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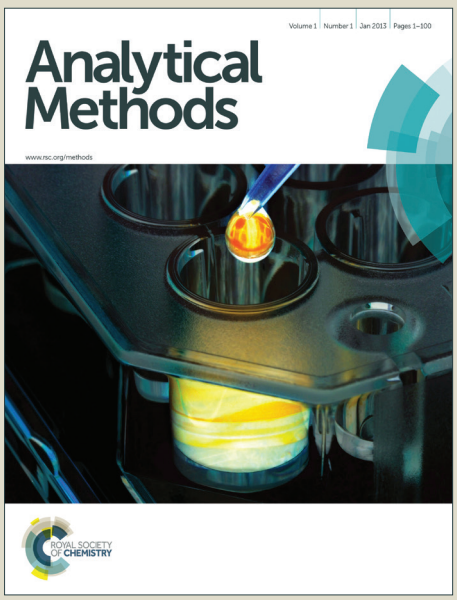

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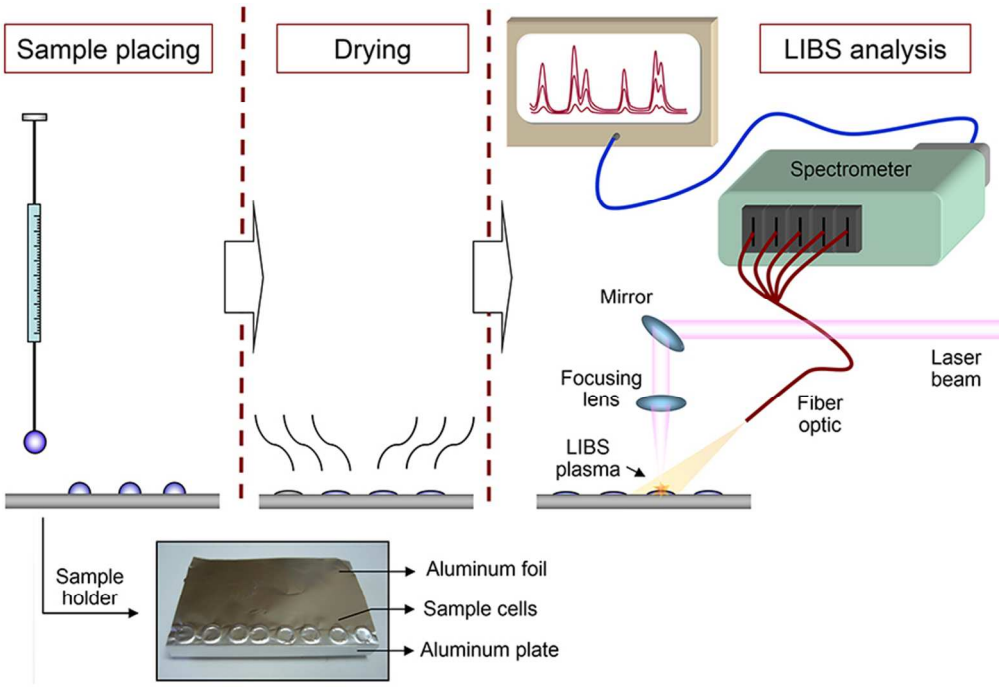

SDME-LIBS as a synergistic association for overcoming LIBS drawback in liquid analysis.
80x55mm (300 x 300 DPI)

HYPHENATION OF SINGLE-DROP MICROEXTRACTION WITH LASER-INDUCED BREAKDOWN SPECTROMETRY FOR TRACE ANALYSIS IN LIQUID SAMPLES: A VIABILITY STUDY†

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† Electronic supplementary information (ESI) available: Further experimental results.

Abstract

In this work, an analytical methodology based on Single Drop Microextraction (SDME) followed by Laser-Induced Breakdown Spectrometry (LIBS) has been tested for trace metals determination in liquid samples. By this method, analytes in the samples were extracted into a small volume of toluene as ammonium pyrroldinedithiocarbamate (APDC) chelates. After that, the analyte-enriched toluene was dried on a solid substrate and, finally, the resulting solid residue was analyzed by LIBS. Analyte extraction by SDME procedure was firstly optimized by using a multivariate optimization approach. Under optimum SDME conditions, analytical figures of merit of the proposed SDME-LIBS methodology were compared to those of the direct LIBS analysis method (i.e., without SDME procedure). An estuarine water certified reference material was analyzed for method trueness evaluation. The results obtained in this study indicate that SDME-LIBS methodology leads to a sensitivity increase

of about 2.0-2.6 times the ones obtained with LIBS. Detection limits of SDME-LIBS decreases accordingly to the obtained sensitivity improvement, reaching values in the range 21-301 μg kg^{-1} for the analytes tested. Measurement repeatability was similar in both SDME-LIBS (13-20% RSD) and LIBS (16-20% RSD) methodologies, being mainly limited by the LIBS experimental setup used in this work for LIBS analysis of liquid samples. The SDME-LIBS analysis of the certified reference material led to recovery values in the range of 96% to 112%.

