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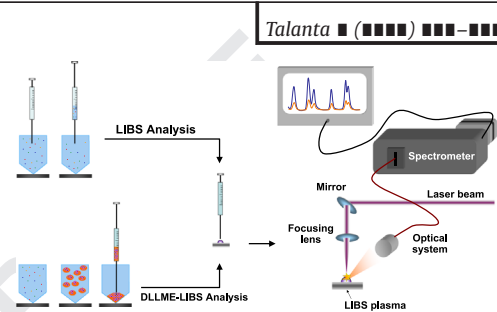
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Graphical Abstract

Dispersive liquid–liquid microextraction for metals enrichment: A useful strategy for improving sensitivity of laser-induced breakdown spectroscopy in liquid samples analysis

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Highlights

- An analytical methodology based on DLLME-LIBS combination is presented.
- This method is aimed to improve sensitivity of LIBS in liquids analysis.
- DLLME-LIBS resulted more efficient than SDME-LIBS for enhancing LIBS sensitivity.



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Short communication

Dispersive liquid–liquid microextraction for metals enrichment: A useful strategy for improving sensitivity of laser-induced breakdown spectroscopy in liquid samples analysis

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ABSTRACT

A rapid and efficient Dispersive Liquid–Liquid Microextraction (DLLME) followed by Laser-Induced Breakdown Spectroscopy detection (LIBS) was evaluated for simultaneous determination of Cr, Cu, Mn, Ni and Zn in water samples. Metals in the samples were extracted with tetrachloromethane as pyrrolidinedithiocarbamate (APDC) complexes, using vortex agitation to achieve dispersion of the extractant solvent. Several DLLME experimental factors affecting extraction efficiency were optimized with a multivariate approach. Under optimum DLLME conditions, DLLME-LIBS method was found to be of about 4.0–5.5 times more sensitive than LIBS, achieving limits of detection of about 3.7–5.6 times lower. To assess accuracy of the proposed DLLME-LIBS procedure, a certified reference material of estuarine water was analyzed.

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1. Introduction

Modern trends in analytical chemistry are toward the development of new miniaturized and field-operable instrumentation allowing *in-situ* and on-line analysis, and on the use of hyphenated techniques having complementary capabilities, leading to analytical methodologies able to both separation and quantification of analytes in complex matrices. New trends also involve continuous advances for improving sensitivity and specificity, reducing sample size and toxic reagent consumption, and achieving lower time and costs per analysis [1,2].

Some of the potentials of Laser-Induced Breakdown Spectroscopy technique (LIBS) fulfill the trends of modern analytical chemistry [3,4]. LIBS allows fast multi-elemental analysis of very small quantities of sample. Moreover, due to the striking technological improvements in lasers and spectrometers during the last decades, a number of portable and easily automatable commercial LIBS instruments are currently available in market [5–7], which makes this technique especially suitable for field measurement. However, in spite of its numerous advantages, the low sensitivity of LIBS when compared with other well established atomic spectrometric techniques constitutes its most

important limitation for (ultra) trace elemental analysis, in special for liquid samples analysis [8–11].

Several strategies, aimed to improve the analytical capabilities of LIBS when applied to liquid samples analysis, have been developed in recent years [12–16]. These strategies, however, even if greatly contribute to enhance LIBS sensitivity in liquid analysis, are still insufficient to make LIBS competitive with other atomic spectrometric techniques for (ultra) trace elemental determination.

One common way to increase sensitivity and decrease limits of detection in analytical chemistry is analyte separation and enrichment, thereby increasing the concentration of an analyte, or analytes, to a level compatible with an analytical technique. Conventional liquid–liquid extraction is the most popular in routine sample preparation, but it uses a great amount of solvent, it is tedious, time consuming and difficult to automate. Nowadays, there are novel microextraction techniques that are faster and more easily automatable than conventional extraction procedures and use negligible volume of extractant solvents, which are often hazardous and expensive [17]. As a consequence, traditional liquid–liquid extraction procedures are being increasingly replaced by Liquid Phase Microextraction (LPME) methodologies, which are now widely used for analyte separation and enrichment. In the field of elemental analysis, LPME has been extensively used in combination with atomic spectrometric techniques such as Electrothermal Atomic Absorption Spectrometry (ETAAS), Flame Atomic Absorption Spectrometry (FAAS), Inductively Coupled Plasma Optic Emission Spectrometry (ICP-OES), or X-ray Fluorescence spectrometry (XRF) for trace metal determination in a great variety of

