Determination of Fluorine in Organic Pigments with the Use of Laser Induced Breakdown Spectroscopy

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ABSTRACT

The aim of this work was to develop a methodology for the determination of fluorine in real samples of organic Pigment Yellow 154. Although several methods are successfully used for determining of fluorine, most of the methods require digestion of the sample. Unfortunately, transferring of fluorine into the solution is frequently not quantitative. It is therefore appropriate to use a method for the analysis of solid samples. A suitable method is laser-induced breakdown spectrometry (LIBS). Samples were measured in air, helium and argon atmosphere in the form of pellets and with a thin layer on the tape. Suitable modification appears as compressed samples to form of pellets, and the ablation chamber filled with helium. The limit of detection was determined as F 0.538% (w / w). The proposed method was successfully applied to the determination of F concentration in a real sample of organic pigment.

1. 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 exacting a sample preparation step. 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 with 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].

The difficulty of F determination follows from its ability to form complexes which are rarely decomposable. The most commonly used methods for the determination of F are ion selective electrode, ion chromatography or isotachophoresis [2,3,4]. The afore-mentioned methods require converting of the solid sample into a solution, where F is present in an ionic form. The transfer of the sample into the solution is often extremely difficult and tedious. Molecular absorption spectrometry with a continuous source is another suitable method for an analysis of F. This method unfortunately requires a high homogeneity in the sample. Gleisner et al. [5] determined the total and soluble F in toothpaste. The method is based on the molecular absorption of gallium mono-fluoride (GaF), with the use of a commercially available high-resolution continuum source atomic absorption spectrometer (HR-CS MAS). The limit of detection was 30 $\mu g.g^{-1}$. The results for the total fluorine were compared with a modified conventional headspace gas chromatographic procedure. The accuracy and precision of the two procedures were comparable, but the proposed procedure was much less labour-intensive and faster than the chromatography. Another possibility for direct analysis of F in solid samples is the use of X-ray fluorescence spectrometry (XRF) and LIBS. Expensive wavelength-dispersive systems are usually needed to analyse F with the use of XRF. A suitable preparation of the sample is

necessary for a quantitative analysis of F with XRF. A study of An et al. [6] was carried out to assess the applicability of WD-XRF in the determination of soil fluorine. This method worked well and was able to determine the extent of contamination of F in soil without previous extraction steps. The limits of detection and quantification were calculated as 1.62 and 5.39 mg F in the absolute mass term. An interesting alternative to the afore-mentioned methods is LIBS. This technique allows for a rapid qualitative and quantitative analysis with minimal sample preparation.

There is a need during the analysis of F to watch the atmosphere in the ablation chamber. The influence of the helium and argon atmosphere for the sensitivity of analysis is described below. It is generally believed that in determining F, the helium atmosphere in the ablation chamber has the effect of increasing in signal intensity while lowering the spectral background. This is confirmed by several studies. The issue of determination of fluorine in pharmaceutical pellets is the subject of the works of the authors St-Onge et al. [7]. When the analysis is performed in a helium atmosphere, the increase in the signal intensity of the analyte is possible up to eight times. An analysis of F in a helium atmosphere allows for detecting lines of F which are not detectable in the air. The limit of detection of F was 0.264 % F (w/w). Similarly, pellets containing F and Cl were analysed in the work of Asimellis et al. [8]. The pellets were placed in an evacuated ablation chamber and helium was supplied. Reproducible results have been obtained for a concentration down to 0.03% F (w/w). A similar effect has been described for argon atmosphere in the work of the authors Williamson et al. [9], which is devoted to an analysis of halons. The analytical line of F is typically located at a wavelength of 685.6 nm, but after filling the chamber with argon, F was also measured at a wavelength of 811.4, 840.8 and 842.5 nm.

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.

