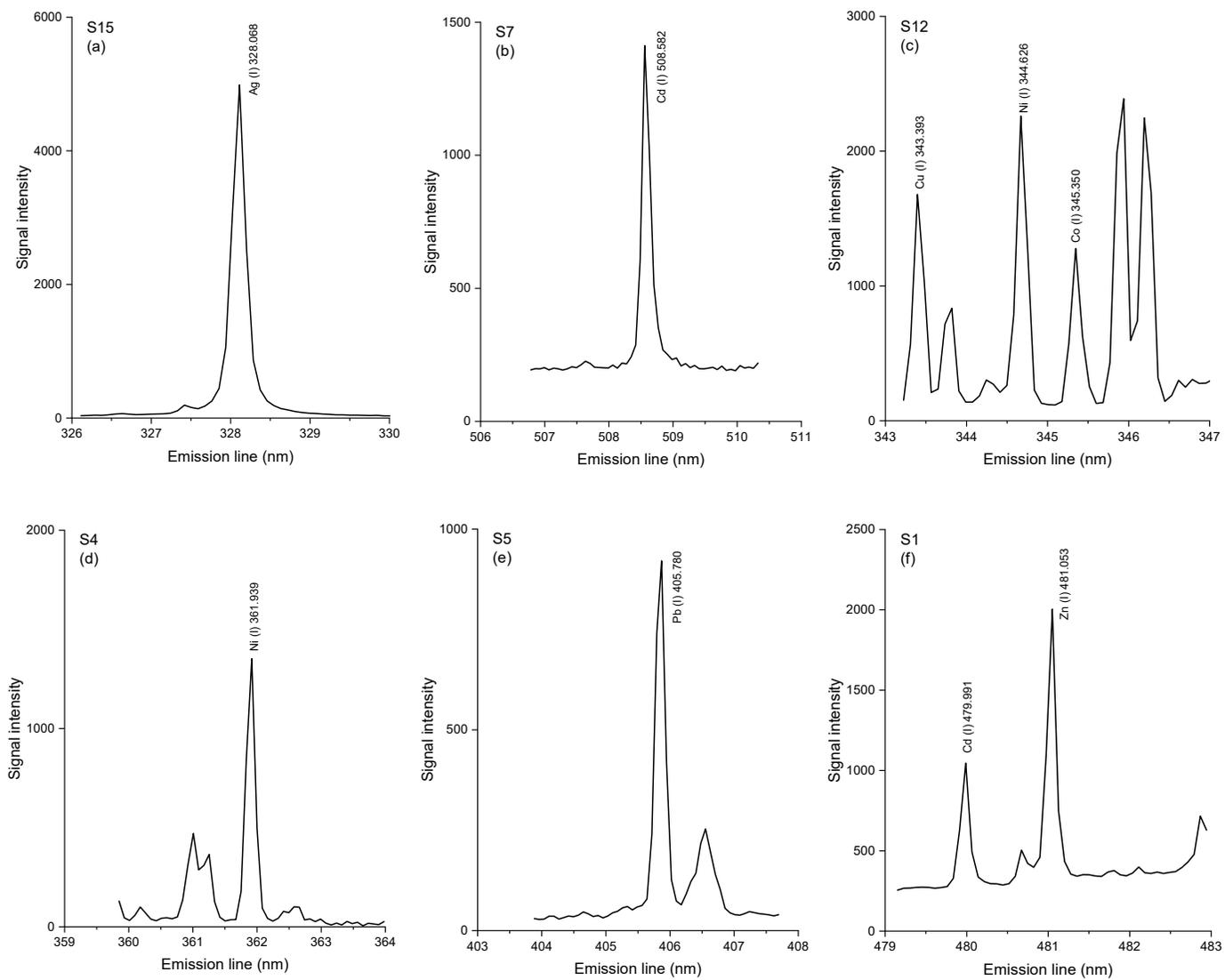
Fig 2. Observed emission lines (nm) from the LIBS recorded spectra for samples S15 (a), S7 (b), S12 (c), S4 (d), S5 (e), and S1 (f).
