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Reversed-phase dispersive liquid-liquid microextraction for elemental analysis in gasoline by inductively coupled plasma optical emission spectrometry

Ezequiel Vidal^a, Anabela S. Lorenzetti^{a*}, Mónica B. Álvarez^a, Claudia Domini^a, Miguel Ángel Aguirre^{b*}, Lorena Vidal^b and Antonio Canals^b

^aINQUISUR, Departamento de Química, Universidad Nacional del Sur (UNS)-CONICET, Av. Alem 1253, 8000 Bahía Blanca, Argentina.

^bDepartamento de Química Analítica, Nutrición y Bromatología, Instituto Universitario de Materiales, Universidad de Alicante, P.O. Box 99, 03080 Alicante, Spain.

*Corresponding authors: anabela.lorenzetti@gmail.com, aguirre.pastor@ua.es

Abstract

In this work a green and fast sample preparation method based on reversed-phase dispersive liquid-liquid microextraction (RP-DLLME) was developed for the separation and preconcentration of several elements (i.e., Ag, As, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, S, Se, Sn and V) in gasoline samples before Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) determination. The extraction procedure was carried out in a reverse mode, since a small volume of aqueous phase (i.e., HCl 8M) is used to extract a relatively high volume of organic phase (i.e., gasoline sample). Unlike conventional DLLME, in the RP-DLLME the analytes were extracted from the organic phase into the aqueous phase. The experimental conditions for the microextraction procedure were: 5 g of sample, HCl 8M as extractant phase, mechanically stirred by vortex as dispersion system, 115 μL of extractant volume, and 2 min for extraction and 5 min centrifugation time. Under optimized extraction conditions the enrichment factor ranged between 3-53, and limits of detection ranged between 0.02 and 50 $\mu\text{g kg}^{-1}$. The proposed analytical method was validated and successfully used to analyze three gasoline samples. All gasoline samples were spiked at 100 $\mu\text{g kg}^{-1}$ for all analytes, except sulfur (in this case at 1000 $\mu\text{g kg}^{-1}$), obtaining recovery and RSD values within the range of 88-109% and 2-9%, respectively.

Keywords: Gasoline; Reversed-phase dispersive liquid-liquid microextraction; Elemental Analysis; Acidic Aqueous Extractant.

1. Introduction

The presence of trace metals in gasoline, unless they are added purposely, is usually undesirable, as they can be responsible for the poor performance of the gasoline, leading to deterioration of some engine components¹. Some of them could catalyze reactions responsible for corrosion of engine parts² (e.g., Ag, Mn, Mo, and Sn), gum formation³ (e.g., Cu and Ni), and/or catalyst poisoning⁴ (e.g., As, Se). Other important reasons are that they are restricted by legislation^{5,6} (e.g., S and Pb) or they are released into the environment as an important source of atmospheric pollution^{7,8} (e.g., Cd, Hg, Ba, V). Although some metals are natural constituents of crude oil, others can be found into the gasoline as contaminants (e.g., in the transport and storage container)⁹. Thus, gasoline chemical composition plays an important and essential role, not only for information about fuel quality but also for pollution monitoring¹⁰.

Metallic elements in gasoline are normally present in very low concentration, therefore, it is required the employment of sensitive techniques such as X-Ray Fluorescence (XRF)^{11,12}, Electrothermal Atomic Absorption Spectrometry (ETAAS)^{1,13}, Inductively Coupled Plasma Mass Spectrometry (ICP-MS)^{14,15}, Flame Atomic Absorption Spectrometry (FAAS)¹⁶, and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)¹⁷. ICP-OES technique is an excellent option for trace element determination due to it allows the simultaneous determination of a great variety of elemental analytes due to its high selectivity and sensitivity¹⁸.

