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Fast emulsion-based method for simultaneous determination of Co, Cu, Pb and Se in crude oil, gasoline and diesel by graphite furnace atomic absorption spectrometry

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ABSTRACT

A method for the simultaneous determination of Co, Cu, Pb and Se in crude oil, gasoline and diesel samples using emulsion-based sampling and GF AAS is proposed. 400 mg of sample was weighted in volumetric flask following the sequential addition of 125 μL of hexane and 7.5 mL of Triton X-100® (20% m v^{-1}). Subsequently, the mixture was stirred in ultrasonic bath, during 30 min, before dilution to 25 mL with deionized water. Aliquots of 20 μL of reference solution or sample emulsion were co-injected into the graphite tube with 10 μL of 2 g L^{-1} $Pd(NO_3)_2$. The pyrolysis and atomization temperatures were 1300 °C and 2250 °C, respectively. The limits of detection ($n=10$, 3σ) and characteristic masses were 0.02 μg g^{-1} (0.32 μg L^{-1}) and 18 pg for Co, 0.03 μg g^{-1} (0.48 μg L^{-1}) and 15 pg for Cu, 0.04 μg g^{-1} (0.64 μg L^{-1}) and 48 pg for Pb, and 0.11 μg g^{-1} (1.76 μg L^{-1}) and 47 pg for Se. The reliabilities of the proposed method for Co and Se were checked by SRM® 1634c Residual Oil analysis. The found values are in accordance to the SRM at 95% confidence level (*Student's t-test*). Each sample was spiked with 0.18 μg g^{-1} of Co, Cu, Pb and Se and the recoveries varied from 92% to 116% for Co, 83% to 117% for Cu, 72% to 117% for Pb, and 82% to 122% for Se.

1. Introduction

Although crude oil is essentially a mixture of organic compounds, it contains a large range of metals and metalloids at trace levels, which can be linked to organic acids or porphyrin groups and dissolved in the water present in the oil on the inorganic form [1]. The importance to know the concentration of metal and metalloid in crude oil is related to their influence on the distillation processes and the final features of the derivate products [1–4].

Some elements, *e.g.* Co, Cu, Pb and Se are naturally present in crude oil and can be transported to the lighter fractions during the distillation process. Thus, gasoline and diesel can also contain metals and metalloids even in low concentrations [2,5]. Additionally, contamination from storage or transport provoked by corrosion of tanks or pipelines is another source of metals and metalloids [3]. Elements, such as Ag, Al, Ca, Ce, Cr, La, Li, Mg, Mn, Mo, Na, Si, Sn, Th, W, Zn and Zr can be intentionally added in the crude oil and derivates as additives to improve some chemical, physico–chemical and mechanical properties [6]. On the other hand, the presence of metals and metalloids in crude oil or derivates can cause undesirable effects, for example: (i) during the heavy oil's cracking process, some elements (*e.g.* Cr, Fe, Ni and V) can link irreversibly on to the catalyst surface, decreasing its activity; (ii) the burning of fuel oils releases potentially toxic elements to the atmosphere; and (iii) the waste waters from the refining processes can contain considerable concentrations of selenium and other metals and metalloids higher than those recommended by the environmental directives [7–10]. Trace metals, such as Cu, Fe, Co and Mn can catalyze the oxidation of the gasoline, gasoline–ethanol mixture and the diesel oil, losing some important properties like combustion power. Moreover, solid particles can be formed and accumulated into the engines, affecting its performance and durability [2].

Therefore, either as additives to improve specific characteristics of the products or as contaminants, the analytical control of petrochemical products for metal and metalloid is frequently performed in routine laboratories. For this reason, a large number of methods dedicated to the metal and metalloid determinations in crude oil and derivates have been proposed [11] and some of the elements monitored by petrochemical industries are cobalt [12], copper [5], lead [13,14] and selenium [15].