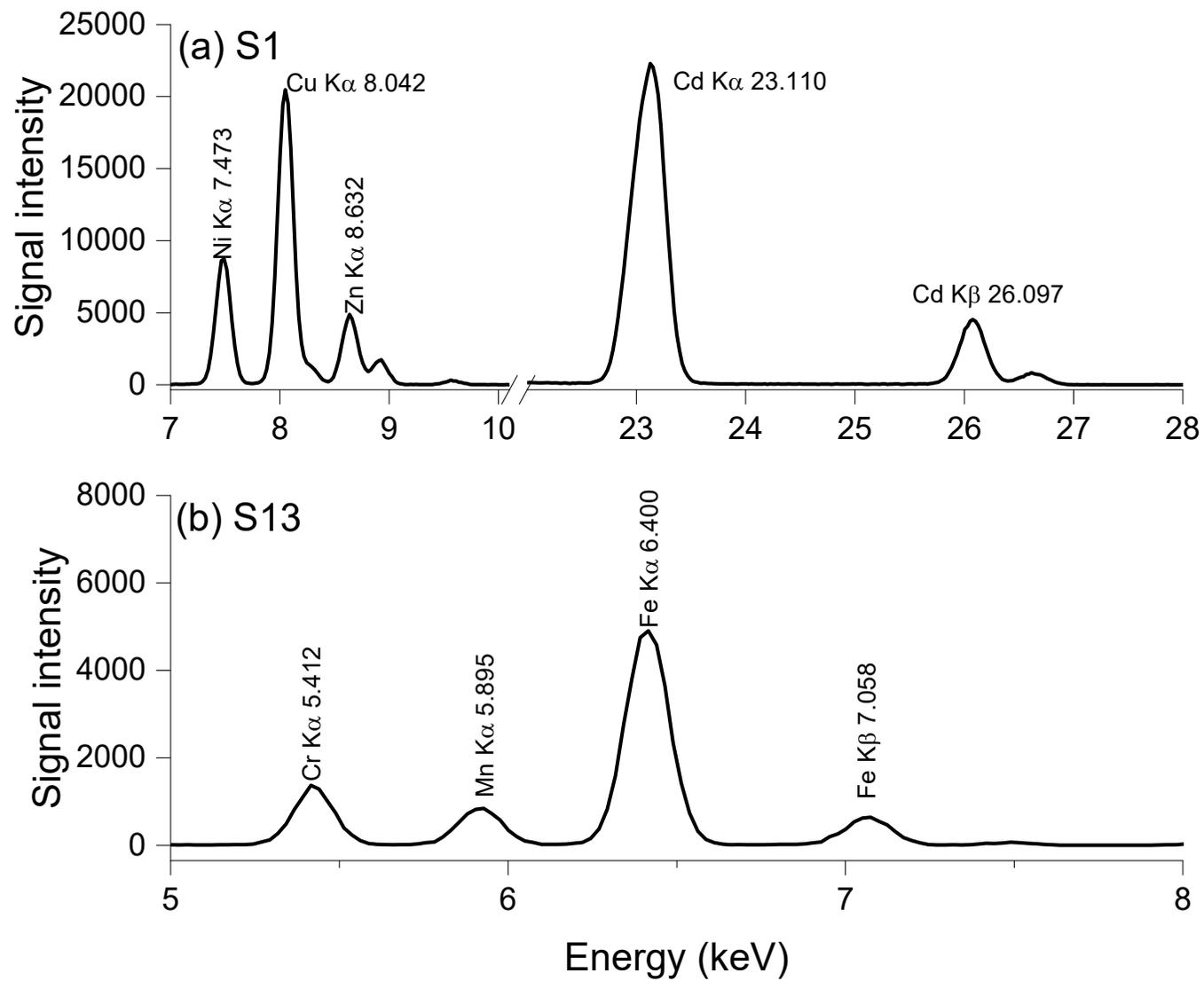
Fig 3. ED-XRF spectra fragments for two representative samples: S1 (a) and S13 (b).
