



Analytical note

Imidazolium-based task-specific ionic liquid for selective Ag, Cu, Pd and Pt determination by means of dispersive liquid-liquid microextraction and inductively coupled plasma optical emission spectrometry

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ABSTRACT

This work explores chelating capabilities of 1-butyl-2-diphenylphosphino-3-methylimidazolium hexafluorophosphate (BDPPIMPF₆) as a task-specific ionic liquid (TSIL) for metal extraction/preconcentration procedures. To this end, metal extraction by BDPPIMPF₆ for 21 elements (Ag, Al, As, Au, Co, Cr, Cu, Fe, Ir, Mn, Ni, Pb, Pd, Pt, Re, Rh, Ru, Sc, Ti, V, and Zn) were evaluated. This TSIL specifically forms chelating complexes with several elements of Group 10 (Pd and Pt) and Group 11 (Ag and Cu) of the Periodic Table. Chelating capabilities of BDPPIMPF₆ has been exploited for developing a novel methodology for the simultaneous determination of Ag, Cu, Pd, and Pt by means of dispersive liquid-liquid microextraction and inductively coupled plasma optical emission spectrometry detection (DLLME-ICP-OES). This methodology afforded enrichment factors of 14 to 70 and limits of detection (LoD) of 0.2–2 µg L⁻¹ for Ag, Cu, Pd and Pt. These LoD values were between 110 and 35-fold lower than those obtained by direct analyses with ICP-OES (i.e., no DLLME treatment). Finally, the proposed method has been applied to the analysis of Ag, Cu, Pd, and Pt in water and pharmaceutical products. Irrespective of matrix characteristics, quantitative recoveries were found for all the elements investigated thus highlighting methodology robustness.

1. Introduction

The use of ionic liquids (ILs) in all fields of chemistry has grown exponentially due to their physicochemical properties are particularly attractive with regard to those afforded by conventional organic solvents (e.g., negligible vapor pressure, thermal stability, toxicity, tunable viscosity) [1–4]. Interestingly, ILs structure can be modified by introducing certain functional groups in such a way that they present additional and unique characteristics (task-specific ILs, TSILs) [5]. Some of the most common TSILs found in the literature are based in 1-alkyl-3-methylimidazolium as organic cation functionalized with metal-chelating groups (e.g., hydroxyl, amino, thiol, thiourea, 2,2'-thiodiacetic acid, pyrrolidinedithiocarbamate, among others) [3]. This type of TSILs has been used in organic chemistry as recyclable catalysts when combined with some metals as well as for selective metal recovery in industry applications. On the other hand, they have also been employed in analytical chemistry for developing highly selective and efficient

extraction/preconcentration procedures for ultra-trace metal and metalloid determination (As, Cd, Cr, Pb, etc.) in complex samples by means of electrothermal atomic absorption spectrometry (ETAAS) or flame atomic absorption spectrometry (FAAS) [3,6–10]. Though inductively coupled plasma optical emission spectrometry (ICP-OES) shows a greater analytical potential than AAS techniques (i.e., simultaneous multi-element analysis, higher sample throughput, etc.), it has been scarcely exploited for such procedures so far.

Our research group has recently demonstrated that Ag and Pd complexes with 1-butyl-2-diphenylphosphino-3-methylimidazolium hexafluorophosphate (BDPPIMPF₆) can be successfully applied in organic chemistry to catalyse 1,3-dipolar cycloadditions [11] (Pd and Ag complexes), and in Suzuki-Miyaura and Tsuji-Trost allylation reactions [12,13] (Pd complexes) for the preparation of natural products, biologically active compounds, and pharmaceuticals. Because the great stability of the complex formed between these metals and BDPPIMPF₆, these chelates can be reuse it 5–8 runs without a significant decrease in

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the catalyst efficiency (i.e., 98% yield) [11–13]. According to these findings, BDPPIMPF₆ seems a promising chelating agent for Ag and Pd extraction/preconcentration procedures. Similarly, it is expected that it could also be employed for the extraction of other metals as well. To the best of our knowledge, the benefits, and drawbacks of this TSIL for metal extraction has not been investigated so far.

The goal of this work was to assess BDPPIMPF₆ as a chelating agent for developing an extraction/preconcentration procedure for simultaneous metal analysis by means of dispersive liquid-liquid microextraction (DLLME) and ICP-OES. To this end, BDPPIMPF₆ extraction capabilities for different hard and soft cations (Ag, Al, As, Au, Co, Cr, Cu, Fe, Ir, Mn, Ni, Pb, Pd, Pt, Re, Rh, Ru, Sc, Ti, V, and Zn) were tested under different pH values. Next, for those species forming chelating complexes with BDPPIMPF₆, DLLME and ICP-OES experimental conditions were optimized. Finally, the method proposed was applied to the analysis of environmental and pharmaceutical samples.