Several analytical methods using different instrumental techniques, such as flame atomic absorption spectrometry (F AAS), graphite furnace atomic absorption spectrometry (GF AAS), inductively coupled plasma optical emission spectrometry (ICP OES), and inductively coupled plasma mass spectrometry (ICP-MS) have been described in the literature for determination of trace

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elements in crude oil and derivates [6,11,16–20]. Among them, GF AAS is still posed as the technique of choice for determination of trace elements in several materials [11,21–26]. The main advantages are the high selectivity and sensitivity, the possibility to carry out *in situ* sample thermal decomposition during the heating program and the operation is simple. Additionally, this technique is not so affected by high amount of organic compounds as ICP OES and ICP-MS. Nevertheless, the mono-element conventional modes of operation and the long heating program (typically 1–3 min) have impaired the analytical frequency of GF AAS. This drawback can be partially attenuated by simultaneous graphite furnace atomic absorption spectrometer with conventional light source (SIMAAS) [7] or with high-resolution continuum source (HR-CS GF AAS) [21–23].

The SIMAAS allows the determination of up to 6 elements, which is favorable for the development of simultaneous methods with high sensitivity, reducing the time and costs related to instrument maintenance. The determinations of elements by SIMAAS have been proposed in the literature for many types of samples, but a small number of applications were devoted to the petrochemical samples. Recently, a direct sampling method was proposed for Cd and Pb determination in fuel ethanol using a combination of W as permanent modifier and Ir as co-injected modifier [24]. The simultaneous determination of Cr, Fe, Ni and V in crude oil using emulsion-based method and SIMAAS was successfully proposed by our group [7].

In general, the sample preparation for element determinations in crude oil and derivates has been performed by digestion using acids or mixtures of acids and hydrogen peroxide in combination with microwave heating [6,23]. However, significant time is needed for sample treatment when conventional digestion procedures are used. Furthermore, contamination, element volatilization and excessive dilution of final digested must be avoided.

Alternatively, the crude oil and derivates can be diluted with organic solvent or as emulsion or micro-emulsion for direct introduction into the equipment [3,7,11,12–18,22,23]. Emulsification seems to solve the problem of sample preparation for several petrochemical products [11]. The non-miscible system water–organic liquid by the formation of emulsions and micro-emulsions, using anionic, nonionic and amphoteric surfactants does not require a previous mineralization and can be used as simple and fast sample preparation procedure. Usually, when emulsion or micro-emulsion sample preparation is adopted the determination is possible using calibration with aqueous solutions instead of the organometallic standards.

Combining the simple sample preparation procedure and the multielement capability, the aim of this work is to propose a fast and reliable emulsion-based method for the direct and simultaneous determination of Co, Cu, Pb and Se in crude oil, gasoline and diesel by graphite furnace atomic absorption spectrometry.

2. Experimental

2.1. Reagents and samples

Titrisol© standard solutions of 1 g L^{-1} of cobalt, copper, lead and selenium in 1% (v v^{-1}) HNO_3 (Merck, Darmstadt, Germany) were appropriately diluted with high-purity double-ionized water (18 MΩ cm), obtained from a Milli-Q® water purification system (Millipore, Bedford, MA, USA). Palladium nitrate (20 g L^{-1}) (Sigma-Aldrich, St. Louis, Missouri, USA) was used to prepare the chemical modifier. Hexane and Triton X-100® (Merck, Darmstadt, Germany) were used, respectively, for crude oil dilution and emulsions preparation.

Standard reference material of residual oil from National Institute of Standards and Technology (Trace Elements in Fuel Oil —SRM® 1634c) was used to confirm the accuracy of the Co and Se determinations. Addition and recovery tests were used to check the reliability of Cu and Pb determinations.

Finally the proposed method was applied for analyses of six crude oil samples, provided by Petrobras (Rio de Janeiro, RJ, Brazil), four gasoline samples, and three diesel samples acquired in different gas stations from Sao Paulo city.

2.2. Apparatus

A simultaneous graphite furnace atomic absorption spectrometer, SIMAA-6000® model (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA), equipped with longitudinal Zeeman-effect background corrector, Echelle optical arrangement, standard THGA tube with integrated pyrolytically coated platform, and solid-state detector was used throughout in this work. The spectrometer was operated in the four-element simultaneous mode using hollow cathode lamps for cobalt, copper and lead, and an electrodeless discharge lamp for selenium. The instrumental parameters are depicted in Table 1. An AS-72 autosampler (Perkin Elmer Life and Analytical Sciences) was used to deliver reference solutions and sample emulsions from the cup to the graphite tube. Argon 99.998% (v v^{-1}) (Air Liquide Brasil, São Paulo, SP, Brazil) was used as the protective and purge gas.