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samples [18–20]. However, it was not till 2013 than Aguirre et al. introduced the idea of combining LPME with LIBS [21]. These authors suggested LPME-LIBS as being a synergistic association for overcoming the well known sensitivity limitation of LIBS for liquid samples analysis, proving LIBS technique to be able to afford the analysis of microamounts of liquids resulting from a microextraction procedure. Recently, the LPME-LIBS combination proposal was experimentally tested by the same authors, using Single Drop Microextraction (SDME) as LPME procedure for metals extraction prior to LIBS detection (SDME-LIBS) [22]. Preliminary results obtained from this research work showed that sensitivity of LIBS analysis of liquid samples improved due to the use of a previous SDME procedure, proving the viability of this association. Such results were considered by the authors as a starting point for future research aimed to improve the analytical capabilities of LPME-LIBS hyphenation, with the final goal focused on the future development of a fully automated system useful for *in-situ* trace elemental analysis of liquid samples.

A possible way for improving the analytical potential of this association is the use of alternative and more efficient LPME procedures. Dispersive Liquid-Liquid Microextraction (DLLME) is a microextraction methodology based on the dispersion of few microliters of an organic extractant solvent in the aqueous sample, which can be accomplished by several ways, such as the use of a disperser solvent or vortex agitation. After extraction, phase separation is achieved by centrifugation and analytes in the organic phase can be determined by the detection technique [23–25]. Since many fine droplets of organic solvent are dispersed throughout the aqueous solution, the very large interfacial area makes DLLME process to be very efficient and quick, being considered easier to handle and faster than SDME.

In this work, combination of LIBS with DLLME procedure for analyte enrichment was evaluated for the first time. Tetrachloromethane (CCl_4) was used as extractant solvent for DLLME of several metals as pyrrolidinedithiocarbamate (APDC) complexes, using vortex agitation to achieve dispersion of the extractant solvent. Multivariate analysis was employed for optimization of the experimental factors affecting metals extraction. Under optimum DLLME conditions, sensitivity of DLLME-LIBS methodology in the analysis of model aqueous samples was tested and compared with that achieved by LIBS. Accuracy of the proposed method was evaluated from the analysis of a Certified Reference Material (estuarine water).

2. Experimental

2.1. LIBS experimental setup

Technical details on the LIBS system used in this work have been previously reported [21]. As shown in Fig. 1, the system basically consists of a 10 Hz pulsed Nd:YAG laser (model HYL Handy-YAG, Q-switched, Quanta System S.P.A., Varese, Italy) for plasma creation, a 100 mm focal length plano-convex lens for laser focusing, a five channel spectrometer (model AvaSpec-2048-SPU, 200 nm–800 nm coverage, Avantes, Eerbeek, The Netherlands) coupled to a five-furcated optical fiber ($5 \times 400 \mu\text{m}$ fiber optic cable, model FC5-UV400-2, Avantes) for plasma emission detection and a delay system consisting of two pulse generators (a Digital delay/pulse generator, model DG 535, Stanford Research Systems Inc., Sunnyvale, USA and 1–50 MHz pulse/function generator, model 8116 A, Hewlett Packard/Agilent Technologies, Santa Clara, USA). In this work, the laser was operated in single pulse mode, emitting at its fundamental wavelength (*i.e.*, 1064 nm) with energy 130 mJ per pulse. Data were acquired 1.3 μs after the laser firing, using 1 ms acquisition time. CrI (357.869 nm), CuI (324.754 nm), MnII (259.373 nm), NiI (352.454 nm) and ZnII (202.548 nm) were the emission lines evaluated.