1 Introduction

Laser-Induced Breakdown Spectrometry (LIBS) is perhaps one of the most versatile techniques for elemental analysis, since it can be applied to a great variety of real-world analytical problems.[1-6] However, in spite of its potential for the analysis of practically any kind of sample, most LIBS applications have been focused on solid samples analysis whereas its applicability to liquid samples has been, in comparison, poorly exploited. The minor interest in LIBS analysis of liquids can be mainly attributed to its inherent experimental drawbacks,[2,7,8] which lead to low sensitivity and precision compared to LIBS analysis of solids or to the analysis of liquids with most conventional spectrometric techniques. Even if numerous LIBS experimental strategies have been developed to solve, or at least to reduce, the experimental drawbacks of LIBS analysis of liquid samples,[9-18] these methodologies still provide analytical results that are, in general, worst than those provided by other well established spectrometric techniques such as ICP-OES.[19]

In spite of its comparatively lower sensitivity, there is still an inherent advantage that could turn LIBS into a very attractive technique for liquid samples analysis compared to the use of conventional techniques; that is the possibility for *in situ* and on-line analysis offered by this technique due to its field-operable and easily automated instrumentation.

A possible way to improve sensitivity and decrease limits of detection in LIBS analysis of liquid samples could be the use of a previous step for analyte enrichment. Liquid Phase Microextraction (LPME) procedures are nowadays extensively used for separation and concentration of both organic and inorganic analytes.[20-22] These novel microextraction methodologies are faster and more easily automatable than conventional extraction procedures and use negligible volume of extraction solvents, which are often hazardous and expensive. Among the different LPME modalities, Single Drop Microextraction (SDME), Dispersive Liquid Liquid Microextraction (DLLME) and Hollow Fibre Liquid Phase Microextraction (HF-LPME) methodologies have been applied to the concentration of inorganic analytes for trace elemental analysis with excellent results.[23-30] The combination of LPME with LIBS could be a promising alternative for trace elemental analysis due to the complementarily of both extraction and detection procedures; LPME usually results in a microvolume of analyte-enriched extraction solvent, which sometimes needs to be subsequently diluted to adequate it (i.e., quantity, chemical or physical properties) to the requirements of the instrumental system used for analysis (e.g., ICP-OES or FAAS). LIBS, however, has proved to be useful for the direct analysis of microvolumes of liquid samples, owing to its ability to interrogate extremely low quantities of material.[31] Therefore, microvolumes of solvent resulting from microextraction procedures could be easily analyzed without the need of previous dilution. An added advantage of this combination could arise from the small dimensions and possibility of automation of both LPME and LIBS instrumentation, which could make LPME-LIBS hyphenation suitable for the future development of portable systems for *in situ* and on-line analysis of liquid samples.

In this work, combination of LIBS with SDME modality has been tested as an analytical methodology aimed to extend the applicability of LIBS to trace elemental analysis of liquid samples, opening a new way of research on LPME-LIBS hyphenation. Here, Single Drop

Microextraction was applied to water samples prior to analyte determination by LIBS, in order to improve the sensitivity of the method. Toluene was used in SDME as extracting solvent of several metals as ammonium pyrrolidinedithiocarbamate (APDC) complexes. SDME procedure was previously optimized by using multivariate analysis. The resulting microvolumes of analyte-enriched solvent were analyzed by LIBS after being dried on an aluminum substrate, as a method for overcoming the experimental difficulties of LIBS analysis of liquids. Analytical figures of merit obtained with both SDME-LIBS and direct LIBS methodologies (*i.e.*, analysis of the water samples by LIBS, after being dried on the aluminum substrate but without previous SDME procedure) are presented and discussed. The proposed methodology was finally tested for determination of several metals in a certified reference material (Estuarine Water, LGC6016).

