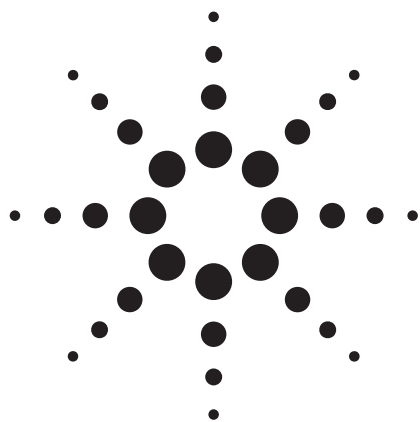




Determination of V, Ni, and Fe in Crude Oils and Bitumen using Sequential ICP-OES and Scandium as an Internal Standard

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Authors

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Abstract

A sequential ICP-OES is used to analyze viscous petroliferous materials (crude oils and residua), using tetralin as a diluent, oil-soluble metal compounds as calibration standards, and Sc as an internal standard. The analytical performance of the procedure was evaluated by employing conventional figures of merit, such as ease of operation (chemical stability of the standards and samples, plasma stability over an extended period of time, and absence of carbon build up), long and short-term precision, limits of detection, and accuracy. The satisfactory long term RSDs of less than 5%, reduced the frequency of re-calibration thus increasing sample throughput. The limits of detection with tetralin as a diluent are similar to those reported previously in other studies, and are better than those obtained with xylene and similar to those obtained with kerosene. The effect of variable viscosity was compensated by using Sc as an internal reference. Relative to a pure tetralin matrix, the effect of a 1:10 crude oil-tetralin matrix did not exceed 10%. Several certified petroliferous reference materials, varying widely in composition, were analyzed for their Fe, Ni and V contents, and the data obtained indicate a satisfactory accuracy and an extended linear range of calibration of 4 orders of magnitude.



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Introduction

The concentration of Ni and V in natural crude oils can amount to several hundred mg/kg. During the processing of these resources, the presence of Ni and V in petroleum fractions can deactivate catalysts. Consequently, there is a need for a rapid and convenient procedure for their determination.

The direct analysis of industrial petroliferous materials (crude oils, lubricating oils, gas turbine fuels, residua, complex oil additives, etc.), for their trace and minor element contents by ICP-OES, is now an accepted method in many laboratories [1–6]. However, some difficulty in the analysis of these organic samples has frequently been encountered. This is due to interference effects in the sample introduction system as a result of viscosity differences and in the plasma due to the interaction with the organic aerosol and vapors formed during nebulization [1–4,7,8]. For several analytes, the limits of detection are impaired due to spectral interferences caused by prominent C-molecular bands. Plasma instability due to RF generator design inadequacies also leads to degraded repeatability and incomplete pyrolysis results in C build up in the torch [1–4].

In the present report, results are given of a study aimed at evaluating the Liberty 220 and its 40.68 MHz generator for the analysis of crude oils and residua using tetralin as a diluent. Since natural crudes contain particulate materials, a high solids nebulizer was used to prevent nebulizer clogging. The use of tetralin (1,2,3,4-tetrahydronaphthalene) as a diluent and solvent was prescribed by the ASTM for the determination of trace elements in gas turbine fuels by atomic absorption spectrometry [9]. The solvent was also used by Botto7 who used H β as a diagnostic criterion for viscosity and plasma effects. In previous studies Y and Co were employed as the internal standards [10,11]. Sc has been widely employed for compensating for salt effects in the analysis of aqueous solutions [12,13], but has not been used for compensating viscosity effects in the analysis of organic samples. In this application, Sc II 361.384 nm was used as the internal standard to compensate for such variations in the samples and calibrating solutions. It was measured sequentially in contrast to the simultaneous detection of previous applications [12,13].