2. Experimental

2.1. Reagents and solutions

All solutions for DLLME experiments were prepared using ultrapure water (Milli-Q water purification system, Millipore Inc., Paris, France). For TSIL synthesis 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆) was mixed with dichlorodiphenylphosphane in the presence of dichloromethane extra dry and *n*-BuLi at $-78\text{ }^{\circ}\text{C}$ (Fig. S1, appendix). A detailed description of BDPPIMPF₆ synthesis procedure is found elsewhere [12]. BmimPF₆ $\geq 97\%$ w w⁻¹, chlorodiphenylphosphine 96% w w⁻¹ and the *n*-Butyllithium (15% w w⁻¹ solution in *n*-hexane) solution were provided by Merck (Darmstadt, Germany) and dichloromethane 99.9% w w⁻¹ extra dry was purchased from Thermo Fisher Scientific (Roskilde, Denmark).

Nitric acid 69% w w⁻¹ hiperpure, hydrochloric acid 37% w w⁻¹, phosphoric acid 85% w w⁻¹, acetic acid 96% w w⁻¹, formic acid 85% w w⁻¹, sodium dihydrogen phosphate and sodium chloride were obtained from Panreac (Barcelona, Spain). Methanol was purchased from Honeywell (Düsseldorf, Germany) and an ICP-IV multi-element 1000 mg L⁻¹ was provided by Merck (Darmstadt, Germany). Finally, Y and Mn 1000 mg L⁻¹ mono-elemental solutions were obtained from Inorganic Ventures (Virginia, United States).

2.2. Samples

A set of seven samples were analysed in this work: (i) CRM-DW1 drinking water reference material (ISC Science, Oviedo, Spain); (ii) tap water; (iii) river water (38° 15' 53.9" N, 0° 42' 00.1" W); (iv) seawater (38° 20' 42.1" N, 0° 28' 37.9" W); (v) ibuprofen suspension (Mylan, Barcelona, Spain); (vi) ibuprofen effervescent (Kern Pharma, Barcelona, Spain); and (vii) ibuprofen tablet (Pensa, Valencia, Spain). These samples were selected to cover different matrix characteristics.

2.3. Sample preparation

Water and oral ibuprofen drug were treated directly by means of DLLME. For the analysis of solid ibuprofen drugs (i.e., table and effervescent granulated), however, a given amount of each sample (0.5 g) was added to 20 mL of water and the mixture obtained was magnetically stirred for 10 min. Finally, all the samples were filtrated with the aid of 0.2 μm syringe filters prior to DLLME analysis.

2.4. Dispersive liquid-liquid microextraction

Because the solid nature of the TSIL BDPPIMPF₆, it should be previously dissolved in an appropriate solvent to be used as chelating agent for metal extraction. Given its chemical similarity and widely use in DLLME applications, BmimPF₆ was selected as a solvent [14,15]. If not

stated otherwise, a 1:35 mixture has been employed through this work.

Optimization of the metal extraction procedure was performed by means of central composite design using Statgraphics Centurion XVI.I software. The DLLME treatment was performed as follows. First, 4 mL sample aliquots (or standards) were spiked with 100 μL of a phosphoric acid-hydrogenphosphate 0.1 M buffer solution (when it is required) to adjust the pH and 500 μL or 1000 μL of a 5% w w⁻¹ NaCl solution to modify the ionic strength of the sample. Next, 230 mg of the extraction mixture solution TSIL/BmimPF₆ was dissolved in 500 μL of methanol (disperser) which was rapidly injected into the aqueous sample. A cloudy solution was formed and, after a centrifugation step (5 min at 4000 rpm), the extractant solution was collected at the bottom of the test tube. Finally, before ICP-OES analysis, the extractant solution was transferred to an Eppendorf tube and diluted with acetic acid containing 250 $\mu\text{g L}^{-1}$ of Mn and Y as internal standards.

