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Optimum phase-behavior formulation of surfactant/oil/water systems for the determination of chromium in heavy crude oil and in bitumen-in-water emulsion

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Abstract

An "oil in water" formulation was optimized to determine chromium in heavy crude oil (HCO) and bitumen-in-water emulsion (Orimulsion-400®) samples by transversally heated electrothermal atomic absorption spectrometry (TH-ET AAS) using Zeeman effect background correction. The optimum proportion of the oil–water mixture ratio was 7:3 v/v (70 ml of oil as the internal phase) with a non-ionic surfactant concentration (Intan-100) in the emulsion of 0.2% w/w. Chromium was determined in different crude oil samples after dilution of the emulsions 1:9 v/v with a 0.2% w/w solution of surfactant in order to further reduce the viscosity from 100 to 1.6 cP and at the same time to bring the concentration of chromium within the working range of the ET AAS technique. The calibration graph was linear from 1.7 to 100 μg Cr l^{-1}. The sensitivity was of 0.0069 s l μg^{-1}, the characteristic mass (m_o) was of 5.7 pg per 0.0044 s and the detection limit (3σ) was of 0.52 μg l^{-1}. The relative standard deviation of the method, evaluated by replicate analyses of three crude oil samples varied in all cases between 1.5 and 2.6%. Recovery studies were performed on four Venezuelan crude oils, and the average chromium recovery values varied between 95.9–104.8, 90.6–107.6, 95.6–104.0 and 98.8–103.9% for the Cerro Negro, Crudo Hamaca and Boscán crude oils and for the Orimulsión®-400, respectively. The results obtained in this work for the Cerro Negro, Crudo Hamaca and Boscán crude oils and for the Orimulsión®-400 following the proposed procedure were of 0.448 ± 0.008, 0.338 ± 0.004 0.524 ± 0.021 and 0.174 ± 0.008 mg Cr l^{-1}, respectively, which were in good agreement with the values obtained by a tedious recommended standard procedure (respectively: 0.470 ± 0.05, 0.335 ± 0.080, 0.570 ± 0.021 and 0.173 ± 0.009 mg Cr l^{-1}).

Keywords: Heavy crude oils; Three-phase behavior; ET AAS; Chromium

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1. Introduction

Petroleum and its products have become the world's principal source of energy as fuel for transport and industries. The "native" crude oil is a complex mixture of organic compounds, which contains a large spectrum of inorganic constituents, among them chromium. This element can be present in a non-porphyrin form [1] at concentration levels between a few $\mu g\ g^{-1}$ and some hundred $\mu g\ g^{-1}$ [1–3]. Although, neither hexavalent nor trivalent forms of chromium may enter the environment in a quantity or concentration that may constitute a danger to the environment on which human life depends, the evaluation of chromium in crude oil and in the liquid effluents released from petroleum refineries will not per se "reduce the risk of exposure", but it may well point to implementing appropriate measures to do so [3].

The American Society for Testing Materials (ASTM) [4] and Institute of Petroleum (IP) standard methods also exist for the determinations of some metal species in crude oil and petroleum products [5,6]. Oil samples can be examined directly or after ashing. Procedures that require sample ashing are time consuming and the complete recovery of the analytes is often affected by some vapor-phase loss due to the high volatility of their chemical species. The wet digestion method and the extraction method involve intricate steps and are time-consuming [7]. The direct procedures involve reduced time, but, in some cases, the composition of the matrix affects the accuracy of the measurements. One important source of error is the contamination of the sample by accidental or systematic introduction of foreign elements during the various analytical operations. These undesirable effects may completely distort the results, and stringent precautions must be taken.

