Use of Emulsion Systems for the Determination of Sulfur, Nickel and Vanadium in Heavy Crude Oil Samples by Inductively Coupled Plasma Atomic Emission Spectrometry*

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A useful and rapid procedure is described for the determination of sulfur, nickel and vanadium in crude oil by inductively coupled plasma atomic emission spectrometry. Samples were prepared by emulsifying crude oil in water. Aqueous inorganic solutions with the same amount of emulsifier and solvent were used as calibration standards. Heavy crude oils were analysed and the results were compared with those obtained by digestion methods. To evaluate the accuracy of the method, National Institute of Standards and Technology Standard Reference Materials, 1622c Sulfur in Residual Fuel Oil and 1634a Trace Elements in Fuel Oil, were analysed. No statistically significant differences were observed between the results obtained by this method and the certified values. The precision of the method was in the range from 1 to 3% relative standard deviation.

Keywords: *Inductively coupled plasma atomic emission spectrometry; sulfur; trace metals; crude oil; emulsion systems*

There is a need in the petroleum industry to quantify sulfur, nickel and vanadium in crude oil samples as they are catalyst poisons and cause corrosion in furnaces and boilers. Also, sulfur contributes to environmental pollution through acid rain.[1] For this reason, sensitive, rapid and precise methods for the determination of sulfur in crude oils, are essential. In this respect, inductively coupled plasma atomic emission spectrometry (ICP-AES) is an attractive technique for the determination of sulfur and trace metals because of its applicability in multi-element determinations and the low detection limits obtainable.

Sulfur, nickel and vanadium can be determined by ICP-AES using different sample preparation methods. These methods are discussed below.

Digestion treatments are used to avoid the matrix problems associated with the analysis of crude oils.[2–4] The physical and chemical properties of samples treated in this manner are similar to those of aqueous standards, therefore, the determination of analytes in various different matrices is possible with the use of a single calibration curve. Digestion processes have some disadvantages, such as, long analysis times and trace metal contamination from acid reagents, digestion vessels and airborne particulates, which can affect the accuracy of the analytical results.

Some workers have determined sulfur, nickel and vanadium in crude oils by direct nebulization of the samples dissolved in organic solvents.[5–9] Direct dilution is simple, can be automated, is less time consuming than alternative procedures, such as, digestion, and is applicable to a wide range of petroleum products. In routine analyses, agreement between values obtained by direct dilution and those obtained by digestion of the sample is very good.[4] Care must be taken to ensure that the chemical characteristics of the standards match those of the samples as closely as possible. This problem can be overcome by selecting a more appropriate standard material.

An evaluation of the effects of a variety of common organic solvents on the analytical signal indicates that problems are experienced with organic solvents because of their volatility.[10] Solvents with greater volatility than water require changes to the normal ICP-AES operating conditions. Some of these changes include an increase in the forward power together with additional plasma gas to protect the torch and the addition of oxygen to the plasma to achieve the combustion of the solvent vapour. Also, addition of oxygen prevents the build-up of carbon.[11,12]

As an alternative to the use of organic solvents, the oil samples were emulsified in water and the emulsions were introduced into the ICP. The use of emulsions can reduce the organic content of the sample solution to less than 95% m/m. Emulsion techniques have been reported in the literature for atomic absorption spectrometry,[13,14] flame photometry[15] and direct current plasma emission spectrometry,[16] however, there are only a few references about the use of emulsion systems for sample introduction into an ICP. Determination of sulfur and trace metals in crude oil and oily products by ICP mass spectrometry (ICP-MS) and ICP-AES have been reported by Lord[17] and Borszeki *et al.*[18] They obtained good accuracy and precision in their methods.

Previous studies did not involve the analysis of heavy crude oils [crude with American Petroleum Institute (API) gravity less than 14] as these samples are difficult to handle because of their viscosity, and stable emulsions are difficult to obtain because of the high asphaltene content of these oils. In this paper, an ICP-AES method is described and evaluated for the determination of sulfur, nickel and vanadium in heavy crude oils by using the emulsification technique for sample preparation.