2 Experimental

2.1 LIBS experimental setup

Fig. 1 shows the LIBS experimental setup used throughout this work for liquid samples analysis. The laser-induced plasmas were generated by focusing a 10 Hz pulsed Nd-YAG laser (model HYL Handy-YAG, Q-switched, Quanta System S.P.A., Varese, Italy), emitting a pulse of energy 180 mJ (pulse width 10 ns FWHM) at 1064 nm, on the sample to analyze. The laser was focused on the sample by a N-BK7 plano-convex lens with 100 mm focal length (model KPX094AR.33, Newport Corporation, Irvine, United States). Plasma emission was collected directly with a five-furcated fiber optic (5x400 μm fiber optic cable, model FC5-UV400-2, Avantes, Apeldoorn, The Netherlands) and was imaged on the entrance slits of a five channel spectrometer with full spectral coverage from 200 nm to 844 nm (model AVS-Rackmount-USB2 housing equipped with five preconfigured AvaSpec-ULS2048-USB2-RM channels, Avantes, Apeldoorn, The Netherlands). A delay system consisting in

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two pulse generators (Digital delay/pulse generator, model DG 535, Stanford Research Systems Inc., Sunnyvale, USA and 1 Hz-50 MHz pulse generator, model PM-5715, Philips Export B.V., Eindhoven, The Netherlands) was used for synchronization of laser firing and data acquisition. Spectra were collected 1.3 μs after the plasma generation (optimum condition), with 1 ms acquisition time (minimum time setting available on the spectrometer).

2.2 Sample preparation

Water samples containing Cr, Mn, Ni, Cu and Zn as target analytes were analyzed by LIBS in two different ways: (i) without applying any previous sample treatment for analyte concentration (*i.e.,* direct LIBS) and (ii) after a microextraction procedure with SDME methodology to separate and concentrate analytes present in the samples (*i.e.,* SDME-LIBS). In both cases, and in order to avoid liquid splashing during LIBS analysis and to enhance LIBS sensitivity and reproducibility, the corresponding liquids (*i.e.,* water sample or analyte-enriched toluene) were converted into solid by drying on an aluminum surface prior to LIBS measurement (i.e., SENLIBS), as already described elsewhere.[31] In direct LIBS, few μL of the water samples were confined into a small cell shaped in an aluminum foil (see Fig. 1). The aluminum foil, placed on an 8 mm thick aluminum plate, was heated by a hot plate to completely evaporate the water. The solid residue was then irradiated with the laser for LIBS analysis.

In SDME-LIBS, metal ions were extracted from the water samples as ammonium pyrrolidinedithiocarbamate (APDC) complexes, using toluene as extraction solvent for SDME. After extraction, few μL of the analyte-enriched toluene were placed on the aluminum foil, were heated by the hot plate to completely evaporate the toluene and, as described above for direct LIBS analysis, were irradiated by the laser for LIBS measurement.

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In both methodologies, the result of the LIBS analysis was the mean of three replicate measurements (*i.e.,* three single laser shots) made on different positions of the same solid residue.

2.2.1 Single Drop Microextraction procedure

For metals extraction by SDME, approximately 9 g of sample was placed in a 20 mL glass vial containing a magnetic stir bar. Solid APDC reagent was added to the vial up to a concentration well in excess of that required to chelate all metals in the solution. Then, the solution pH was adjusted with diluted NH_3 and HCl solutions and, finally, the sample weight was brought to 10 g with deionized water. A microsyringe, containing a known volume of toluene, was clamped above the vial and its needle was immersed into the sample. The plunger was depressed and a microdrop of toluene was exposed to the sample at room temperature for a certain period of time, to allow partition of the analytes between the aqueous phase and the organic droplet. During this time, the solution was continuously stirred with a magnetic stirrer to accelerate the mass transfer process. After extraction, the toluene drop was retracted into the microsyringe and a microvolume of this analyte-enriched solvent was placed on the aluminum foil for LIBS analysis (Figure 1).

2.3 Reagents and solutions

Aqueous calibration standards were prepared by appropriate dilution of a 1000 mg L^{-1} mono-element standard solutions of Cr, Mn, Ni, Cu and Zn (High-purity mono-element standard solutions, Charleston, United Kingdom) in distilled deionized water (18 MΩ cm resistivity). Ammonium pyrrolidinedithiocarbamate (APDC) (Fluka, Buchs, Switzerland) was used as chelating agent. Diluted hydrochloric acid solution, prepared from a Suprapur 30% (w w^{-1}) HCl solution (Merck, Darmstadt, Germany) and diluted ammonia solution, prepared from a

Reagent Grade 32% (w w^{-1}) (in NH_3) solution (Scharlau, Barcelona, Spain) were used for pH adjustment. HPLC grade toluene (Scharlau, Barcelona, Spain) was used as extraction solvent in the microextraction procedure. Estuarine water certified reference material (LGC6016, LGC Deselaeres S.L., Middlesex, United Kingdom) was used for evaluation of method trueness.

