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FACULTY OF CHEMICAL TECHNOLOGY

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Analysis of samples in form of thin layer using LIBS spectrometry

Doctoral thesis

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2017

Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is an instrumental analytical method which can be used for qualitative and quantitative elemental analysis. It has achieved great popularity primarily due to the speed of analysis, easy direct analysis of solid samples and good detection limits for a wide range of elements, including light ones. Another advantage is the possibility of quasi-non-destructive, multi-analyte analysis without the necessity of a sample preparation. The LIBS technique is one of the methods in the optical atomic emission spectrometry. The principle of the LIBS spectroscopy is generating microplasma above the sample surface by a laser pulse. This process is known as laser ablation. Laser ablation is a summary of the processes, which lead to heating, fusion and evaporation of the material sample to be analysed due to interaction with the laser pulse. Interaction of the laser beam with the surface of the sample leads to excitation of microplasma, formation of free atoms and subsequent emission of the characteristic radiation of the resulting plasma (1 - 3).

The main aim of this dissertation was to gain knowledge about the possibilities of using laser-induced microplasma spectrometry (LIBS) for the quantitative elemental analysis of samples in the form of a thin layer and to create methodologies for practical application of this technique. Emphasis was placed mainly on the optimization of experimental conditions and on the preparation of samples for analysis, which are parameters that fundamentally influence the accuracy and precision of the obtained results.

Analysis of powder sample in form of thin layer

The first partial aim of the dissertation was to investigate the possibility of using laser-induced breakdown spectrometry (LIBS) for the quantitative analysis of light but hardly excitable element present in the organic matrix. Powdered organic pigment samples were transferred to the thin layer when the powder pigment was applied by the brush to the surface of the adhesive tape. Fulfillment of the target should lead to a significant reduction in sample consumption. The use of LIBS should also allow analysis of elements that are difficult or impossible to analyze by alternative techniques. Practical implementation of the specific target was realized within the development of a methodology for the determination of fluorine in samples of organic pigments. Fluorine is a light element difficult to analyze by conventional techniques used to analyze of solid samples. The goal of our work was to evaluate the influence of sample preparation and the influence of the atmosphere in the ablation chamber for analysis of samples of organic pigments (pigment yellow 154). Two methods of sample preparation were used for the actual analysis, pressed into pellets and the preparation of a thin layer was deposited on the tape. The influence of the atmosphere of air and helium and argon in the ablation chamber was also observed at the same time.

Experimental conditions were optimized for each form of the samples - energy of pulse, delay, diameter of analytical point and flow of inert gas (He and Ar). Parameters set during the analysis are listed in Tables 1 and 2. Calibration curves were constructed under optimum conditions and are shown below (Fig. 1-4).

Table 1 - Optimal parameters for analysis of thin layer

Optimised parameter	Atmosphere		
	Air	Helium	Argon
Flow of gas [l.min^{-1}]	-	3,7	1,3
Laser pulse energy [mJ]	130	140	120
Diameter analytical point [μm]	400	400	400
Interpulse delay [μs]	6	6	6

Table 2 - Optimal parameters for analysis of pellets

Optimised parameter	Atmosphere		
	Air	Helium	Argon
Flow of gas [l.min^{-1}]	-	5,3	1,5
Laser pulse energy [mJ]	140	135	120
Diameter analytical point [μm]	300	300	300
Interpulse delay [μs]	6	6	6

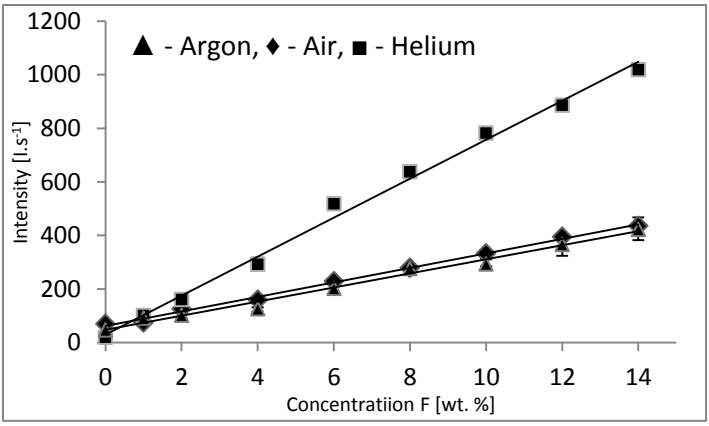

Fig. 1- Calibration curves obtained using pellets standards
The intensity of the F 685.6 nm analytical line is evaluated as peak height

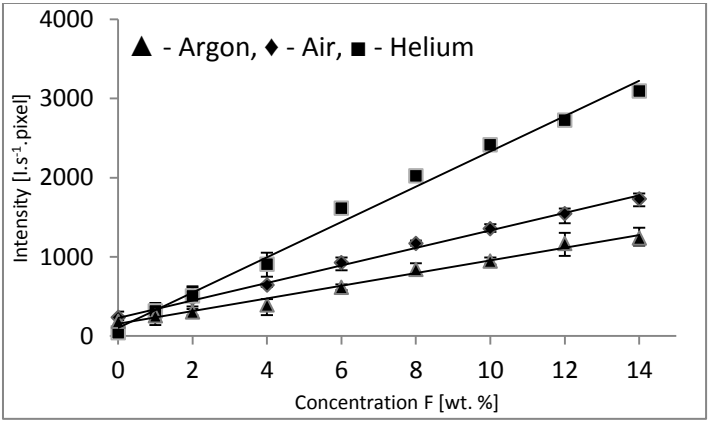

Fig. 2 - Calibration curves obtained using pellets standards
The intensity of the F 685.6 nm analytical line was evaluated as peak area