Instrumentation and Methods

A 40.68 MHz RF generator in the Agilent Liberty 220 vacuum high resolution sequential spectrometer was employed. An Agilent high solids V-groove nebulizer (catalog no. 99 100574 00), permitting the injection of suspended and viscous materials, together with a Sturman-Masters double pass cylindrical spray chamber (01-104236-90), was used. A conventional one piece quartz torch with a central injector (1.4 mm in diameter) was employed (catalog number 20 100696 90).

ICP Operating Conditions

ICP operating conditions are listed in Table 1. The plasma was operated at 1.2 kW using the Ar gas flows set out in Table 1; the gap between the plasma base and the injector was about 2 mm. The samples and standards were delivered at a rate of 1.5 mL/min through organic solvent resistant Viton peristaltic tubes (0.76 mm ID, Gilson, WI., catalog no. 475103). A fast pump of 10 s was used to minimize memory effects between sample analyses. The position of the torch and the pressure of the aerosol carrier was adjusted so that the visible carbon molecular emission bullet extended about 1 mm above the top of the torch. The height of observation above the load coil was determined using the automated profiling routine provided in the Liberty 220 software.

Table 1. ICP Operating Conditions

Argon cooling gas	12 L/min
Auxiliary gas flow	2.25 L/min
RF generator	40 MHz crystal locked
Power	1.2 kW
Nebulizer pressure	120 kPa
Aerosol carrier	0.7 L/min
Sample delivery rates	1.5 mL/min
Delivery tube	Gilson cured Viton
Integration	Three 1 s replicates
Sample delay	30 s
Rinse time	10 s, fast pump

Spectral Line Selection

Spectral lines for the determination of V, Ni, and Fe were selected on the basis of minimum spectral interferences and maximum signal-to-background ratios, and are listed in Table 2. Background positions were selected by scanning the lines and selecting positions in automatic mode. Spectral line interferences due to the analytes present in the standards and samples were not observed. Lack of spectral line interference is due to the high resolution of the spectrometer.

Sample Preparation

In previous investigations it was concluded that the use of xylene and toluene as diluents had several disadvantages [8]. During nebulization of these solvents, vaporization takes place in addition to aerosol formation and, as a result of high plasma loading, a high operating power is necessary. In addition, carbon formation on the sample injector and on the auxiliary gas tube appears to be more frequent when these diluents are employed. The only advantage of these solvents appears to be an increase in stability of the sample solutions and standards. Although the use of kerosene results in increased plasma stability, less intense molecular carbon emissions, and absence of carbon build up, numerous natural crude oils and bitumen do not dissolve completely even in high kerosene-sample ratios, and those that did, are unstable. In this application, tetralin (Fluka catalog no. 87450) was used as a diluent. The plasma could be operated for extended periods of time without operator intervention, and the samples readily dissolved and remained in solution.

Calibration and Quality Control Standards

A 100 mg/kg multi-element standard (Spex Industries, Edison, NJ, catalog no. MIO-21A) was diluted by mass with tetralin to produce a series of standards containing 0.1–10 mg/kg of Fe, Ni, and V. The calibration graph for V was extended by diluting the Spex 1000 mg/kg V in oil standard to produce a standard containing 50 mg/kg V. The zero value was determined using a blank consisting of tetralin containing 5 mg/kg Sc. Alternatively, the blank contained a 1:10 dilution of Spex base oil with tetralin. The calibration standards are listed in Table 2.

Table 2. Spectral Wavelengths, Calibration Standards, Precision and Correlation Coefficients of the Calibration Graphs for the Determination of Fe, Ni, and V in Crude Oils and Residua. All Data in $\mu\text{g}/\text{kg}$

Blank	STD-1	STD-2	STD-3	STD-4	STD-5	%RSD	R
Ni II 231.604	0	0.1	1	10	—	0.19	0.9991
Fe II 259.940	0	0.1	1	10	—	0.6	0.9994
V II 292.402	0	0.1	1	10	50	0.35	0.99998
V II 310.230	0	0.1	1	10	50	0.94	0.99997
Sc II 361.384	Internal standard						
C I 193.026							
C I 247.857							
Ar I 763.511							

