JAAS

Journal of Analytical Atomic Spectrometry

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: R. Serrano, G. Grindlay Lledó, P. Niedzielski, L. Gras and J. Mora, *J. Anal. At. Spectrom.*, 2020, DOI: 10.1039/D0JA00113A.

# Evaluation of MIP-OES as a detector in DLLME procedures. Application to the Cd determination in water samples.

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## Abstract

High-power microwave induced plasma optical emission spectrometry (MIP-OES) constitutes a serious alternative to inductively coupled plasma optical emission spectrometry (ICP-OES) for elemental analysis. To improve the analytical capabilities of MIP-OES, dispersive liquid-liquid microextraction (DLLME) procedures seems to be, *a priori*, a very promising choice for trace and ultra-trace analysis in complex matrices. Nevertheless, up to date, DLLME has never been coupled to MIP-OES. The goal of the present work is to investigate the capability of MIP-OES as a detector in DLLME procedures. To this end, spectral and non-spectral interferences caused by the presence of common DLLME extractants (i.e., chloroform and supramolecular solvent based on 1-decanol and THF) in MIP-OES have been evaluated. Results reveal the occurrence of both spectral and non-spectral interferences due to carbon-based molecular bands emission in MIP-OES. Carbon-based molecular emission (i.e. $C_2$ and CH) significantly affects analyte wavelengths above 328 nm. By the

appropriate selection of experimental conditions (i.e. analyte wavelength and nebulizer gas flow rate), both spectral and non-spectral interferences could be mitigated allowing elemental analysis by means DLLME-MIP-OES. Different DLLME methodologies have been developed for Cd determination in water samples (i.e., tap, sparkling and synthetic seawater) by MIP-OES. These methodologies afford an enrichment factor of 46 and 42 for chloroform and supramolecular-based solvent DLLME procedures, respectively, and a limit of detection (LoD)of 1 μg $L^{-1}$. This LoD is 100-fold lower than that obtained by conventional MIP-OES (i.e. no DLLME) due to both analyte preconcentration and the beneficial effect of organics on aerosol generation and transport. These analytical figures of merit are equivalent to those previously reported for DLLME-ICP-OES and allows Cd determination in water samples according to current international policies.

**Keywords:** dispersive liquid-liquid microextraction, microwave induced plasma, optical emission spectrometry, matrix effects, cadmium, water analysis.

## Introduction

In the past few years, microwave induced plasma optical emission spectrometry (MIP-OES) has generated a great interest as an alternative technique to inductively coupled plasma optical emission spectrometry (ICP-OES) for elemental analysis. [1] Early MIP-OES instruments were limited by the lack of power and the poor energy transfer between the plasma and the sample aerosol, thus giving rise to poor analytical figures of merit and strong matrix effects. Recent advances in instrumentation have mostly solved these shortcomings [2,3]

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and detection capabilities afforded by current MIP-OES instruments are closed to those obtained in ICP-OES. Moreover, operational costs with MIP-OES are significantly reduced due to the use of nitrogen as plasma gas. This technique has been successfully employed to analyse complex organic samples such as ethanol, gasoline, crude oils, petrochemical products, etc. [4–6]

Dispersive liquid-liquid microextraction (DLLME) is widely employed in atomic spectrometry (mainly flame and graphite furnace atomic absorption spectrometry) [7] as a fast and green sample preparation methodology to improve analytical figures of merit and reduce matrix effects from complex matrices. [8] In DLLME procedures, few microliters of an organic solvent are injected into the sample to generate a cloudy solution with the aid of a disperser solvent miscible with both the extractant and the aqueous phase. Due to the limited solubility of metals and metalloids in the organic phase, a chelating agent is required to accomplish analyte extraction. The main advantages of DLLME are simplicity, high sample throughput, low reagent consumption, minimum waste generation and high enrichment factors. It is interesting to note that DLLME has been scarcely coupled to plasma-based techniques (i.e., ICP-OES, and ICP-MS) due to the limited volume available after the microextraction process and the negative effect of organics on plasma characteristics. [8,9] However, Martínez et al., [10] have recently demonstrate that DLLME-ICP-OES coupling is feasible by the appropriate selection of both sample introduction system and plasma experimental conditions. Thus, by a judicious selection of the experimental conditions, 1-undecanol, 1-butyl-3-methylimidazolium hexafluorophosphate and chloroform can be directly introduced into the ICP source by means of a flow injection manifold in a highly reproducible way and minimum matrix effects.

Operating this way, neither oxygen addition nor additional sample pre-treatment are required to analyse DLLME extracts. [11] According to these authors, coupling DLLME to ICP-OES affords a noticeable improvement on the analytical figures of merit because the preconcentration process itself but also by the beneficial effect of organics on the aerosol generation and transport to the plasma regarding aqueous solutions.