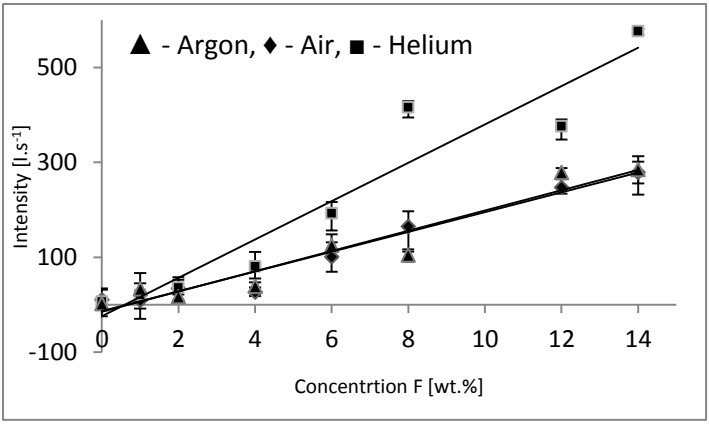

Fig. 3 - Calibration curves obtained using standards on the tape
The intensity of the F 685.6 nm analytical line is evaluated as peak height

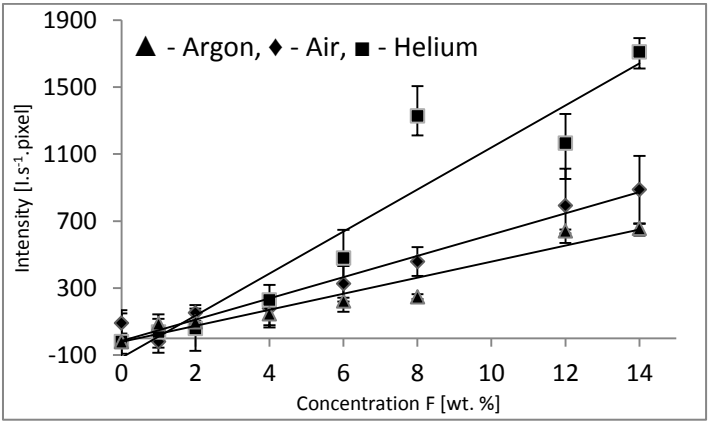

Fig. 4 - Calibration curves obtained using standards on the tape
The intensity of the F 685.6 nm analytical line was evaluated as peak area

Table 3 summarizes the statistical regression parameters calculated for each calibration dependency. Parameter R^2 serves to describe the quality of the measured data. In the case of calibration dependencies for pellets, the parameter reached the highest values in He atmospheric measurements. For the calibration obtained by measuring thin film standards, R^2 was significantly lower. The AIC and MEP values describe the quality of the regression model and can be used to select the best of way of interleaving the measured data. In the case of calibration for pellets measured in He atmospheres, the AIC and MEP values are significantly lower if the intensity of the analytical line is calculated as the height of the peak - the given model can therefore be considered more appropriate. In addition, the calculated detection limits (LODs) for each analyzed sample form are plotted in the table. By computing by the $3\ \sigma / s$ concept, where σ is the standard deviation and s is directive of the calibration line, much lower LOD values were obtained, which in our measurements corresponded rather to the background intensity. The second method of calculating the LOD was made using the statistical software Adstat. In this case, detection limits were calculated from the confidence bands of the calibration curves. The calculated LOD values are higher than when using the $3\ \sigma / s$ concept. Comparable LOD values obtained by computation from confidentiality bands and using the $3\ \sigma / s$ concept were obtained for measurement in a helium atmosphere.

Table 3 - Regression parameters for individual calibration dependencies

		LOD [wt. % F]		Basic characteristics of linear regression		
Sample form	Atmosphere	Confidental bands	3 σ/ s	MEP	AIC	R^2
Pellets - height	Air	1,389	0,1134	579,6	170,8	0,971
	He	0,5383	0,2238	952,3	185,6	0,993
	Ar	1,749	0,2166	698,2	176,2	0,963
Pellets - area	Air	1,114	1,950	7705	241,1	0,977
	He	0,6083	0,2185	15460	260,7	0,988
	Ar	2,001	0,6737	7674	231,9	0,958
Tapes - height	Air	-	2,488	1023	166,3	0,921
	He	4,829	0,6018	4551	202,5	0,906
	Ar	4,861	3,392	1226	170,8	0,910
Tapes - area	Air	5,231	2,621	15459	230,3	0,882
	He	-	2,949	6571	266,9	0,864
	Ar	3,259	3,291	5912	208,7	0,913

Determination of F in unknown samples

To verify the applicability of the proposed methods of determination of F in organic pigments, we measured two more samples of pigments of unknown concentration F (from another set and lot of samples, but the synthesis procedure was the same as for calibration standards) from the company HEUBACH Research Center s.r.o. The samples were prepared in the form of pellets and measured under optimal conditions in a helium atmosphere. Subsequently, a calibration curve method was used to calculate the concentration of F in unknown samples. Calculated data are given in Table 4 together with the declared content F by the manufacturer and the calculated yield (R). The measured F-values were in good agreement with the theoretical concentrations.

Table 4 - Theoretical and measured content F in unknown patterns

Samples	Theoretical concentration [wt. % F]	Measured concentration [wt. % F]	R [%]
Sample A	3,37	3,34 ± 0,3	0,967
Sample B	11,3	11,1 ± 0,3	0,986

Analysis of liquid in the form of a thin layer on a carrier

The second part of the dissertation thesis was to verify the possibility of elemental analysis of small volumes of liquid samples deposited as a thin layer on a solid support using a LIBS spectrometer. Filling the target should allow a rapid analysis of liquids in laboratories equipped with either solid sample analysis techniques (XRF, LIBS), or in laboratories equipped with techniques which needs higher specimen consumption.