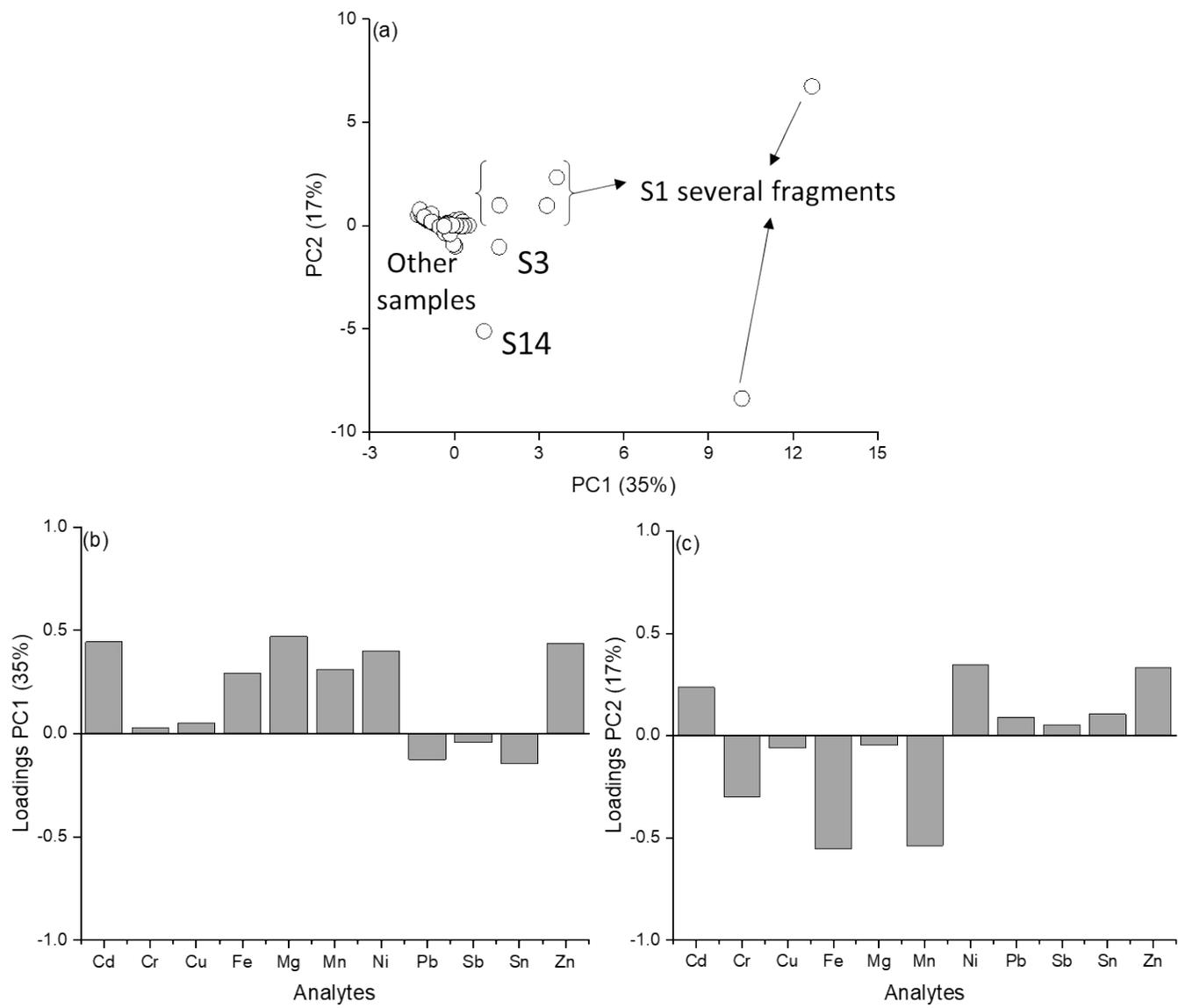
Fig 4. Score (a) and loading plots of PC1 (b) and PC2 (c).