Considering the previous findings in ICP-OES, [10] it would be expected that combining DLLME with MIP-OES would also result in a noticeable improvement of the analytical figures of merit afforded by this technique. The goal of the present work is to evaluate, for the first time, the feasibility of coupling DLLME to MIP-OES for elemental analysis. To this end, both the potential spectral and non-spectral interferences caused by two common DLLME organic extractants (i.e., chloroform and a supramolecular solvent based on THF/1-undecanol) [12,13] with different physicochemical properties (i.e., viscosity and volatility) on the emission signal of 23 elements in MIP-OES have been studied. Next, after a careful optimization of the experimental conditions, different DLLME procedures have been tested and optimized for Cd determination in water samples (i.e. tap, sparkling and synthetic seawater) by means MIP-OES.

# Experimental

## Chemicals

Chloroform, 1-decanol, ammonium diethyl dithiophosphate 95% (DDTP), 85% w $w^{-1}$ phosphoric acid, 99% w $w^{-1}$ sodium dihydrogen phosphate anhydrous and 0.45 µm nylon syringe filters were purchased from Sigma-Aldrich (Steinheim,

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Germany). A 200 mg $L^{-1}$ multi-element organometallic solution (Ag, Al, B, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Sn, Ti, V, and Zn) and mono-elemental 200 mg $L^{-1}$ Co, K, Li, Sr, Tl, and Y organometallic solutions were obtained from ASI standards (Texas, USA). Sodium chloride, 96% w $w^{-1}$ ethanol and 1000 mg $L^{-1}$ mono-element inorganic solutions (Ag, Al, B, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sn, Sr, Ti, Tl, V, Y, and Zn) were purchased from Panreac (Barcelona, Spain). Tetrahydrofuran (THF) 99.9% w $w^{-1}$ and nitric acid 65% w $w^{-1}$ were obtained from Honeywell (New Jersey, USA). Deionised water produced in a Milli-Q device (Millipore, USA) were used.

## Solutions

*MIP-OES characterization operating organic extracts*

Different analyte standard solutions have been employed to investigate both spectral and non-spectral interferences operating organic extracts in MIP-OES. For chloroform, analyte standards were directly prepared by diluting the appropriate aliquots of a 200 mg $L^{-1}$ multi-elemental and mono-elemental organometallic solution in this solvent. A two-step procedure has been employed to prepare analyte standards with the supramolecular solvent. First, the supramolecular solvent was generated by injecting a mixture of THF (400 mg) and 1-decanol (100 mg) on a pH 2 buffered solution with 1 M phosphoric/dihydrogen phosphate. Next, after a centrifugation step, the upper layer of THF/1-decanol micelles was transferred to an Eppendorf tube and diluted with an analyte spiked pure ethanol solution (1:0.5 THF/1-decanol micelles:ethanol ratio). Finally, analyte standards in 1.0% w $w^{-1}$ nitric acid were employed as a reference to evaluate matrix effects. These solutions were

prepared from the corresponding 1000 mg $L^{-1}$ mono-element inorganic solutions.

*DLLME optimization*

The following solutions were employed to optimize Cd extraction by means of DLLME operating either chloroform or the supramolecular solvent: *(i)* 0.5 mg $kg^{-1}$ Cd aqueous standard prepared by the appropriate dilution of a 1000 mg $kg^{-1}$ standard one; *(ii)* 1 M phosphoric/dihydrogen phosphate buffer; *(iii)* 0-3.3% w $w^{-1}$ DDTP solution; and (iv) 0-8% w $w^{-1}$ NaCl.

**Dispersive liquid-liquid microextraction**

In this work, two different DLLME procedures for Cd determination in water samples based on the use of chloroform and a supramolecular solvent have been developed. In both cases, extraction conditions have been optimized by means of a central composite design using the Statgraphics Centurion® software.

*Chloroform-based extraction*

The extraction/preconcentration procedure for Cd determination with chloroform was performed as follows. First, 5 mL of water sample or analyte standard were placed on a glass tube with 100 µL of phosphoric/dihydrogen phosphate buffer, 200 µL of DDTP (60% w $w^{-1}$ in pure ethanol) and 300 µL of NaCl (17% w $w^{-1}$l) solutions. Next, a mixture of chloroform (extractant) and ethanol (disperser) was injected into the glass tube containing the sample. A cloudy solution is formed, and after centrifugation (5 min at 3500 rpm), chloroform was collected at the bottom of the conical test tube and transferred into an Eppendorf tube, before to

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analyse by MIP-OES.