The determination of chromium in crude oils and fractions can be achieved routinely using a number of techniques such as flame (F AAS) [8,9] and electrothermal (ET AAS) [7,8] atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry (ICP-AES) [10], X-ray fluorescence spectrometry [11], neutron activation analysis (NAA) [10] and inductively coupled plasma mass spectrometry (ICP-MS) [12]. A problem posed by many of the samples from crude oils and by-products is their high viscosity, therefore, the direct analysis of crude oil using these techniques generally requires: (i) dilution with an organic solvent which may cause serious technical problems, e.g. in the case of ICP-AES, the dilution with an organic solvent which has high vapor pressure overload the plasma with solvent vapors changing its physical characteristics and make it unstable [13–15]; further, most of the plasma energy is consumed in evaporation of the solvent hence not sufficient energy is left for atomization of the analyte reducing the sensitivity of measurements. In the case of F AAS, irregular sample aspiration and volatilization processes cause low sensitivity and poor reproducibility. In the case of ET AAS the presence of analyte species in different organo metallic forms having different properties such as volatilization or mechanism of atomization in samples and standards may lead to different sensitivities [16,17]. (ii) Ashing or wet digestion procedures to prepare suitable specimens for direct XRF [11]. The choice of sample preparation is varied [18], each method having its own particular advantages and limitations.

When samples are diluted with an organic solvent changes in the concentration of sample/standard due to evaporation losses of the organic solvent can occur, but emulsification can reduce such losses, which is very important for a slow technique such as ET AAS [16]. Therefore, the analysis call for the use of emulsions consisting of surfactant/heavy crude oils/water mixtures, which three-phase systems require selection of optimum parameters [17,18]. The potential of phase-behavior formulations of surfactant/heavy crude oils/water systems for metals determination by ET AAS has not yet been investigated. The purpose of this study was to investigate for the first time, the analytical potential of an optimized phase behavior for the determination of chromium in heavy crude oils (HCO).

2. Experimental

2.1. Instrumentation

The measurements were carried out with a Perkin–Elmer Zeeman 4100ZL atomic absorption spectrometer with Zeeman effect background correction and equipped with a chromium hollow-cathode lamp operated at a current of 10 mA. Pyrolytic graphite coated tubes were used with pyrolytic graphite coated graphite platforms. Time-resolved absorbance signals were recorded on an Epson EL-486UC printer and integrated absorbance values were computerized using the PERKIN–ELMER software 4100 PC (version 3.7) for evaluating results.

Measurements were made at 357.9 nm with a slit of 0.2 nm and an integration time of 5 s. All measurements were made with at least three replicates and based on integrated absorbance, unless otherwise specified. Argon was used as the protective gas throughout. The volumes injected by the instrument autosampler were 10 μl of the emulsion solution.

A Contraves Rheomat 30 Couette-type rheometer (Oerlikon Contraves AG, Zürich, Switzerland) at 25 °C was used to measure the viscosity of emulsions. A double-gap bell-shaped cell was used for the low viscosity range. A two speeds and 6000 rpm Shimadzu electrical mixer (Tokyo, Japan) was used to emulsify oil samples.

The American Petroleum Institute (API) gravity scale, arbitrary scale designating an oil specific gravity in API° or degrees API, was based on the ratio of the weights of equal volumes of oil and pure water at 16 °C and one atmosphere pressure.

2.2. Reagents

All reagents were of analytical grade unless otherwise stated. Double de-ionized water of 18 MΩ cm^{-1} specific resistivity, obtained in a Millipore (Bedford, MA, USA) system, was used to prepare all the solutions and to rinse the previously cleaned laboratory material. The nitric acid was Suprapur® grade (Merck, Elmsford, NY, USA).

The nonionic surfactants used for this study were ethoxylated tri-terbutyl phenols: Sapogenat T-100, -180 and -300 with an average number of ethylene group per molecule (generally referred to as the ethylene oxide number or EON) ranging from 6 to 13 and manufactured by Hoechst (Franfurt-Höchst, Franfurt am Main, Germany); and Intan-100 nonionic surfactant, with an EON = 17.5 and manufactured by Kao Atlas Japan. All solutions of surfactants were prepared by appropriate dilution with water.

A 1000 mg l^{-1} stock solution of Cr(VI) was made by dissolving 3.3735 g of potassium chromate (K_2CrO_4 from Riedel de Haen, Seelze, Germany) in 0.2% (v/v) nitric acid solution. Working standards were prepared daily by dilution with the same nitric acid solution.

The argon used in this study was from AGA (Maracay, Venezuela), which certifies a purity of 99.9%.