Nevertheless, the aforementioned techniques are often not sufficient to achieve the required sensitivity in complex matrices, thus sample pretreatment methods must be used to reach high preconcentration factors. In recent years, Dispersive Liquid-Liquid Microextraction (DLLME) has emerged as an attractive preconcentration method, allowing the extraction and preconcentration of analytes from complex samples¹⁹. The DLLME technique offers many advantages such as rapid analysis time, simple setup, inexpensive equipment, high extraction efficiency and enrichment factor²⁰. The conventional DLLME is carried out in a ternary system composed of an aqueous sample, extractant and dispersant solvents. Thus, the dispersant (e.g., acetonitrile) solvent dispersed the extractant solvent (e.g., chlorinated solvents) into fine droplets increasing the contact area between the sample and the extractant phase, transferring rapidly the analyte from the sample to the extractant phase^{21,22}. After extraction and centrifugation

1 steps, the direct analysis of the enriched organic phase into the elemental detection system
2 is discouraged due to incompatibility of the solvent with the technique^{23,24}. For this
3 reason, an additional step of dilution or back extraction is required. When the sample is
4 immiscible with water, aqueous extractant solvent is an excellent option, appearing a new
5 modality of DLLME called Reverse Phase Dispersive Liquid–Liquid Microextraction
6 (RP-DLLME). In this modality, aqueous solvents are employed as extractant solvent²⁵.
7 The RP-DLLME provides the ability of introducing the extract (i.e., acidic aqueous
8 solution) directly into the elemental detection system²⁶. Recently, Özzeybek et al.
9 reported the determination of cadmium traces in fish and olive oil samples²⁷, achieving
10 both green and sensitive analytical methods.

11 Due to the importance of the elemental analysis in gasoline samples explained above, the
12 purpose of this work is to present a simple, fast, efficient, and environmentally friendly
13 RP-DLLME procedure, using acidic aqueous (i.e., HCl 8M) solution as a valuable
14 extractant solvent for the simultaneous separation and preconcentration of several
15 elements (i.e., Ag, As, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, S, Se, Sn and V) in gasoline
16 samples for subsequent measurement by ICP-OES.

17 2. Experimental

18 2.1. Reagents and samples

19 Working solutions were prepared from: (i) multi-element standard Conostan S-21
20 (Conostan, SCP Science, Baie D'Urfé, Canada) containing 500 µg g⁻¹ of Ag, Ba, Cd, Cr,
21 Cu, Mn, Mo, Ni, Pb, Sn, and V, and (ii) mono-element stock solution (Conostan)
22 containing 10,000 µg g⁻¹ of S, 500 µg g⁻¹ of As and Se, and 100 µg g⁻¹ of Hg. The solvent
23 used in the calibration standards and as a blank was kerosene (Panreac, Barcelona, Spain;
24 boiling range 190-250 °C). The extractant phase was prepared by an appropriate dilution
25 of an ultra-pure HCl acid (32% w w⁻¹, Merck Pro Analysis, Darmstadt, Germany) in
26 distilled deionized water (18 MΩ.cm resistivity).

27 The applicability of the analytical method proposed was evaluated using three
28 commercial fuel samples of 95 RON gasoline. The samples were purchased at different
29 petrol stations close to the University of Alicante and were stored in polyethylene
30 terephthalate (PET) containers and kept in the refrigerator until analyzed. Before
31 performing the analysis, the samples were allowed to reach room temperature.

2.2. Instrumentation

All measurements were performed with an inductively coupled plasma optical emission spectrometer (model 720-ES, Agilent Technologies, Melbourne, Australia) working in axially viewed plasma mode. **Table 1** shows the optimum operating conditions and emission lines used in ICP-OES. The RF generator power and gas flow rates (i.e., plasma, auxiliary, and nebulizing gas flow rates) were optimized achieving the maximum analyte intensities, after RP-DLLME procedure, using a standard solution containing 1 $\mu\text{g g}^{-1}$ of all analytes in kerosene (Panreac), except sulfur in which concentration was 10 $\mu\text{g g}^{-1}$.