An ultrasound bath (50 Hz), model 75D (VWR, New York, USA) was used for emulsion stirring.

2.3. Procedure

All glassware and polypropylene bottles were first cleaned with detergent solution, soaked in 10% (v v^{-1}) of HNO_3 for 24 h, rinsed with Milli-Q® water and stored in a closed polypropylene container. The reference solutions and sample preparations were conducted in a class 100 laminar flow bench (Veco, Campinas, SP, Brazil) to avoid airborne contamination.

Considering the complexity of crude oil, the optimization for sample preparation and heating program was carried out only for this matrix and tested subsequently for gasoline and diesel. Hexane was used only for crude oil emulsion preparation to improve the sample dissolution. The sequence of reagents addition (hexane, Triton X-100® and dilution with water) was also investigated. Taking into account the low concentration of the analytes in the samples, it was necessary to increase the sample mass for emulsion preparation and, consequently, the sensitivity of the method. Then, the crude oil masses were studied from 100 to 1000 mg in 0.5% (v v^{-1}) of hexane and 6% (m v^{-1}) of Triton X-100®. After the mixture of sample with hexane and Triton X-100® the influence of ultrasonic stirring was investigated over the emulsion

Table 1
Instrumental parameters and SIMAAS heating program for the simultaneous determination of Co, Cu, Pb and Se.

Element		λ (nm)	Current (mA)	Model
Co		242.5	15	HCL
Cu		324.8	15	HCL
Pb		283.3	12	HCL
Se		196.0	290	EDL
Step	**Temperature (°C)**	**Ramp (s)**	**Hold (s)**	**Ar (mL/min)**
Drying 1	110	10	20	250
Drying 2	130	5	20	250
Pyrolysis 1	200	10	10	250
Pyrolysis 2	1300	10	10	250
Atomization	2250	0	5	0
Cleaning	2600	1	3	250

HCL=Hallow Cathode Lamp; EDL=Electrodeless Discharge Lamp.

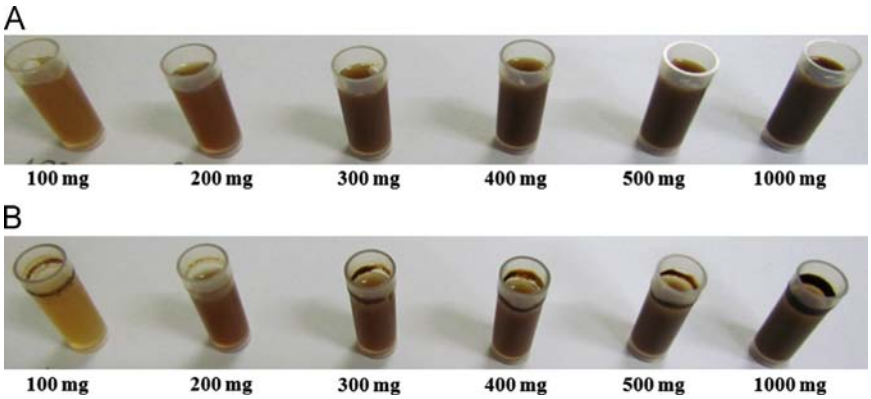

Fig. 1. Emulsions with different crude oil masses: (A) $t=2$ min and (B) $t=12$ h.

stability. Thus, crude oil mixtures were stirred in an ultrasound bath (50 Hz) for 30 min.

The optimization of SIMAAS heating program for Co, Cu, Pb and Se determination was simultaneously performed by pyrolysis and atomization temperatures, ramp and hold time variations. This study was carried out using reference solution of 20 μg L^{-1} of Co, Cu, Pb and Se in 0.5% (v v^{-1}) of hexane and 6% (m v^{-1}) of Triton X-100® and crude oil emulsion, prepared by dissolving 200 mg crude oil in 0.5% (v v^{-1}) of hexane and 6% (m v^{-1}) of Triton X-100®. The influence of 20 μg Pd as chemical modifier was evaluated in both cases.