Short term % RSD for standard containing 5 mg/kg

Several standard reference materials varying widely in composition (S content varies from 0.45–4.3%) were employed to evaluate the accuracy of the procedure for the determination of Fe, Ni and V. These consisted of NIST 1618 Vanadium and Nickel in Residual Fuel Oil, 1634a Trace Elements in Fuel Oil, NIST 1085a Wear Metals in Lubricating Oil, and NIST RM 8505 V in Crude Oil. The recommended values used were those listed in the NIST certificates of analyses [14]. Standards and samples were diluted by weight using a 1:10 sample:tetralin ratio. Usually 10 g were used and brought up to 100 g. Sc in tetralin was used as the internal standard, and was added so that the final Sc content was 5 mg/kg. A Sc stock solution of 100 mg/kg in tetralin was prepared from a 1000 mg/kg metal organic concentrate supplied by Spex Industries (Edison, NJ). Viscous samples were heated on a hot water bath (90 °C) until they could be poured readily. All standards and samples were mixed thoroughly with a vortex mixer (Fisher Scientific, Genie, catalog number 12-812) for several minutes. Several ml of stabilizer were added (Sta-Sol, Spex, Edison, New Jersey), followed by mixing.

Results

Effect of Nebulizer Pressure

The influence of the nebulizer pressure on the intensities of the ion lines of Fe, Ni, V, and Sc is illustrated in Figures 1 and 2. The observed variations appear to be in accordance with the excitation potential of the spectral lines. C I 193.026 and 247.851 nm – 7.69 and 7.68 eV, respectively have maximum intensities at low nebulizer pressure <100 KPa; Fe II 259.940, V II 292.402 and 310.230, and Ni II 231.604 nm – 4.77, 4.63, 4.36, and 6.39 eV respectively, were highest at 100–125 KPa, and Sc II 361.384 nm – 3.45 eV was maximum at 150 KPa. An operating pressure of 125 KPa was used for quantitative analysis.

Limits of Detection

The limits of detection (LOD) for the tetralin matrix are compared with values cited in the literature in Table 3. The LODs in tetralin in this application are better than those obtained using xylene [6], slightly higher than those obtained with kerosene [15], and compare favorably with the values quoted by other workers for tetralin [5,7,8]. However, the prominent C₂ Mullikan band structure in the vicinity of Ni II 231.604 nm placed constraints on the limits of detection of this line.

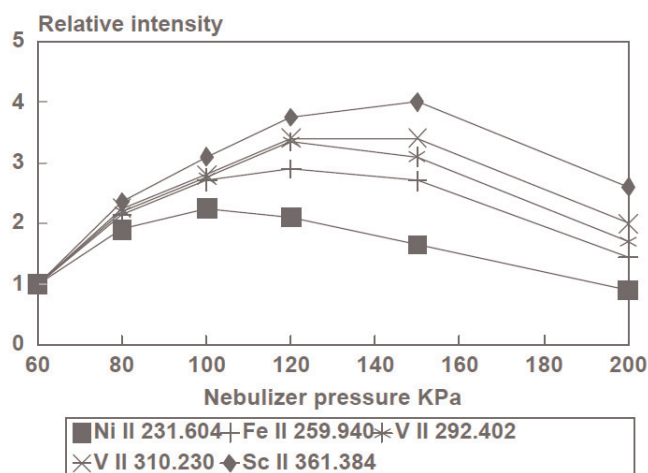


Figure 1. Effect of nebulizer pressure on the intensities of Ni, Fe, V, and Sc lines.

