

LIBS analysis of chromium in samples of dyed wool fabric

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A method for the analysis of chromium in wool fabric samples was developed. It is fast and cheap with no sample preparation. This method involved the use of double pulse Laser Induced Breakdown Spectrometry (LIBS) for the wool fabric samples dyed by two types of metal complex dyes (C.I. Acid Orange 173 and C.I. Acid Black 60). A commercially available LIBS spectrometer was calibrated with the aid of authentic wool fabric samples previously analysed by F-AAS after microwave digestion. Comparable results can be obtained using this unique procedure if the same set of standards is used for XRF and LIBS calibration. Limits of detection for chromium achieved by suggested LIBS methods (from 5 to 10 mg kg⁻¹) are comparable with the WD XRF ones (from 4 to 5 mg kg⁻¹).

Introduction

In LIBS, a high power laser pulse is focused on a small spot of the sample which ablates the surface layer, and successively heats and ionises the vaporised matter, producing the plasma. The spectral emission, which occurs as a result of the subsequent relaxation of constituent excited species, is measured by an appropriate spectrometer.¹

There are a number of industrial applications for this technique in areas where simple, fast and inexpensive analysis is desired.^{1–4}

When compared to other spectrometric methods, LIBS's disadvantages are low sensitivity and poor limits of detection. The substantial improvement in analytical capabilities of LIBS can be achieved through the use of the double pulse configuration.⁵ The emission enhancement in double pulse LIBS strongly depends on sample matrix composition.⁶

The main aim of the present study was to apply the above-mentioned technique as a routine analysis of metal content in wool fabric dyed by metal complex dyes. Usually ICP OES after microwave digestion or extraction⁷ as well as ICP MS⁸ is used for the analysis of metal constituents in dyed fabric. Traces of metals present in textile matrix can be analysed after solid sample extraction by AAS⁹ or after microwave digestion using ICP OES.^{10,11} When a non-destructive analytical process is required (analysis of forensic and archaeological samples), X-ray fluorescence spectroscopy is used.^{12–14}

Acceleration of analytical processing, radical simplification of sample pre-treatment steps and quasi non-destructive character of measurements are the main advantages of LIBS in this area of application.

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Experimental

Wool fabric standards preparation and characterisation

The wool fabric with an area weight of 250 g m⁻² was dyed using two different chromium containing dyes: orange (C.I. Acid Orange 173) and grey (C.I. Acid Black 60). Metal complex dyes were dosed in the range 0.5–5 mg of dye g⁻¹ of fabric to obtain samples with different Cr content. Microwave digestion in HNO₃ (Speedwave™ MWS-3+, Berghof, Germany) and F-AAS (SensAA, GBC, Australia) were employed for precise quantitative analysis of Cr in dyed wool fabric samples.

LIBS analysis

The LIBS spectrometer (LEA S500, Solar TII Ltd., Belarus) used is fully described elsewhere.¹⁵ The instrument integrates a dual pulse Q-switched Nd:YAG laser, operating at 1064 nm. The laser emits two colinear pulses of about 10 ns duration with energy per pulse variable between 80–150 mJ at maximum repetition rate of 20 Hz. The inter-pulse delay can be set from 0 to 20 μs. The spectrograph with focal length 500 mm and grating 1800 lines mm⁻¹ provides dispersion 1 nm mm⁻¹. The wavelength range of the spectrograph is 170–800 nm. Recording of spectra is carried out by means of a back thinned and front illuminated CCD-camera (2048 × 14 pixels) with a minimal integration time of 1 μs.

The chromium line with wavelength 360.53 nm was chosen for analysis from the set of intensive Cr lines positioned in the spectral window 345–365 nm (Fig.1). The experimental parameters were adjusted to optimise the analytical line intensity and measurement reproducibility. In the end, the final combination of spectrometer conditions used for measurement were: energy per pulse – 90 mJ, inter-pulse delay – 7 μs, focal spot diameter – 450 μm, spectrometer slit width – 40 μm, number pulses collected per spectrum – 8, measure window – 1 ms.