*Supramolecular solvent based extraction*

In this procedure, 5 mL of the sample were spiked with a phosphoric/dihydrogen phosphate buffer solution to adjust the pH (2). Next, 200 µL of DDTP (60% w $w^{-1}$ in pure ethanol) and 600 µL NaCl (17% w $w^{-1}$) solutions were added to the sample. A mixture of 1-decanol (extractant) and THF (self-assembly agent and disperser solvent) was injected into the sample to form a cloudy solution of micelles. The sample was then centrifuged (5 min at 3500 rpm) and micelles collected at the top of the sample solution were finally transferred into an Eppendorf tube. Finally, before MIP-OES analysis, the supramolecular solvent was diluted with ethanol (1:0.5) to decrease its viscosity and thus favouring solution handling and nebulization.

**Instrumentation**

MIP-OES measurements were performed using an Agilent 4200 MP-OES (Agilent, Santa Clara, USA) with axial viewing using the operating conditions reported in Table 1. The sample introduction system consisted of a OneNeb® pneumatic nebulizer coupled to a double pass glass cyclonic spray chamber (Agilent, Santa Clara, USA). Because of the limited sample volume available after the DLLME treatment, organic extracts were drove to the nebulizer by means of a Rheodyne 9725i FIA manifold (Bristol, USA) equipped with a 25 µL loop valve. Samples were injected using a 1 mL plastic syringe with a stainless-steel needle. Chloroform extracts were directly introduced into the valve. For the supramolecular solvent extracts, as explained before, a preliminary dilution with

ethanol (1:0.5) is mandatory. Instrument peristaltic pump was employed to control FIA carrier solution (1% w $w^{-1}$ $HNO_3$). Operating this way, chloroform and the supramolecular solvent can be analysed without requiring the external gas control module for air introduction into the plasma.

Because of MIP-OES software (MP expert®) does not allow the continuous register of the analyte emission signal, detection parameters (i.e. integration time and number of replicates) were optimized to fully register FIA transient analyte emission peak. After some preliminary tests, the integration time was fixed at 1 s whereas the number of replicates was adjusted to 25. Operating this way, well defined and highly reproducible analyte emission signal peaks were obtained. It is not advisable to use integration times lower than 1 second since communication lag between the spectrometer and the computer (1-2 s) affects negatively to peak resolution. [14] Microsoft Excel® was employed for manually signal integration.

The emission lines employed in this work are listed in the Supplementary material (Table S1). Several molecular emission bands were monitored for plasma diagnostics. Emission bands for CN (388.340 nm), CH (431.420 nm) and $C_2$ (473.700 nm) were selected to assess potential spectral interferences due to carbon molecular species on analyte emission. [1] On the other hand, $N_2^+$ (391.439 nm) and OH (308.970 nm) emission bands were employed to evaluate plasma thermal conditions. Because none of the above-mentioned bands are included in the instrument software, nearby emission lines from different elements were employed (Table S1, supplementary material).

**Samples**

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Three water samples covering a wide range of matrix characteristics were selected: (i) tap water (Adam Mickiewicz University, 52º 27' 59.5" 16º 55' 28"); (ii) commercial sparkling water (Muszyna Skarb Zycia, Poland); and (iii) synthetic seawater. [15] All water samples were stored in polyethylene bottles after a filtration step with a 0.45 µm Nylon syringe filter.

# Results and discussion

## MIP-OES optimization for organic extracts analysis

MIP-OES has been recently applied for the elemental analysis of complex matrix samples, such as high carbon- or salt-content samples. [4–6,16] Nevertheless, up to date, no previous attempt to combine DLLME and MIP-OES has been reported. In the present work, the behaviour of chloroform and a supramolecular solvent mixture of 1-decanol and THF (i.e., two DLLME extractants) in MIP-OES have been tested. These solvents have been selected to cover different physico-chemical properties (viscosity, volatility, etc.) thus allowing to assess the main problems arising from coupling DLLME to MIP-OES. The potential occurrence of both spectral and non-spectral interferences operating these solvents was investigated. To compare the results obtained for organic solvents, a 1% w $w^{-1}$ nitric acid solution was used as a reference.

### *Spectral interferences*

MIP appearance (i.e., shape, colour and bright) is strongly affected by the presence of organics, thus suggesting the occurrence of carbon-based molecular emission due to the incomplete atomization of these solvents in the plasma. [3] To check this hypothesis, spectral interferences have been evaluated monitoring