2.3. Samples

The HCOs, namely, Boscan (gravity from 10.3 to 12.0 API° and viscosity of 7.0×10^3–8.5×10^3 cP at 100 °F), Cerro Negro (gravity from 8.0 to 8.9 API° and viscosity of 8.0×10^3–5.0×10^4 cP at 100 °F) and Hamaca (gravity from 8.8 to 10.5 API° and viscosity of 3.0×10^3–8.0×10^3 cP at 100 °F) [19,20]. These samples were sent to INTEVEP (Venezuelan Institute for oil industry analysis, Los Teques, Venezuela) directly from oil-drilling and refining companies for their respective analyses. The crude oil was a random sample taken directly from a barrel and stored in a gallon acid rinsed/deionized water plastic container.

Natural bitumen is a highly viscous (> 10 000 cP at 30 °C) and complex mixture of hydrocarbons which is difficult to pump in its natural state. To facilitate its transportation, natural bitumen is mixed with water in the production of a bitumen emulsion known as Orimulsion®. Orimulsion®-400, is the most current formulation of the fuel. Orimulsion®-400, a fuel manufactured by PDVSA-BITOR [21], is an emulsion of natural bitumen (ca. 70%), freshwater (ca. 30%), and a surfactant package (< 0.2%); therefore, this fuel

has not single molecular formula. The resulting fuel, Orimulsion®-400, has viscosity more than 20-times lower than that of natural bitumen.

In our case, all samples were kindly provided by INTEVEP, Caracas, Venezuela.

2.4. Procedure

The temperature program in Table 1 was followed. Calibration graphs were constructed by evaluating the integrated absorbance obtained by injecting 10 μl of standards solutions containing 0, 10, 20, 30, 40 50, 60 70, 80, 90 and 100 μg l^{-1} of chromium on the atomizer platform. The characteristic mass (m_o) was the amount in pg of analyte which gave a signal of 0.0044 s. The limit of detection (LOD, μg l^{-1}), was calculated from the equation $LOD = 3 \times S_{BL}/b$, where S_{BL} was the standard deviation of ten blank firings. Three to four sample replicates were analyzed in each case.

3. Results and discussion

3.1. Mixing rules for optimum formulations

The emulsion type (oil in water (O/W), water in oil (W/O) or multiple), drop size distribution, stability and rheological behavior are known to depend upon three types of variables, i.e. physicochemical formulation, composition and fluid mechanical conditions, as well as the way these variables are handled or programmed during the formulation protocol [22]. Thus, the amount of oil, surfactant, water and form of agitation were optimized in order to produce stable and low viscosity emulsions.

3.2. Surfactant/oil/water system preparation

The crude oil was warmed up to 60 °C, stirred and weighted. Due to the high viscosity of samples, the preparation of the emulsions by the moderate (magnetic) stirring of the system or by phase inversion [23] of both phases was not possible. Instead the emulsion preparation was performed following the classical way [24], which consisted in mixing both phases at 60 °C with a shaft turbine blender at a speed of 3000 rpm during 30 s. The total volume of the surfactant-oil-water systems was of 100 ml, which were prepared by changing the water-to-oil ratio (WOR) by increasing the volume of the internal phase (Φi) of oil from 10 to 100 ml and correspondingly decreasing the volume of the external phase (Φe) of surfactant–water. The 100 ml systems were prepared in 250 ml beakers. First the surfactant was added in aqueous solution and this solution was then mixed with the oil phase. The optimum WOR was of 3:7 (see below). After mixing, the system was left to equilibrate at room temperature for 1–2 h. (ca. 22 °C) and then the viscosity was evaluated. The beakers were then closed with a plastic wrap and kept at room temperature. Before the ET AAS measurement, the previously prepared emulsions were mixed again 1:9 (v/v) with an aqueous solution of 0.2% (v/v) Intan-100 in order to reduce the viscosity to 1.6 cP, at which values the sample behaves similarly to an aqueous solution, and to lower the concentration of chromium in the sample to the working range level of ET AAS determinations. This final dilution of the emulsion was done with the Intan-100 solution instead of water, because the sample transfer efficiency from the sampler tip to the graphite tube was improved