Practical fulfillment of the second partial goal was realized by the development of methodology for determination of Cd in samples of jewelry leachates.The extraction of jewelry was carried out in solutions of acidic and alkaline artificial sweat. High salt content and small volumes can complicate ICP OES analysis. The application of liquid samples on the solid support and subsequent drying should improve the detection limits. The obtained results providing information about the mobility of the toxic element and were used in the process of assessing the health risks of analysed jewelry.The leaching of 13 jewelry samples was performed with two types of artificial sweat - acidic and alkaline. Acidic sweat was prepared dissolving 0,5 g of L-histidine mono-chloride monohydrate ($C_6H_9O_2N_3.HCl.H_2O$), 5 g of NaCl, and 2,2 g of $NaH_2PO_4.2H_2O$ in 1 l of demineralized water.The pH value was adjusted by 0,1 $mol.l^{-1}$ NaOH to 5.5. To prepare 1 l of alkaline sweat, 0,5 g of $C_6H_9O_2N_3.HCl.H_2O$, 5 g of NaCl and 5 g of $Na_2HPO_4.12H_2O$ was diluted in demineralized water. A solution of NaOH of a concentration of 0,1 $mol.l^{-1}$ was added for a pH adjustment to 8. The prepared solutions

were used to prepare a calibration series of a known concentration of Cd. (4)

The analyzed samples were provided by the Czech Environmental Inspectorate (CEI). Altogether 13 samples were obtained, 3 pairs of earrings, 6 pendants and 1 ring. The volume of the leaching agent (ml) was calculated for each jewelry analyzed based on the size of its area (cm^2). 1 cm^2 of the area of jewelry corresponds to 2 ml of the used leaching agent. Those parts of samples that were not supposed to be in contact with the skin (decorative stones, etc.) were not counted in the area of the article. Prior to leaching, these parts were sealed with adhesive tape to prevent release of Cd from these parts. To obtain leachate, the samples were immersed in a suitable volume of artificial sweat solution in a plastic container for 168 hours and at 37 ° C according to EN 1811 (5) and No. 84/2001 (4), after the leaching time, 20 µl of the leachate were applied on the paper carrier. Subsequently, drying under a lamp (50-60 °C) was performed and the carriers were analyzed.

Optimization of the measurement conditions was carried out using a solution of artificial sweat with a Cd concentration of 10 $mg.l^{-1}$. The SBR value was chosen as the optimization criterion, taking into account also the RSD value. Optimization was carried out for diameter of analytical point, energy of laser pulse and entrance slit of spectrometer. Another optimizations were for delay time between pulses, the number of analytical points and the number of laser pulses per analytical point. The final conditions were set as follows: analytical point diameter 200 µm, laser beam energy 110 mJ, entrance slit 25 µm, delay time 7 µs, 1 laser pulse per analytical point and 9 analytical points. After optimization of

the conditions, both calibration series of prepared standards were measured (Fig. 5-6). Statistical parameters are shown in Table 5.

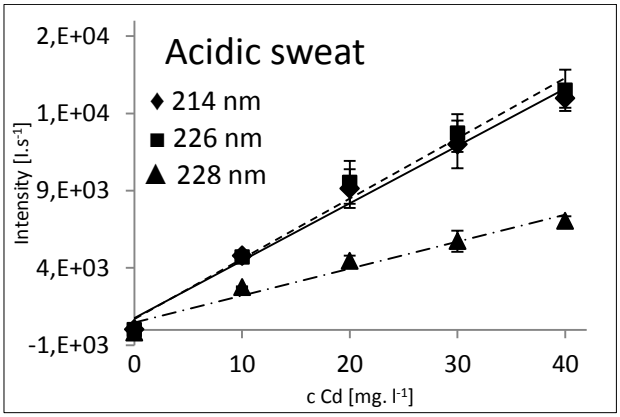

Fig. 5 - Calibration curves designed for a solution of artificial acid sweat

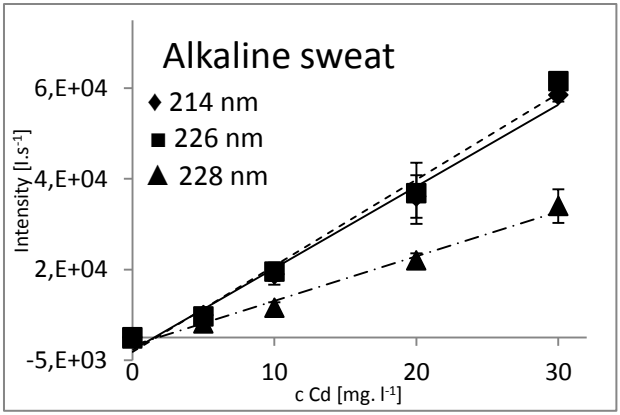

Fig. 6 - Calibration curves designed for a solution of artificial alkaline sweat

Table 5 - Statistical parameters calculated for each calibration model

Type of sweat	WL [nm]	β_1	*Intr*	R^2	*MEP*	*AIC*	*p value*
Acidic	214	370	767,3	0,986	$2{,}32 \cdot 10^6$	70,3	$6{,}8 \cdot 10^{-4}$
	226	389,3	710,3	0,985	$1{,}81 \cdot 10^6$	69,3	$7{,}3 \cdot 10^{-4}$
	228	174,5	469,3	0,964	$9{,}35 \cdot 10^5$	65,6	$2{,}9 \cdot 10^{-3}$
Alkaline	214	1802	-2729	0,989	$1{,}91 \cdot 10^7$	80,1	$4{,}8 \cdot 10^{-4}$
	226	1901	-3204	0,985	$2{,}92 \cdot 10^7$	82,2	$7{,}5 \cdot 10^{-4}$
	228	983,9	-1730	0,987	$6{,}11 \cdot 10^6$	74,9	$6{,}1 \cdot 10^{-4}$