different carbon-based molecular emission bands (i.e., CN 388.340 nm, CH 431.420 nm and $C_2$ 473.700 nm). Carbon molecular emission was studied for nebulizer gas flow rates ($Q_g$) ranging from 0.3 to 0.8 L min (i.e. MIP-OES standard values) since this parameter exerts a great influence on aerosol generation and transport as well as on plasma characteristics.[21] As expected, carbon-based molecular emission (CN, CH and $C_2$) operating organic matrices was significantly higher than that measured using the reference 1% w $w^{-1}$ nitric acid solution (Fig. 1). Results show that these carbon-based molecular emission signals strongly depend on the solvent and the nebulizer gas flow rate ($Q_g$) employed. Though the low sample volume injected with the FIA manifold (i.e., 25 µL) when operating both chloroform and the supramolecular solvent, the emission signal of the CN band saturates the detector (Fig. 1.A). Irrespective of the organic solvent considered, carbon-based molecular band emission intensities followed the order CN>$C_2$≈CH. Finally, as expected from its volatility values, [9] chloroform affords higher emission signals for the carbon-based molecular species tested than the supramolecular solvent. Thus, at a $Q_g$ value of 0.3 L $min^{-1}$, $C_2$ and CH molecular emission signals operating chloroform were, respectively, 20- and 9-fold higher regarding the supramolecular solvent. The behaviours above described are magnified when increasing $Q_g$ values due to the higher solvent load into the plasma. Thus, when $Q_g$ raises up from 0.3 to 0.8 L $min^{-1}$, carbon-based molecular emission for chloroform and the supramolecular solvent increased on average 2.1- and 1.3-fold. Because the high carbon-based molecular emission, the potential occurrence of spectral interferences on the most sensitive emission wavelength of 23 elements (Ag, Al, B, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sn, Sr, Ti, Tl, V, Y and Zn) was examined. Table 2 shows the background

ratios obtained for the 23 elements operating organic solvents regarding the 1% w $w^{-1}$ nitric acid solution at a $Q_g$ of 0.3 L $min^{-1}$. For all the elements investigated, the most sensitive wavelength in MIP-OES was employed. It is observed that background emission for organics significantly increased for those analyte wavelengths located mostly above 328 nm, particularly chloroform due to its higher volatility. Thus, interfered elements by the presence of carbon in the plasma includes Ag, Al, Co, Cr, Cu, Fe, K, Li, Mn, Mo, Na, Ni, Pb, Sn, Sr, Tl and Y. No significant carbon-based molecular emission was found below this wavelength (i.e. background differences lower 2-fold). Elements free from interferences include Ag, B, Cd, Cu, Mg, Ti, Sn, V and Zn.

From a practical point of view, these carbon-based spectral interferences can be mitigated by means of different strategies: (i) injecting air into the plasma. Several authors have successfully demonstrated that the use of $N_2/O_2$ mixed plasmas improves discharge stability with organics and minimized carbon-based background emission.[17,18] Nevertheless, oxygen addition into the plasma could lead to an increase of the background emission spectra in the wavelength range between 200-328 nm due to the emission of NO molecular species,[19] thus affecting the determination of those elements with its most sensitive emission line located in this range; (ii) organics removing by means additional sample preparation step prior to MIP-OES analysis. Thus, for instance, chloroform could be evaporated and then the solution reconstituted with diluted acid.[20] However, this approach counterbalances most of the main benefits of DLLME (e.g. simplicity, high sample throughput, etc.) and it is not useful for non-volatile solvents such as the supramolecular ones; (iii) employing a desolvation system after the spray chamber exit to reduce solvent load into the plasma. Nevertheless,

this approach is not efficient to reduce spectral interferences from low volatile solvent such as the micelles. In addition, it is expected to affect negatively sample throughput due to the longer wash-out times required; and, (iv) choosing wavelengths on the spectrum region free from carbon-based molecular emission (<328 nm). Though this strategy might affect negatively limits of detection (LOD) due to the use of a less sensitive wavelength, it would be counterbalanced by using DLLME.

*Non-spectral interferences*

To evaluate non-spectral interferences due to the presence of DLLME extractants in MIP-OES, a line free from spectral interferences must be employed. In this work Cd I 228.802 nm signal has been selected for this purpose.

Non-spectral matrix effects in MIP-OES are mostly related to changes in the aerosol characteristics and transport to the plasma and/or on the plasma excitation conditions. These parameters strongly depend on the physical properties of the solvents used and on the experimental conditions selected. Among the experimental parameters, RF power, $Q_l$ and $Q_g$ are the most relevant. The MIP-OES instrument employed in this work only operates at a constant plasma power of 1000 W and, therefore, the influence of this parameter on analyte signal cannot be investigated. As regards sample uptake rate, it is well known that sensitivity decreases when increasing $Q_l$ due to the generation of coarser aerosols and plasma robustness deterioration.[10] Consequently, this parameter was fixed at 0.6 mL $min^{-1}$ as a compromise between sensitivity and sample throughput. Finally, given the strong influence of $Q_g$ on molecular background emission, the influence of this parameter on the analyte emission