Table 1
Temperature program for the graphite furnace

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (ml min^{-1})
Drying	110	1	20	250
Drying	130	5	30	250
Pyrolysis	1500	10	20	250
Atomization	2400	0	5 (without reading)	0
Cleaning	2600	1	2	250
Cooling	20	3	5	250

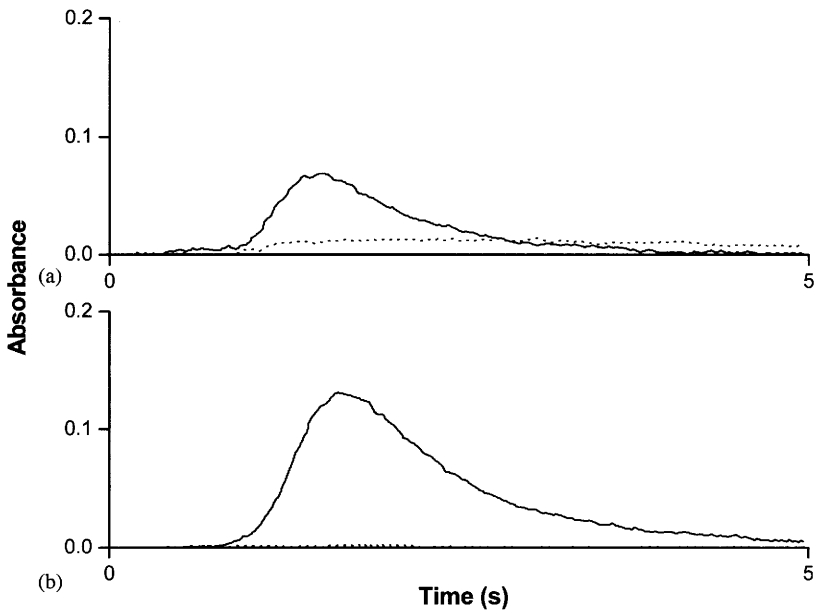

Fig. 1. Analytical responses for chromium in an emulsified HCO sample with final dilutions with water (a) and a 0.2% (v/v) Intant-100 solution (b). Other conditions as specified in Table 1.

and hence, higher sensitivity (Fig. 1). This effect could be attributed to the moiety of the surfactant, due to the presence of EON, which increases the surfactant/oil/water preparation solubility and wettability [25,26].

3.3. Formulation variables

Formulation variables are related to the components of the system, such as surfactant type and concentration. From the practical point of view, the actual surfactant–O/W system is quite more complex that any idealized ternary system. As a general rule, the water phase is an aqueous electrolyte solution which may contain several anions and cations, the oil phase may be an intricate blend such as crude oil and the surfactant is in most cases a complex mixture of chemical species, which make difficult to ascertain the number of independent formulation variables. The emulsion stability is estimated by measuring the time required for 2/3 volume coalescence ($t_{2/3}$), according to a standard procedure discussed elsewhere [27]. When a so-called optimum formulation is attained, a system is formed which exhibits features with built-in potential applications, such as ultra-low interfacial tension, high solubilization, reduced viscosity and long term stability [23].

In this work, the surfactant-rich phase becomes the emulsion external phase and the oil phase becomes the Φi upon stirring, resulting in an O/W emulsion. According to this, the phase transition start as an oil phase microemulsion, that takes up more and more water, then becomes the middle phase and starts rejecting oil by some nucleation process, until it ends up finally as a water phase microemulsion in equilibrium with an excess oil phase [23].

Emulsions are not thermodynamically stable and the time interval associated with the worsening of their stability appears to depend on the surfactant used [24]. Therefore, in this study the effect of two nonionic surfactant's concentrations on the optimum formulation to obtain an O/W emulsion was studied. For this purpose, the Sapogenat-100, -180 and -300 and Intan-100 surfactants were added at the concentration range from 0.1 to 1.0% (v/v) in water. When the different Sapogenat surfactants were used rather unstable emulsions were obtained with coalescence times

within 10 and 80 min, regardless of the surfactant concentration. In this case, the plugging of the autosampler tip was not uncommon. However, stable emulsions were observed when 0.2–0.4% (v/v) Intan-100 solutions were added. As the surfactant concentration increased, the viscosity minimum feature tended to fade away, whereas at lower surfactant concentrations the stability of the emulsion greatly decreased (ca. 12 h for a 0.1% (v/v) Intan-100 solution and a 7/3 O/W ratio).