2.2. Sample preparation and analysis

Since the main aim of the work was to evaluate the possible sensitivity improvement of DLLME-LIBS hyphenation over LIBS in the analysis of liquid matrices, both LIBS and DLLME-LIBS methodologies were tested, in parallel, to the determination of different analytes in water samples. For LIBS analysis, the aqueous samples were converted into solid by drying on an aluminum substrate, as already described elsewhere [21]. In order to do this, 10 μL of standard (or sample) aqueous solution were transferred to an aluminum foil, where the solution was confined into a small circular cell (3.2 mm diameter) to avoid liquid spreading. After that, the aluminum foil, placed on a thicker (8 mm) aluminum plate, was heated by a hot plate (model 500 Darlab Egara S.L., Barcelona, Spain) to completely evaporate the water. The remaining solid residue was then analyzed by LIBS. In all cases, the result of LIBS analysis was the mean of three replicate measurements

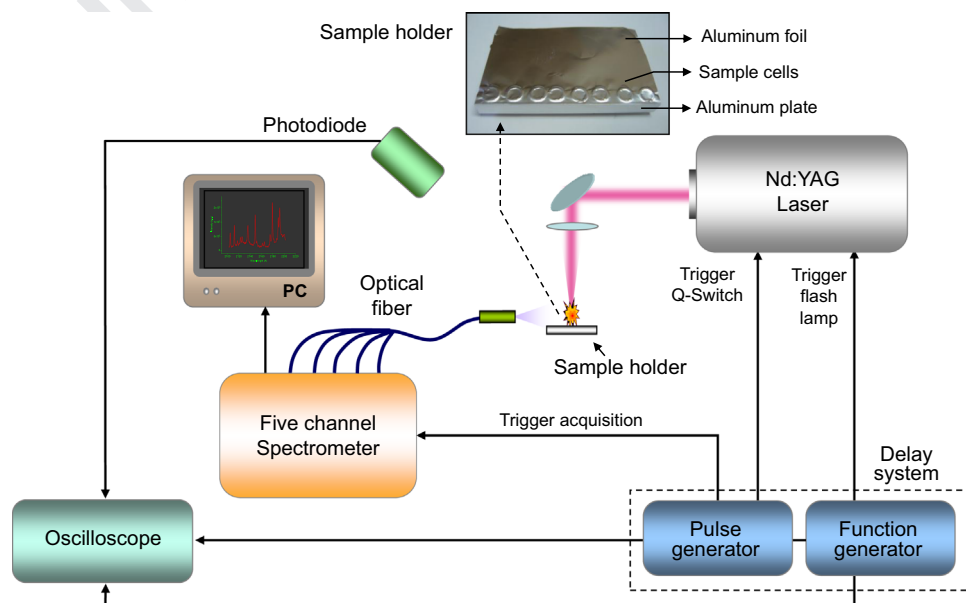


Fig. 1. LIBS experimental system used in the analysis of liquid samples.

(*i.e.*, three single laser shots) made on different positions of the same solid residue.

On the other hand, for DLLME-LIBS analysis, analytes were firstly extracted from the aqueous samples and concentrated in a small volume of extractant solvent (*i.e.*, tetrachloromethane) using the DLLME procedure. After that, 10 μL of the analyte-enriched extractant solvent (*i.e.*, the same volume than that used for direct LIBS analysis of the aqueous samples) were transferred to the aluminum foil, heated by the hot plate to completely evaporate the tetrachloromethane and, as described above for direct LIBS analysis, irradiated by the laser for LIBS measurement.

For DLLME procedure, 9 g of aqueous sample was placed in a 12 mL conical centrifuge tube. An excess of chelating agent (solid ammonium pyrrolidinedithiocarbamate (APDC)) was added to the solution and pH was adjusted with diluted hydrochloric acid and ammonia solutions. pH measurements were carried out using a pH meter (model micropH 2000, Crison Instruments S. A., Barcelona, Spain). Additionally, sodium chloride was added to this mixture up to a concentration of 5% w w⁻¹ in order to evaluate the influence of the medium ionic strength on extraction (*i.e.*, salting out phenomenon [23,25]. See Sections 2.5 and 3.1 below). The sample weight was then brought to 10 g with deionized water. The resulting metal-APDC complexes were extracted from the aqueous solution by injecting few μL of extractant solvent (tetrachloromethane), shaking vigorously the mixture with a vortex agitator in order to obtain a cloudy solution, and finally achieving phase separation by centrifugation (model 2690/5 centrifuge, Nahita). The analyte-enriched organic phase, settled at the bottom of the conical tube, was then retrieved with a microsyringe (model 1702, Hamilton, Bonaduz, Switzerland) for LIBS analysis.