2.3. RP-DLLME optimization

A multivariate optimization strategy was carried out to determine optimum conditions for RP-DLLME. The statistical software NEMRODW[®] ("New Efficient Methodology for Research using Optimal Design") from LPRAI (Marseille, France) was used to build the experimental design matrix and evaluate the results. In this study, the individual emission intensities were the response functions for optimization.

RP-DLLME optimization was performed using a multivariate approach consisting of a Plackett–Burman (**Table 2**) design in order to identify the significant factors²⁸. In these studies, the experiments were randomly performed in order to nullify the effect of extraneous or nuisance factors. After the screening study, only one significant factor was found and univariate optimization was carried out by monitoring the effect of this variable (i.e., extractant volume) on the signal intensity values. On these investigations, a standard solution containing 100 $\mu\text{g kg}^{-1}$ of all analytes was used, except sulfur. In this case, a concentration of 2000 $\mu\text{g kg}^{-1}$ was employed.

2.4. RP-DLLME procedure

Under optimized conditions, 5 g of calibration standards or 95 RON gasoline samples were placed in a glass centrifuge tube. Then, 115 μL of aqueous solution (i.e., HCl 8M) were added and the mixture was shaken for 2 min using vortex agitation. Then, phases were separated by centrifugation for 5 min at 4000 rpm. The upper organic phase was carefully removed with a glass pipette and the remaining acidic aqueous phase (i.e., 100 μL) was retrieved with a syringe for final analysis by ICP-OES. **Figure 1** shows a scheme of the overall procedure.

1 3. Results and discussion

2 3.1. RP-DLLME optimization

3 Numerous factors can affect extraction yield in the RP-DLLME procedure. Therefore,
4 optimization through a multivariate approach was carried out.

5 3.1.1. Screening study

6 A Plackett-Burman design was used to construct the matrix of experiments, including six
7 factors in twelve runs. The factors investigated at two levels in this work were: amount
8 of sample, type of extractant phase, extractant volume, dispersion system, and extraction
9 and centrifugation time. **Table 2** shows the considered experimental factors and levels in
10 the Plackett-Burman design.

11 Pareto charts of this screening study are shown in **Figure 2**. The relative influence of the
12 corresponding factor, and those bars that exceed reference vertical lines (dashed lines)
13 can be considered significant with 95% probability. In addition, rightward bars indicate a
14 positive effect in the response when increasing from a lower to high level, while leftward
15 bars indicate a negative effect upon the response when passing from a lower to upper
16 level of the corresponding factor. **Figure 2** shows that all the Pareto charts present a
17 similar response for almost all of the factors, varying degrees of significance depending
18 on the analyte. The exceptions are the extraction and centrifugation time which present
19 different effects (i.e., positive or negative) depending on the evaluated analyte. However,
20 the majority of the analytes show a positive effect in the extraction and centrifugation
21 time. Besides, these variables were non-significant. Thus, they were fixed at 2 min (the
22 extraction time) and 5 min (centrifugation time).

23 Interpretation of the graphic study presented in **Figure 2** leads to conclude that only three
24 factors (i.e., extractant phase type, extractant volume and dispersion system) are
25 statistically significant in the emission lines evaluated. Amount of sample was non-
26 significant with negative effect, and therefore, this factor was fixed at its low level (i.e.,
27 5 g). The type of extractant phase and dispersion system had both positive effects, and
28 they were chosen at their high level (i.e., 8M HCl as extractant phase and vortex agitation
29 as dispersion system). According to a previous publication, this acid plays a significant
30 role in the extraction step, in both organic and inorganic analytes^{29,30}. On the other hand,
31 some authors suggest that using the vortex in a mixture of two immiscible liquids directly

1 provides the mechanical energy needed to break up the drop. However, it should be noted
2 there are three different steps that are generated during emulsion formation: deforming,
3 breaking up and rejoining the droplets^{31,32}. In accordance with the result of the screening
4 study, the extractant volume was the only factor to be optimized and it was thoroughly
5 studied varying the extractant volume from 115 to 285 μL , with the other factors at the
6 corresponding fixed level.

