Dispersive liquid–liquid microextraction combined with laser-induced breakdown spectrometry and inductively coupled plasma optical emission spectrometry to elemental analysis

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ABSTRACT

In this paper, two analytical methodologies based on the combination of dispersive liquid–liquid microextraction with inductively coupled plasma optical emission spectrometry and laser-induced breakdown spectrometry, respectively, were evaluated for simultaneous preconcentration and detection of Cd, Co, Ni, Pb and Zn. The microextraction procedure was based on the injection of appropriate quantities of 1-undecanol and methanol into the sample solution containing the complexes formed between metal ions and 1-(2-pyridylazo) 2-naphtol (PAN). The main experimental factors affecting the complexation and the extraction of metals (pH, PAN concentration, salt addition and extractant solvent and disperser solvent volume) were optimized using a multivariate analysis consisting of two steps: a Plackett-Burman design followed by a Circumscribed Central Composite Design (CCCD). Under optimum microextraction conditions, the analytical features of the proposed methodologies were assessed. Accuracy was evaluated by analyzing two certified reference materials, yielding results in agreement with the certified values. Both methodologies were applied to the analysis of a number of beverage samples.

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1. Introduction

Inductively coupled plasma optical emission spectrometry (ICP-OES), flame atomic absorption (FAAS), electrothermal atomic absorption spectrometry (ETAAS), molecular spectrophotometry and other atomic and molecular conventional instrumental techniques have all been extensively used to quantify metals in many samples. Laser induced breakdown spectroscopy (LIBS), even if not yet considered a conventional instrumental technique, has also been used for elemental analysis since its introduction, providing a significant number of applications [1–4].

Irrespective of the recent advancements in analytical instrumentation, extraction and preconcentration procedures prior to the detection step are still necessary, either for decreasing detection limits or for eliminating matrix effects [5–13].

The use of procedures resulting in low consumption of reagents and, consequently, in drastically reducing residue discharge, has been an attractive field of research for the development of analytical methods tied to environmental-friendly analytical chemistry [14–16]. As a consequence, traditional extraction procedures are being increasingly replaced by microextraction methodologies, which are nowadays widely used for analyte separation and enrichment. Among others, dispersive liquid–liquid microextraction (DLLME) is a liquid–liquid extraction procedure that allows for a low consumption and discharge of chemical reagents. It is based on the mixing of an extractant solvent and a disperser solvent (with high miscibility in both aqueous and organic media). The quick addition of an appropriate mixture of these two solvents into the sample leads to the formation of a great number of small droplets of extractant solvent, which remain dispersed in the aqueous solution. As a result, analyte is extracted to the extractant solvent droplets (generally hydrophobic organic compounds), which is then separated from the aqueous phase by centrifugation. Some advantages of DLLME are operation easiness, quickness, low cost and high recovery factors and preconcentration [17–21].

Different conventional atomic spectrometric techniques have been already combined with DLLME for trace-metals analysis. Among them, ETAAS has been, by far, the most widely used due to its requirement of microamounts of sample for analysis [12]. In contrast, few papers propose the combination of this microextraction technique with ICP-OES, probably due to the intrinsic difficulties of this analysis method of organic matrices [22–25].

LIBS, as ETAAS, only needs a very low quantity of sample for analysis. Moreover, this technique presents some other added advantages, such as quick multi-elemental determination and possibility for *in situ* analysis. This technique can be used for direct analysis of gases, liquids and

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solids. However, its low sensitivity when compared to other atomic spectrometry techniques constitutes the most important limitation for (ultra) trace elemental analysis, especially for liquid samples [1,26,27]. Aguirre et al. [26] proposed the combination of LIBS with microextraction techniques as a method to extend the applicability of LIBS to trace elemental analysis in liquid samples. The capability of the technique to analyze microvolumes of sample was tested by evaluating two different experimental strategies for LIBS analysis: (i) direct laser irradiation of microdroplets suspended from the tip of a microsyringe and (ii) analysis by laser irradiation of microdroplets dried on metallic substrates (surface-enhanced LIBS – SENLIBS). Jesus et al. [28], using the combination of DLLME and LIBS, developed a method for the determination of V and Mo. The proposed method was applied to the analysis of different real samples (i.e., pharmaceutical, multimineral formulation, soil and mineral water) and a beef liver reference material.

In this context, the aim of this work was, on the one hand, to propose a DLLME method based on the use of 1-undecanol (extractant solvent) and methanol (disperser solvent) for extraction of metal ions as 1-(2-pyridylazo) 2-naphtol (PAN) complexes and, on the other hand, to evaluate the combination of the proposed DLLME procedure with ICP-OES and LIBS techniques (i.e., DLLME-ICP-OES and DLLME-LIBS) for trace elemental analysis of liquids samples. To this end, the main experimental factors affecting the DLLME of several metals (Cd, Co, Ni, Pb and Zn) were optimized using a multivariate analysis. Under optimum DLLME conditions, analytical figures of merit of the DLLME-ICP-OES and DLLME-LIBS combinations were estimated. Accuracy of the proposed methods was evaluated from the analysis of two Certified Reference Materials (estuarine water and hard drinking water). Finally, several beverage samples (drinking water, alcoholic beverages and soft drink) were analyzed in order to assess the applicability of the methods to real samples analysis.