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signal in MIP-OES has been investigated. Fig. 2 shows the influence of $Q_g$ on the Cd I 228.802 nm integrated emission signal for all the matrices tested in this work (i.e., 1% w $w^{-1}$ nitric acid solution, chloroform and the supramolecular solvent). As it can be observed in Fig. 2, Cd signal shows a maximum at a $Q_g$ of 0.5-0.6 mL $min^{-1}$ for the 1% w $w^{-1}$ nitric acid solution. For the supramolecular solvent, the maximum Cd signal is obtained at lower $Q_g$ values (i.e., 0.3-0.5 mL $min^{-1}$), whereas for chloroform, analyte signal decreases when increasing $Q_g$. It is interesting to note that, under optimum conditions, organics afford higher Cd I 228.802 nm emission signal than the nitric acid reference solution (i.e., 1.9- and 1.6-fold, for chloroform and the supramolecular solvent, respectively). This signal improvement can be explained considering the influence of solvents' physicochemical properties (mainly surface tension and volatility) on the aerosol generation and transport to the plasma.[11] However, considering the high carbon-based molecular background emission signals and the differences in the optimum $Q_g$ observed between the matrices tested, data in Fig. 2 suggest a deterioration of the plasma excitation conditions for organics regarding the nitric acid solution. Different methods have been reported in the literature to evaluate plasma energetic conditions. Thus, the measurement of the excitation temperature by means of the Boltzmann plot using Fe atomic lines is one of the most extensively employed. [22] Unfortunately, this method cannot be used when operating organics since the region of the spectrum used for the measurement of Fe lines (i.e., 371–382 nm) is severely interfered by the CN band. Neither the $N_2^+$ (391.439 nm)/OH (308.970 nm) emission signal ratio proposed by Williams et al., [23] as a plasma diagnostic tool in MIP-OES can be used, since $N_2^+$ emission signal is also interfered by the CN band (Fig. S1, supplementary material). The same occurs

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with the strategy proposed by Serrano et al., [21] who used $N_2^+$ and OH emission signal profiles to evaluate plasma energetic conditions. Alternatively, background emission at a given wavelength free from carbon-based molecular emission can be monitored to estimate changes in the plasma conditions. [24] Fig. 3 shows the Cd I 228.802 nm emission signal profile for both blank and analyte solutions at $Q_g$ values of 0.3 L $min^{-1}$ and 0.8 L $min^{-1}$ for all matrices investigated. As it can be observed in this figure, regardless of $Q_g$, the introduction of the 1.0% w $w^{-1}$ nitric acid solution does not significantly affect background emission and Cd signal shows the typical flow injection peak-shape. When operating organics (mainly chloroform), however, some changes were noticed on both background and analyte emission. For chloroform, background emission is significantly reduced due to sample introduction, being this effect more pronounced at higher $Q_g$ values. Thus, for instance, background emission signal for chloroform at 0.3 and 0.8 L $min^{-1}$ was reduced 17% and 57%, respectively, regarding the values afforded by the 1% w $w^{-1}$ $HNO_3$ acid solution. These results clearly suggest that plasma discharge is indeed negatively affected by the presence of organics. In fact, at $Q_g$ of 0.8 L $min^{-1}$, it is observed how these changes in the background emission have a negative impact on the Cd signal peak shape. Probably, this change on plasma discharge characteristics is the main reason why the signal enhancement factor for chloroform in MIP-OES is lower than in ICP-OES (i.e. 8-fold). [10]

**Cadmium determination in water samples by means of DLLME-MIP-OES**

To evaluate the benefits derived from DLLME-MIP-OES coupling for trace metal analysis, different strategies to determine Cd in water samples operating with

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both chloroform and the supramolecular solvent as extractants have been developed. Cadmium has been selected as a model analyte for metal extraction due to its: (i) environmental and toxicological significance; and (ii) most sensitive wavelength is free from carbon-based spectral interferences.

*Optimization of DLLME experimental conditions for Cd determination*

Cadmium extraction conditions were optimized by means of experimental design using a central composite model. [25,26] Diethyl dithiophosphate (DDTP) was employed as chelating agent for Cd extraction since its capability to form stable complexes with divalent metals. [27] Because the DDTP-Cd complex is favoured under acidic conditions, [28] sample pH was fixed at 2.0 with a phosphoric/dihydrogen phosphate buffer solution. After checking previous works in the literature, the following variables were investigated for Cd extraction with chloroform and the supramolecular solvent at five levels: (i) NaCl concentration; (ii) DDTP concentration; (iii) extractant (i.e., chloroform or 1-decanol) mass; and (iv) dispersant/self-assembly agent (i.e., ethanol/THF) mass (Table S2 and S4, supplementary material). A total of 26 experiments were performed by triplicate operating a 0.5 mg $L^{-1}$ Cd solution for each organic solvent (Table S3 and S5, supplementary material). To assess the significance of each variable on Cd extraction, data were analyzed by ANOVA and the effects were summarized by means the corresponding Pareto charts (Fig. S2, supplementary material). For chloroform, ANOVA data analysis reveals that Cd extraction is significantly affected by the chloroform mass, dispersant mass and the NaCl two factor term. Thus, chloroform mass has a negative influence on Cd extraction since the analyte concentration in the organic phase (enrichment factor) is favoured by