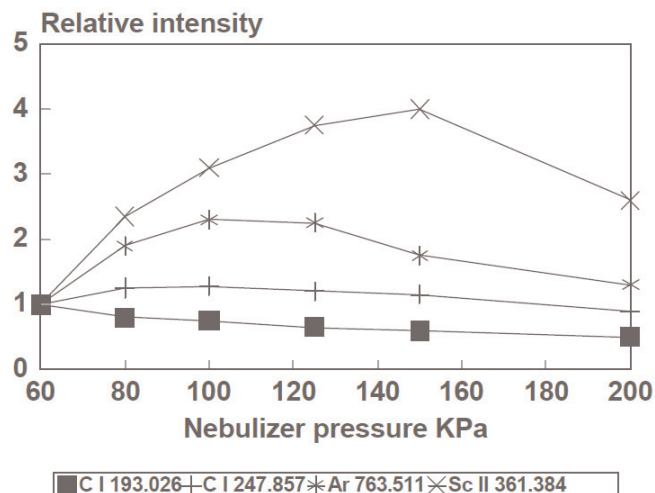


Figure 2. Effect of nebulizer pressure on the intensities of Sc, C and Ar lines.

Table 3. Comparison of Limits of Detection. All Data in $\mu\text{g/kg}$

Method	1	2	3	4	5
Ni II 231.604	12	90	6.5	6	23
Fe II 259.941	5	15	1.3	3	5.6
V II 292.402	5	10	2	—	15
V II 310.181	2	—	—	3	—

1. This application
2. Xylene (Brown, [6])
3. Kerosene (Nham and Bombelka, [15])
4. Tetralin (Brenner, [8])
5. Tetralin (Botto, [7])

Internal Standard

In the present study, tetralin-based standards were used for calibration. The samples, represented by several standard reference oils and crudes were prepared in a 1:10 mass ratio. Consequently, the effect of the amount of oil was evaluated. Several tetralin-based standards containing 1 mg/kg trace elements and oil contents amounting to 35% were aspirated. The intensity variations of the analyte lines with and without Sc II 361.384 nm as the internal standard are shown in Figures 3 and 4. From Figure 3, it is evident that the Fe, Ni, V, and Sc lines vary similarly in response to increasing oil contents. The effect due to 10% oil was less than 10% RSD, and in the presence of 35% oil, the intensities decreased by 10–20%. These relatively small effects can be attributed to the high tolerance of the high solids Vgroove nebulizer. Figure 4 shows that these effects are reduced when Sc was applied as the internal standard. In order to demonstrate further the efficiency of Sc II as an internal standard, the elemental "recoveries" were determined. A calibration using pure tetralin calibration solutions was performed, followed by the analysis of the oil-tetralin solutions. The data in Table 4 indicate that the accuracy is satisfactory. It can be concluded that crudes and oils of varying viscosities can be analyzed using simple tetralin-based calibration standards with Sc as the internal standard. Changes in the intensity of C and Ar lines were not correlative with those of Sc, however, the former may serve as criteria of plasma conditions.

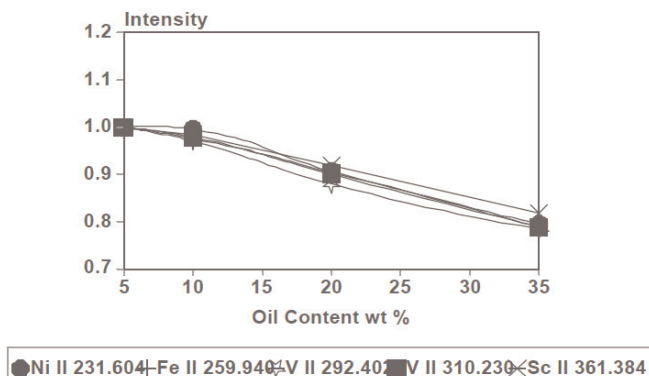


Figure 3. Variation of Ni, Fe, V, and Sc as a function of the oil concentration. All solutions contained 1 mg/kg trace elements, and 5 mg/kg Sc.