The analytical calibration solutions were prepared simultaneously for Co (4.0–50 μg L^{-1}), Cu (4.0–50 μg L^{-1}), Pb (4.0–50 μg L^{-1}) and Se (8.0–50 μg L^{-1}) in 0.5% (v v^{-1}) of hexane and 6% (m v^{-1}) of Triton X-100®.

The sample preparation was performed using 400 mg of the crude oil, gasoline or diesel samples and fuel oil SRM® 1634c into polypropylene tubes (25 mL) with addition of 125 μL hexane (only for crude oil) and 7.5 mL Triton X-100® (20% m v^{-1}), submitted to ultrasound stirring for 30 min and subsequent dilution with deionized water. After this, the emulsions were manually homogenized and a volume of about 1 mL was transferred to the autosampler cup for analyzing. All measurements were based at least in three repetitions and in integrated absorbance.

3. Results and discussion

3.1. Emulsion sample preparation

Hexane was used to facilitate the dissolution of the crude oil in the water/Triton X-100® medium. Additionally, it was observed adsorption of crude oil on the sample preparation flasks' wall that was circumvented by using hexane as diluent. For hexane concentrations above 0.5% (v v^{-1}), the emulsions were not stable and black solid residues were observed, probably due to the asphaltenic precipitation. Different concentrations of Triton X-100® (2–10% m v^{-1}) were tested and the best relation between the amount of surfactant and the stability of emulsions was 6% (m v^{-1}). In the present work, the mixture of 0.5% (v v^{-1}) of hexane and 6% (m v^{-1}) of Triton X-100® was selected to optimize the mass of crude oil to prepare the emulsion.

Previous results showed that up to 50 mg of crude oil was possible to produce a stable emulsion in 25 mL of 0.5% (v v^{-1}) of hexane and 6% (m v^{-1}) of Triton X-100® without ultrasonic stirring [7]. For higher masses of crude oil the ultrasonic stirring was necessary to produce a stable emulsion. However, the sequence of reagents mixture and the exact step of ultrasonic stirring were decisive to achieve the best results for emulsion preparation. The stability of the emulsions increased when masses of crude oil (100–1000 mg) were mixed with 125 μL of hexane and 7.5 mL of Triton X-100® (20% m v^{-1}) and submitted to ultrasonic stirring, during 30 min, before dilution to 25 mL with deionized water. In this case, the ultrasound stirring before dilution induced the formation of micro-drops of crude oil that were better stabilized in the micelle medium formed by the higher concentration of Triton X-100® (20% m v^{-1}). On the other hand, when the crude oil masses (100–1000 mg) were mixed with 125 μL of hexane and 7.5 mL of Triton X-100® (20% m v^{-1}) and diluted to 25 mL with deionized water, before of the ultrasonic stirring, stable emulsions were not obtained. Although the concentration of 6% (m v^{-1}) of Triton X-100® is above to the Critical Micelle Concentration (CMC) the stabilization of crude oil in the system was not possible. This behavior should be related to the difficult to form micro-drops of crude oil and the low concentration of Triton X-100® in the system, which takes the break of emulsions.

Fig. 1 shows the auto sampler cups pictures representing the stability of emulsions prepared using increased masses of crude oil (100–1000 mg) at different time. As can be seen, stable emulsions were obtained for all crude oil masses up to 2 min (Fig. 1A). After this time, the stability of the crude oil emulsion using 1000 mg was broken, while the emulsions of 100, 300, 400 and 500 mg were maintained stable up to 120, 30, 20, and 10 min, respectively. The emulsion prepared with 200 mg of crude oil was the most stable, keeping homogeneous up to 8 h. Even after this time, the amount of emulsion supernatant containing 200 mg of crude oil was lower than emulsion containing 100 mg of crude oil (Fig. 1B). Probably, the higher stability of the emulsion with 200 mg of crude oil is related to the better ratio between the amount of species that act as co-surfactant (*e.g.* naphthenic acids) and the mass of crude oil. In Fig. 1B it is also possible to see that after 12 h there was a formation of a visible ring of crude oil on the polypropylene flask's wall due to the solvent evaporation.