2.4 Apparatus

A 25 µL syringe (model 1702, Hamilton, Bonaduz, Switzerland) was used to suspend the toluene microdrop inside the standard/sample solutions in the SDME procedure and to place a microvolume of water sample/extraction solvent on the metallic substrate (*i.e.*, aluminum foil) for LIBS analysis. pH measurements were performed with a pH meter (model micropH 2000, Crison, Alella, Spain). The solutions were stirred with a magnetic stirrer (model 501, Darlab Egara S.L., Barcelona, Spain). A hot plate (model 500 Darlab Egara S.L., Barcelona, Spain) was used to dry the droplets before LIBS analysis.

3 Results and discussion.

3.1 Optimization of SDME experimental parameters

A multivariate approach was employed to optimize the main experimental factors affecting metals extraction. Several factors including pH, APDC concentration, drop volume, extraction time and stirring speed were studied in order to maximize the extraction yield of the SDME procedure. In order to identify the most important experimental factors affecting SDME, among the ones initially considered, a previous screening study (Placket-Burman design) was carried out. After that, significant factors were optimized by means of a Circumscribed Central Composite Design (CCCD). In the screening and optimization studies, the experiments were randomly carried out in order to nullify the effect of extraneous or

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nuisance variables. In both cases, emission signal obtained from LIBS analysis of the resulting extractions was used as the output variable (response) of interest. Statistical software (NemrodW® version 2007, LPRAI, Marseille, France) was used for generation of the experimental design matrices and for data processing.

3.1.1 Screening study

A Plackett-Burman design was used for identification of the significant factors affecting SDME (screening). In this particular type of experimental design, interactions between the different factors are considered to be negligible and, therefore, significant factors can be identified using a limited number of experiments. In this study, a five-factor 12-experiments Plackett–Burman screening design was used. Each factor was represented at two levels, defining the upper and lower limits of the range covered by each factor (see Table 1). Levels chosen for the different factors were based on literature data and preliminary experiments.

Synthetic aqueous solutions containing 1 μg g^{-1} of the analytes were used as samples in all the screening experiments. After the extractions, the resulting analyte-enriched solvents were analyzed by LIBS, evaluating the emission signal obtained for the different analytes.

Fig. S1 in ESI† shows the main effects Pareto charts obtained from the screening experiments. Since microextraction conditions are usually analyte-dependent, a separate screening evaluation was performed for each analyte in order to identify the common significant factors affecting the overall extraction process. Pareto charts in Fig. S1 in ESI† illustrate the order of significance of the variables affecting SDME for the different emission lines evaluated. As can be seen, these charts contain a bar for each factor, with the length of the bar being proportional to the relative influence of that factor on the metal extraction. Those bars that extend over the dashed vertical line indicate factors that are statistically significant at 95% probability. The direction of the bar is related to the "sign" of the effect

produced by that factor. That is, those bars to the right of the origin indicate positive effect in the response when increasing the value of the factor and, on the contrary, those bars to the left indicate negative effect.

As observed from Fig. S1 in ESI,† the screening study provides similar results for all the emission lines evaluated. Drop volume, extraction time and pH can be considered significant factors affecting the extraction with a positive effect, with pH being the most critical parameter. On the other hand, APDC concentration and stirring speed, even if having a slightly positive effect on the response, do not produce any significant impact on extraction. These two factors were, therefore, fixed at their higher level for subsequent extractions (*i.e.*, 1% (w v^{-1}) APDC concentration; 1700 rpm stirring speed), and only drop volume, extraction time and pH were considered for optimization in the following study.

3.1.2 Optimization study

The three main factors identified in the previous screening study were optimized by using a Circumscribed Central Composite Design (CCCD). This experimental design requires 5 levels for each factor: a central level (0), a low level (-1), a high level (+1) and two star points located at ±α (α = 1.682) from the centre of the experimental domain (0). The levels chosen for the three factors considered (*i.e.*, drop volume, extraction time and pH), as well as the location of their start points, are given in Table 2. The design matrix for this CCCD design involved a total of 18 runs. As in the previous screening study, all the experiments were carried out using synthetic solutions containing 1 μg g^{-1} of the target analytes. LIBS signals of the different emission lines were evaluated in order to compare the optimum conditions for extraction of the different analytes and to decide, accordingly, a common optimum conditions for extraction of all of them.