2.3. Reagent and solutions

Aqueous calibration standards containing all analytes under study were prepared by appropriate dilution of 1000 mg L⁻¹ mono-element standard solutions of Cr, Cu, Mn, Ni and Zn (High-Purity mono-element standard solutions, Charleston, United Kingdom) in distilled deionized water (18 M Ω cm resistivity). Solid ammonium pyrrolidinedithiocarbamate (APDC) (Sigma-Aldrich Co., St. Louis, United States) was used as chelating agent. Diluted hydrochloric acid solution and diluted ammonia solution, used for pH adjustment, were prepared from Suprapur 30% (w w⁻¹) HCl solution (Merck, Darmstadt, Germany) and Reagent Grade 32% (w w⁻¹) (in NH₃) solution (Scharlau, Barcelona, Spain), respectively. Tetrachloromethane (Panreac, Barcelona, Spain) was used as extractant solvent in the microextraction procedure. Sodium chloride (Scharlau, Barcelona, Spain) was added to the samples for evaluation of salting out phenomenon. Estuarine water certified reference material (LGC6016, LGC Deselaeres S.L., Middlesex, United Kingdom) was used for evaluation of method accuracy.

2.4. Optimization of DLLME experimental parameters

DLLME procedure was optimized by using a multivariate analysis consisting of two steps: (i) a Plackett–Burman design to assess the significance of the experimental factors affecting DLLME (*i.e.*, extraction time, pH, extractant volume, concentration of chelating agent and salt concentration) followed by (ii) a Circumscribed Central Composite Design (CCCD) to optimize those factors identified as significant in the step (i). Both the screening study using Plackett–Burman design and the optimization with CCCD involved 12 microextraction experiments each, (in CCCD, these 12 experiments included three replicate experiments in the central point for estimation of the experimental variance). In both studies, the experiments were randomly performed in order to minimize

the effect of uncontrolled variables. A standard solution containing 0.5 $\mu\text{g g}^{-1}$ of the analytes was used for all the extractions. LIBS emission signal obtained in the analysis of the organic solvent resulting from the microextraction procedures was always used as response variable. Data were evaluated with the NemrodW statistical software (NemrodW[®] version 2007, LPRAI, Marseille, France). Since optimum microextraction conditions is usually analyte-dependent, a separate data evaluation was performed for each analyte (*i.e.*, for each emission line evaluated) in both screening and optimization studies.

3. Results and discussion

3.1. DLLME procedure: screening and optimization studies

Table 1 shows the experimental factors and levels considered in the Plackett–Burman design. The result obtained from this screening for DLLME of Zn is shown in Fig. 2a, represented as a main effects Pareto chart. Pareto charts obtained for all analytes under study can be seen in Fig S1 (Appendix A). In these Pareto charts, the bar lengths are proportional to the relative influence of that factor on the metal extraction, and the direction of the bar is related to the “sign” of the effect produced by that factor (*i.e.*, bars to the right of the origin indicate positive effect in the response when increasing the value of the factor and bars to the left indicate negative effect). The charts also include two vertical reference lines corresponding to the 95% confidence level. A bar exceeding a reference line indicates the corresponding factor to be significant for the extraction.

As observed in Fig. 2a, pH and extractant volume can be considered significant factors and extraction time, concentration of chelating agent and salt concentration (*i.e.*, salting out phenomenon) do not have significant impact on the microextraction. Similar results were obtained for most target analytes (Fig. S1). Therefore, extraction time and salt concentration were fixed at their lower level (*i.e.*, extraction time: 1 min; NaCl concentration: 0%), concentration of chelating agent was fixed at its higher level (*i.e.*, APDC concentration: 0.5%) and, under these conditions, pH and extractant volume were optimized by using a CCCD.

Table 2 shows the different level values chosen in the CCCD. An example of the results obtained in this study is given in Fig. 2b, corresponding to the extraction of Zn. In this figure, LIBS emission signal variation versus pH and extractant volume is represented as both a contour plot and a response surface. The same graphics are included in Figs. S2–S6 (Appendix A) for all analytes under study.