7 3.1.2. Optimization study of extractant volume

8 **Figure 3** shows the resulting normalized signal of the average of all emission lines
9 evaluated. The signal of each element was normalized with respect to the maximum signal
10 for each one. In **Figure 3**, the signal intensity decreases by increasing the extractant
11 volume from 115 to 285 μL . It is well known that increasing the extractant volume leads
12 to an increase in metal extraction. In contrast, an excessive extract volume could lead to
13 a dilution effect, thus decreasing the preconcentration factor. It is easy to predict that the
14 optimum extract volume is below 115 μL . However, it was impossible to perform the
15 analysis using a lower volume than 115 μL , since it was the minimum volume required
16 to measure all emission lines analyzed.

17 Summarizing, optimal RP-DLLME conditions were: 5 g of sample weight, HCl 8M as
18 extractant phase, vortex as dispersion system, 115 μL of extractant volume, and 2 min for
19 extraction and 5 min centrifugation time.

20 3.2. Validation of the method

21 The main analytical figures of merit of the proposed method are summarized in **Table 3**.
22 The working range showed good linearity with correlation coefficients (r) from 0.9752 to
23 0.9997, being the majority of values higher than 0.995. The repeatability of the method
24 was evaluated by analyzing five spiked solutions at 10 and 100 $\mu\text{g kg}^{-1}$, except sulfur
25 where the spiked concentrations were 500 and 2000 $\mu\text{g kg}^{-1}$. The obtained RSD % values
26 varied between 3 and 12% (**Table 3**). Enrichment factors (EFs) were calculated as the
27 ratio of the sensitivity obtained with and without RP-DLLME. Arsenic gave the highest
28 extraction performance of the studied analytes, with an EF value of 53, whereas barium
29 showed the lowest extraction performance (i.e., EF=3). LOD values were calculated
30 following the $3 \sigma_{\text{blank}}$ criteria, being σ_{blank} the standard deviation of 10 blank
31 measurements, in accordance with Eurachem guidelines³³. Overall emission lines
32 evaluated, barium offered the most sensitive results in the analysis, obtaining a sensitivity

1 of 4000 ± 300 cps ($\mu\text{g kg}^{-1}$)⁻¹ and a LOD of $0.02 \mu\text{g kg}^{-1}$. Conversely, the highest LOD
2 value was obtained for sulfur (i.e., $50 \mu\text{g kg}^{-1}$).

3 3.3. Analysis of samples

4 Both calibration standards and samples were submitted to the same RP-DLLME
5 procedure and external calibration was used to measure all gasoline samples. It is
6 worthwhile to remark that both calibration standards and samples have the same matrix
7 after RP-DLLME procedure, and therefore, the matrix effects generated by HCl in ICP-
8 OES are compensated.

9 The original concentrations of the analytes in the three commercial samples analyzed by
10 external calibration were below the LOD, except for sulfur in the three samples and
11 selenium in samples 1 and 2. Hence, in order to assess the applicability of the proposed
12 analytical method, spiked commercial fuel samples were analyzed. Consequently, the
13 three gasoline samples were spiked at $100 \mu\text{g kg}^{-1}$ levels of all analytes, except sulfur. In
14 this case, all samples were spiked with $1000 \mu\text{g kg}^{-1}$ (**Table 4**). According to these results,
15 there were no significant differences between the concentrations added and those found
16 in all gasoline samples, obtaining relative recoveries ranged between 88 and 109%.
17 Therefore, non-significant matrix effects were found with the proposed methodology.