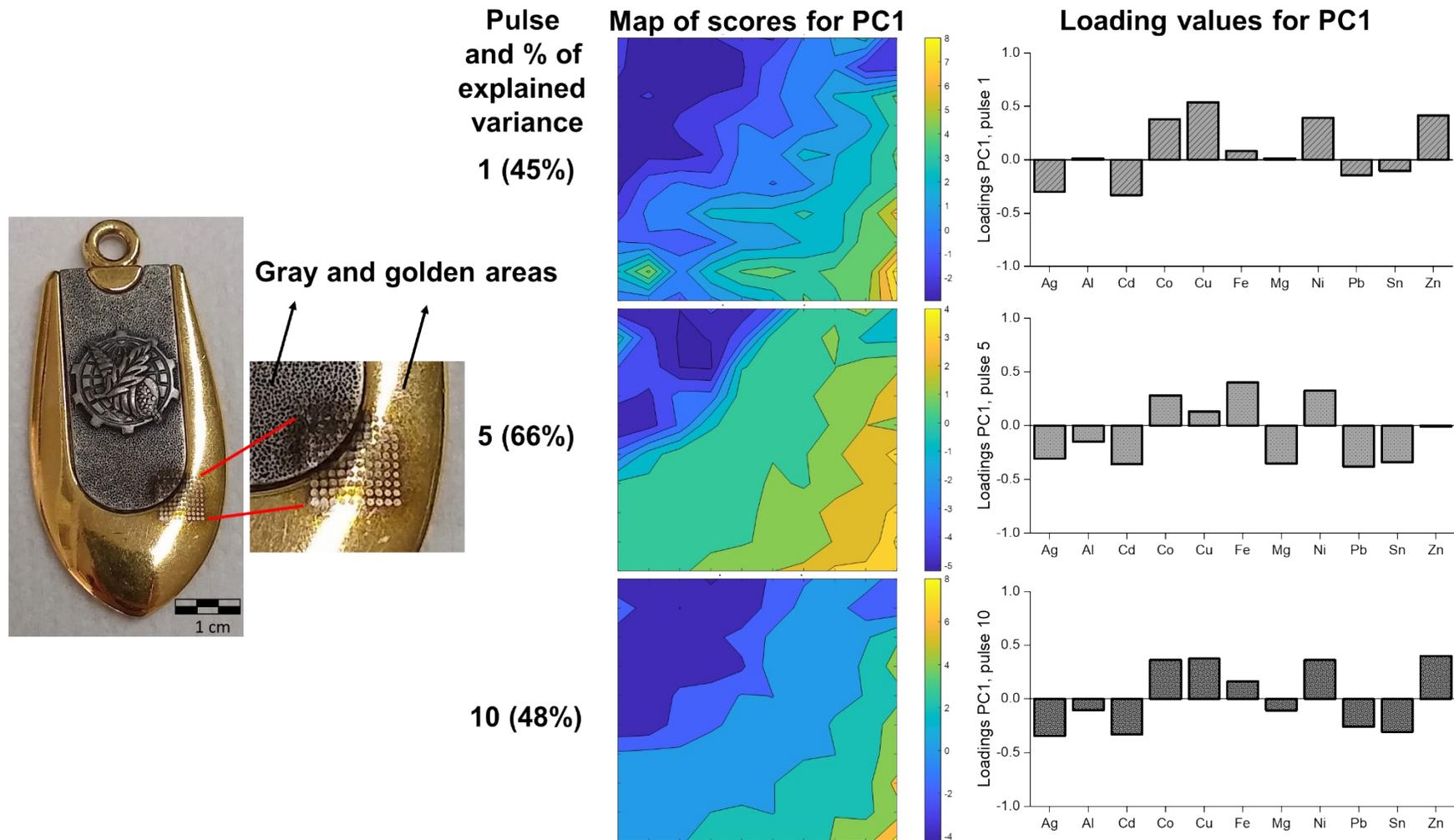
Fig 5. Scores maps and loadings are valued at PC1 for S5, considering pulses 1, 5, and 10.