Although the emulsion using 400 mg of crude oil was stable only for few minutes (~20 min), it was enough to do the simultaneous determination of Co, Cu, Pb and Se with better sensitivity. Consequently, this mass was adopted for emulsion preparation of all samples. However, to maintain the stability during 20 min, the following steps of the procedure must be observed: (step 1) 400 mg of sample+125 μL of hexane+7.5 mL of Triton X-100® (20% m v^{-1})+30 min of ultrasonic stirring; (step 2) dilution with deionized water to 25 mL; and (step 3) manual shaking. This procedure was also used for gasoline and diesel sample preparation, but without using hexane for dilution. Fig. 2 presents a picture of the final emulsions of the crude oil (A), gasoline (B), diesel (C) and SRM® 1634c (D) prepared according to the proposed procedure. The optically transparent and thermodynamically stable dispersion formed by gasoline sample (Fig. 2B) confirms that in this case the system was a micro-emulsion.

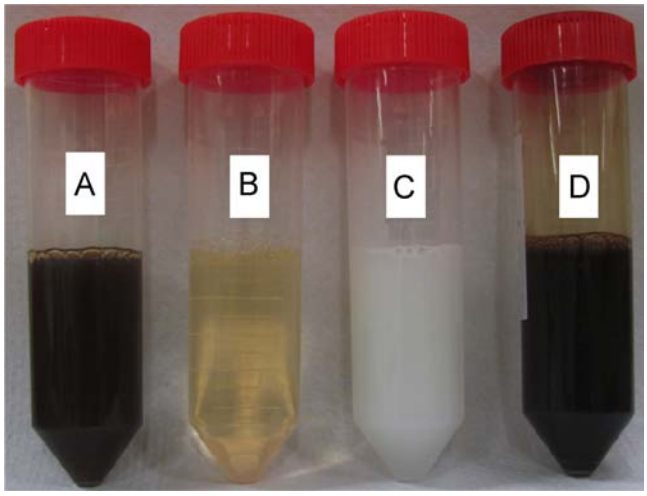

Fig. 2. Emulsions containing 400 mg of crude oil (A); gasoline (B); diesel (C) and SRM® 1634c of residual oil (D) prepared according to the proposed method.

3.2. Heating program for simultaneous determination

The thermal behavior of Co, Cu, Pb and Se was simultaneously evaluated during the optimization of the heating program. Pyrolysis temperatures in the crude oil emulsion and in aqueous solution were assessed. Taking into account the differences between the thermal behavior of the analytes and the necessity to adopt compromised conditions for the simultaneous determination the use of chemical modifier was mandatory. For this study 20 μg of Pd was used as chemical modifier. The main motivation for the choice of this chemical modifier was the excellent performance in terms of thermal stabilization of the selenium species.

In the absence of chemical modifier the pyrolysis temperatures of the elements in aqueous solution (0.5% (v v^{-1}) of hexane and 6% (m v^{-1}) of Triton X-100®) and crude oil emulsion were 1100 °C and 1150 °C for Co, 900 °C and 750 °C for Cu, 700 °C and 550 °C for Pb, and 300 °C and 550 °C for Se. For Co and Se the pyrolysis temperatures in aqueous solution were lower than those observed in presence of crude oil. The difference was more expressive for Se (150 °C). It is well know the low thermal stability of selenium inorganic species that volatilize at temperature around 250 °C. The higher pyrolysis temperature observed in presence of crude oil should be related to the presence of Se–organic species that increased the thermal stability of Se in absence of chemical modifier. Opposite results were observed for Cu and Pb. The pyrolysis temperatures in presence of aqueous solution were higher than those obtained in crude oil emulsion. Using 20 μg of Pd as chemical modifier, the thermal stability for all elements increased, mainly for Pb and Se. In this condition, the pyrolysis temperatures in aqueous solutions, crude oil, gasoline and diesel emulsions were close to 1400 °C for Co, 1500 °C for Cu, 1300 °C for Pb, and 1400 °C for Se.

The pyrolysis and atomization temperatures for simultaneous determination must be selected based on the analytes with higher and lower volatile characteristics. Considering this statement, the pyrolysis and atomization temperatures for the simultaneous determination of Co, Cu, Pb and Se were 1300 °C and 2250 °C, respectively.