Each one of the fabric samples were measured at sixteen separate points placed in the square with the side-length 4 mm. Therefore, the perpendicular distance between each measured point was 1 mm. As a result, the total sample area covered by the

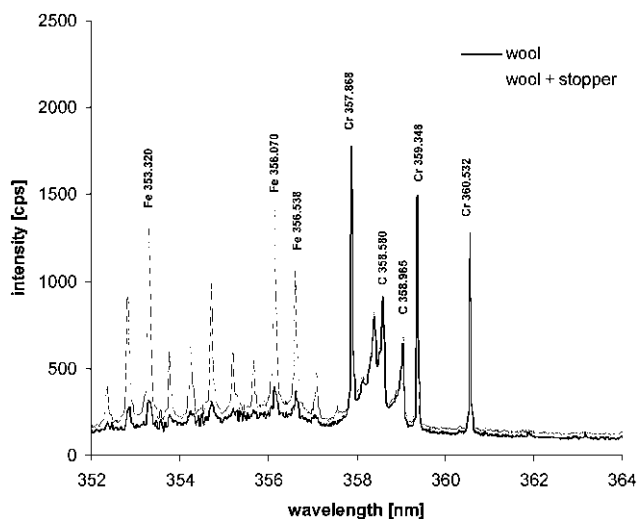


Fig. 1 LIBS spectrum of dyed wool fabric and gap flash with Fe lines originated from metal stopper of sample holder.

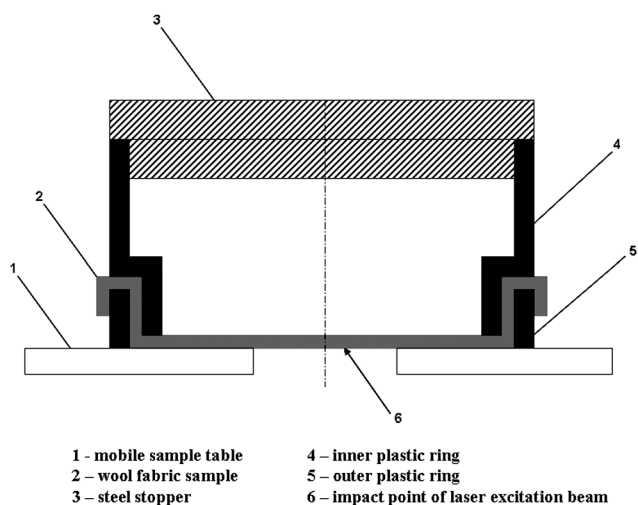


Fig. 2 Sample holder for LIBS analysis of wool fabric.

LIBS spectrum was similar to the area of corresponding XRF measurement. Due to knots and gaps in the fabric and the automated sample movement, abnormal gap flashes sometimes occurred. Such a case was characterised by the appearance of Fe lines originating from the metal stopper of the sample holder (Fig. 2). Spectra with obvious Fe lines (Fig. 1) were rejected from calculation of the final average spectra of the particular sample. If it was necessary to reject more than four spectra per sample, measurement of all sixteen points was repeated on another spot of the same sample.

WD XRF analysis

A bench-top vacuum wavelength dispersive X-ray fluorescence spectrometer (Spectroscan MAKC-GV, Spectron NPO Ltd., Russia) that was used for XRF analysis is equipped with a Pd X-ray tube. It has five diffraction crystals in Johansson's arrangement and sealed gas proportional detector filled with Xe. The Cr K_{α} (2291 mÅ) analytical line was measured with fixed

two-point background correction (2255 and 2330 mÅ). Integration time for the analytical line was 30 s and 15 s for background points. The set up of the X-ray tube was 40 kV and 2 mA. To compensate for in-homogeneity of the fabric, sample rotation (1 rps) was chosen.