decreasing the extraction solvent mass. [7,29] Both dispersant and the NaCl two factor term have a positive influence on Cd extraction. The former variable favours chloroform dispersion in the samples whereas the later favours analyte-chelate transfer between both phases. [30] Regarding the supramolecular solvent, ANOVA data analysis shows that Cd extraction is significantly influenced by alcohol mass (1-decanol) as well as by alcohol and THF two-factor terms. The influence of alcohol mass on Cd extraction is rather complex since the alcohol mass two-factor term has a positive influence but the single term has the opposite behaviour. The increase of 1-decanol mass affects negatively to Cd extraction because the higher the alcohol amount, the higher the extraction phase obtained thus decreasing analyte enrichment factor. [13,31] The THF two-factor term has a positive influence since it favours the 1-decanol assembly and improve its dispersion on the aqueous phase. Nevertheless, above a certain level, THF favours both coacervate phase and Cd-DDTP complex solubility in the THF-water bulk phase [13,32] and, hence, analyte extraction. Table 3 shows the optimum Cd extraction conditions derived from the experimental design for chloroform and the supramolecular solvent. Despite the different nature of the extractants employed, similar experimental conditions were obtained for both extractants. Optimum experimental conditions for Cd extraction with chloroform and the supramolecular solvent agree with previous studies in the literature.[33,34]

*Analysis of Cd water samples*

To validate Cd determination in water samples by means of DLLME-MIP-OES, several samples covering different matrix characteristics were selected (i.e. tap, sparkling and synthetic sea water). Method validation was performed according

to European conformity guidelines for analytical methods of food contaminants [35] since this normative is significantly more restrictive than those usually employed for water analysis in environmental samples. [36,37]

Because Cd levels in all the samples were below the limits of detection (LoD) in MIP-OES, a recovery test was performed to evaluate the method accuracy. To this end, water samples were spiked with Cd for a final concentration of 60 μg $L^{-1}$. Dispersive liquid-liquid microextraction procedure was applied to both analyte standards and water samples. Table 4 shows Cd recovery values obtained operating both chloroform and supramolecular solvent-based DLLME treatments. Irrespective of the DLLME procedure, analyte recoveries for tap and sparkling water were quantitative since they were within the limits established by the EU for analyte concentrations above 10 μg $kg^{-1}$ (-10%/+10%).[35] The repeatability of Cd determination in tap and sparkling water (5 replicates) was within the 2%–4% range. Accuracy and precision for the synthetic sea water, however, was severely deteriorated regarding the above-mentioned water samples. Thus, Cd recoveries operating chloroform and the supramolecular solvent were 117±8 and 86±15 %, respectively. It was observed that, when analyzing DLLME extracts, plasma color becomes bright orange stating the presence of Na in the organic phase. This phenomenon is expected considering that NaCl is employed in DLLME and it could be co-extracted with the Cd-DDTP chelate. Nevertheless, it was more significant for the synthetic sea water due to the higher NaCl content regarding tap and sparkling water samples. Several authors have shown that MIP-OES are highly sensitive to the presence of easily ionizable elements and, consequently, Cd analysis in synthetic sea water samples is affected by non-spectral matrix effects due to the presence of Na. [21] The reproducibility (inter-assay precision) of

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each methodology was evaluated as the relative standard deviation of the measurements obtained for six replicates on three different days. In this case, the relative standard deviation for tap and sparkling waters ranged from 2 to 6% whereas for the sea water sample was between 10 and 16%. Next, method selectivity was evaluated by means a recovery assay operating a Cd standard spiked with the most significant major elements usually found in water samples (i.e. Na, K, Mg and Ca). It was observed that, for the concentration range tested (major elements: 0-4000 mg $L^{-1}$) Cd recovery was quantitative, thus confirming method selectivity. Preconcentration factor (defined as the ratio between analyte concentration in the extractant phase to the initial concentration in the aqueous phase) for chloroform and supramolecular-based DLLME treatments were 46 and 42, respectively. Finally, the LoD and limit of quantification (LoQ) values (estimated from the analyte calibration graph according to IUPAC guidelines [38]) were, respectively, 1 µg $L^{-1}$ and 3 µg $L^{-1}$ for both methodologies. When compared to conventional DLLME analysis (i.e. no preconcentration), LoD are improved 100-fold due to the combined effect of the preconcentration treatment and the beneficial effect of organic extractants on aerosol generation and transport. The LODs obtained for DLLME-MIP-OES allow the Cd control in drinking and bottled water according to USA[39,40] and European [36] regulations (5 µg $L^{-1}$ Cd). As regards environmental waters (i.e. surface and marine), Cd levels can be monitored according to USA policy (7.9 – 33 µg $L^{-1}$ Cd)[41] but not to the European one (0.45-1.5 µg $L^{-1}$ Cd). [37]