Experimental

Instrumentation

The inductively coupled plasma spectrometer employed for this study was a Jobin-Yvon Model JY24. Details of the instrument and the operating conditions used throughout this work are listed in Table 1.

Reagents

Sulfur solutions were prepared by diluting a 1000 μg ml^{-1} standard prepared from *pro analysi* sodium sulfate (Merck). Nickel and vanadium solutions were obtained from 1000 μg ml^{-1} stock solutions (BDH). Ethoxy nonilphenol (Etoxyl) and sulfur free xylene (BDH) were used as emulsifier and solvent, respectively, for emulsion preparation. De-ionized water (MilliQ grade, Millipore) was used throughout this work.

Table 1 Instrumental and experimental parameters

Spectrometer	Jobin-Yvon Model JY24
Grating	Holographic grating having 3600 grooves mm^{-1}
R.f. generator/MHz	40
Forward power/W	900
Nebulizer	Meinhard C type (with peristaltic pump)
Spray chamber	Scott type
Gas flow rates/l min^{-1}	
Plasma	12
Intermediate	2
Sheathing	0.1
Carrier	0.9
Purge	10
Observation height	15 mm above load coil
Measurement time/s	0.5
Working wavelength/nm	
Sulfur	181.9
Vanadium	309.311
Nickel	231.604

Samples

The samples tested were various Venezuelan crude oils having an API gravity of less than 14 (heavy crude oils). To assess the accuracy of the proposed method National Institute of Standard and Technology (NIST) Standard Reference Materials (SRM), 1622c Sulfur in Residual Fuel Oil and 1634a Trace Elements in Fuel Oil were tested.

Sample Preparation

Portions ($\leqslant 0.2500$ g) of crude oil are weighed into a tared 30 ml glass bottle. A 0.5000 g portion of xylene is added to each sample and the contents are mixed until a homogenous solution is obtained. Each sample is then mixed with 0.40 g of emulsifier and the mixture is mechanically agitated until a homogenous solution phase is produced again. The mechanical agitation can be accomplished by use of an ultrasonic bath. De-ionized water is added with continual agitation until a final mass of 20 g is obtained. The time required to prepare an emulsion is approximately 10 min per sample.

## Results and Discussion

Emulsion Preparation

A number of factors, such as, concentrations of crude oil, surfactant and water; chemical composition of the crude oil; temperature; and the technique used to mix and homogenize the components, can influence the stability of an emulsion. These variables are too numerous to evaluate their effect on the stability of the emulsions, experimentally. Becher[19] reported that a non-ionic emulsifier with an hydrophile–lipophile balance (HBL) of 8–18 should be used in order to form a stable oil-in-water emulsion. In this sense, 10 mol of ethoxylation nonilphenol (HBL ≈ 14) were selected as an emulsifier. This nonilphenol is a more efficient emulsifier for heavy crude oils than others used for crude oils and some of their products.[17,18] The optimum concentration of surfactant required to obtain a stable emulsion was obtained experimentally by varying the amount of emulsifier. Homogenization of the emulsion was evaluated visually. The best surfactant concentration obtained was 2.00% m/m for emulsions with a 1.25% m/m oil phase. A little xylene was used for emulsion preparation to reduce the viscosity of heavy crude oils. This pre-treatment facilitates effective mixing and interaction between the oil and surfactant that must be accomplished prior to the addition of water.

## Analytical Conditions for Sulfur, Nickel and Vanadium Determination by ICP-OES.

Ionic to atomic line intensity ratios were used to optimize the operating parameters of the plasma.[20] The magnesium lines Mg II (280.270 nm) and Mg I (285.213 nm) were selected for the optimization of the following parameters: carrier, plasma, intermediate and sheathing gas flow rates, forward power and purge gas flow rate (for sulfur determination). The operating parameters are presented in Table 1.