WL - Wavelength, β_1 - slope of the curve, *Intr* - curve segment, R^2 - coefficient of determination, *MEP* - mean square prediction error, *AIC* - Akaik´s information criterion, *p value* - Fisher-Snedecor test

After the leaching time, the samples were removed from the sweat solution and the extracts were filtered. For analysis by LIBS spectrometer 3 solid carriers were prepared for each leachate and a 20 μl solution of leachate was applied. The carriers were dried under lamp and analyzed under previously optimized conditions. In case of analysis of 3 pairs of earrings (1B, 2B, 3B), one piece from the pair was leached in acidic and the second in alkaline sweat. Other samples were selected randomly for leaching in both types of sweats. Data in Table 6 show that the total amount of Cd that has been released into alkaline sweat amounts to approximately 20% of the amount of Cd released into the acidic sweat.

Tabulka 6 - The total amount of Cd released from jewelry into artificial sweat

Sample	Type of sweat	TRA Cd [µg/week]	TRA Cd * [µg/cm^2/week]	MADD [µg/kg/day]	RCR [%]
1B	Alkaline	370,4	61,73	4,54 x 10^{-3}	1,13 x 10^{-1}
2B	Alkaline	72,70	8,078	8,90 x 10^{-3}	2,23 x 10^{-2}
3B	Alkaline	49,01	12,25	6,00 x 10^{-4}	1,50 x 10^{-2}
4A	Alkaline	29,37	9,789	3,60 x 10^{-4}	8,99 x 10^{-3}
6A	Alkaline	24,55	24,55	3,01 x 10^{-4}	7,52 x 10^{-3}
7A	Alkaline	24,00	3,840	2,94 x 10^{-4}	7,35 x 10^{-3}
9A	Alkaline	29,09	3,232	3,56 x 10^{-4}	8,90 x 10^{-3}
1B	Acidic	1517	252,9	1,86 x 10^{-2}	4,64 x 10^{-1}
2B	Acidic	340,5	37,82	4,17 x 10^{-3}	1,04 x 10^{-1}
3B	Acidic	222,3	55,59	2,72 x 10^{-3}	6,81 x 10^{-2}
5A	Acidic	44,14	3,532	5,41 x 10^{-4}	1,35 x 10^{-2}
10A	Acidic	16,36	4,089	2,00 x 10^{-4}	5,01 x 10^{-3}
Ring	Acidic	154,6	51,53	1,89 x 10^{-3}	4,73 x 10^{-2}

TRA Cd - total release of Cd in 1 week, TRA Cd* - total released amount of Cd from 1 cm^2 of jewelry per 1 week, MADD - maximum absorptive daily dose, RCR - Ratio of risk characterization

Systemic Non-Carcinogenic Health Risk of Released Cd

A reference dose (RfD) is the regulatory limit established by the United States Environmental Protection Agency (US EPA) representing the maximum oral dose of a toxic substance, below which no adverse non-carcinogenic health effects should result from a lifetime of exposure. According to the Integrated Risk Information System (6), the calculation of RfD for chronic oral exposure was based on the assumption of increased proteinuria occurring when the Cd content in the renal cortex exceeds the value of 200 μg Cd/g wet tissue. Cd daily intake of 0,352 mg (or 0,005 mg/kg/day for 70-kg adult), which is necessary in order for the concentration of this element in the renal cortex to reach the critical value, was estimated based on the work of Friberg et al. (7). This work assumed a Cd biological half-life ($t_{1/2}$) of 19 years, an exposure duration of 50 years, and an absorption of 4,5% of Cd contained in the food. US EPA postulated only 2,5% absorption of Cd from the food and consequently established the NOAEL (No-Observed-Adverse-Effect Level) value of 0,01 mg of Cd/kg/day. RfD of 0,001 Cd/kg/day was then obtained dividing NOAEL by the uncertainty factor (UF) of 10. The US EPA document shared at the IRIS (Integrated Risk Information System) database unfortunately does not provide any further information regarding the used toxicokinetic model. When the one-compartment standard first-order elimination model with bolus administration described by Amzal et al. (8) was used, the same value of NOAEL (0,01 mg Cd/kg/day) was obtained for the subsequent set of parameters: a Cd gastrointestinal absorption index equal to 2,5%; a fraction of absorbed Cd transported to the kidney equal to