2.5. Instrumentation

ICP-OES measurements were performed using an Agilent 720 ICP-OES instrument with axial viewing (Agilent, Santa Clara, United States). Table 1 summarizes the operating conditions employed with this instrument. The sample introduction system was made of a OneNeb® nebulizer (Ingeniatics, Seville, Spain) coupled to a single pass with impact bead PTFE spray chamber (Thermo Scientific, Germany). Sample and standards were introduced into the nebulizer by means of a V-451 flow injection manifold (Upchurch Scientific, Silsden, United Kingdom) equipped with a 25 μL loop valve. An in-house built 300 μL plastic syringe with PEEK (Poly Ether Ether Ketone) coated quartz capillary needle (200 μm i.d., PEEKSIL, Upchurch, Oak Harbor, Washington, USA) was employed with the FIA manifold. Samples were introduced into a carrier stream (i.e., either 1% w w⁻¹ HNO₃ or air) controlled by a peristaltic pump (Model Minipuls 3, Gilson, France). Signal acquisition was performed by means of the transient signal software of Agilent's ICP-OES. Microsoft Excel® software was employed for manually signal integration. To improve accuracy and precision, internal standardization was employed. To this end, considering wavelengths characteristics and potential matrix effects due to carbon [16], Mn and Y were selected as internal standards. Analyte and internal standard wavelengths in this work are reported in the Supplementary material (Table S1, appendix).

2.6. Description of the fundamental calculations on TSIL selectivity by means of density functional theory

Density functional theory (DFT) was applied to gain insight about metal/BDPPIMPF₆ complexes. To this end, DFT calculations for optimization of saddle points were performed in terms of ONIOM method implemented in Gaussian16 software. The electron correlation was considered by using the hybrid functional B3LYP3. In order to consider nonbonding interactions and dispersion forces, single-point calculations

Table 1
ICP-OES operating conditions.

Plasma forward power (W)	1400
Argon flow rate (L min ⁻¹)	
Plasma	16.5
Auxiliary	2.25
Nebulizer (Q _g)	0.7
Torch injector diameter (mm)	2.4
FIA carrier	1% w w ⁻¹ HNO ₃ /air
FIA carrier flow rate (Q _i) (mL min ⁻¹)	1.0
FIA sample loop volume (μL)	25
Sample introduction:	
Nebulizer	OneNeb®
Spray Chamber	Single pass with impact bead
View mode	Axial
Acquisition time (s)	60
Replicates	3

of the optimized ONIOM structures were carried out employing the Truhlar functional M06. All stationary points were characterized by harmonic analysis. Reactants, intermediates and cycloadducts have positive definite Hessian matrices.

3. Results

3.1. Metal chelating capabilities of BDPPIMPf₆

In this work, for the first time, BDPPIMPf₆ has been evaluated as chelating agent for elemental extraction. First of all, TSIL extraction capabilities were evaluated for different hard and soft cations (i.e., Ag, Al, As, Au, Co, Cr, Cu, Fe, Mn, Ni, Pb, Pd, Pt, Re, Rh, Ru, Sc, Ti, V, and Zn). To this end, 0.5 mg kg⁻¹ multi-element standard was prepared at different pH values (i.e., pH 2, 4 and 6) and 200 mg of the extraction solution (i.e., TSIL/BmimPF₆ ratio 1:50) were added. Next, the mixture was shaken vigorously for 30 s using a vortex agitator and the organic phase was analysed by means of ICP-OES. Since the ionic nature of ILs, metals could also be extracted by anion exchange mechanisms with the BmimPF₆ [14]. Therefore, an extraction with BmimPF₆ was also carried out in the same conditions as those described above to be used as a reference. Fig. 1 shows the signal ratio between TSIL/BmimPF₆ and BmimPF₆ extracts for Ag, Cu, Pd and Pt under different pH values. Signal ratio values above 1 means that a given metal is selectively extracted by the TSIL.

In general, signal ratio for these four elements was above 1 for all the conditions tested thus confirming that BDPPIMPf₆ is a highly specific chelating agent for these species [11,13]. Interestingly, extraction efficiency for all these elements was strongly dependent on solution pH values. Silver and Cu extraction improved with solution pH whereas Pd and Pt extraction were favored at highly acid conditions. Similar findings have been observed by other authors operating alternative TSILs [9]. Regardless solution pH, no extraction was found for the remaining elements investigated (As, Al, Au, Co, Cr, Fe, Mn, Ni, Pb, Rh, Ru, Sc, Ti, V, and Zn) and, hence, it can be concluded that BDPPIMPf₆ is not an efficient chelating agent for these species.

Finally, the optimal mixture ratio between BDPPIMPf₆ and BmimPF₆ for Ag, Cu, Pd, and Pt extraction was investigated. Mixtures of BDPPIMPf₆/BmimPF₆ ranging from 1:20 to 1:50 were tested for a 0.5 mg kg⁻¹ of Ag, Cu, Pd, and Pt standards under optimum pH conditions for each element. No improvement on metal extraction occurred for ratios below 1:35 and, hence, this mixture ratio was used throughout

this work.