The viscosity of the emulsion, which depends essentially upon the internal phase content, can be used as a guide of its usefulness for analytical purposes. The viscosity an emulsified HCO sample (Cerro Negro) decreased to an almost constant value (between 1.2 and 1.6 cP) for 10 and 20 Φi values (Fig. 2). This constant value stays at the optimum formulation as low viscosity values are required to ease the sample injection into the atomizer by means of the instrument autosampler and to avoid irreproducibility due to adherence of the oil phase to the capillary tube. Also, the emulsified system is clearly shifted to the formation of a stable O/W binary system at higher Φi values. Indeed, the coalescence time was of 20, 30 and 40–50 min for 1/9, 2/8 and 3/7–4/6 WOR values. However, the coalescence time for a 60/40 O/W relationship (Φi = 60 ml) was of 30 days (Fig. 3), while the coalescence time for a 70/30 O/W

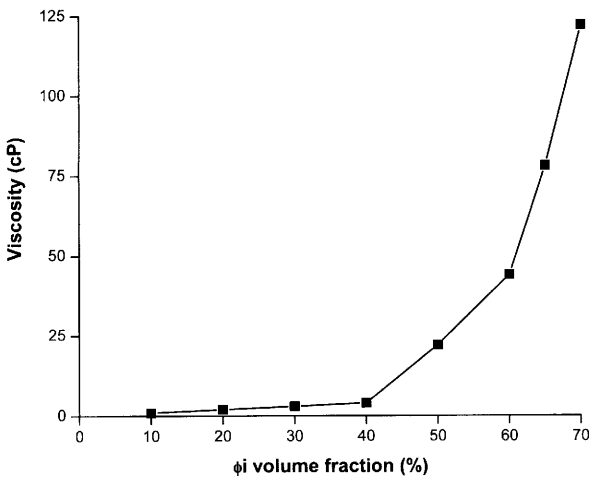

Fig. 2. Viscosity of a HCO emulsion at different Φi volume fractions.

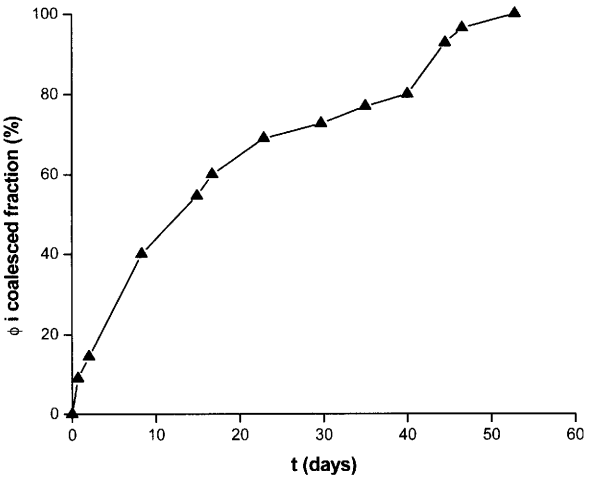

Fig. 3. Stability (as the coalesced time to clear of the aqueous phase) of a HCO for a 70 ml Φi value.

relationship (Φi = 70 ml) exhibits a stability value over 40 days. At this stage, the criterion was to choose the Φi value which provided the higher stability of the O/W emulsion, fact that is strictly related with the analyte homogeneity in the emulsion; otherwise, sampling errors can occur due to changes in the amount of analyte in the organic and aqueous phase. Therefore, an emulsion with a 70 ml Φi value was further diluted by adding a 0.2% (v/v) Intan-100 solution, to decrease the viscosity of this emulsion but without reducing the coalescence time below certain values (at least 6 h) that would not make possible the analysis of samples. When a ratio of 1:9 v/v (7/3 WOR emulsion: 0.2% Intant-100 solution) was used, the viscosity value was of 1.6 while the stability of the final emulsified solution was well above 20 h. This stability was appropriate for the analytical purpose of this work.