Results and discussion

Calibration of LIBS spectrometer

Fig. 3 shows spectra of grey and orange dyed wool fabric samples with the same concentration of chromium ($\approx 100 \text{ mg kg}^{-1}$) scanned at the same above-mentioned conditions. As can be seen, the grey dyed sample gives less intensive spectra with lines slightly shifted to the shorter wavelengths. This effect can be observed at all chromium concentration levels tested, which probably could be connected to the different reflectivity of dyes when excited with the laser beam.^{6,16}

Due to the above mentioned observations separate calibrations of LIBS spectrometer for orange and grey dyed wool fabric were used. Thirty real samples of each fabric type, which were preliminarily analysed for chromium content by F-AAS were used in the process of LIBS calibration. The concentration of chromium varied from 10 to 130 mg kg^{-1} in orange standards and from 8 to 160 mg kg^{-1} in grey standards.

The area of the 360.53 nm line of chromium was calculated after a Gaussian fit of the peak in the integration window 360.50–360.60 nm (7 pixels). The left background point was calculated as an average intensity in the integration window 360.43–360.46 nm (2 pixels) while the corresponding integration window for the right background point was 360.64–360.68 nm (3 pixels).

Three of the most typical approaches for compensation of some matrix effects and fluctuation of conditions for plasma formation are: normalisation by a line of the matrix species, normalisation by the background and normalisation by the area under the whole spectrum.¹⁷ In this case, only normalisation by a line of the matrix species was possible to use because of the spectrometer software design. An area of a 358.58 nm carbon line was measured in the integration window 358.53–358.61 nm (6 pixels) for this purpose. Integral windows for average intensity measurements of background points were 358.33–358.50 nm (3 pixels) and 358.67–358.71 nm (3 pixels) respectively.

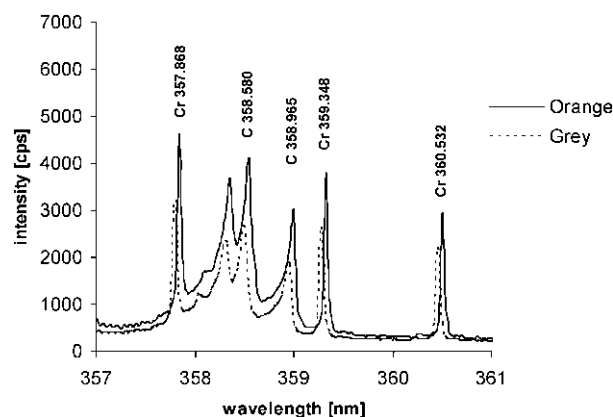


Fig. 3 LIBS spectrum of orange and grey dyed wool fabric with equal content of chromium (100 mg kg^{-1}).

The following regression model was suggested for the description of experimental data

$$C_{Cr} = \beta_0 + \beta_1 I_{Cr} + \beta_2 I_{Cr}^2 + \beta_3 I_{Cr}/I_C + \beta_4 (I_{Cr}/I_C)^2$$

where C_{Cr} is concentration of chromium in calibration standards (mg kg^{-1}), I_{Cr} is net peak area of 360.53 nm Cr analytical line (counts s^{-1}) and I_C is the net intensity of 358.58 nm C comparison line (counts s^{-1}).

The final calibration relationship obtained by the least square method for orange dyed wool fabric was

$$C_{Cr} = 7.28 \times 10^{-3} I_{Cr} - 3.23 \times 10^{-7} I_{Cr}^2 + 1.16 \times 10^2 (I_{Cr}/I_C)^2$$

$(R^2 = 0.996, \text{MEP} = 18.1)$

and for the grey dyed fabric

$$C_{Cr} = 8.18 \times 10^{-3} I_{Cr} + 1.04 \times 10^2 (I_{Cr}/I_C)^2$$

$(R^2 = 0.995, \text{MEP} = 39.0)$

Calibration of WD XRF spectrometer

Identical sets of thirty orange and grey dyed wool fabric standards were used for WD XRF calibration. The following regression model was suggested for the description of experimental data

$$C_{Cr} = \beta_0 + \beta_1 I_{CrK\alpha} + \beta_2 I_{CrK\alpha}^2$$

where C_{Cr} is concentration of chromium in calibration standards (mg kg^{-1}) and $I_{CrK\alpha}$ is Cr K_{α} line intensity (counts s^{-1}).