3.2. Insight into metal extraction selectivity by BDPPIMPf₆

Experimental data in Fig. 1 reveal that phosphine group present in BDPPIMPf₆ specifically favours the extraction of elements in Group 10 (Pd and Pt) and 11 (Ag and Cu) of the Periodic Table [11,13] with the exception of Au and Ni. To gain insight about TSIL affinity against Group 10 and Group 11 elements, DFT has been employed for a qualitative analysis of the stabilization energies of the corresponding complexes between BDPPIMPf₆ and these metals (Table S2, appendix). According to the general coordination geometries of the transition metals, planar geometries (trig or tetra) or pyramidal TPY-3 are favored [17]. The TSIL is ready to be complexed with transition metals through the phosphorous atom and by one of the nitrogen atoms of the imidazolium unit (Fig. S2, appendix). Employing a basic DFT model (B3LYP) for Ag⁺, the two types of feasible ligations (P and N-Methyl or P and N-butyl) have been examined. A priori, both ligation approaches are feasible since there were no differences in terms of energy. Possibly the slightly higher hyperconjugative effect of the butyl group is counteracted by its higher steric hinderance. Thus, the N-methyl and phosphorous atoms coordination was selected for further studies.

The stabilization energies for Group 11 elements were examined first. To this end, the analysis was performed using hydroxides due to pH increase resulted to be optimal for metal extraction. Silver nitrate and phosphate were coordinated to the TSIL and submitted to calculations, affording both the same energy (Table S2, appendix) but higher than in the complex TSIL-AgOH indicating that stabilized anions, whose negative charge is delocalized, gave weaker chelations. Similar findings were also observed for Cu²⁺ derived complexes. To justify the hypothesis of the geometry, the Au⁺ complex TSIL-AuOH_{N-Me} and TSIL-AuOH bonded only to the phosphorous atom were analysed and afforded very high energies. Consequently, Ag⁺ and Cu²⁺ extraction is favored with regard Au⁺.

In other side, under acidic conditions, it is known that the poor nucleophilic and non-coordinative PF₆⁻ anion can be decomposed liberating hydrogen fluoride in ionic liquids [14,18,19]. The influence of the acidic media in the complex can produce the interchange of the counter-anion of the IL and also the substitution of the anions bonded to the metal sphere. Initially, it was compared the relative stability of bidentate complexes of the two selective extracted Pd²⁺ and Pt²⁺ with the analogous planar complexes formed with Ni²⁺ using nitrate as anion

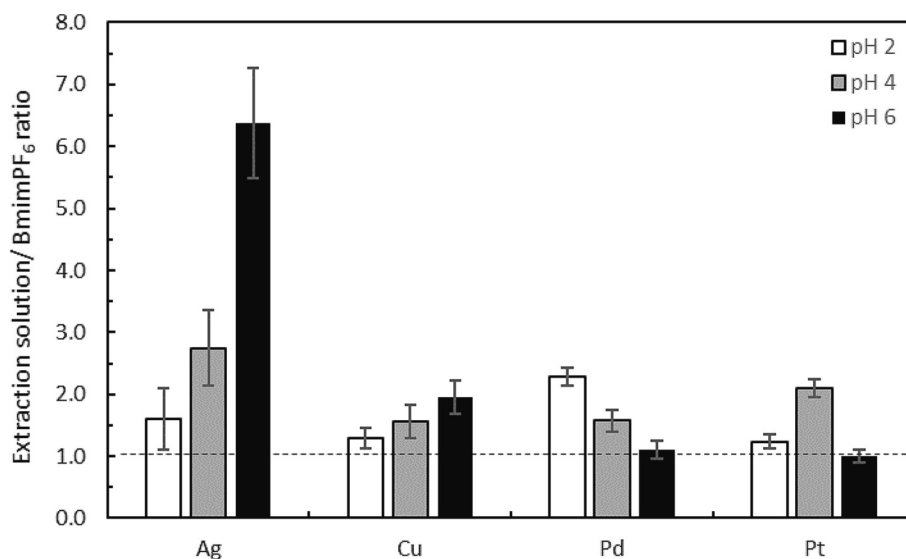


Fig. 1. Signal ratio between TSIL/BMIMPf₆ and BMIMPf₆ extracts for Ag, Cu, Pd and Pt under different pH values. Error bars calculated by error propagation calculation taking into account the uncertainty of the areas obtained (n = 3) for TSIL and BMIMPf₆.