As observed from Fig. 2b, extractant solvent volume reaches an optimum value for extraction of Zn at 106 μL . Increasing the extractant volume in DLLME leads to an increase in the quantity of tiny droplets dispersed throughout the aqueous solution, therefore increasing the interfacial contact area for analyte diffusion and, consequently, the extraction efficiency. On the other hand, increasing the volume of extractant solvent also leads to an increase in the sedimented phase, and therefore to a decrease in

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

| Experimental factor | Level | |
|-------------------------------------|----------|-----------|
| | Low (-1) | High (+1) |
| pH | 4 | 10 |
| Extraction time (min) | 1 | 3 |
| [NaCl] (% w w ⁻¹) | 0 | 5 |
| [APDC] (% w w ⁻¹) | 0.25 | 0.50 |
| Extractant volume (μL) | 50 | 100 |

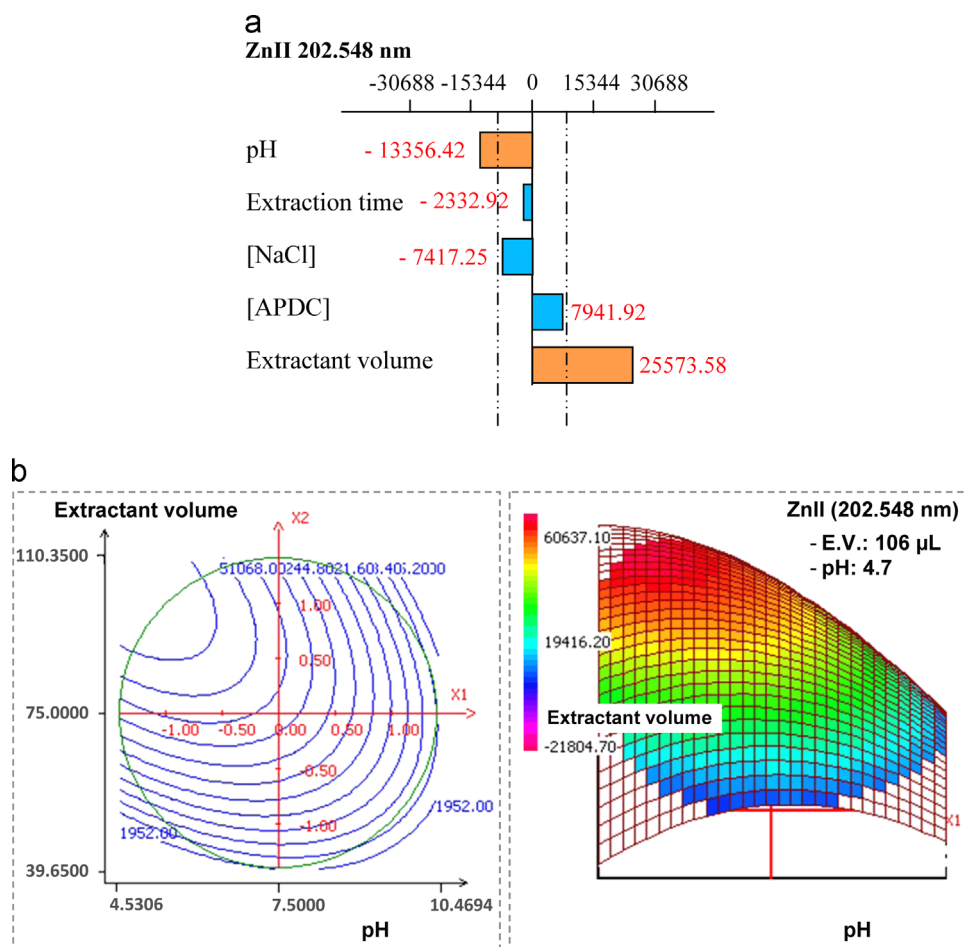


Fig. 2. Optimization of DLLME of zinc (ZnII (202.548 nm) emission line): (a) Pareto chart from Plackett-Burman design and (b) contour plot and response surface from circumscribed central composite design.

Table 2

Experimental factors and levels of the Circumscribed Central Composite Design (CCCD).

| Experimental factor | Level | | | Star points ($\alpha=1.4142$) | |
|-------------------------------------|----------|-------------|-----------|---------------------------------|-----------|
| | Low (-1) | Central (0) | High (+1) | $-\alpha$ | $+\alpha$ |
| pH | 5.6 | 7.5 | 9.4 | 4.5 | 10.5 |
| Extractant volume (μL) | 50 | 75 | 100 | 110 | 40 |

the analyte concentration in the organic phase [24,26]. The observed optimum value for extractant solvent volume could therefore be explained as a consequence of these two competitive effects.