However, when the heating program was applied using only one pyrolysis step at 1300 °C, micro-explosions were heard into the graphite tube (during pyrolysis step), impairing the standard deviation and accuracy of the results. Additionally, micro-holes over the platform surface were observed, reducing the graphite tube lifetime. This behavior can probably be associated to the formation of instable nitro compounds resulting from the thermal decomposition of the large amount of organic matrix (~320 μg) in combination with the nitric acid (1% w w^{-1}) present in the chemical modifier.

To circumvent this problem, a systematic study was executed changing ramps and holds times for drying and pyrolysis steps. After the optimization, an additional pyrolysis step, at 200 °C for 10 s, was mandatory to eliminate the micro-explosions, probably due to the better decomposition of organic compounds before the pyrolysis 2 step. The optimized heating program is depicted in Table 1.

3.3. Analytical figures of merits

The analytical parameters of the calibration curves are shown in Table 2. The limits of detection (LODs) were calculated considering the variability of 10 consecutive measurements of a mixture of 0.5% (v v^{-1}) of hexane and 6% (m v^{-1}) of Triton X-100® as the blank solution, according to $3s_{blk}/b$ (s_{blk} = standard deviation of the blank and b = calibration curve slope). To calculate the LODs in μg g^{-1} a mass of 400 mg and a final volume of 25 mL were considered. As the same method was used for all samples the LODs obtained for crude oil were also adopted for gasoline and diesel analysis. Excepting Pb, all characteristic masses (m_0) of elements were quite close to those observed for mono-element determinations (Table 2).

The analytical frequency of the method was approximately 10 samples per hour. This estimation was made considering measurements in triplicate, the heating program and time spent for the data acquisition. Taking into account the simultaneous determination of Co, Cu, Pb and Se, it was possible to have up to 40 analytical results per hour, lowering costs associated with the replacement of graphite parts.

3.4. Analytical results

The accuracy of the proposed method was checked by analysis of the Standard Reference Material of residual oil (SRM® 1634c). The found values for Co and Se concentrations are in accordance to the acceptable range at 95% confidence level (*Student's t-test*), as

Table 2
Figures of merits of the proposed method.

Parameters	Co	Cu	Pb	Se
Slop	0.0047	0.0022	0.0012	0.0006
Correlation coefficient	0.9968	0.9972	0.9957	0.9971
LOD (μg g^{-1})	0.02	0.03	0.04	0.11
LOD (μg L^{-1})	0.32	0.48	0.64	1.76
RSD (%)[a]	3.7	4.8	2.9	2.8
m_0 (pg)	18	15	48	47
m_0 (pg)[b]	17	17	30	45

[a] Reference solution: 4 μg L^{-1} of Co, Cu, Pb and Se in 0.5% (v v^{-1}) of hexane and 6% (m v^{-1}) of Triton X-100® (n=3).
[b] The THGA Graphite Furnace: Techniques and Recommended Conditions, Perkin Elmer, 1991.

Table 3
Results of the analysis of certified reference material.

Element	Certified value (μg g^{-1})	Determined value (μg g^{-1})	Recovery (%)
Co	0.15 ± 0.01	0.15 ± 0.10	100
Cu	–	0.45 ± 0.04	105[a]
Pb	–	0.43 ± 0.01	92[a]
Se	0.10 ± 0.01	0.11 ± 0.01	110

[a] Addition of 0.18 μg g^{-1}.

Table 4
Results of the determination of the analytes in crude oil (O1–O6), gasoline (G1–G4) and diesel (D1–D3) samples.