for simplicity (Table S2, appendix). The energy gap between Pd and Pt complexes is around 6 kcal·mol⁻¹, Pd²⁺ chelate being more stable than the corresponding platinum²⁺ aggregate. In addition, Ni²⁺ complex had strong configurational and steric barriers to raise the square planarity giving very high energy gaps. Similar findings were observed for other transition metals (e.g., Co²⁺, Mn²⁺, etc.). In view of the high concentration of phosphate anions in the acidic mixture, the Pd²⁺ phosphate was also examined revealing a stabilization energy very similar to the obtained for the Pd²⁺ nitrate complex (0.2 kcal mol⁻¹ gap). From these data, it can be concluded that BDPPIMPf₆ complexes with Pd²⁺ and Pt⁺² are more favorable than with Ni²⁺.

3.3. Development of a metal extraction procedure based on DLLME and ICP-OES detection

According to the selectivity and the affinity of the TSIL with Ag, Cu, Pd, and Pt, an extraction/preconcentration procedure based on BDPPIMPf₆ as the chelating agent was further investigated. To this end, DLLME was combined with ICP-OES detection since this coupling is highly beneficial from analytical point of view (e.g., analyte enrichment factors, simplicity, sample throughput, multi-element detection capabilities, etc.).

3.3.1. Optimization of ICP-OES experimental conditions

Direct analysis of DLLME extracts by ICP-OES is challenging due to the limited volume available (i.e., <50–70 µL) and the potential occurrence of both spectral and non-spectral interferences caused by the organic matrix [20]. In addition, because the high viscosity of extraction mixture solution (i.e., BmimPF₆ 382 mPa·s at 25 °C) [14], strong memory effects and pumping issues are expected. According to previous findings by Martinez et al. [14], several strategies have been simultaneously implemented to operate TSIL extracts with ICP-OES: (i) selection of robust plasma conditions to favour sample decomposition (i.e., r. f. power 1400 W and nebulizer gas flow 0.7 L min⁻¹); (ii) dilution of the extraction mixture with acetic acid (1:1 ratio) to reduce sample viscosity [14,21]; and (iii) operating a FIA manifold coupled to the conventional sample introduction system operating a 1.0% w w⁻¹ nitric acid solution as a carrier for microsample introduction. Though the above-mentioned strategies allowed the introduction of the extraction mixture solution into the plasma, it was observed that the emission signal of the elements monitored was highly irreproducible due to the formation of TSIL precipitate through the sample introduction system (tubing, nebulizer, etc.) due to the low solubility of this compound in the carrier solution. For this reason, air segmented sample introduction was investigated to prevent precipitation issues. This sample injection methodology reduces sample dispersion and shows a positive effect on the analytical figures of merit (i.e., sensitivity, interferences, etc.) [22] Operating this way, TSIL precipitation through the sample introduction system was avoided but signal reproducibility was severely deteriorated due to the extraction mixture was segmented during its path towards the nebulizer. This pattern is typical of a high viscous substance [14] and, hence, different extractant mixture solution:diluent ratios (1:1–1:10), Q_i (100–500 µL min⁻¹) and tubing i.d. (i.e., 0.191–1.016 mm) were tested to eliminate sample segmentation. Thus, operating a 1:2 extractant solution:acetic acid ratio at 250 µL min⁻¹ with a tubing i.d. of 1.016 mm, sample segmentation disappears without compromising sample throughput.

3.3.2. DLLME optimization

The optimization of the DLLME extraction conditions for the elements of interest (i.e., Ag, Cu, Pd and Pt) was carried out by means of a central composite experimental design (CCD) [23]. According to previous works [24,25] and some preliminary experiments, the amount of extractant mixture solution, volume of dispersant, pH, and ionic strength were identified as the main relevant variables controlling metal extraction. Based in previous works reported in the literature [24,25], each of the four variables selected were investigated in five levels: (i)