The optimum pH value for extraction of Zn is obtained at 4.7 (Fig. 2b). Separation of metals ions by DLLME involves the previous formation of metal complexes with enough hydrophobicity to be extracted in the organic phase and, as already well known, pH plays an essential role in metal complexes formation. Increasing pH leads to an increase in the formation of uncharged metal complexes that are readily extracted into organic phase. However, further increase in solution pH can also lead to the formation of stable hydroxo complexes of the metal ions, thus decreasing extraction efficiency.

As can be seen from Figs. S2 to S6, no substantial differences were obtained for the different analytes studied, with optimum

extractant volumes ranging from 93 μL (Mn) to 106 μL (Zn) and optimum pH values ranging from 4.1 (Mn) to 6.2 (Cr). Therefore, average values were chosen as the common pH and extractant volume optimum condition for simultaneous extraction of all the analytes from the samples.

In summary, optimum experimental conditions for DLLME procedure were set at: extraction time, 1 min; pH, 5.5; extractant volume, 100 μL ; APDC concentration, 0.5% and salt concentration, 0%.

It is worth mentioning here that this optimization study was performed on model aqueous solutions prepared in deionized water. Therefore, possible matrix effects influencing DLLME procedure due, for instance, to competitive chelate formation with concomitant metals, or to preferential diffusion of such concomitant metals chelates into the organic phase, were not considered. However, in order to evaluate possible matrix effects, estuarine water certified reference material containing Ca, Mg, K and Na, among others, as majority elements [27], was successfully analyzed by using the proposed DLLME procedure (see Section 3.2. below). In any case, for application of the proposed DLLME procedure to more complicated aqueous samples matrices (e.g., residual water); an exhaustive matrix effect study should be carried out.

3.2. Comparison of LIBS with DLLME-LIBS methodologies for analysis of aqueous samples

In order to compare the analytical capabilities of both LIBS and DLLME-LIBS methodologies, six-point calibration curves were constructed in both cases. For LIBS analysis, aqueous calibration

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

| Emission line (nm) | LIBS | | DLLME-LIBS | | Enhancement factor ^b | LOD ratio ^c |
|--------------------|---|-------------------------------|---|-------------------------------|---------------------------------|------------------------|
| | Sensitivity ^a (cts Kg μg^{-1}) | LOD ($\mu\text{g Kg}^{-1}$) | Sensitivity ^a (cts Kg μg^{-1}) | LOD ($\mu\text{g Kg}^{-1}$) | | |
| CrI (357.869) | 4.1 \pm 0.7 | 184 | 19 \pm 3 | 41 | 4.8 | 4.5 |
| CuI (324.754) | 12.8 \pm 1.4 | 84 | 52 \pm 2 | 23 | 4.0 | 3.7 |
| MnII (259.373) | 13.0 \pm 1.0 | 276 | 71 \pm 5 | 49 | 5.5 | 5.6 |
| NiI (352.454) | 1.5 \pm 0.3 | 475 | 7.1 \pm 0.8 | 107 | 4.7 | 4.4 |
| ZnII (202.548) | 13 \pm 2 | 90 | 71 \pm 6 | 18 | 5.5 | 5.0 |

^a Uncertainty expressed as standard deviation.

^b Calculated as the ratio of sensitivity values obtained with DLLME-LIBS and LIBS.

^c Calculated as the ratio of LOD values obtained with LIBS and DLLME-LIBS

standards with analyte concentration increasing up to 1 $\mu\text{g g}^{-1}$ were used. These standards were directly analyzed by LIBS as described in the experimental part of this work (Section 2.2). For DLLME-LIBS analysis, concentration of the standards was reduced to a half of the used for LIBS analysis, being 0.5 $\mu\text{g g}^{-1}$ the maximum concentration used. In this case, analytes were first extracted from the aqueous standards under optimum DLLME conditions. Afterward, the resulting analyte-enriched organics were analyzed by LIBS (Section 2.2). In both methodologies, LIBS signal corresponding to the different emission lines evaluated was found to be linear in the concentration range studied.