The resulting calibration relationship adopted for orange dyed wool fabric was

$$C_{Cr} = -9.63 + 1.48 \times 10^{-1} I_{CrK\alpha} - 1.72 \times 10^{-5} I_{CrK\alpha}^2$$

$(R^2 = 0.997, \text{MEP} = 11.3)$

and for the grey dyed fabric

$$C_{Cr} = -7.83 + 1.35 \times 10^{-1} I_{CrK\alpha} - 8.34 \times 10^{-6} I_{CrK\alpha}^2$$

$(R^2 = 0.999, \text{MEP} = 7.1)$

Analysis of samples

Eight samples of orange dyed and eight samples of grey dyed wool fabric were analysed by WD XRF and LIBS using the above mentioned calibration relationships. The chromium concentration range for both sample sets was approximately 20–130 mg kg^{-1} . Values of RSD (relative standard deviation)

calculated from three replicate measurements varied between 1.4–5.4% for LIBS analysis of orange samples and 1.5–6.1% for grey samples. Corresponding RSD values for WD XRF measurements varied between 0.2–5.3% for orange samples and 1.2–6.1% for grey samples.

The parameters of the following regression equation were calculated to evaluate parity between WD XRF and LIBS results:

$$C_{Cr-LIBS} = \beta_0 + \beta_1 C_{Cr-WDXRF}$$

where $C_{Cr-LIBS}$ represents concentration of Cr in wool fabric sample (mg kg^{-1}) measured by LIBS and $C_{Cr-WDXRF}$ is Cr content measured by WD XRF. The statistical parameters of regression for orange and grey dyed samples are summarised in Table 1.

The 95% reliability intervals for the slope include a value of 1 and the 95% reliability intervals for the intercept includes 0. Consequently it can be stated, that there is no statistically significant difference between results obtained by LIBS and WD XRF measurements of chromium content in orange and grey dyed wool fabric samples.

Limits of detection (LOD) for suggested LIBS and WD XRF procedures were defined according to the 3σ concept, where σ was the standard deviation calculated from ten replicated determinations of chromium in the real sample with a very low concentration of measured element (5 mg kg^{-1}). The following values of LODs were obtained for LIBS measurements of orange and grey dyed wool fabric respectively: $\text{LOD}_{\text{LIBS-orange}} = 5.3 \text{ mg kg}^{-1}$ and $\text{LOD}_{\text{LIBS-grey}} = 9.5 \text{ mg kg}^{-1}$. Corresponding values of LODs calculated for WD XRF were even lower: $\text{LOD}_{\text{WD XRF-orange}} = 4.88 \text{ mg kg}^{-1}$ and $\text{LOD}_{\text{WD XRF-grey}} = 4.35 \text{ mg kg}^{-1}$.

Conclusion

The procedure for the analysis of chromium in a dyed wool fabric using commercially available LIBS spectrometer was developed. Real samples previously analysed by F-AAS after microwave digestion were used as calibration standards. The statistically significant parameters of the calibration equation as well as statistic characteristics, which describe quality of calibration, were dependent on the type of dye used. The calibration equation for grey dyed samples contained fewer terms with statistically significant parameters than the equation for orange ones. However, corresponding statistical characteristics showed a worse quality of the model adopted for the grey samples. The congruence of WD XRF and LIBS results were also worse for grey samples than for orange ones. Re-optimisation of LIBS analytical parameters performed separately for grey sample set seems to be necessary.

Acknowledgements

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Table 1 Parameters and statistical characteristic of regression equation comparing WD XRF and LIBS results

Colour	Equation	95% interval of reliability		R^2
		β_0 —intercept	β_1 —slope	
Orange	$C_{Cr-LIBS} = -0.36 + 1.01 C_{Cr-WDXRF}$	−5.91 to 5.25	0.94 to 1.08	0.9949
Grey	$C_{Cr-LIBS} = 1.47 + 0.96 C_{Cr-WDXRF}$	−6.67 to 9.62	0.85 to 1.06	0.9883

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