2. EXPERIMENTAL

2.1 Sample preparation

Samples of organic pigments from Heubach Research Centre Ltd. were analysed. Pigments were prepared by a diazotization of the individual active components: aniline and trifluoromethylaniline. Particular samples of pigments were milled in a rotary grinder to achieve optimum particle size distribution. A set of 8 real samples was used to optimize the conditions and calibration of the spectrometer . The concentration range of F in these samples declared by the pigment producer was 0-14% F (w/w). The optimized method was used for the analysis of two real samples of unknown F concentration. Theoretical concentrations of F in these samples were calculated from the stoichiometry of the chemical reaction describing the pigment production process. The reaction is shown in Fig. 1.
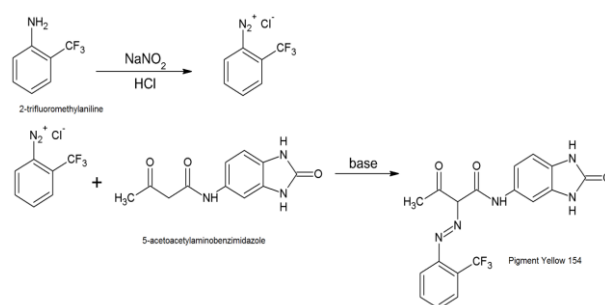

Figure 1: Reaction of production Pigment Yellow 154

Samples were prepared for LIBS analysis in two directly analysable forms. For preparing pellets, samples were dispensed into the crimping head using a manual hydraulic press (diameter 15 mm, height 5 mm). The pressure used was 195 bar. The second applied sample preparation method was the deposition of the thin layer of pigment on the surface of adhesive tape. This sample preparation minimizes clogging of the optical system of the spectrometer during the analysis. The sample was transferred by plastic spoon on the surface of commercially available single-sided adhesive tape and spread over the entire surface with a metal spatula and a soft brush. This procedure has proven itself already in previously published work [10, 11].

3. INSTRUMENTATION

We used a commercially available, fully automated LIBS spectrometer LEA-S500, for the analysis. This spectrometer uses a two-pulse nanosecond Nd:YAG laser operating in a co-linear arrangement. The energy pulse may be optimized in the range of 80-150 mJ. The delay between two consecutive pulses can be adjusted from 0 to 20 microseconds. The scanned wavelength range of the spectrometer is from 170 to 800 nm. Detailed technical parameters of the device were described in our previous work [10, 11]. For analysing the measured data, we used the statistical program ADSTAT version 2.0.

4. METHOD DEVELOPMENT

The intense fluorine spectral lines are located at wavelengths of 683.4; 685.6; 687.02 and 690.2 nm. Primarily due to the high sensitivity and applicability for analytical purposes throughout the calibration range, a line lying at a wavelength of 685.6 nm was evaluated as the best one.

Optimisation of analytical conditions was performed with regard to the signal-to-background ratio (SBR) and the relative standard deviation (RSD) of the analytical line intensity. An evaluation was made of the effect of the laser pulse energy, the delay between pulses (delay), spot size and the flow of inert gas. Optimization of the parameters was performed for the sample with the highest concentration of fluorine, in order to record the possible saturation of the detector signal of the analyte. The width of the entrance slit, the number of laser pulses at one point and the analytic number of the analytical points, or the number of analysed locations on the sample were selected as fixed parameters for which optimal values were chosen based on the authors' experience. The average spectrum of the points obtained from a single measurement was used for the evaluation. To optimize the measurement parameters, we initially selected the initial conditions and subsequently optimized each parameter one by one. The other parameters remained unchanged.
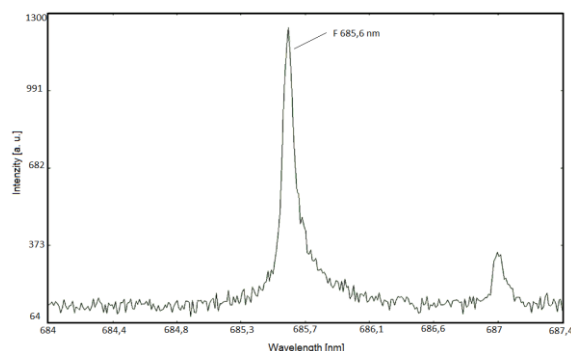

Figure 2: Line of F measured at a wavelength of 685.6 nm in the helium atmosphere

5. RESULTS AND DISCUSSION

5.1 Optimization of the parameters

Table I shows the parameters optimized for the analysis of the tape and pellets The fixed parameters were as follows for the analysis of the tape: the width of the entrance slit 20 μm, the number of laser pulses 1, the analytical values of the fixed points 9. The fixed parameters for the analysis pellets were as follows: the width of the entrance slit 20 μm, the number of laser pulses 4, the number of analysis points 4. The parameters of the delay and the width of the spot were optimized for measurement in air. The measurement in helium and argon atmosphere remained the same.