33%; a ratio of Cd content in the entire kidney and renal cortex of 1,25; a kidney weight of equal to 300 g; and a Cd biological half-life $t_{1/2}$ of 18,3 years. The EPA did not establish a limit of a similar meaning as the RfD for dermal exposure. To be able to assess the health risk of Cd released from low-cost jewelry, we performed our own approximation of dermal RfD based on the same toxicokinetic model. The parameters mentioned above were used except for the absorption index, which was set to 0,6%. The calculated value of NOAEL for dermal exposure was 0,042 mg/kg/day. The resulting dermal RfD in this case was also obtained dividing NOAEL by the uncertainty factor UF = 10 with a value of 0,004 mg/kg/day. The dermal RfD estimated in such a way represents a kind of worst-case scenario, in as much as the Cd absorption into the plasma could be lower than the absorption into the renal cortex with published data for absorption into the plasma varying between 0,1% and 0,6% (9). The total amounts of Cd in μg released from a particular piece of jewelry (TRA - Total Released Amount) into acidic or alkaline artificial sweats over one week of leaching are summarized in Table 6. The maximum absorbable daily dose (MADD) of Cd from a particular piece of jewelry was calculated based on the assumed Cd bioavailability of 0,6% and an average human body weight of 70 kg according to the following equation: MADD = 0,006 x TRA/(70 x 7). A factor of 7 in the denominator was used to convert the amount of Cd released over one week of leaching to the daily exposure. The risk characterization ratio (RCR) was then calculated as the hundredfold ratio of MADD and RfD. This factor serves as an estimate as to what percentage of the safe daily dose can be covered by Cd released from the jewelry. The amount of Cd

leached into alkaline artificial sweat typically represents about 0,01–0,02% of the safe daily dose, while the maximal RCR for Sample 1B was 0,1%. In the case of acidic artificial sweat, RCR values are higher and more variable (ranging from 0,05% to 0,46%). Although the process of health risk estimation used is extremely simplified, it can be concluded that the evaluated set of Cd containing jewelry do not pose any serious health risk in terms of systemic non-carcinogenic effects.

Analysis of ultra-thin surface layer

Finding accurate quantitative method for characterization of nanometer layers constituting the surface of anti-corrosion protective coatings is a task of crucial importance for industrial laboratories. The standard procedure is based on the wet process, where the surface layer is etched by acids and the obtained leachate is subsequently analyzed with atomic spectrometry techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectroscopy (ICP OES), and inductively coupled plasma mass spectrometry (ICP MS) (10). This process requires work with highly corrosive chemicals, it is time-consuming and the results are strongly dependent on the working experience of the analyst. The process is not able to provide information about the homogeneity of the layer. The results are usually calculated as averages of concentrations measured on the obverse and reverse side of the steel sheet sample. A common alternative is the use of energy-dispersive or wavelength-dispersive X-ray fluorescence spektrometry (ED XRF, WD XRF). Serious problems can be caused if the analyzed element is contained in both the substrate and the

surface layer. In order to construct reliable calibration models, a high number of substrate matrix matched calibration standards is necessary and the quality of the results strongly depends on the variability of the steel and coating composition. There is often a need to create several separate material specific calibrations.

The third part deals with a quantitative analysis of Cr deposited in a several nanometer-thick layer on the surface of a Zn-based anticorrosive layer on top of Cr-containing steel sheets. The LIBS was supposed to provide an advantage in terms of speed and cost of analysis. The possibility to develop a method using single calibration for more steel types without the negative influence of the composition of the base material on the measured results was also assumed.

In order to optimize the measurement and calibration conditions of the LIBS spectrometer, 5 real samples of steel sheets with anticorrosive surface treatment (S1 - S5) were used. A 25 μm anti-corrosion Zn layer contained on its surface an ultra-thin layer of Cr of a thickness of several nanometers. The thickness of this layer was variable and greatly dependent on the sample preparation process. The Cr concentration in the surface layer of the calibration standards was determined using the lagging method in the industrial laboratory that provided and worked on the samples in the GLP (Good Laboratory Practice) system. Concetration of Cr was determined 11 – 21 $mg.m^{-2}$. Another set of 4 samples (V1 - V4) was first analyzed in the same GLP laboratory using the standard ED XRF method and these samples were subsequently used to verify the proposed LIBS method.

The following parameters were optimized: diameter of analytical point (200; 400; 500 μm with energy of laser beam 130 mJ), laser beam energy (110; 130, 140 mJ with diameter of analytical point 400 μm), and the single or double pulse mode (85; 90 and 100 mJ laser bem energy with diameter of analytical point 400 μm) of the LIBS spectrometer. The fixed experiment parameters were set as follows: 21 μm entrance slit, pulse delay (DP mode) 7 μs, number of analytical points 4, and number of pulses per analytical point 1.Subsequently, a set of calibration standards was repeatedly measured under different analytical conditions, and the concentration-intensity of the analytical line (the so-called c-I curve) was constructed (Fig 7-9).

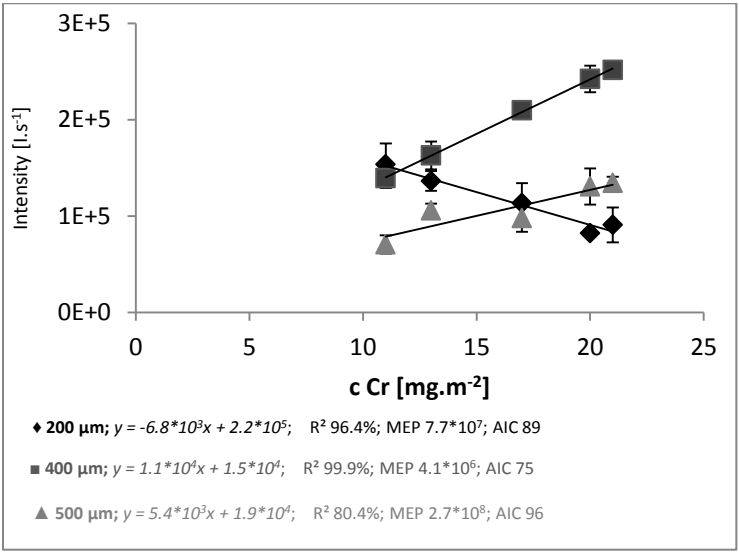

Fig 7 - c-I curves measured for the variable diameter of the analytical point (SP mode)