extractant amount: 450 mg (++) , 350 mg (+) , 275 mg (0) , 175 mg (–) and 135 mg (–); (ii) dispersant volume: 650 µL (++) , 500 µL (+) , 350 µL (0) , 200 µL (–) and 100 µL (–); (iii) pH: 9 (++) , 7 (+) , 5 (0) , 1 (–) and 3 (–); and (iv) Ionic strength: 7.5% w w⁻¹ (++) , 5% w w⁻¹ (+) , 2.5% w w⁻¹ (0) , 0.5% w w⁻¹ (–) and 0% w w⁻¹ (–). Methanol was selected as dispersant agent since it usually affords better extraction efficiencies than other polar solvents (e.g., acetonitrile, ethanol, etc.) [14,15,21]. A total of 26 experiments were performed by triplicate using a 1 mg L⁻¹ multi-element standard containing Ag, Cu, Pd and Pt. After each DLLME treatment, and prior to ICP-OES analysis, 250 µg L⁻¹ of two different internal standards were added to all extracts for improving precision and minimizing carbon matrix effects on atomic and ionic emission [16]. Manganese (Mn I 280.108 nm) was selected for Ag, Cu, and Pd whereas Y (Y II 324.228 nm) was employed for Pt emission signal. To evaluate the significance of each of the variables investigated on the elemental extraction, data was analysed by ANOVA and the effects were summarized by means of the corresponding Pareto charts.

The results obtained for Ag and Pd are gathered in Fig. S3 (Appendix). Similar findings were, respectively, observed for Cu and Pt. Extraction for these species mainly depended on both the amount of extractant and dispersant. Analyte extraction was enhanced by reducing the extractant volume due to the higher enrichment factor achieved whereas metal extraction increased with the dispersant volume by improving the dispersion of the acceptor phase (ionic liquid) on the sample [26]. Solution pH and the ionic strength were less significant than the above-mentioned variables.

As expected from previous experiments (Section 3.1), Ag extraction was favored at higher pH values (i.e., neutral values). The ionic strength showed a negative influence on Ag extraction, probably due Cl⁻ ions affects negatively Ag solubility. As regards Pd, extraction for this element improved by decreasing pH and was independent of solution ionic strength. The optimum extraction conditions for each element are gathered in Table S3 (appendix). No significant differences were observed except for pH and ionic strength. To take advantage of ICP-OES multielemental capabilities, the CCD model was examined to look for a compromise set of pH and ionic strength allowing the simultaneous determination of Ag, Cu, Pd and Pt. However, no compromise conditions were found due to extraction efficiency for each pair of elements decreased under non-optimum pH and ionic strength. For instance, Group 11 elements (i.e., Ag and Cu) extraction decreased on average 30% operating the optimum pH and ionic strength conditions (i.e., pH 1.2 and 1.2 and 2.4% w w⁻¹ NaCl) for Group 10 elements. From these findings, the following compromise conditions were selected for metal extraction by means of DLLME: (i) extractant amount: 140 mg; (ii) dispersant volume: 500 µL; (iii) pH: 1.2 (Pd and Pt) and 6.8 (Ag and Cu); and (iv) Ionic strength: 1.8% w w⁻¹ (Pd and Pt) and 0% w w⁻¹ (Ag and Cu).

3.3.3. Comparison with other methodologies

Table 2 summarizes analytical figures of merit afforded by the proposed method: (i) LoD (3 times the standard deviation of the blank signal divided by the calibration curve slope according to IUPAC guidelines [27]); (ii) sample volume required; (iii) enrichment factor, EF (the ratio of the analyte concentration in the organic phase to the initial concentration in the sample); (iv) consumption index, CI (ratio between the sample volume and EF). Though this parameter is not usually reported, it is particularly useful to evaluate extraction efficiency since, unlike EF values, it does not depend on sample volume. Moreover, it does not take into consideration detection capabilities of the atomic spectrometry technique selected [28]; and (v) greenness metric, calculated with AGREEprep the tool proposed by Wojnowski et al. [29] to assess the analytical sample preparation greenness based on the green analytical chemistry principles. When compared to direct analysis by means of ICP-OES (i.e., no DLLME treatment), LoD improvement for Ag, Cu, Pd and Pt were, respectively, 110-, 35-, 40- and 36-fold (Table 2). These results can be explained by both the preconcentration procedure itself (EF) and the

Table 2

Comparison of the analytical figures of merit afforded by different microextraction methodologies.