Calibration Mode

To choose the correct calibration method for the determination of sulfur, nickel and vanadium, the slopes of calibration curves obtained by using inorganic aqueous solutions, emulsified crude oil solutions and emulsified inorganic aqueous solutions (with the same amount of emulsifier as used in emulsified crude oil solutions) were compared. These calibration curves were obtained by using the single off-peak background correction method. The results are presented in Figs. 1–3. For sulfur and nickel (Figs. 1 and 2), the slopes of the emulsified crude oil and emulsified inorganic aqueous solutions were the same. This means that emulsified inorganic aqueous solutions can be used for calibration purposes under the working conditions selected. This conclusion cannot be applied to aqueous solutions because the slopes have a different behaviour when compared with the slopes obtained for emulsified solutions. In the case of vanadium (Fig. 3), all the calibration curves exhibit similar behaviour. Therefore, emulsified inorganic aqueous solutions were chosen for calibration purposes.
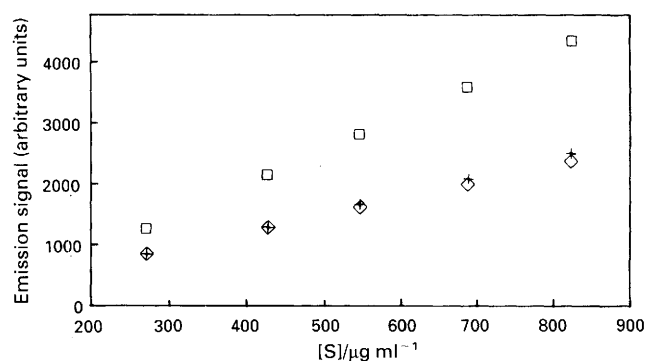
Fig. 1 Calibration curves for sulfur obtained by using: □, aqueous solutions; ◇, emulsified aqueous solutions, and +, emulsified crude oils solutions
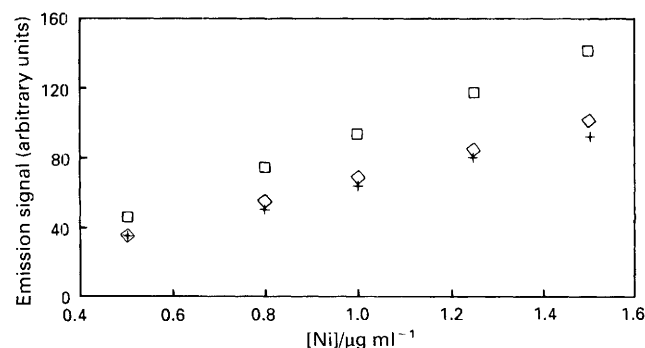
Fig. 2 Calibration curves for nickel obtained by using: □, aqueous solutions; ◇, emulsified aqueous solutions; and +, emulsified crude oils solutions
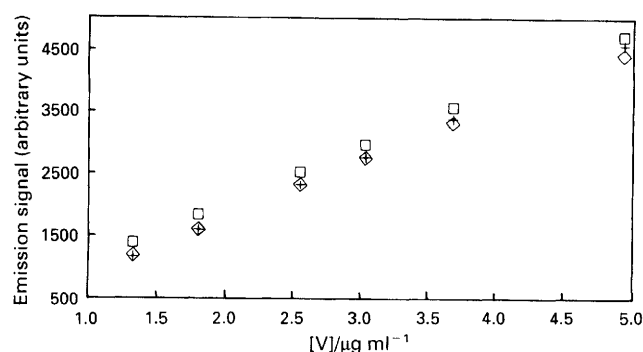
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Fig. 3 Calibration curves for vanadium obtained by using: □, aqueous solutions; ◇, emulsified aqueous solutions; and +, emulsified crude oils solutions