18 3.4. Comparison with other methods

19 In order to compare the developed method with previously reported ones, various
20 publications were found in which the same analytes were determined in fuel samples. The
21 techniques used in the studies consulted differ in either the detection technique or the
22 microextraction technique, or both. In **Table 5** it can be seen that the number of analytes
23 quantified simultaneously is the highest for the developed method. Besides, the time used
24 for the microextraction of the analytes is one of the lowest used thanks to the speed
25 obtained by the RP-DLLME procedure. It should be noted that acidic water solution is a
26 solvent significantly cheaper and greener than other organic solvents and sorbents
27 employed in the bibliography. Even though these publications determinate heavy metals
28 in gasoline samples, to our knowledge, the use of water solution as an extract solvent has
29 not been reported in elemental analysis in gasoline samples. In addition, the analytical
30 method proposed meets with the majority of the 12 principles of Green Analytical
31 Chemistry³⁴, especially those related with the reduction of reagents, the use of non-
32 hazardous reagents obtained from renewable sources, the use of miniaturized methods,

1 the safety of the operator, multi-analyte methods, low sample consumption and analytical
2 waste.

3 **4. Conclusions**

4 A RP-DLLME has been investigated for the elemental analysis in commercial fuel
5 samples by ICP-OES. The results obtained in this work showed that the RP-DLLME is a
6 successful analytical method for the separation and preconcentration of several analytes
7 from gasoline samples, improving their figures of merits (i.e., a high enhancement factor
8 is obtained) by ICP-OES. The application of this microextraction procedure avoided a
9 laborious and time-consuming digestion procedure that is a mandatory step before the
10 injection of high carbon content samples, resulting in a procedure with very low LOQ.
11 The method was applied to the elemental analysis of three commercial gasoline samples
12 with the additional advantages of using an aqueous extractant (i.e., HCl 8M) solution.
13 The proposed method was carried out using only 115 μ L of aqueous 8 M HCl as
14 extractant, reducing drastically the reagent consumption and also the generation of lab
15 residues. In addition, the analytes were extracted to an aqueous phase completely
16 compatible with ICP-OES instrumentation, in comparison with the use of organic
17 extractant employed with conventional DLLME. The results clearly showed that this
18 analytical method is promising and satisfactorily accurate to be used for elemental
19 analysis of gasoline samples by ICP-OES.

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31

1 **Table 1.** Operating conditions for ICP-OES.View Article Online
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Parameters	Value
Nebulizer type	OneNeb [®]
Spray chamber	Cyclonic
RF generator power	1200(W)
Plasma gas flow rate (L min ⁻¹)	15
Auxiliary gas flow rate (L min ⁻¹)	1.5
Nebulizing gas flow rate (L min ⁻¹)	0.75
Sample liquid flow (μL min ⁻¹)	100
Replicates	3
Viewing mode	Axial
Emission lines (nm)	Ag (328.068), As (193.696), Ba (455.403), Cd (214.439), Cr (267.716), Cu (324.754), Hg (253.652), Mn (257.610), Mo (202.032), Ni (216.555), Pb (220.353), S (181.972), Se (196.026), Sn (283.998) and V (311.837).

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1 **Table 2.** Experimental factors and levels of the Plackett-Burman design.
2View Article Online
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Experimental factor	Low level (-1)	High level (+1)
Amount of sample (g)	5	7
Type of extractant phase	HNO ₃ (8M)	HCl (8M)
Extractant volume (μL)	150	250
Dispersion system	Ultrasound	Vortex
Extraction time (min)	1	2
Centrifugation time (min)	3	5