Because no previous works about Cd determination by means of DLLME-MIP-OES have been reported in the literature so far, data in this work have been compared with those reported for DLLME-ICP-OES[10,42-44] (Table 5). Limits of

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detection obtained by DLLME-MIP-OES operating with both chloroform and the supramolecular solvent are similar to those afforded by DLLME-ICP-OES. On this regard, DLLME treatments developed in this work are highly efficient since they afford high Cd enrichment factors, EF (ratio between the slopes of the regression equations with and without pre-concentration), thus giving rise to low consumption indexes, CI (the ratio between the sample volume and EF).[45]

## Conclusions

This work demonstrates that, after a carefully optimization of the experimental conditions, DLLME coupling to MIP-OES is totally feasible and it could be employed to determine Cd in water samples. Organic extracts could be directly introduced into the plasma by means a flow injection manifold and without requiring air addition. However, special attention must be paid to both spectral and non-spectral interferences operating organic extractants. Carbon-based molecular bands emission has a negative influence on the analytical figures of merit for analyte emission wavelengths above 328 nm. Results in this work demonstrate that DLLME significantly improves the detection capabilities afforded by MIP-OES, thus allowing Cd determination at ultratrace levels in water samples. In fact, DLLME-MIP-OES affords similar figures of merit than those previously reported for DLLME-ICP-OES. Therefore, it is expected that MIP-OES could be employed for more challenging applications than those traditionally address by this technique.

## Acknowledgments

The authors would like to thank the Generalitat Valenciana

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DOI: 10.1039/D0JA00113A

(CONSELLERIAAGRICULTURA4-17T) and the University of Alicante (VIGROB-050; UADIF17-42; UAUSTI16-02) for the financial support of this work.

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## Figure captions

**Fig. 1.** Emission spectra for (A) CN, (B) CH and (C) $C_2$ molecular bands operating (●) 1.0 w $w^{-1}$ nitric acid, (▲) the supramolecular solvent and (■) chloroform. $Q_g$ 0.3 L $min^{-1}$.

**Fig. 2.** Influence of the nebulizer gas flow rate on Cd I 228.802 nm integrated emission signal operating (●) 1.0 w $w^{-1}$ nitric acid, (▲) the supramolecular solvent and (■) chloroform.

**Fig. 3.** Cadmium I 228.802 nm emission signal profile for blank (- -) and analyte solution (—) for the different matrices tested.

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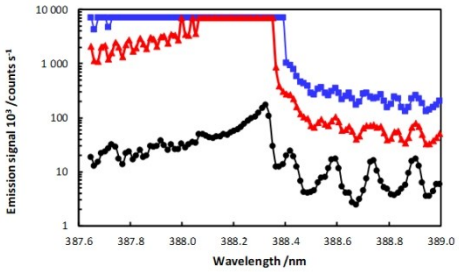


Fig 1.A

338x190mm (96 x 96 DPI)

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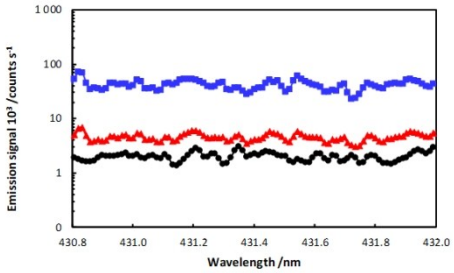


Figure 1.B

338x190mm (96 x 96 DPI)

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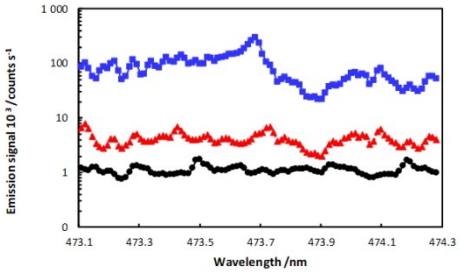


Figure 1.C

338x190mm (96 x 96 DPI)

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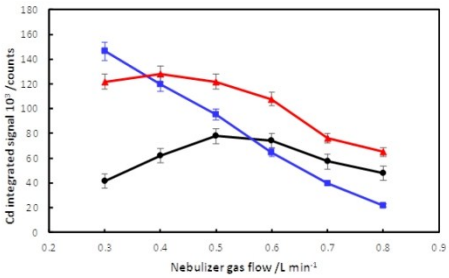


Fig. 2

338x190mm (96 x 96 DPI)

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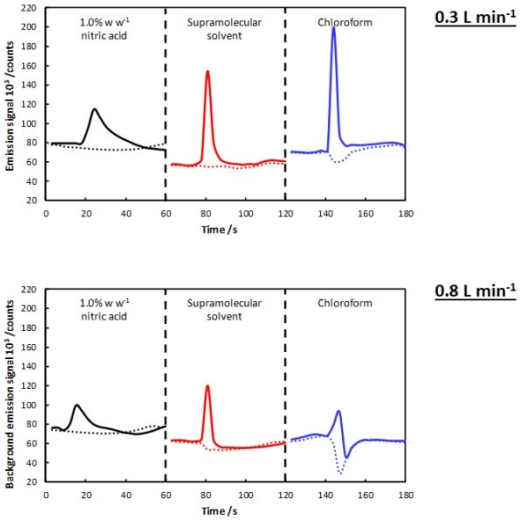