OPTIMIZED CONDITION	Thin layer on the tape					
	Air	SBR	Helium	SBR	Argon	SBR
ENERGY [MJ]	130	4.06	140	8,89	120	2,70
SPOT [μM]	400	6.21	400	6,21	400	6,21
DELAY [μS]	6	4,03	6	4,03	6	4,03
FLOW OF GAS [L/MIN]	-		3,7	6,17	1,8	2,56
	Pellets					
	Air	SBR	Helium	SBR	Argon	SBR
ENERGY [MJ]	140	2,04	135	7,98	120	2,14
SPOT [μM]	300	2,23	300	2,23	300	2,23
DELAY [μS]	6	7,75	6	7,75	6	7,75
FLOW OF GAS [L/MIN]	-		5,3	7,42	1,5	1,84

Table 1: Optimized conditions of measurement

5.2 Calibration

During the process of the calibration curves construction, each sample with a declared concentration of F was measured three times. These samples were analysed in the form of pellets and as a thin layer on the tape. The evaluation was carried out by integrating the peak area and peak height. The obtained dependencies are listed for both types of sample preparation on the following charts (Fig. 3-6). The obtained coefficients of determination, equations of regression, LOD and statistical parameters are given in Table II. The LOD and statistical characteristics were calculated with the use of the statistical program ADSTAT 2.0, module Calibration - Linear Spine.

As can be seen from the graphs and table, the sample form has the greatest influence on the analysis. Regression parameters were significantly worse for the measurement of thin layers on tape. The results indicate that the pellets are a more suitable form of sample than the thin layers on the tape.

Another important factor is the selected atmosphere in the ablation chamber. It is evident that the changing of the atmosphere in the ablation chamber significantly affected the quality of the calibration. The helium atmosphere was evaluated as advantageous for analysing these samples of organic pigments. The slope of curve and linearity were higher than for the other examined atmospheres. The effect of the argon atmosphere is comparable with the measurement of the air.

The means of evaluation of the measured lines of F has a certain effect on the result of the analysis. Higher linearity is obtained with the use of the peak height. The peak area integration is less accurate for small inequality on the plot of the peak.
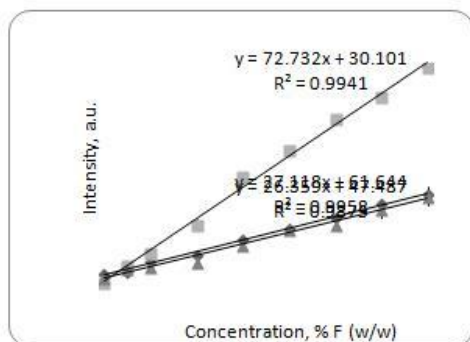
Figure 3: Calibration curve - pellets (peak height)
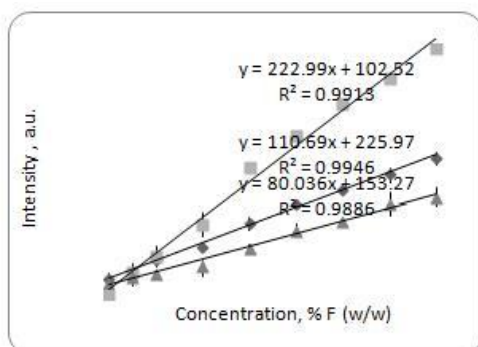▲ - Argon, ♦ - Air, ■ – Helium

Figure 4: Calibration curve - pellets (peak area)
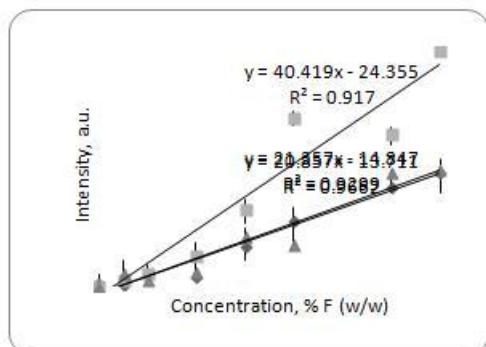▲ - Argon, ♦ - Air, ■ – Helium