Table 4. Recovery of Fe and Ni from Various Oilbased Standards using Sc II: 1 mg/kg trace elements and 5 mg/kg Sc

%Oil	V %Recovery	%RSD	Fe %Recovery	%RSD
35	90	0.89	97	1.45
20	96	1.4	101	1.25
10	105	1.9	105	1.7
5	108	0.9	111	0.6
0	104	0.7	99	0.42

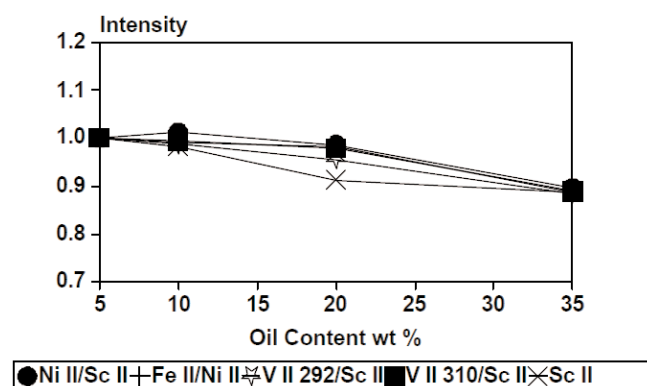


Figure 4. Compensation of the effect of the oil content using Sc as the internal standard.

Precision

The short term RSDs at the 5 mg/kg level for tetralin were usually less than 1%, and frequently < 0.5% (Tables 2, 4, and 5). The medium-term RSDs (2 h) were determined by nebulizing the calibrating standards for several times over a period of 2 h (Table 5). For the 10 mg/kg standard, the % RSDs for Ni, Fe and V II 292.402 and V II 310.181 were 0.8, 0.1, 0.5, and 0.4, respectively. The calibrations obtained for Ni and V over this period of time are illustrated in Figure 5. The repeatability for Ni, Fe and V in a 1:10 dilution of NIST 1634a (2.7, 1.9, and 5.2 mg/kg), was 0.3, 0.3 and 0.76%, respectively). These values are satisfactory considering the relatively low concentration levels.

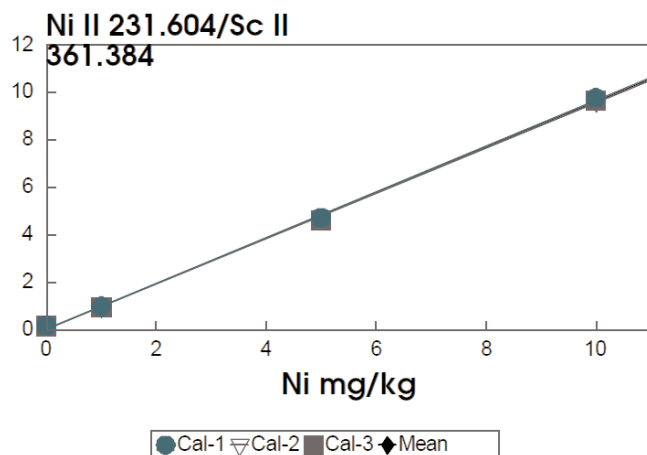


Figure 5. Long term calibration variation for Ni II 231.604 nm in crude oils - 2 hour.

The long-term variation (Table 5) was estimated by recalibrating the instrument 24 h after an analytical run, without changing any of the operating parameters. At the 1 mg/kg concentration level the relative deviation for all elements was < 2%.

Table 5. Long and Medium Term Variation (%RSD) of the V and Fe Calibrations for the Analysis of Crude Oil. Long Term was for a Period of 24 Hours, Medium was for a Period of Two Hours

Concentration (mg/kg)	0.1	1	5	10
Ni II 232.604 nm				
Medium term	—	1.2	0.9	0.8
Long term	—	3.5	2.2	1.5
Fe II 259.940 nm				
Medium term	2.6	0.3	0.6	0.1
Long term	2.8	2	1.8	1.9
V II 292.402 nm				
Medium term	2.8	1	1	0.5
Long term	12	1.6	1.7	1.8
V II 310.181 nm				
Medium term	0.8	0.5	0.6	0.4
Long term	10	1.7	2.1	1.7

Accuracy

The internal accuracy of the calibration was satisfactory based on the correlation coefficients listed in Table 2. The accuracy of the procedure was evaluated by analyzing of NIST 1634a, 1085a, 1618, and 8505 using Spex synthetic standards and with Sc as the internal standard. Comparison of the data with the recommended values [16] (Table 6) indicates that the accuracy is satisfactory and that analytical bias is absent.