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The results obtained in this study are given in Figs. S2 to S6 in ESI† as response surfaces and contour plots. Each figure shows the results obtained for a different analyte. Graphics (a), (b) and (c) in these figures show the variation of LIBS emission signal as a function of each pair of factors, while keeping fixed the third one at its optimum value. As can be observed from the plots, all response surfaces show maximum points which are, in general, similar for all the analytes evaluated.

Emission signal increases with drop volume to reach a maximum at approximately 7.5 µL. In any case, the use of larger volumes was difficult to handle since the droplet became unstable and easily fell off from the tip of the syringe needle.

Similar behavior was observed for pH, with signal increasing up to pH of approximately 10 and decreasing thereafter. For metal cations extraction, pH plays a crucial role in the formation of the neutral chelates which can be efficiently transferred to the organic phase. Low pH values favor the protonated form of the complexing reagent, therefore limiting chelates formation and, consequently, metals extraction. On the other hand, insoluble hydroxides or soluble ammonia complexes are preferentially formed at high pH values, avoiding the neutral chelates to form and leading also to a decrease in metals extraction.

As expected, increasing the extraction time results in an increase in the total amount of analyte extracted, reaching a maximum at around 10 minutes. Mass transfer is, indeed, a time-dependent process in which transfer rate decreases as the system approach equilibrium.

Due to the similarity between the optima obtained for the different analytes, average values were chosen as the common optimum condition for SDME of all of them. Thus, experimental conditions for extraction were set at pH, 10; drop volume, 7.5 µL; extraction time, 10 min.; APDC concentration, 1% (w v^{-1}) and stirring speed, 1700 rpm.

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3.2 LIBS and SDME-LIBS: analytical figures of merit

In order to assess the analytical capability of SDME-LIBS procedure versus LIBS for the analysis of trace metals in liquid samples, analytical figures of merit (*i.e.*, sensitivity, repeatability and LOD) of both analytical procedures were evaluated and compared. To this end, calibration standards were analyzed by both methods in order to obtain the corresponding calibration graphs: (i) without a previous extraction procedure (direct LIBS analysis of the standards) and (ii) after extraction of the analytes by SDME at optimum conditions. In the former method, calibration was performed by directly analyzing five calibration standards with concentrations of Zn, Mn, Cu and Cr increasing up to 2500 μg kg^{-1} and Ni increasing up to 8000 μg kg^{-1}. In the latter, analytes were extracted from the same number of calibration standard solutions, but with concentrations of Ni, Mn, Cu and Cr increasing up to 1000 μg kg^{-1} and Zn increasing up to 800 μg kg^{-1}. Afterward, the resulting analyte-enriched toluene microdroplets were analyzed by LIBS. In both cases, the experimental procedure for LIBS analysis of the liquids was that described in the experimental section (section 2.2.). That is, 7.5 μL of the calibration standard (direct LIBS analysis) or 7.5 μL of the resulting analyte-enriched toluene (SDME-LIBS analysis) were placed on the aluminum foil, heated to dryness and analyzed by LIBS. In all cases, LIBS analysis was carried out by averaging the LIBS signal obtained from three single laser shots in different positions on the same dried residue. Even if more laser firings could have been possibly performed on the dried residue, this number was chosen in order to completely avoid a possible overlapping of the ablated zones created in the residue by previous laser shots.

Table 3 summarizes the analytical figures of merit obtained by both methods. Here, sensitivity was derived from the slope of the calibration graphs. Repeatability, expressed as RSD, was estimated from the analysis of eight aliquots taken from the same vial of 1 μg g^{-1} calibration standard. For SDME-LIBS procedure, this means from eight extractions, one per

aliquot. LOD calculation was based on 3 times the standard deviation of 10 blank determinations (*i.e.*, deionized water for LIBS and toluene for SDME-LIBS). LIBS signal was found to be linear in the concentration range evaluated for each method.