3.4. Temperature program

The temperature program developed in this study, as given in Table 1, was followed. Complete dryness of aqueous standards and emulsified samples was ensured with two drying steps; a 5 s ramp for the second drying temperature at 130 °C avoided spattering of the liquids and resulted in a

uniform solid deposit on the surface of the atomizer platform.

The pyrolysis and atomization curves for 0.2 ng of chromium in aqueous solutions and a HCO sample (Cerro Negro) are shown in Fig. 4. The variation of the pyrolysis and atomization temperatures was different in both matrices. The atomic absorption signal from chromium in standard solutions was thermally stable up to 1500 °C in the absence of chemical modifiers with a pronounced decrease of sensitivity above this temperature. However, it should be pointed out that the standard solutions of chromium were prepared in a 0.2% (v/v) nitric acid solution, and this acid may eventually acts as chemical modifier [5,28,29]. In the case of the emulsified crude oil solution the sensitivity slightly decreased from 1000 to 1500 °C, but the pyrolysis temperature range was widened up to 1800 °C. This effective stabilization of the analyte between 1500 and 1800 °C are decisive factors that are more important than better sensitivity. The organic crude oil and/or Intan-100 probably promoted the stability of the absorbance signals at higher pyrolysis temperatures. The maximum temperature of pyrolysis (T_{pyr}) that could be used without loss of chromium in both solutions was of 1500 °C. This T_{pry} is similar to that previously reported in previous publications in the presence of Eu as chemical modifier [30].

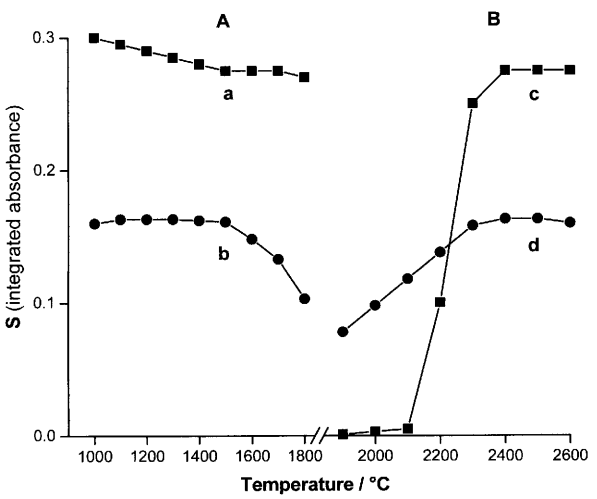

Fig. 4. Pyrolysis (A) and atomization (B) curves of chromium; (b, d) from an aqueous standard containing 0.2 ng of chromium; (a, c) from an emulsified Cerro Negro HCO sample.

Atomization curves were obtained by varying the atomization temperature while keeping the T_{pyr} constant at 1500 °C. In both cases, the optimum atomization was found to be 2500 °C. The furnace program included a cleaning stage at 2600 °C, as the temperature used for atomization of this element made such a stage necessary in order to minimize the build-up of a carbonaceous residues observed after 150 successive injections. Otherwise, frequent recalibrations (usually after 50 cycles) were required.

3.5. *Analytical figures of merit and application to real samples*

The calibration carried out with chromium alone followed the equation: $s = b + m[Cr]$ ($s = 0.0025 + 0.0069[Cr]$), where s is the integrated absorbance (peak area), b is the intercept with the *Y*-axis, m is the slope within the linear range, and [Cr] is the chromium concentration in the range 1.7–100.0 μg l^{-1}. Analyte addition graphs for the different samples were established in the same range. A paired Student *t*-test indicated that the calibration slopes obtained for aqueous chromium solutions were not statistically different ($P < 0.05$) from those for analyte additions to the real samples and subsequently emulsified as previously described, hence, the standard calibration technique with simple aqueous standards could be used for the determination of chromium in the crude oil samples investigated in this work. The limit of detection under the optimized conditions was 0.52 μg l^{-1} and m_o was 5.7 pg.