Sensitivity values obtained from these calibration graphs for the different analytes are shown in Table 3. In this Table, limit of detection (LOD) values, based on 3 times the standard deviation of 10 blank determinations (*i.e.*, deionized water for LIBS and tetrachloromethane for DLLME-LIBS), are also included. As observed, DLLME-LIBS methodology improves sensitivity compared to LIBS. Sensitivity improvement was very similar for all analytes studies, as can be seen from the enhancement factors calculated (Table 3). From these data, it can be concluded that, on average, sensitivity of the DLLME-LIBS methodology was about 5-fold higher than that provided by LIBS. This fact led to a decrease of about 4.5-fold, on average, in the detection limits obtained with DLLME-LIBS.

As already mentioned in the introductory part of this work (Section 1), a different liquid phase microextraction procedure (*i.e.*, Single Drop Microextraction (SDME)) was previously evaluated by the authors as a possible way to increase sensitivity of LIBS analysis of liquid samples [22]. Preliminary results obtained in that work shown that sensitivity of the tested SDME-LIBS methodology led to about 2.0–2.6 times improvement, depending on the analyte, compared with direct LIBS analysis of the samples. Consequently, LOD values were found to be 1.4–2.9 times lower in SDME-LIBS analysis. As can be seen from the results obtained in this work, the use of DLLME procedure leads to further improvements in sensitivity and detection limits compared with SDME method, proving that DLLME-LIBS is a more efficient combination than SDME-LIBS for enhancing the analytical capability of LIBS analysis of liquid samples.

Accuracy of the DLLME-LIBS method was evaluated from the analysis of a certified reference material (estuarine water). Table 4 shows the results obtained in this study. As can be seen, concentration values obtained with DLLME-LIBS match the certified concentration intervals for all the elements studied. Recovery values were in the range of 81–109%, with the lower and upper limits corresponding to recoveries obtained for Zn and Ni, respectively. For both elements, certified concentrations in the CRM were below their respective theoretical limits of quantification (*i.e.*, 357 $\mu\text{g Kg}^{-1}$ for Ni and 60 $\mu\text{g Kg}^{-1}$ for Zn). Nevertheless, an acceptable recovery value was obtained for Ni. On the other hand, Zn was, by far, the analyte with the worst recovery. However, as stated in the certificate of measurement provided by the material

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

| Emission line (nm) | Certified value ^a | DLLME-LIBS | |
|--------------------|------------------------------|--------------------------|--------------------|
| | | Found value ^a | Recovery value (%) |
| CuI (324.754) | 190 \pm 4 | 204 \pm 40 | 107 \pm 21 |
| MnII (259.373) | 976 \pm 31 | 906 \pm 157 | 93 \pm 16 |
| NiI (352.454) | 186 \pm 3 | 202 \pm 29 | 109 \pm 16 |
| ZnII (202.548) | 55 ^b | 45 \pm 10 | 81 \pm 20 |

^a In $\mu\text{g L}^{-1} \pm$ confidence interval at 95%.

^b Indicative value. In $\mu\text{g L}^{-1}$.

supplier [27], concentration of Zn was not a certified value in this CRM, because the last stability test performed by the supplier pointed out that Zn concentration had decrease since the release of the material in July 2000. Therefore, Zn concentration in the recently distributed CRM is marked as indicative value rather than certified.

4. Conclusions

This work presents a new advance in the use of analytical methodologies based on LPME-LIBS combination for trace elemental analysis of liquid samples. In previous preliminary studies, hyphenation of LIBS with Single Drop Microextraction (SDME-LIBS) was shown to improve approximately 2.3 times both sensitivity and LOD of LIBS [22]. The work presented here demonstrates that further improvement can be achieved just by using a more efficient microextraction procedure. The use of DLLME-LIBS methodology leads to sensitivity and LOD enhancements of about 5.0 and 4.5-fold, respectively, that of LIBS, therefore proving DLLME to be approximately twice more efficient than SDME for LPME-LIBS hyphenation.

The results shown with DLLME reassert the viability of the LPME-LIBS hyphenation as a way to extend the applicability of LIBS to trace elemental analysis of liquid samples and, in addition, demonstrate the possibility of improvement of analytical methodologies based on this combination. However, these results should be only considered as a small step forward the pursued goal. That is, the development of a LPME-LIBS based analytical methodology useful for multielement determination at trace level, with on-line capabilities for liquid samples analysis. The use of different extracting solvents and chelating agents with this or others microextraction procedures, the improvement of LIBS measurement reproducibility and the development of possible strategies for automation of the whole analytical process are all possible ways for further improving the method performance, which are currently under study in our laboratory.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2014.07.090>.

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