Table 2 Detection limits for sulfur, nickel and vanadium

Analyte	Aqueous solution/ $\mu g\ ml^{-1}$	Emulsified aqueous solution/ $\mu g\ ml^{-1}$	Emulsified crude oil solution/ $\mu g\ ml^{-1}$
Sulfur	0.04	0.5	0.6
Nickel	0.03	0.06	0.08
Vanadium	0.01	0.02	0.02

Table 3 Determination of sulfur, nickel and vanadium in different SRMs using the proposed method

SRM	Sulfur (% m/m) Experimental*	Certified
NIST 1622c	2.2±0.1	2.012±0.025
NIST 1634a	2.7±0.1	2.85±0.05

SRM	Nickel/$\mu g\ ml^{-1}$ Experimental*	Certified
NIST 1622c	—	—
NIST 1634a	27±2	29±1

SRM	Vanadium/$\mu g\ ml^{-1}$ Experimental*	Certified
NIST 1622c	—	—
NIST 1634a	54±2	56±2

* Mean of five determinations and ±RSD at the 95% confidence level.

Detection Limit

Detection limits (expressed as the concentration associated with the smallest signal that can be distinguished with a predetermined change from the random fluctuations of the background) were determined for sulfur, nickel and vanadium in aqueous, emulsified inorganic aqueous and emulsified crude oil solutions by the method of Miller and Miller.[21]

The detection limits are presented in Table 2. Results show that the detection limits for emulsified crude oil and emulsified aqueous solutions are the same. Also, these detection limits are higher than those obtained for aqueous solutions. These differences were mainly due to the different background emission signals obtained for aqueous solutions and emulsified solutions.

Accuracy and Precision of the Method

To assess the accuracy of the method, two Standard Reference Materials, NIST SRM 1622c and NIST SRM 1634a, were analysed. The results are presented in Table 3. Significance tests[21] (*t*- and *F*-tests) at a confidence level of 95% indicated that the results obtained were in good agreement with the certified values. The precision of the method was in the region of 2% expressed as relative standard deviation (RSD).

Reliability of the Method

In order to test the applicability of the proposed method to the analysis of real samples, several heavy crude oils were analysed. The results obtained by ICP-AES for emulsion samples were compared with those obtained by digestion methods (sulfate ash[2] and bomb digestion[3]). The different sulfur, nickel and vanadium contents obtained are listed in Table 4. Results show that ICP-AES values are in agreement with digestion method values, when *t*- and *F*-tests[21] were applied to the results at a confidence level of 95%.

Conclusions

The direct determination of sulfur, nickel and vanadium in heavy crude oil was successfully achieved by using emulsion systems for sample introduction in ICP-AES. Good precision and accuracy were obtained using emulsified inorganic aqueous solutions for calibration purposes, with no internal standard.

Emulsion sample preparation is extremely quick and the problems experienced with organic solvents, such as, carbon build-up, are avoided because of the reduction of the organic content of the sample solution.

Table 4 Determination of sulfur, nickel and vanadium in various crude oils using the proposed method; results given as mean±RSD, $n=3$, at the 95% confidence level

Sample	Gravity (API*)	Sulfur (% m/m) ICP-AES	R.M.(A)†	Nickel/$\mu g\ ml^{-1}$ ICP-AES	R.M.(B)‡	Vanadium/$\mu g\ ml^{-1}$ ICP-AES	R.M.(B)
A	8	2.8±0.1	2.54±0.05	81±5	81±2	280±25	249±5
B	9	4.7±0.1	4.78±0.07	99±7	102±3	468±50	478±9
C	10	5.7±0.2	5.51±0.08	107±7	107±3	1200±62	1188±30
D	12	3.8±0.1	3.66±0.07	88±7	87±3	415±50	415±8
E	13	3.0±0.1	2.80±0.06	54±7	57±2	451±37	439±8

* API=American Petroleum Institute.
† R.M.(A)=Reference method, values obtained using combustion bomb digestion method.[3]
‡ R.M.(B)=Reference method, values obtained using sulfate ash method.[2]

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