The precision expressed as the relative standard deviation (R.S.D.%) was established using the mean absorbance values of five replicate injections of chromium in aqueous standards and in each of the real samples varied in all cases between 1.5 and 2.6%.

Recovery studies were performed following the proposed procedure on four Venezuelan crude oils, and the average chromium recovery values varied between 95.9–104–8, 90.6–107.6, 95.6–104.0 and 98.8–103.9% for the Cerro Negro,

Crudo Hamaca and Boscán crude oils and for the Orimulsión® 400, respectively.

The accuracy of the recommended procedure was further investigated by also analyzing the three crude oils and the Orimulsion®-400 samples under study with a reported sample pretreatment recommended standard method for ET AAS determination of metal species [31]. The results are given in Table 2. The mean concentrations given by the two methods have been compared by using the two tail Student's t-test for a confidence limit of 95%. For four degrees of freedom the calculated value of t was of 0.47, while the critical value of t was of 2.78, indicating that the two methods do not give significantly different values for the mean chromium concentration found in all cases [32]. Although, good agreement was obtained for all samples by using both procedures, obviously the reported recommended standard procedure for ET AAS determination is less suitable as it is cumbersome for the determination of chromium, e.g. it requires of wet digestion and ashing procedures, among others. The concentrations vary considerable and are dependent on the actual location where the crude oil is originally obtained. However, all of them were below the value of 1 mg Cr l^{-1}, which is the upper limit of chromium in crude oils, and were close to the value of 0.43 mg l^{-1}, which is the approximately chromium concentration in Venezuelan crude oils [33].

Table 2
Results of the determination of chromium in HCOs and in Orimulsion®-400

Sample	Chromium concentration[a] (mg g^{-1})	
	Recommended procedure for ET AAS [31]	Proposed procedure
Cerro Negro	0.480±0.000	0.448±0.008
Hamaca	0.335±0.080	0.338±0.004
Boscan	0.570±0.020	0.524±0.021
Orimulsion®-400	0.173±0.008	0.174±0.008

[a] Mean±standard deviation of five determinations.

4. Conclusions

When the oil is evenly dispersed in the water phase, the sample similarly behaves to an aqueous solution, so it was possible to use the inorganic water soluble standards of chromium to prepare calibration curves, minimizing the time and cost of analysis. Stable emulsions with low viscosity are the only requirement needed to use this methodology. The main advantage of the proposed methodology as compared with the traditional ashing, dilution or wet digestion methods is that the optimum phase-behavior formulation of surfactant/oil/water methodology does not require a long time sample pretreatment or large amounts of organic solvents or inorganic acids, is easy to follow and it shows good accuracy and reproducibility.

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References

[1] J. Wieckowska, Mikrochim. Acta 98 (1982) 195.
[2] B. Du, Q. Wei, S. Wang, W. Yu, Talanta 44 (1997) 1803.
[3] Canadian Environmental Protection Act, Chromium and its Compounds, Government of Canada-Environment Canada and Health Canada, Catalogue No. En 40-215/39E, Ottawa, Ont., Canada, 1994.
[4] 1991 Annual Book of ASTM Standards, vol. 5.01, American Society for Testing and Materials, Philadelphia, 1991, pp. 580–583.
[5] Standard Methods for Analysis and Testing of Petroleum and Related Products, The Institute of Petroleum, vol. 2, Wiley, London, 1990, Sect. 285.
[6] Standard Methods for Analysis and Testing of Petroleum and Related Products, The Institute of Petroleum, vol. 2, Wiley, London, 1990, Sect. 288.
[7] M. Turunen, S. Peräniemi, M. Ahlgrén, H. Westerholm, Anal. Chim. Acta 311 (1995) 85.
[8] J. Alvarado, A.R. Picón, C. Manganaro de Vecchi, Acta Cient. Venezolana 41 (1990) 306.
[9] E. Pramauro, E. Pelizzetti, in: S.G. Weber (Ed.), Surfactants in Analytical Chemistry: Applications of Organized