Analyte	Chelating agent/solvent	Detection technique	V _{sample} (mL)	EF	CI (μL)	LOD (μg L ⁻¹)	Greenness Metric ^c	Ref.
Ag	BDPPMPF ₆ /BMIMPF ₆	ICP-OES	4	70	60	0.2 (22) ^b	0.51	This work
	8-HQ/CHCl ₃	FAAS	10	65	150	2	0.47	[36]
	2-mercaptobenzimidazole/CCl ₄	FAAS	12	35 ^a	340	0.4	0.49	[37]
	TSCC4P/2-DCB	GFAAS	5	92	50	0.02	0.57	[38]
Cu	Aliquat®/CHCl ₃	ICP-MS	35	58	600	0.0003	0.40	[39]
	BDPPMPF ₆ /BMIMPF ₆	ICP-OES	4	14	280	0.4 (14) ^b	0.51	This work
	Triton X-100/[Hmim][PF ₆]	GFAAS	10	28	360	0.5	0.52	[40]
	DDTC/[Bmim][PF ₆]	FAAS	10	62	160	0.8	0.51	[41]
	5-Br-PADAP/acetone nitrile	FAAS	30	11 ^a	2700	1.4	0.38	[42]
	dithizone/CHCl ₃	FAAS	5	20	250	1.2	0.51	[43]
Pd	salophen/CHCl ₃	FAAS	10	49 ^a	200	0.6	0.51	[44]
	BDPPMPF ₆ /BMIMPF ₆	ICP-OES	4	16	250	2 (80) ^b	0.51	This work
	PAN/[Hmim][PF ₆]	FAAS	5	16	310	3	0.53	[45]
	MPPT/CCl ₄	FAAS	10	20 ^a	500	2	0.51	[46]
Pt	Aliquat®/CHCl ₃	ICP-MS	35	51	690	0.00005	0.40	[39]
	BDPPMPF ₆ /BMIMPF ₆	ICP-OES	4	15	270	1 (36) ^b	0.51	This work
	Aliquat®/CHCl ₃	ICP-MS	35	75	470	0.00004	0.40	[39]

DDTC: Diethyldithiocarbamate; PAN: 1-(2-Pyridylazo)-2-naphthol; [Hmim][PF₆]: 1-hexyl-3-methylimidazolium hexafluorophosphate; HQ: 8-hydroquinoline; TSCC4P: mesotetraspirocyclohexylcalix[4]pyrrole; DCB: Dichlorobenzene; 5-Br-PADAP: 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)-phenol; MPPT: *N*-(6-morpholin-4-ylpyridin-3-yl)-*N'*-phenylthiourea.

^a Enhancement factor: ratio of the calibration curve slope with and without the extraction–preconcentration procedure.

^b Limits of detection obtained without the extraction–preconcentration procedure.

^c The possible score values are between 0 and 1, where 0 indicates that the method is not at all sustainable while 1 indicates that it is very sustainable.

beneficial effect of organics (i.e., acetic acid) on aerosol generation and transport [21]. Analytical figures of merit for the proposed method have also compared with those previously reported in the literature for alternative DLLME procedures (with or without TSILs as the chelating agent). Silver, Pd and Pt extraction efficiencies (CI values) for the proposed method were better than those reported by other authors. The BDPPMPF₆/BMIMPF₆ mixture was less attractive for Cu extraction. For this element, better CI values were obtained for other extraction mixtures. Because the limited use of ICP-OES as a detector for DLLME procedures, it is not feasible to compare Ag, Cu, Pd and Pt LoD with those afforded by alternative DLLME-ICP-OES methodologies. So far, flame atomic absorption (FAAS), graphite furnace atomic absorption (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) have been used for Ag, Cu, Pd and Pt determination in DLLME extracts. As expected, LoD for the proposed method were equivalent to those achieved by means of FAAS, but they were higher than those obtained with more sensitive techniques such as GFAAS and ICP-MS. Finally, the sustainability of the methodology proposed was also evaluated and compared with other methodologies reported in the literature. As it can be observed, the value obtained for the TSIL-based DLLME procedure was similar to that obtained for other methodologies. The variables with the higher influence on the score value for liquid-liquid microextraction procedures are based mainly on (i) the extractant amount; (ii) the waste generated; (iii) the energy consumption; and (iv) the number of pictograms labelled of the reagents employed.

3.4. Analysis of real samples

In order to check the applicability of the developed methodology, Ag, Cu, Pd and Pt were analysed in different water and pharmaceutical samples (ibuprofen containing drugs). These samples were selected for covering the different fields in which concentration levels of these elements should be controlled. For instance, Ag, Cu, Pd and Pt could be found in environmental samples because of different anthropogenic activities (e.g., copper-based fungicides, catalysers in combustion engines, etc.) [30]. Similarly, Ag, Pd and Pt are found in pharmaceutical products due to their use as catalysers during drug synthesis [31,32] and their levels should be carefully monitored according to European Medicines Agency (EMA) regulations [33].