As expected, the use of a microextraction procedure leads to sensitivity improvement for all the emission lines evaluated. The extent of this improvement can be easily assessed by looking at the enhancement factor in Table 3, which was calculated as the ratio of sensitivities obtained with and without SDME. As can be seen, all enhancement factors were in the range 2.0-2.6, without any appreciable analyte-dependence. Since sensitivity improvement for a given analyte can be directly associated with its extraction efficiency into the organic phase, this result probably indicates that all metal-APDC chelates were similarly extracted by the applied SDME procedure. As a matter of example, Figs. 2a and 2b show the signal increase observed for ZnII (202.548 nm) and NiI (352.454 nm) emission lines, respectively, when a 1 μg g^{-1} calibration standard is analyzed by SDME-LIBS. In general terms, it seems that SDME-LIBS procedure results in analytical sensitivities that are approximately 2.3 times the ones obtained with LIBS (mean value over the five emission lines evaluated).

Repeatability was found to be in the range 13% - 20% RSD, without any clear trend with respect to analyte or analytical procedure. Repeatability of both analytical procedures was observed to be mainly limited by the current LIBS experimental setup for liquid samples analysis. It could be seen, by visual inspection, that the solid residue resulting from the liquid sample drying was not homogeneously distributed over the aluminum foil, thus leading to low repeatability even from replicate measurements performed on different positions on the same sample residue.

Detection limits were all below 0.5 mg kg^{-1} for both LIBS and SDME-LIBS methodologies. Without the use of SDME, LOD values ranged from 463 μg kg^{-1} for NiI (352.454nm) to 49

µg kg^{-1} for ZnII (202.548 nm). These values were reduced to 189 µg kg^{-1} and 21 µg kg^{-1} respectively, with the use of SDME. As can be observed from Table 3, relative LODs obtained for the different emission lines were in good agreement with the corresponding enhancement factor, with the exception of Mn. This fact, as well as the comparatively high limit of detection obtained for this element, can be probably due to the presence of Mn as an impurity in the aluminum foil used as solid substrate, which leads to poor reproducibility of the blank measurements. Without considering this element, it can be seen from Table 3 that the use of SDME-LIBS results in LOD values that are approximately 2.5 times lower than those obtained with direct LIBS.

3.3 Analysis of a certified reference material

Method trueness was evaluated from the analysis of a certified reference material (estuarine water). Trueness test was only carried out with the proposed SDME-LIBS procedure, since certified concentrations were all below the quantification limits obtained for direct LIBS analysis. Table 4 shows the results of the estuarine water analysis. Here, percent recovery was used as estimation of method trueness. As observed, the results obtained with SDME-LIBS methodology were in good agreement with the certified values, with recovery values ranging from 96% to 112%.

4 Conclusions

The results obtained in this preliminary study demonstrate that LIBS detection preceded by a single drop microextraction procedure for analyte enrichment allows performing liquid samples analysis with higher sensitivity than direct LIBS. Therefore, SDME-LIBS could be considered a synergistic association for improving LIBS sensitivity drawback in liquid analysis. With the proposed SDME-LIBS analytical methodology, approximately 2.3 fold

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sensitivity enhancement and 2.5 fold LOD improvement were obtained, compared to the direct LIBS analysis of the liquid samples (i.e., without SDME procedure). Under optimum SDME conditions, SDME-LIBS methodology lead to LOD values in the range of 21-301 µg kg^{-1} for the analytes tested, being LIBS analysis performed in almost single pulse mode. However, even if the use of SDME, as LPME modality chosen in this work, has been proved to improve sensitivity of direct LIBS analysis, the obtained results can not be considered completely satisfactory for the proposed goal and should be only considered as a starting point for exploring the potentialities of this hyphenated techniques for trace elemental analysis of liquid samples. Therefore, much more research work in this field should be done in the future, aimed to improve the capability of the method.

On one hand, sensitivity could be further improved with the use of different reagents for metal chelation and extraction, with the use of different microextraction methodologies such as DLLME or HF-LPME, which could lead to enrichment factors higher than those obtained with SDME, or even with the application of double pulse LIBS configuration for LIBS analysis instead of single pulse LIBS, which has been demonstrated to be an efficient strategy for LIBS signal enhancement.[18] On the other hand, the precision of the method, currently limited by the low repeatability of LIBS measurements, could be also improved by using alternative strategies for deposition of the microdroplets on the aluminum substrate, leading to predictable and homogeneous deposits morphology, or by optimizing the LIBS system optical setup, allowing the integration of a higher number of laser shots on the solid residue without the risk of overlapping between the several ablated zones. Last but not least, future studies should also be focused on the possibility to convert the three currently separated, but independently automatable processes (i.e., microextraction, sample deposition/drying and LIBS analysis) in a fully automated SDME-LIBS analytical procedure for stand-alone operation, useful for in-situ trace metals analysis of liquid samples.