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1 **Table 3.** Analytical figures of merit of the proposed method (RP-DLLME/ICP-OES). View Article Online
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Analyte	Working range ($\mu\text{g kg}^{-1}$)	r^a	Sensitivity (cps ($\mu\text{g kg}^{-1}$) ⁻¹) ^b	RSD (%) ^c		LOD ($\mu\text{g kg}^{-1}$)	LOQ ($\mu\text{g kg}^{-1}$)	EF ^d
				10 ($\mu\text{g kg}^{-1}$)	100 ($\mu\text{g kg}^{-1}$)			
Ag	10-150	0.9 967 (4)	232±6	11	8	1.5	5	9
As	50-200	0.9 752 (4)	10.5±0.2	-	7	6	20	53
Ba	0.10-150	0.9 985 (6)	4000±300	4	7	0.02	0.05	3
Cd	1.0-150	0.9 987 (5)	179±7	9	8	0.15	0.5	14
Cr	1.0-150	0.9 988 (5)	176±5	11	7	0.3	1.0	7
Cu	1.0-150	0.9 955 (5)	275±13	13	6	0.12	0.4	9
Hg	10-150	0.9 997 (4)	89.9±1.9	9	8	0.9	3	24
Mn	0.10-200	0.9 977 (6)	1340±70	6	10	0.03	0.10	13
Mo	10-150	0.9 959 (4)	70±3	12	11	1.2	4	20
Ni	10-150	0.9 945 (4)	55±4	11	8	1.2	4	17
Pb	10-150	0.9 964 (4)	18.78±0.05	11	5	3	9	15
S	500-2000	0.9 832 (4)	3.22±0.09	12*	3*	50	150	5
Se	50-200	0.9 975 (4)	2.2±0.5	-	10	12	40	5
Sn	10-150	0.9 996 (4)	20.4±0.8	12	7	3	10	8
V	1.0-150	0.9 981 (5)	640±70	10	11	0.09	0.3	25

3 ^a Correlation coefficient (r): number of calibration standards in parentheses.

4 ^b Slope ± standard deviation.

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3 ^c Relative standard deviation (RSD): mean value for 5 replicate analyses of 10 and 100 View Article Online
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4 $\mu\text{g kg}^{-1}$ spiked solution. * In case of sulfur the spiked concentrations were 500 and 2000
5 $\mu\text{g kg}^{-1}$.

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7 ^d Enrichment factor (EF): calculated as the ratio of the sensitivity obtained with and
8 without RP-DLLME.
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Table 4. Analytical results obtained in the analysis of three spiked gasoline samples. The concentration and recovery values are expressed as the mean \pm standard deviation of the three replicates.

Analyte	Spike ($\mu\text{g kg}^{-1}$)	Sample 1		Sample 2		Sample 3	
		Concentration ($\mu\text{g kg}^{-1}$)	R (%)	Concentration ($\mu\text{g kg}^{-1}$)	R (%)	Concentration ($\mu\text{g kg}^{-1}$)	R (%)
Ag	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	101 \pm 5	101 \pm 5	91 \pm 6	91 \pm 6	105 \pm 5	105 \pm 5
As	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	93 \pm 4	93 \pm 4	95 \pm 5	95 \pm 5	93 \pm 4	93 \pm 4
Ba	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	102 \pm 3	102 \pm 3	91 \pm 4	91 \pm 4	105 \pm 4	105 \pm 4
Cd	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	92 \pm 6	92 \pm 6	103 \pm 3	103 \pm 3	106 \pm 7	106 \pm 7
Cr	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	90 \pm 4	90 \pm 4	94 \pm 4	94 \pm 4	93 \pm 5	93 \pm 5
Cu	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	106 \pm 5	106 \pm 5	105 \pm 3	105 \pm 3	108 \pm 3	108 \pm 3
Hg	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	90 \pm 7	90 \pm 7	92 \pm 4	92 \pm 4	107 \pm 4	107 \pm 4
Mn	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	102 \pm 5	102 \pm 5	93 \pm 4	93 \pm 4	105 \pm 4	105 \pm 4
Mo	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	98 \pm 7	98 \pm 7	94 \pm 3	94 \pm 3	96 \pm 5	96 \pm 5
Ni	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	99 \pm 6	99 \pm 6	93 \pm 4	93 \pm 4	91 \pm 7	91 \pm 7
Pb	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	88 \pm 6	88 \pm 6	101 \pm 3	101 \pm 3	99 \pm 5	99 \pm 5
S	-	1978 \pm 81	-	1674 \pm 113	-	1354 \pm 138	-
	1000	2936 \pm 147	96 \pm 5	2604 \pm 87	93 \pm 6	2394 \pm 79	104 \pm 7
Se	-	97 \pm 6	-	51 \pm 4	-	<LOQ	-
	100	199 \pm 12	102 \pm 6	160 \pm 8	109 \pm 4	103 \pm 8	103 \pm 8
Sn	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	98 \pm 2	98 \pm 2	107 \pm 9	107 \pm 9	106 \pm 4	106 \pm 4
V	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	94 \pm 4	94 \pm 4	98 \pm 5	98 \pm 5	107 \pm 5	107 \pm 5