Method accuracy was initially evaluated by means both recovery test and the analysis of a water certified reference material (CRM-DW1: Ag

25 ± 2 μg L⁻¹; and Cu 1900 ± 140 μg L⁻¹). To the best of authors knowledge, there is no certified material available in the market for pharmaceutical products [34,35]. Because Cu levels on CRM-DW1 are particularly high, this element was determined after 1:100 dilution. Silver, however, was directly determined (no dilution). Analyte recoveries for both elements were quantitative (Ag 22 ± 4 μg L⁻¹; and Cu 1900 ± 150 μg L⁻¹) thus demonstrating method accuracy.

Alternatively, a recovery test was carried out using water and pharmaceutical samples of different composition to investigate method robustness and matrix effects. To this end, water samples were spiked directly with Ag, Cu, Pd and Pt for a final concentration of 0.2 mg kg⁻¹, while for the drug samples, an amount of each drug (0.5 g) was added to 20 mL of water and the mixture obtained was then spiked with the same elements for a final concentration of 0.2 mg kg⁻¹ (0.32 mg kg⁻¹ for Pd/Pt in the tablet drug sample). Then, the samples were analysed by means of DLLME-ICP-OES. To fully exploit ICP-OES multielement detection capabilities, DLLME extracts containing Group 10 and Group 11 elements were mixed together (1:1 proportion) for the analysis. Though this strategy partially deteriorates LoD (i.e., 2-fold), it is clearly beneficial in terms of sample throughput, costs, and method sustainability. Prior to carry out the recovery test, selected samples were directly analysed, and Ag, Cu, Pd and Pt levels were below the LoD values in ICP-OES (Table 2).

Table 3 gathers analyte recoveries for all the samples investigated expressed as the percentage of the ratio between the observed concentration and spiked concentration (i.e., 0.2 mg kg⁻¹ approximately). As can be observed, irrespective of the sample considered, Pd and Pt recoveries were quantitative for all the samples investigated (−10%/+10%). Therefore, it can be concluded that extraction for these species is robust since it is not affected by matrix concomitants. Nonetheless, no

Table 3

Analyte recovery test values expressed in % (mean ± 95% confidence level; n = 3) obtained for the elements selected by means of DLLME-ICP-OES.

Sample	Ag	Cu	Pd	Pt
Tap water	92 ± 6	102 ± 4	101 ± 5	102 ± 6
River water	50 ± 10	10 ± 6	90 ± 3	93 ± 4
Sea water	–	4 ± 2	95 ± 6	103 ± 7
Suspension drug	108 ± 4	55 ± 2	102 ± 3	107 ± 5
Effervescent drug	75 ± 3	2 ± 1	105 ± 6	85 ± 5
Tablet drug	34.1 ± 1.6	91 ± 6	98 ± 5	110 ± 8

quantitatively values were registered for Ag and Cu in tap water, and some drug samples. The lack of accuracy for these species can be attributed to the negative influence of ionic strength on metal extraction. To verify this hypothesis, matrix matched standards were prepared by simulating major sample concomitants. Operating this way, recoveries were quantitative ($85 \pm 10/105 \pm 10\%$). Finally, method precision was determined by analysing six replicates of each sample performed in the same day. The relative standard deviation for all the elements was within the 3–8% range for the different samples tested. As regards method reproducibility, it was evaluated analysing five independent replicates in four different days, and it was lower than 16% for all the samples tested.

4. Conclusions

In this work, metal chelating capabilities of the BDPPIMPf₆ have been successfully exploited for developing a novel multielement DLLME-ICP-OES procedure for Ag, Cu, Pd and Pt determination at ultrace levels in environmental and pharmaceutical samples. Though extraction conditions for Group 10 (Pd and Pt) and Group 11 (Ag and Cu) elements are different, it is feasible to combine DLLME extracts for the simultaneous determination of all the analytes in a single run by means of ICP-OES. Consequently, this approach is highly beneficial in terms of sample throughput, costs, and method sustainability regarding previous DLLME procedures based on atomic absorption spectrometry.

DFT has been applied to gain insight into BDPPIMPf₆ affinity for Group 10 and 11 elements. The energies of stabilization of the bidentate complexes could justify the experimental results found due to the dual affinity of the silver and copper atoms to N- and P- ligands which was adapted to their pyramidal/trigonal geometries. In addition, other different divalent metal cations exhibited many difficulties to get a square planar geometry, such as Pd²⁺ and Pt²⁺ cations got. From these findings, there is no doubt that DFT can be a powerful analytical tool for developing TSILs designed for metal extraction as well as to evaluate whether previously reported chelating agents can be employed for multielement determination purposes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.sab.2023.106672>.

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