Figure 6 further illustrates the accuracy and linear dynamic

range for both V spectral lines employed. All SRMs and calibration data are plotted as a function of the V /Sc ratio. The statistics of these graphs are listed in Table 7, and the highly significant R^2 values indicate that the method provides accurate data over the concentration range studied.

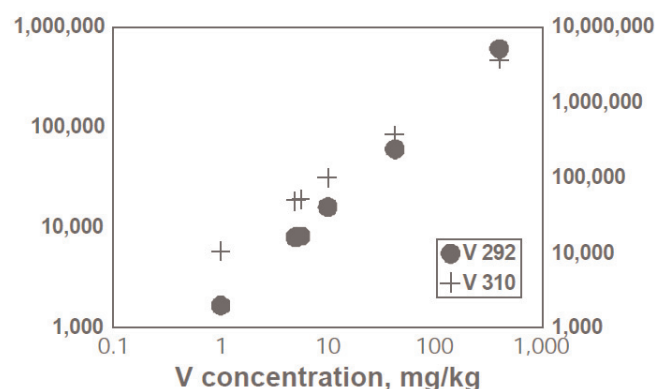


Figure 6. Calibration graphs for V determination in crude oil and residua. SRM data inserted to illustrate goodness of fit.

Table 6. Analyses of Certified Standard Materials (NIST), using Tetralin as the Diluent and Sc as the Internal Standard. Data in mg/kg Except Where Indicated in %. N=4 Separate Determinations. 3 Replicate Nebulizations

	Ni 231.604	Fe 259.940	V 242.402	V 310.181
NIST 1634a				
Mean	28.0	23.0	53.6	53.3
%RSD	0.57	1.5	0.76	0.51
Rec val	29.0	26.0	56.0	56.0
NIST 1618				
Mean	73.0	4.5	423.0	418.0
%RSD	0.8	0.2	0.56	0.90
Rec val	75.0	—	423.0	423.0
NIST 1085a				
Mean	288.0	295.0	288.0	290.0
%RSD	0.68	0.03	0.33	0.47
Rec val	303.0	297.0	292.0	292.0
NIST 8505				
Mean			386.0	387.0
%RSD			0.24	0.65
Rec val			390.0	390.0

Table 7. Statistical Data for the Calibration Graphs of V in Crude Oils. SRM Data Inserted to Illustrate Goodness of Fit

Standard	STD concentration mg/kg	V 292.402 Intensities	V 310.181 Intensities
Blank	0	22	367
NIST 1634a	5.6	8193	50640
Spex 10	10	16060	98750
Spex 5	5	8029	48780
Spex 1	1	1660	10345
NIST 1618	42.3	60456	371366
Regression outputs			
Constant		596	3723
Std err of Y est		763	4581
R Squared		0.9991	0.9991
No. of observations		6	6
Degrees of freedom		4	4
Coefficient(s)		1422	8731
Std err of coef.		21.4	129

Conclusion

Carbon build up was not observed when using tetralin. With the conservative operating conditions, the short term RSDs for tetralin – based standards amounted to < 1 % and the long term to < 5 %. In this application more than two standards were used for calibration. Based on the good comparison of the SRM data, and the high level of linearity between the intensity and the concentration, it can be concluded that a two point calibration is sufficient for analysis. Based on the similar behavior of Sc and analyte lines in the plasma, and the satisfactory data obtained for various certified materials it can be concluded the tetralin is a suitable diluent for the determination of V, Fe and Ni in crudes and residua.

Acknowledgement

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