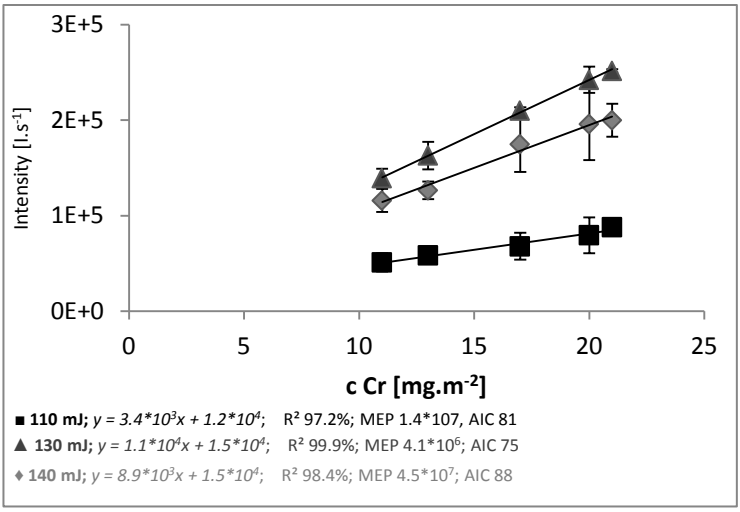

Fig 8 - c-I curves measured for variable laser energy (SP mode)

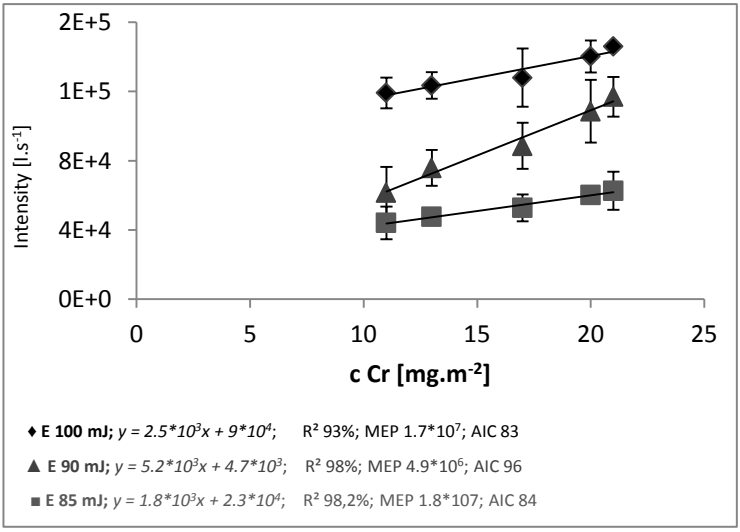

Fig 9 - c-I curves measured for variable laser energy (DP mode)

The calibration dependence shows a good linearity and the RSD values in this case ranged from 0.6 to 8.7%. The detection limit (LOD) was determined according to the 3 σ / s, where σ represents the standard deviation of the intensity calculated from the 12 repeated measurements of the lowest calibration sample performed under optimal conditions and s is the calibration curve directive. The calculated LOD value was 0,7 $mg.m^{-2}$. From a technological point of view, the quantitative analysis of Cr at concentrations below 0,7 $mg.m^{-2}$ in this type of sample has no practical significance and the metrological parameters of the proposed LIBS are fully satisfactory for practical use.

As can be seen from graph 7, when using a focal spot diameter of 200 μm and corresponding fluence of 413.8 J/cm^2, a c-I curve with a negative slope was obtained. The highest intensities of the Cr analytical line were measured for a sample with the lowest Cr content in the surface layer and vice versa. The phenomenon could be explained by the unique relationship between Cr content in the surface layer and the total mass of ablated material, which is strongly dependent on the value of the focal spot diameter. To verify the above-mentioned assumption, we carried out an inspection of the ablation craters using an optical microscopy and mechanical profilometer.

Sharp borders of circular craters with a diameter partly exceeding the set value of the focal spot diameter and the irregular darker area representing heat-affected zone (HAZ) (Fig. 10). The size of HAZ was determined as the longest possible line of the zone and the line perpendicular to the first

one. The measured HAZ lengths are shown in the upper left corner of each image. For samples with a different content of Cr in the surface layer, the dimensions of HAZs are similar when the focal spot diameter of 400 µm (fluence of 103.5 J/cm^2) was used (the observed differences did not exceed the value of the typical experimental error). In the case of the 200 µm focal spot diameter, the size of HAZ is inversely related to the Cr surface concentration. The diameter of HAZ in the sample with a Cr concentration of 11 mg/m^2 was approximately 600 µm and around 300 µm in the sample with 21 mg/ m^2.

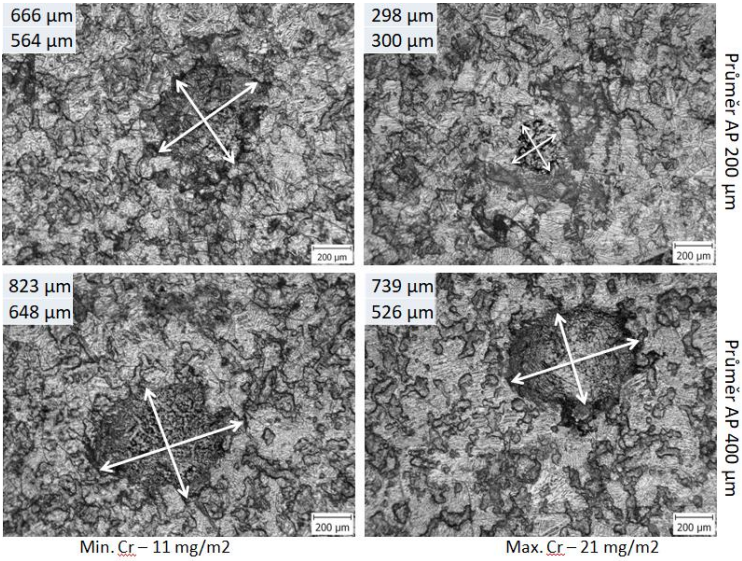

Fig 10 - Picture from optical microscope for sheets with concentrations of 11 and 21 mg.m^{-2}