Sample	Determination ($\mu g\ g^{-1}$)				Determination after addition of 0.18 $\mu g\ g^{-1}$				Recovery (%)			
	Co	Cu	Pb	Se	Co	Cu	Pb	Se	Co	Cu	Pb	Se
O1	0.80 ± 0.02	0.06 ± 0.01	0.05 ± 0.01	0.11 ± 0.01	0.99 ± 0.02	0.28 ± 0.01	0.24 ± 0.02	0.31 ± 0.04	103	117	105	107
O2	1.26 ± 0.01	0.18 ± 0.01	0.08 ± 0.01	< 0.11	1.47 ± 0.01	0.38 ± 0.01	0.26 ± 0.01	0.18 ± 0.02	102	106	100	100
O3	0.97 ± 0.02	0.05 ± 0.01	0.06 ± 0.02	< 0.11	1.18 ± 0.02	0.25 ± 0.01	0.24 ± 0.02	0.18 ± 0.01	103	118	98	100
O4	1.07 ± 0.02	< 0.03	< 0.04	< 0.11	1.27 ± 0.01	0.19 ± 0.04	0.20 ± 0.02	0.22 ± 0.03	102	106	111	122
O5	0.20 ± 0.02	0.09 ± 0.01	0.04 ± 0.01	0.17 ± 0.02	0.44 ± 0.01	0.32 ± 0.01	0.26 ± 0.01	0.38 ± 0.03	116	119	118	109
O6	0.20 ± 0.02	0.06 ± 0.01	0.06 ± 0.01	0.23 ± 0.01	0.41 ± 0.01	0.28 ± 0.01	0.25 ± 0.01	0.39 ± 0.02	108	117	104	95
G1	< 0.02	< 0.03	< 0.04	0.16 ± 0.01	0.20 ± 0.01	0.18 ± 0.01	0.19 ± 0.01	0.33 ± 0.03	111	100	106	97
G2	0.06 ± 0.01	0.29 ± 0.02	0.14 ± 0.01	0.39 ± 0.02	0.22 ± 0.02	0.48 ± 0.01	0.23 ± 0.02	0.47 ± 0.02	92	102	72	82
G3	0.04 ± 0.01	< 0.03	0.06 ± 0.01	0.18 ± 0.03	0.20 ± 0.01	0.18 ± 0.01	0.20 ± 0.01	0.37 ± 0.02	91	100	83	103
G4	0.03 ± 0.01	0.05 ± 0.01	< 0.04	0.14 ± 0.01	0.22 ± 0.01	0.28 ± 0.01	0.19 ± 0.01	0.36 ± 0.02	105	83	106	113
D1	0.03 ± 0.01	0.24 ± 0.03	0.05 ± 0.01	< 0.11	0.21 ± 0.01	0.28 ± 0.02	1.57 ± 0.01	0.19 ± 0.01	100	117	113	100
D2	< 0.02	0.24 ± 0.03	1.32 ± 0.19	< 0.11	0.19 ± 0.01	0.44 ± 0.01	1.57 ± 0.01	0.19 ± 0.01	106	105	105	105
D3	0.05 ± 0.01	0.38 ± 0.03	0.05 ± 0.01	0.13 ± 0.01	0.26 ± 0.02	0.56 ± 0.0	0.27 ± 0.01	0.36 ± 0.01	113	100	117	116

shown in Table 3. Copper and lead are not certified in this SRM. In this case, addition of 0.18 $\mu g\ g^{-1}$ was used to check the reliability of the proposed method. Good recoveries were obtained for Cu (105%) and Pb (92%), corroborating the absence of interferences caused by matrix constituents.

Table 4 presents the results of crude oil, gasoline and diesel analysis. Each sample was spiked with 0.18 $\mu g\ g^{-1}$ of Co, Cu, Pb and Se and the recoveries varied in the ranges of 92–116% for Co, 83–117% for Cu, 72–117% for Pb, and 82–122% for Se. The obtained recoveries attested the good reproducibility of the proposed method.

4. Conclusions

The proposed method for the simultaneous determination of Co, Cu, Pb and Se in crude oil, gasoline and diesel oil samples by SIMAAS is simple and fast, with good accuracy and precision. The mixture of sample with Triton X-100® associated with ultrasound stirring, before dilution step, was essential to obtain stable emulsions for analysis. Additionally, it was not necessary to use any co-surfactant for emulsion preparation. Therefore, the combination of the fast emulsion-based method with the good analytical frequency of SIMAAS can be a good prerequisite to elect this method for quality control of crude oil, gasoline and diesel.