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1 **Table 5.** Comparison between different methods for elemental analysis in fuel samples. View Article Online
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Detection Technique	Sample preparation	Sample	Analyte	Extraction time (min)	Enrichment Factor	LOQ ($\mu\text{g L}^{-1}$)	Reference
EDXRF	MSPME	Ethanol Fuel	Cu, Cd, Pb, Cr, V, Mn	11	NI	36 (Cu), 39 (Cd), 48 (Pb), 36 (Cr), 27 (V), 33 (Mn)	4
EDXRF	RP-VALLME	Diesel oil	Cu, Mn, Ni, Pb	<1	34 (Cu), 62 (Mn), 59 (Ni), 64 (Pb)	47 (Cu), 26 (Mn), 34 (Ni), 23 (Pb)	5
ETAAS	MIL DLLME	Gasoline and diesel	Cd	2	220	0.28*	1
ETAAS	Emulsion breaking and DLLME	Biodiesel and oil	Cu, Pb	30	18 (Cu), 2.5 (Pb)	0.76 (Cu), 0.81 (Pb)	6
ICP-MS	Emulsion breaking	Gasoline	Cd, Mn, Pb, Sb	<1	NI	0.1 (Cd), 2 (Mn), 0.2 (Pb), 0.07 (Sb)	7
ICP-MS	HF-SPME	Gasoline and diesel	Cd, Cu, Fe, Pb, Zn	40	NI	0.4 (Cd), 0.3 (Cu), 0.5 (Fe), 0.9 (Pb), 0.3 (Zn)	8
FAAS	Emulsion breaking	Gasoline	Cu, Fe, Pb	10	2.4 (Cu), 2.5 (Fe), 2.0 (Pb)	11 (Cu), 77 (Fe), 48 (Pb)	9
ICP-OES	HF-LPME	Gasoline and diesel	Ag, Al, As, Mn, Ti	55	150 (Ag), 291 (Al), 112 (As), 405 (Mn), 367 (Ti)	0.27 (Ag), 0.18 (Al), 0.29 (As), 0.15 (Mn), 0.17 (Ti)	10
ICP-OES	RP-DLLME	Gasoline	Ag, As, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni,	2	9 (Ag), 53 (As), 3 (Ba), 14 (Cd), 7 (Cr), 9 (Cu),	5 (Ag), 20 (As), 0.05 (Ba), 0.5 (Cd), 1.0 (Cr), 0.4 (Cu), 3 (Hg),	This work