Profiles of HAZ and ablation craters were also studied using a mechanical profilometer. Typical profiles are shown in Figs. 11 and 12. It is apparent that the sample surface itself shows a high roughness. The beginning of the HAZ is topologically reflected by an abrupt profile decrease of 100–150 nm, without a dependence on the LIBS setting and the sample type. Depth profiles of ablation craters as such are strongly dependent on the used LIBS parameters and on the Cr content. For a focal spot diameter of 200 μm, the depths of craters are positively correlated with the Cr concentration. A crater depth of 1200 nm was at the highest concentration of 21 mg/m^2, while it was only 800 nm at the lowest concentration of 11 mg/m^2.

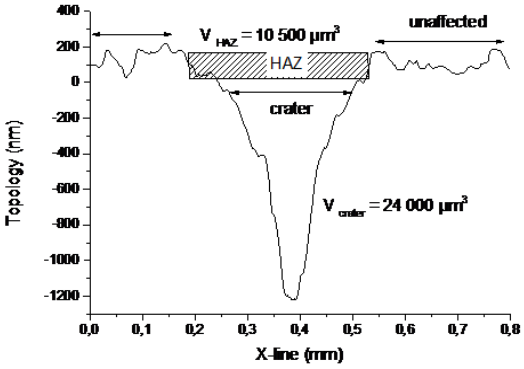

Fig. 11 - Crater profile for sample S5 - diameter of analytical point 200 μm

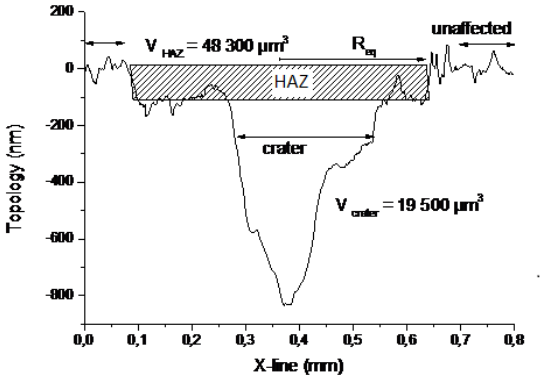

Fig. 12 - Crater profile for sample S1 - diameter of analytical point 200 µm

The profile of craters was also changing as the Cr concentration increased, with the shape of the profile becoming more symmetrical. The relationship between the ablated volume of the sample and the Cr concentration has an inverse character.

In order to verify the functionality of the proposed LIBS method, four steel sheet samples with different types of surface modification and surface concentration of Cr were measured. The results of the LIBS analysis were compared with the ED XRF results obtained from an industrial laboratory working under GLP. Data summarized in Table 7 represent arithmetic means and standard deviations calculated from three (ED XRF), respectively, four (LIBS) repeated measurements of particular samples.

Table 7 - Results of LIBS and ED XRF analysis of unknown samples

Sample	LIBS [mg.m^{-2}]	ED XRF [mg.m^{-2}]	R [%]
V1	21,95 ± 0,7	21,54 ± 0,7	101
V2	18,77 ± 1,5	18,92 ± 0,2	99,2
V3	13,68 ± 1,4	13,66 ± 0,5	100
V4	< LOD	0,82 ± 0,3	-

Conclusion

The dissertation thesis is focused on the quantitative elemental analysis of samples in the form of a thin layer using laser-induced breakdown spectrometry (LIBS). The aim of the thesis was to create methodologies that will allow practical application of this technique. The main objective of the thesis was divided into three partial objectives, which focused mainly on the optimization of experimental conditions and the preparation of samples for analysis, since both factors significantly influence not only the course of the analysis but also the accuracy and correctness of the experiment results.

The first partial aim of this dissertation thesis was focused on the verification of the possibility of using laser-induced breakdown spectrometry for the quantitative analysis of light but hardly excitable elements present in the organic matrix of powdered samples transferred to the thin layer. Specific fulfillment of this objective was achieved by

analyzing samples of organic pigments with declared fluorine content, which were sputtered by brush on an adhesive tape. In this part several factors influencing the analysis were considered - the influence of the sample form and the atmosphere in the ablation chamber and optimization of the experimental conditions. Samples of organic pigments were prepared in two analyzing forms - as a thin layer on the tape and pressed pellets. For both types of sample, the analysis conditions were optimized, the calibration standards were measured, and then the calibration curves were constructed. Higher linearity showed for the calibration built for samples prepared in the form of pellets. The results measured for thin films on the tape showed not only a lower linearity but also higher RSD values. We assume that the reason was the different affinity of the individual samples used as calibration standards for the used tape. Furthermore, the influence of the atmosphere in the ablation chamber was monitored, static air and a dynamic helium and argon atmosphere were tested. In each atmosphere type, calibration standards in both forms were measured. Measuring in a helium atmosphere, there was a significant background reduction and increased fluorine line intensity; on the contrary, the results of the analysis in air and in the argon atmosphere were almost comparable. For the above reasons, the helium atmosphere was evaluated as optimal for fluorine analysis in organic pigments. It is obvious that in the case of this type of sample analysis, the most suitable form of sample is pellet and subsequent analysis in a helium atmosphere. In this particular case, the deposition of thin-film of samples on the adhesive tape appears to be inappropriate due to the small amount of captured material and the possible influence of different physical properties of

the calibration standards and samples. The process for preparing a powder sample in the form of pellets can be used in routine fluorine analysis in solid samples at concentrations above 1 wt. % F.