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References

[1] J.G. Speight, The Chemistry and Technology of Petroleum, Taylor & Francis Group, New York, USA, 2006.
[2] E.S. Chaves, F.G. Lepri, J.S.A. Silva, D.P.C. Quadros, T.D. Saint'Pierre, A.J. Curtius, J. Environ. Monit. 10 (2008) 1211–1216.
[3] C. Duyck, N. Miekeley, C.L.P. Silveira, P. Szatmari, Spectrochim. Acta B 57 (2002) 1979–1990.
[4] G.P. Brandão, R.C. Campos, E.V.R. Castro, H.C. Jesus, Spectrochim. Acta B 62 (2007) 962–969.
[5] D.S.S. Santos, M.G.A. Korn, M.A.B. Guida, G.L. Santos, V.A. Lemos, L.S.G. Teixeira, J. Brazilian Chem. Soc. 22 (2011) 552–557.
[6] M.G.A. Korn, D.S.S. Santos, B. Welz, M.G.R. Vale, A.P. Teixeira, D.C. Lima S.L.C. Ferreira, Talanta 73 (2007) 1–11.
[7] M.S. Luz, P.V. Oliveira, Anal. Methods 3 (2011) 1280–1283.
[8] C.M.S. Almeida, A.S. Ribeiro, T.D. Saint'Pierre, N. Miekeley, Spectrochim. Acta B 64 (2009) 491–499.
[9] N. Miekeley, T.R.C. Pereira, E.A. Casartelli, A.C. Almeida, M.F.B. Carvalho, Spectrochim. Acta B 60 (2005) 633–641.
[10] R.J. Cassella, O.D. Sant'Ana, A.T. Rangel, M.F.B. Carvalho, R.E. Santelli, Microchem. J. 71 (2002) 21–28.
[11] J.L. Burguera, M. Burguera, Talanta 96 (2012) 11–20.
[12] I.M. Dittert, J.S.A. Silva, R.G.O. Araujo, A.J. Curtius, B. Welz, B.H. Helmut, J. Anal. At. Spectrom. 25 (2010) 590–595.
[13] R.J. Cassella, D.M. Brum, C.F. Lima, T.C.O. Fonseca, Fuel Process. Technol. 92 (2011) 933–938.
[14] I.C.F. Damin, M.B. Dessuy, T.S. Castilhos, M.M. Silva, M.G.R. Vale, B. Welz D.A. Katskov, Spectrochim. Acta B 64 (2009) 530–536.
[15] R.Q. Aucélio, A.J. Curtius, J. Anal. At. Spectrom. 17 (2002) 242–247.
[16] F.A.C. Amorim, B. Welz, A.C.S. Costa, F.G. Lepri, M.G.R. Vale, S.L.C. Ferreira, Talanta 72 (2007) 349–359.
[17] C. Duyck, N. Miekeley, C.L.P. Silveira, R.Q. Aucélio, R.C. Campos, P. Grinberg G.P. Brandão, Spectrochim. Acta B 62 (2007) 939–951.
[18] R.Q. Aucélio, R.M. Souza, R.C. Campos, N. Miekeley, C.L.P. Silveira, Spectrochim. Acta B 62 (2007) 952–961.
[19] A.B. Volynskii, J. Anal. At. Spectrom. 66 (2011) 1049–1058.
[20] G.P. Brandão, R.C. Campos, A.S. Luna, E.V.R. Castro, H.C. Jesus, Anal. Bioanal. Chem. 385 (2006) 1562–1569.
[21] M. Resano, E. García-Ruiz, Anal. Bioanal. Chem. 399 (2011) 323–330.
[22] D.P.C. Quadros, E.S. Chaves, F.G. Lepri, D.L.G. Borges, B. Welz, H. Becker-Ross A.J. Curtius, Energy Fuels 24 (2010) 5907–5911.
[23] I.M. Dittert, J.S.A. Silva, R.G.O. Araujo, A.J. Curtius, B. Welz, H. Becker-Ross, J. Anal. At. Spectrom. 25 (2010) 590–595.
[24] L.N. Santos, J.A.G. Neto, N.M. Caldas, Fuel 99 (2012) 9–12.
[25] F.A.C. Amorim, D.C. Lima, J.A.A. Amaro, M.G.R. Vale, S.L.C. Ferreira, J. Brazilian Chem. Soc. 18 (2007) 1566–1570.
[26] R.Q. Aucélio, A. Doyle, B.S. Pizzorno, M.L.B. Tristão, R.C. Campos, Microchem. J. 78 (2004) 21–26.