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Figures

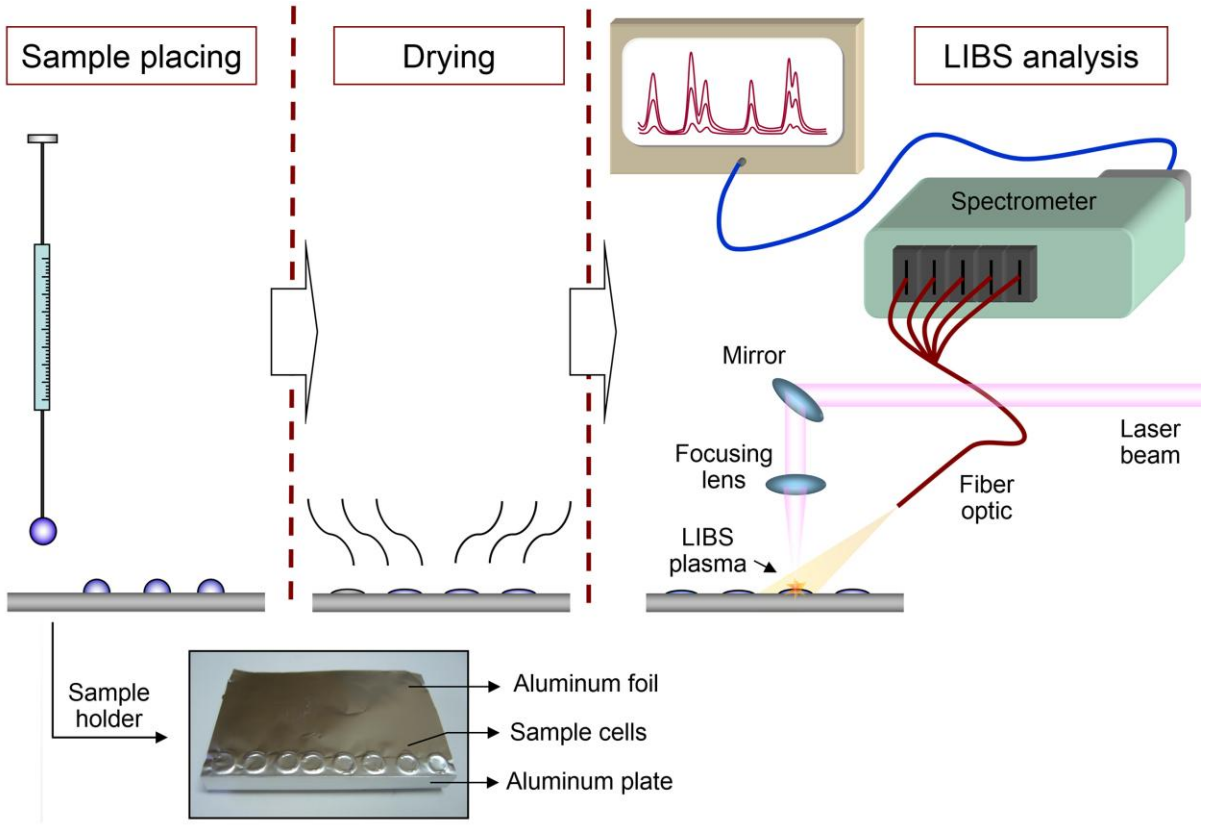

Fig. 1 LIBS experimental setup used in the analysis of liquid samples.