Based on the obtained results, LIBS spectrometry is a method suitable for direct analysis of F in powder samples without the need of decomposition of the sample. The preparation of the powder sample into the thin-film form brings considerable savings not only to the material, but also to the preparation time and the space required for the storage of the samples. However, it is necessary to take into account the properties of the sample and it is desirable that both the calibration standards and the analyzed samples have the same adhesion. The advantage of the developed method of fluorine determination using a LIBS spectrometer is its simplicity and speed. The advantage of the developed method of fluorine determination using a LIBS spectrometer is its simplicity and speed. The detection limit is relatively high but sufficient for some types of applications (analysis of dental cements, pigments and other materials).

The second part of the dissertation thesis was to verify the possibility of elemental analysis of small volumes of liquid samples deposited in the form of a thin layer on a solid support using a LIBS spectrometer. Practical implementation of this sub-goal was carried out within the framework of the development of a methodology for determining Cd in samples of jewelry leachates. First, composing the surface layer of 13 samples of cheap Cd high quality jewelry was analyzed by ED XRF. These samples were leached in model acidic and alkaline sweat, the resulting leachates were deposited on a

solid support and analyzed by LIBS. Several factors influencing the analysis were considered in this part of the thesis - the choice of a suitable solid carrier, the volume of the solution applied to the solid carrier and the optimization of the measurement conditions. As best suited, based on the SBR value, a carrier made from paper-based paper has been selected which has a suitable degree of water absorption. Subsequently, the volume of the leachate applied to the carrier was optimized. The volume of 20 μl was evaluated as the most appropriate. Experimental conditions were then optimized. Under optimal conditions, calibration standards with known Cd content were measured. The detection limit was calculated using the 3σ / s concept. The determined value for the acidicsweat was 0,08 $mg.l^{-1}$ Cd and for the alkaline sweat 0,06 $mg.l^{-1}$. The results obtained provided information on the mobility of the toxic element and were used in the process of assessing the health risks of the analyzed jewelry. The Cd concentration values measured in the surface layer of jewelry markedly exceeded the allowed limits in the EU or USA. Analysis of the leachates suggests that an amount of Cd is released in the acidic sweat roughly five times higher than in alkaline sweat. The relationship between the surface composition of the samples and the amount of Cd released into the artificial sweat was not clearly demonstrated. The low bioavailability of Cd in dermal exposure together with a small amount of Cd released from the surface layer of jewelry leads to the conclusion that neither the long-term use of these jewelry does not pose a significant health risk from the non-carcinogenic toxic effects of Cd because the maximum amount of released Cd of the analyzed jewelry is about 0, 5% of acceptable daily intake.

LIBS can provide several benefits in this type of analysis and enable its use in laboratories which are not equipped with solution analysis techniques or when long-term storage of the sample is required. By applying a small sample volume on a solid carrier, it is possible to eliminate the space required for storing samples after drying. In the case of a well-designed methodology, it is possible to achieve results that are comparable to the results of the solution techniques. This method of sample preparation can minimize the effect of the matrix, reduce the LOD, the analysis time and the amount of sample.

The third goal was focused to verify the possibility of quantitative analysis of the elements which forming the thin anticorrosive layer of steel sheets using LIBS. Practical fulfillment of the partial target was done on the basis of the quantitative LIBS analysis Cr in the thin anticorrosion zinc layer on the steel sheets that also contained Cr. In this part of the thesis the influence of the experimental conditions on the results of the analysis was evaluated. During the optimization of the LIBS spectrometer parameters it was found that the surface layer of the steel sheets strongly influences the interaction of the laser beam with the sample and the subsequent ablation process, especially the amount of ablated material. The diameter of the analytical point and energy of the laser beam were evaluated as the most important parameters. Calibration standards were analyzed under various conditions, calibration curves were then constructed, and based on their statistical parameters, optimal conditions for the determination of Cr in the surface layer of unknown samples were selected. The limit of detection was determined

(0.7 mg $Cr.m^{-2}$). At optimization it was found that at smaller analytical point diameter (200 μm) and under certain laser beam energy values, into plasma is not transfer only of the surface anticorrosive layer, but also of the material of the steel sheet itself. The matrix effect associated with the ablation of the underlying material caused the calibration curve constructed under such experimental conditions to have a negative value of the directive.

The standard procedure for preparing a similar type of sample for analysis is based on wet pathway where the surface layer is etched by acidictreatment and the resulting solution is analyzed by a suitable solution method. This procedure is demanding both in time and in material terms. In the case of inappropriately selected conditions, a thicker layer may be etching. This process does not provide information about the homogeneity of the surface layer. The proposed analysis procedure using LIBS spectrometry is very fast, but the sensitivity and range of calibration strongly depends on the appropriate conditions of analysis. Another advantage of the proposed method is the possibility of routine analysis in operation with minimal cost and operator demands. The proposed method provides results that are in good agreement with the results obtained using the ED XRF method, which is currently being used as part of the quality control process of this type of production. The great advantage of LIBS spectrometry in this case is that no individual calibration is required for each type of steel sheet, which, in the case of ED XRF, is intended to eliminate the interferences caused by the variable Cr concentration in the sheet material.

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