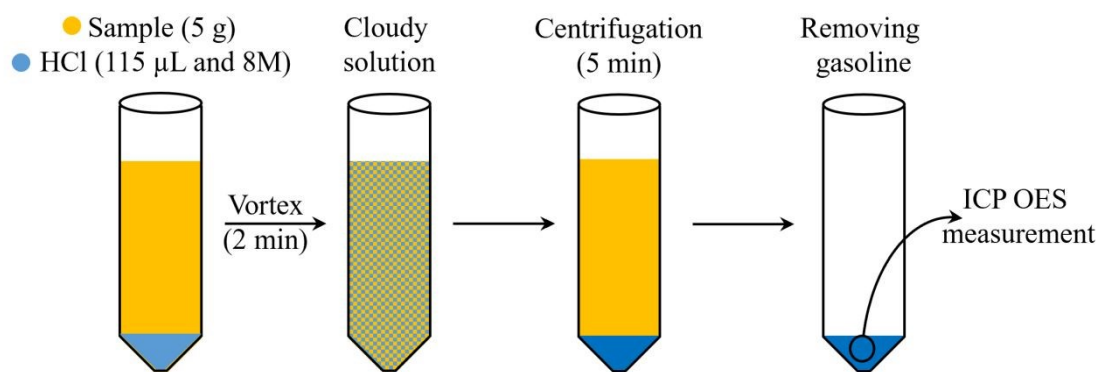
Pb, S, Se, Sn and V.	24 (Hg), 13 (Mn), 20 (Mo), 17 (Ni), 15 (Pb), 5 (S), 5 (Se), 8 (Sn), 25 (V)	0.10 (Mn) 4 (Mo), 4 (Ni), 9 (Pb), 150 (S), 40 (Se), 10 (Sn), 0.3 (V)*
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^a ET, extraction time; NI, not indicated; MIL DLLME, magnetic ionic liquid dispersive liquid-liquid microextraction; EDXRF, energy dispersive X-ray fluorescence spectrometry; MSPME, magnetic solid phase microextraction; HF-SPME, hollow fiber solid phase microextraction; HF-LPME, hollow fiber-liquid phase microextraction; RP-VALLME, reversed-phase vortex-assisted liquid-liquid microextraction.

*LOQ values expressed in $\mu\text{g kg}^{-1}$.

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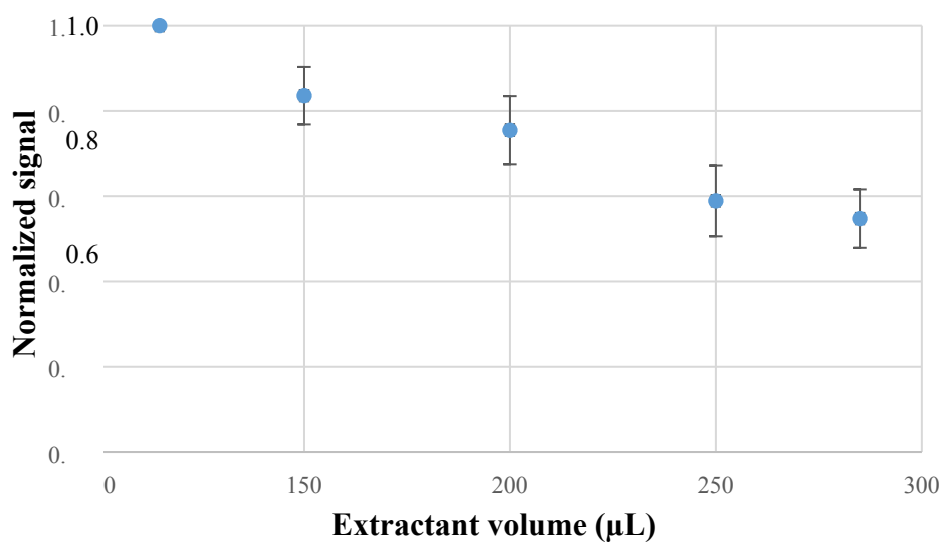
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Figure 1. Scheme of the analytical procedure.

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Figure 2. Pareto charts obtained in the screening study of the experimental factors affecting the RP-DLLME for all the evaluated emission lines. Bars to the right indicate a positive effect and bars to the left indicate a negative effect. Bars extending beyond the dashed vertical line indicate statistically significant factors at 95% probability.



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Figure 3. Effect of the extractant volume in RP-DLLME. Error bars represent the standard deviation of all emission lines evaluated. The experimental conditions for the microextraction procedure were: 5 g of amount of sample, HCl 8M as extractant phase, vortex as dispersion system, and 2 min for extraction and 5 min centrifugation time.

1 **Declarations**

2 There are no conflicts of interest to declare

4 **References**

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