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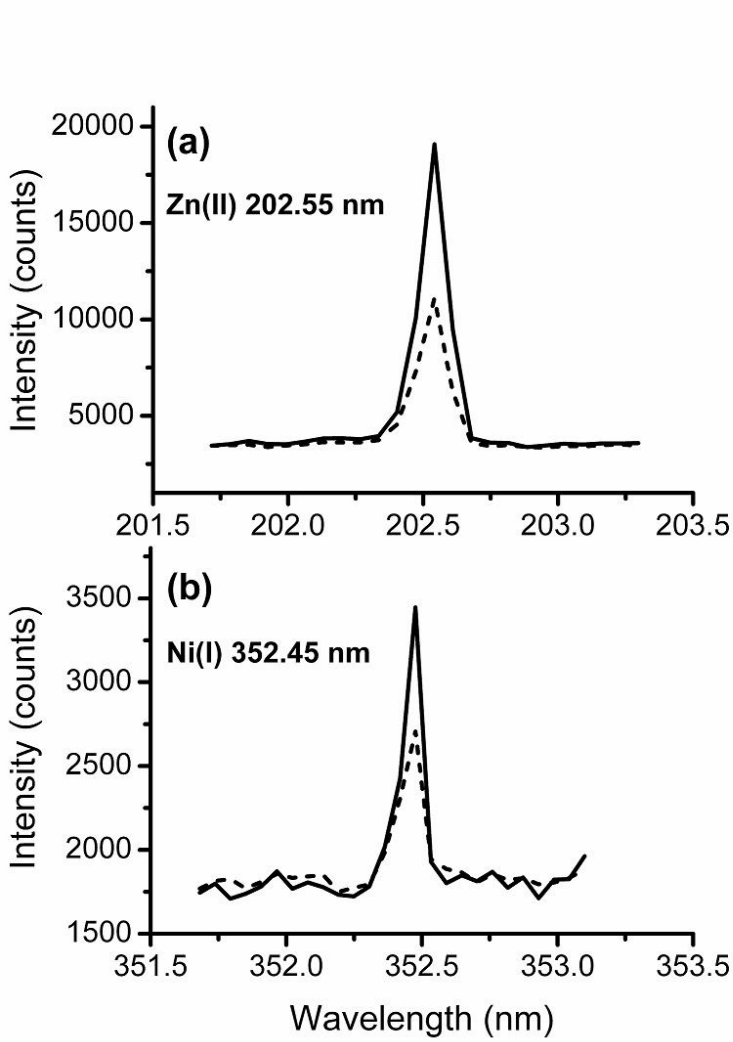

Fig. 2 LIBS signals obtained for (a) ZnII (202.548 nm) and (b) NiI (352.454 nm) emission lines when a 1 μg g^{-1} standard solution is analyzed by LIBS (dash line) and SDME-LIBS (solid line) methodologies.

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Tables

Table 1 Experimental factors and levels of the Plackett-Burman design.

Experimental factor	Level	
	Low (-1)	High (+1)
[APDC] (%, w v^{-1})	0.5	1
Drop volume (μL)	5	7.5
pH	5	10
Strirring speed (r.p.m.)	850	1700
Extraction time (min)	5	10

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Table 2 Experimental factors and levels of the Circumscribed Central Composite design (CCCD).

	Level			Star points (α=1.682)	
Experimental factor	Low (-1)	Central (0)	High (+1)	-α	+α
Drop volume (µL)	2.5	5	7.5	0.8	9.2
pH	6	8	10	4.6	11.4
Extraction time (min)	4	7	10	1.9	12.1

Table 3 Analytical figures of merit obtained with LIBS and SDME-LIBS analytical methodologies.

Emission line (nm)	LIBS			SDME-LIBS			Enhancement Factor[c]	LOD Ratio[d]
	Sensitivity[a] (cts kg μg^{-1})	RSD[b] (%)	LOD (μg kg^{-1})	Sensitivity[a] (cts kg μg^{-1})	RSD[b] (%)	LOD (μg kg^{-1})		
ZnII (202.548)	19.5±1.1	17	49	51±2	13	21	2.6	2.3
MnII (259.373)	29±4	16	427	59±4	15	301	2.1	1.4
CuI (324.754)	26±5	20	141	55±5	18	54	2.2	2.6
NiI (352.454)	1.64±0.10	16	463	3.3±0.3	20	189	2.0	2.4
CrI (357.869)	7.0±1.0	19	143	17.6±1.2	16	50	2.5	2.9

[a] Uncertainty expressed as standard deviation.
[b] Evaluated from the analysis of eight aliquots taken from the same vial of 1 μg g^{-1} calibration standard.
[c] Calculated as the ratio of sensitivities obtained with SDME-LIBS and LIBS.
[d] Calculated as the ratio of LODs obtained with LIBS and SDME-LIBS.

Table 4 Analysis of LGC6016 certified reference material (estuarine water) by SDME-LIBS.

		SDME-LIBS	
Emission line (nm)	Certified value[a]	Found value[a]	Recovery value (%)
ZnII (202.548)	75±2	84±21	112±25
MnII (259.373)	976±31	1026±215	105±21
CuI (324.754)	190±4	183±35	96±19
NiI (352.454)	186±3	n.q. [b]	n.q. [b]

[a] In μg L^{-1} ± confidence interval at 95%. [b] not quantified.