Figure 5: Calibration curve - tapes (peak height)
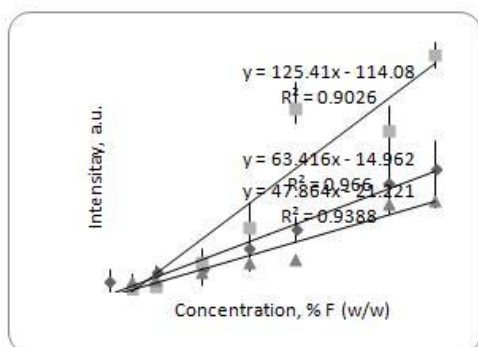▲ - Argon, ♦ - Air, ■ – Helium

Figure 6: Calibration curve - tapes (peak area)
▲ - Argon, ♦ - Air, ■ - Helium

LOD [% F (w/w)]			Basic characteristics of the linear regression			
Form of samples	Atmosphere in ablation chamber	LOD	MEP	AIC	R^2	Regression equation
Pellets - peak height	Air	1,389	579,6	170,8	0,9714	27,118x + 61,644
	Helium	0,538	952,3	185,6	0,9961	72,732x + 30,101
	Argon	1,749	698,2	176,2	0,9633	26,359x + 47,487
Pellets - peak area	Air	1,114	7705	241,1	0,9767	110,69x + 225,97
	Helium	0,6083	15460	260,7	0,9953	222,99x + 102,52
	Argon	2,001	7674	231,9	0,9575	80,036x + 153,27
Tapes - peak height	Air	- *	1023	166,3	0,9209	20,857x - 13,711
	Helium	4,829	4551	202,5	0,9063	40,419x - 24,355
	Argon	4,861	1226	170,8	0,9099	21,357x - 14,847
Tapes - peak area	Air	5,231	15459	230,3	0,8819	63,416x - 14,962
	Helium	- *	6571	266,9	0,8638	125,41x - 114,08
	Argon	3,259	5912	208,7	0,9125	47,864x - 21,221

* The value was not calculated by the program ADSTAT

Table 2: Limits of detection and linear regression parameters for each calibration curve

5.3 Determination of F in unknown samples

Samples of an unknown concentration of F were measured as well as the samples for calibration. The samples were measured three times under optimum conditions in the form of pellets in a helium atmosphere. The measured values are listed in Table III. The measured values of F concentrations were in good agreement with the theoretical concentrations calculated with the use of the reaction scheme depicted in Fig. 1.

	Theoretical conc. (% F)	Measured conc. (%F)	Ratio
Sample A	3.37	3.26 ± 0.3421	0.9674
Sample B	11.30	11.14 ± 0.3073	0.9858

Table 3: Theoretical and measured concentration of F in unknown samples

The results obtained by analysing thin films were not reproducible, based on the small thickness of the layer applied on the tape and due to the lack of homogeneity. The obtained intensity did not correspond with the F concentration in the sample, the different amounts of the sample were ablated. This problem is usually solved with the use of the compare line. This was not possible in our case since the scanned window has a size of 30 nm and this window cannot find any suitable comparative line.

CONCLUSION

The described method allows for the determination of fluorine in samples of Yellow 154 organic pigment with use of a laser-induced breakdown spectroscopy. The best results were obtained for analysing samples in the pellet form and in an atmosphere of helium. The helium atmosphere in the ablation chamber reduces the spectral background and increases the analyte signal intensity. Compression of organic pigments into pellets seems a more appropriate form. The samples analysed in the form of a thin layer on the tape were not suitable for analysis of this type of pigments. The RSD and LOD values in this case are significantly higher than for the samples prepared as pellets. The advantage of the developed method determination of F with the use of the LIBS spectroscopy is its simplicity, speed and accuracy. The knowledge acquired could be used for creating a routine procedure for an analysis of fluorine in solid samples.

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