2. Material and Methods

2.1. Instrumentation

A pH meter (model Basic 20+, Crison Instrument, Barcelona, Spain) with a combined glass electrode was used for pH measurements. A centrifuge (model 2690/5, Nahita Centrifuges, Beriain, Spain) was used to accelerate the phase separation. The disperser and extractant solvent mixture was added to the sample using a 1000 μL syringe (Gastight®, Hamilton Co, Reno, Nevada, USA).

An inductively coupled plasma-optical emission spectrometer (model 720-ES, Agilent Technologies, Melbourne, Victoria, Australia) was used for ICP-OES measurements. Table 1 shows the instrumental parameters used and the emission lines evaluated with this system.

For LIBS analysis, the laser-induced plasmas were generated in air at atmospheric pressure 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 beam was focused on the micro samples by a biconvex lens with a 100 mm focal length. Plasma emission was collected and sent, through a five-furcated optical fiber (5×400 μm fiber optic cable, model FC5-UV400-2, Avantes, Eerbeek, Netherlands), to the entrance slit of a five-channel spectrometer (model AvaSpec-2048-SPU, Avantes, Eerbeek, Netherlands) where plasma's light was spectrally resolved and detected. A delay system consisting of two pulse generators (digital delay/pulse generator, model DG 535, Stanford Research Systems, Inc. and 1 MHz–50 MHz pulse/function generator, model 8116A, Hewlett Packard/Agilent Technologies, Santa Clara, USA) was used for synchronization of laser firing and data acquisition. Spectra were collected 1.3 μs after the plasma generation, with 1 ms acquisition time. Cd I (214.44 nm), Ni I (352.54 nm) and Zn I (202.55 nm) were the emission lines evaluated with this system. LIBS spectra were processed using the spectroscopic software LIBS++®, v. 3.12.4.1., IPCF-CNR (Pisa, Italy).

2.2. Reagents and solutions

All solutions were prepared with analytical grade chemicals and deionized water obtained from Milli-Q system (Millipore, Bedford, USA). A 2.3×10^{-3} mol L^{-1} PAN stock solution was prepared by dissolving appropriate amounts of reagent (Sigma Aldrich, St. Louis, USA) in absolute ethanol (Sharlau, Sentmenat, Spain). Buffer solutions were prepared from acetic acid (Merck, Darmstadt, Germany) and sodium hydroxide (Merck, Darmstadt, Germany) at pH 3.5, 4.5 and 5.0, ammonium acetate (Merck, Darmstadt, Germany) at pH 7.0, ammonia solution 32% (Sharlau, Sentmenat, Spain) and ammonium chloride (Panreac Químicas S.A., Castellar del Vallès, Spain) at pH 9.5 and 10.5. Ethanol, methanol, acetone and acetonitrile (Sigma Aldrich, St. Louis, USA) were used as disperser solvent and 1-undecanol (Acros Organics, Geel, Belgium) as extractant solvent. Cadmium, cobalt, nickel, lead and zinc standard solutions were prepared by appropriate dilutions of 1000 mg L^{-1} monoelemental aqueous stock solutions (High-Purity mono-element standard solutions, Charleston, UK).

2.3. Samples

Two certified reference materials (CRM) from European Reference Material (ERM): Estuarine water (LGC6016) and Hard drinking water (ERM® CA011a), both furnished by the Laboratory of the Government Chemist (LGC, Teddington, Middlesex, UK), were analyzed to assess methods accuracy.

Several beverages purchased from a local market: Drinking water, two alcoholic beverages (obtained by distillation of fermented fruit and brand whisky – both containing 40–60% alcohol) and a soft drink, were also analyzed to evaluate the applicability of the methods to real samples.

2.4. DLLME procedure

For extraction of the analytes by DLLME, different amounts of sample or standard solutions were transferred to 10-mL glass tubes. An excess of chelating agent PAN was added to the solution, ethanol absolute and buffer solution (NH$_4$OH/NH$_4$Cl pH 9.0) were added – maintaining final ethanol percentage at 28%. After a complexation time of around 15 min [13], the mixture was filled with deionized water up to 9 mL. A mixture of 70 μL of extractant solvent (1-undecanol) and 150 μL of disperser solvent (methanol) was added using a glass syringe. Phase separation was then achieved by centrifugation at 3000 rpm for 3 min. The organic phase was retrieved with a micropipette for ICP-OES and with a microsyringe for LIBS analysis.

For ICP-OES detection, around 40 μL of the analyte-enriched solvent was diluted to 100 μL with 1-propanol in order to reduce viscosity and

Table 1
Instrumental parameters for ICP-OES measurements.

Parameter	Value
RF generator power (kW)	1.2
Plasma gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	1.5
Nebulizer type	OneNeb®
Spray chamber type	Cyclonic
Nebulizer gas flow rate (L min^{-1})	0.75
Sample flow rate (mL min^{-1})	0.1
View mode	Axial
Read time (s)	3
Replicates	3
Analytical lines (nm)	Cd II (226.502)
	Co II (228.616)
	Ni II (230.299)
	Pb II (220.353)
	Zn I (213.857)