Amphiphilic Media, vol. XXXI, Elsevier, Amsterdam, Netherlands, 1975, pp. 256–260.
[10] S.D. Olsen, R.H. Filby, T. Brekke, G.H. Isaksen, Analyst 120 (1995) 1379.
[11] K. Iwasaki, K. Tanaka, Anal. Chim. Acta 136 (1982) 293.
[12] M. Bettinelli, S. Spezia, U. Baroni, G. Bizzarri, J. Anal. At. Spectrom. 10 (1995) 555.
[13] A.W. Broon, R.F. Browner, Anal. Chem. 54 (1982) 1402.
[14] C.J. Lord, III, Anal. Chem. 63 (1991) 1594.
[15] S.J. Kumar, S. Gangadharan, J. Anal. At. Spectrom. 14 (1999) 967.
[16] N.N. Meeravali, S.J. Kumar, J. Anal. At. Spectrom. 16 (2001) 527.
[17] J.L. Burguera, I.A. Quintana, J.L. Salager, M. Burguera, C. Rondón, P. Carrero, R. Anton de Salager, Y. Petit de Peña, Analyst 124 (1999) 593.
[18] S.C. Nielsen, S. Stürup, H. Spliid, E.H. Hansen, Talanta 49 (1999) 1027.
[19] I. Layrisse, H. Rivas, S. Acevedo, R. Medina, M. Sánchez, M. Utrera, Rev. Tec. Intevep 4 (1984) 3.
[20] M.L. Chirinos, J. González, I. Layrisse, Rev. Tec. Intevep 3 (1983) 103.
[21] Orimulsion® Fact Sheet, Physical and Chemical Properties of Orimulsion®-400, http://www.orimulsionfuel.com.
[22] J.L. Salager, R. Antón, C.L. Bracho, M.I. Briceño, A. Peña, M. Rondón, S. Salager, Attainment of emulsion properties on design a typical case of formulation engineering, in: G. Flamant (Ed.), Product Engineering and Chemical Engineering Now, vol. 64, Société Française de Génie, 1999.
[23] M. Miñana-Perez, C. Gutron, C. Zundel, J.M. Anderez, J.L. Salager, J. Dispersion Sci. Technol. 20 (1999) 893.
[24] A.J.F. Sing, A. Graciaa, J. Lachaise, P. Brochette, J.L. Salager, Colloids Surf. Part A 152 (1999) 31.
[25] C.E. Rondón, M. Burguera, J.L. Burguera, M.R. Brunetto, P. Carrero, J. Trace Elem. Med. Biol. 9 (1995) 20.
[26] J.L. Burguera, R. Anton de Salager, M. Burguera, J.L. Salager, C. Rondón, P. Carrero, M. Gallignani, M.R. Brunetto, M. Briceño, J. Anal. At. Spectrom. 15 (2000) 549.
[27] J. Lachaise, T. Breul, A. Graciaa, G. Marion, A. Monsalve, J.L. Salager, J. Dispersion Sci. Technol. 11 (1990) 443.
[28] K. Pyrzynska, Spectrochim. Acta Part B 50 (1995) 1595.
[29] J.L. Burguera, C. Rondon, M. Burguera, M.E. Roa, Y. Petit de Peña, Spectrochim. Acta Part B 57 (2002) 561.
[30] J.L. Burguera, M. Burguera, C. Rondon, L. Rodríguez, P. Carrero, Y. Petit de Peña, E. Burguera, J. Anal. At. Spectrom. 14 (1999) 821.
[31] J.N. Miller, J.C. Miller, Statistics and Chemometric for Analytical Chemistry, fourth ed, Prentice Hall, Harlow, UK, 2000.
[32] Covenin 2044-83 Method for the Oil and Petrochemical Industry, Determination of Metals by Atomic Absorption Spectrometry in Crude Oils and its Products, first ed., Caracas, 1983.
[33] R.H. Filby, K.R. Shah, in: T.F. Yen (Ed.), The Role of Trace Metals in Petroleum, Ann Arbor Science, Ann Arbor, MI, USA, 1975.