Fig. 3

338x190mm (96 x 96 DPI)

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**Table 1**

MIP-OES operating conditions

| | |
|---|---|
| Plasma forward power (W) | 1000 |
| Plasma gas (L $min^{-1}$) | 15 |
| Auxiliary gas (L $min^{-1}$) | 1.5 |
| Nebulizer gas (L $min^{-1}$) | 0.3 - 0.8 |
| Carrier flow rate (mL $min^{-1}$) | 0.6 |
| Sample introduction system: | |
| Nebulizer | OneNeb® |
| Spray chamber | Double pass cyclonic |
| View mode | Axial |
| Flow injection loop volume (µL) | 25 |
| Integration time (s) | 1 |
| Replicates | 25 |

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**Table 2**

Background ratio for the emission signal obtained at the different wavelength for the organic solvents and the 1% w $w^{-1}$ nitric acid solution.

| Element | Wavelength (nm) | Chloroform | Supramolecular solvent |
|---|---|---|---|
| Zn | 213.857 | 0.8 | 0.9 |
| Cd | 228.802 | 0.9 | 1.0 |
| B | 249.772 | 0.6 | 0.8 |
| Mg | 285.213 | 0.9 | 1.0 |
| Ti | 308.804 | 1.0 | 1.0 |
| V | 309.311 | 1.0 | 1.0 |
| Sn | 317.505 | 1.4 | 0.7 |
| Cu | 324.754 | 1.9 | 0.9 |
| Ag | 328.068 | 1.7 | 0.8 |
| Co | 340.512 | 15.0 | 7.5 |
| Ni | 352.454 | 83.5 | 41.8 |
| Y | 371.029 | 59.9 | 29.9 |
| Fe | 371.993 | 76.5 | 38.2 |
| Mo | 379.825 | 90.7 | 18.1 |
| Al | 396.152 | 30.3 | 3.4 |
| Mn | 403.076 | 38.6 | 7.7 |
| Pb | 405.781 | 50.0 | 17.1 |
| Sr | 407.771 | 151.5 | 50.5 |
| Cr | 425.433 | 34.8 | 3.9 |
| Tl | 535.046 | 22.7 | 2.3 |

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| | | | |
|---|---|---|---|
| Na | 588.995 | 28.2 | 2.8 |
| Li | 670.784 | 84.9 | 8.5 |
| K | 766.491 | 28.8 | 2.9 |

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**Table 3**

Optimum extraction conditions for Cd extraction with DLLME operating chloroform and the supramolecular solvent as extractants.

| DLLME parameters | Chloroform | Supramolecular solvent |
|---|---|---|
| DDTP concentration (% w $w^{-1}$) | 2.2 | 1.8 |
| Extractant mass (mg) | 230 | 100 |
| Dispersant mass (mg) | 490 (EtOH) | 400 (THF) |
| Ionic strength (NaCl % w $w^{-1}$) | 1.0 | 2.2 |

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**Table 4**

Recoveries obtained for water samples spiked for a final concentration of 60 μg $L^{-1}$ Cd by means of DLLME-MIP-OES operating chloroform and the supramolecular solvent as extractants.

| Sample | Recovery values (%) | |
|---|---|---|
| | Chloroform | Supramolecular solvent |
| Tap | 92 ± 4 | 95 ± 3 |
| Sparkling | 111 ± 3 | 95 ± 2 |
| Sea | 117 ± 8 | 86 ± 15 |

**Table 5**

Comparison of different methodologies proposed in the literature for Cd determination in water samples by means DLLME coupled to ICP-OES.

| Extractant | Chelanting agent | Technique | LODs (μg $L^{-1}$) | EF | $V_{sample}$ (mL) | Cl (μL) | Ref. |
|---|---|---|---|---|---|---|---|
| Chloroform | DDTP | MIP-OES | 1 | 70 | 5 | 110 | This work |
| Supramolecular solvent | DDTP | | 1 | 63 | 5 | 120 | |
| 1-undecanol | TTA | ICP-OES | 6 | 1.4 | 5 | 4000 | 10 |
| Chloroform | DDTC | | 6 | 6.3 | 5 | 800 | 10 |
| Trichloroetilene | BTAC | | 0.3 | 13 | 40 | 3000 | 41 |
| 1-undecanol | PAN | | 0.8 | 56 | 9 | 160 | 42 |
| THF/1-decanol | APDC | | 0.6 | 44 | 4 | 90 | 43 |