

Determination of Vanadium, Nickel, and Iron in Crude Oil by High-Performance Liquid Chromatography

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Abstract

A reversed-phase high-performance liquid chromatography method for the separation and simultaneous determination of vanadium, nickel, and iron is described. The chelates of the metal ions with 4-(2-pyridylazo)resorcinol are separated on a octadecyl-siloxane column with methanol and 0.01M $(\text{NH}_4)_2\text{HPO}_4\text{-NH}_4\text{H}_2\text{PO}_4$ (35:65, v/v) buffer (pH 6.5) as the mobile phase at a flow rate of 1.0 mL/min. The chelates are detected at 510 nm. The detection limits of vanadium, nickel, and iron are 0.9, 0.4, and 0.7 ng, respectively.

Introduction

Crude oil is a very complex natural organic product that is the source of energy and basic substances of the petrochemical industry. Metal derivatives are a group of the components of crude oil associated with either the aqueous layer or organic layer. The first category contains metals such as zinc, calcium, and titanium that arise from the contact between oil and underground waters. Vanadium, nickel, iron, and copper as oil soluble porphyrin complexes are the second category. This group of metals has been found in crude oil, and its separation and determination are the subject of many investigations (1,2). V, Ni, and Fe at low levels are important in oil stores and crude oil refining. The Ni-to-V ratio is one of the evaluation factors for crude oil. In trace quantities, Ni and Fe can also poison cracking process catalysts and effectively reduce their catalytic activity (3,4). Because of their role and the fact that these elements are in trace quantities, their assessment is very important.

During the last 20 years, techniques such as neutron activation analysis, X-ray fluorescence, inductively coupled plasma atomic emission spectrometry, and others have been applied to these analyses (5-7). Today, the most common method for the determination of these metals is the UOP method via atomic absorption spectrometry (AAS) (8). The ash of the oil sample is prepared for this determination. It is established that porphyrin

complexes of Ni are lost by vaporization in ashing.

Reversed-phase high-performance liquid chromatography (HPLC) with bonded stationary phases has been shown to be one of the most effective separation methods presently available, and this method seems to be convenient for the separation and simultaneous determination of elements that have similar chemical properties (9).

4-(2-pyridylazo)resorcinol (PAR) is one of the best chelating reagents for the precolumn complexation of many metal ions because of its sensitivity and solubility in water (10). The reagent has been used for the separation and determination of molybdenum, chromium, vanadium, cobalt, copper, and nickel (11-14).

The present study demonstrates that the reversed-phase liquid chromatographic separation and determination of V, Ni, and Fe as PAR chelates are feasible at the nanogram level. This method is applied for the detection and determination of V, Ni, and Fe in crude oil.

Experimental

HPLC system and conditions

The liquid chromatograph was a Shimadzu (Tokyo, Japan) LC-2A equipped with a model SPD-6AV spectrophotometric detector and a CTO-2A column oven. The ultraviolet-visible (UV-vis) detector was set at 510 nm. A 5- μm particle-size octadecyl siloxane (ODS) column (Dupont, Wilmington, DE) (250 \times 4.6 mm) was used in all experiments.

The mobile phase composition was 65% 0.01M $(\text{NH}_4)_2\text{HPO}_4\text{-NH}_4\text{H}_2\text{PO}_4$ (pH 6.5) buffer and 35% methanol. Other factors included a flow rate of 1 mL/min and an injection loop of 50 μL .

Preparation of reagents

Standard solutions of V, Ni, and Fe were prepared by dissolving these metals in the least quantity of HNO_3 and then diluting

them with 1% (v/v) HNO₃ solution. The PAR solution was prepared by dissolving the compound in a 50:50 (v/v) methanol–water mixture. All the other reagents were of analytical grade.

Preparation of sample

One bituman and two crude oil samples were analyzed. They included a sample of 545°C from the Siri Island area and two samples of crude oil named Froozan and Tehran entering the Tehran (Iran) refinery. One gram of bitumen was adsorbed onto 10 g of active alumina and introduced to the top of 100 g of alumina in a glass column. The saturated and aromatic hydrocarbons were eluted with 10% ether in hexane. The metalloporphyrins were eluted with methylenechloride (15).

Two other extraction techniques were employed. Crude oil samples (approximately 4 g) were extracted with 5 mL of pyridine–water–toluene (4:1:1) for consecutive determinations. The extract was then evaporated to dryness, and the residue was dissolved in toluene (16). Three grams of crude oil was introduced to toluene (9 mL), to which anhydrous methanol (9 × 5 mL) was added. The mixture was sonicated (approximately 3 min). Centrifugation (approximately 3000 rpm for 5 min) produced an upper layer (wine-red) containing the crude metalloporphyrins that was removed by pipet (17). The extracts were constantly monitored by UV–vis spectrometry for the quantitative isolation of porphyrins. The metals were removed from the metalloporphyrin concentrate by treatment with HNO₃ (1M), and the free bases were recovered as previously outlined.

The oil sample was wet ashed with fuming sulfuric acid, and the resultant char was burned off in a muffle furnace. The remaining inorganic residue (ash) was dissolved in sulfuric and hydrochloric acids.

Results and Discussion

Selection of experimental conditions

Effect of pH on color development

Absorption-versus-pH curves for the metal–PAR chelates are shown in Figure 1. An (NH₄)₂HPO₄–NH₄H₂PO₄ solution (pH 6.5)

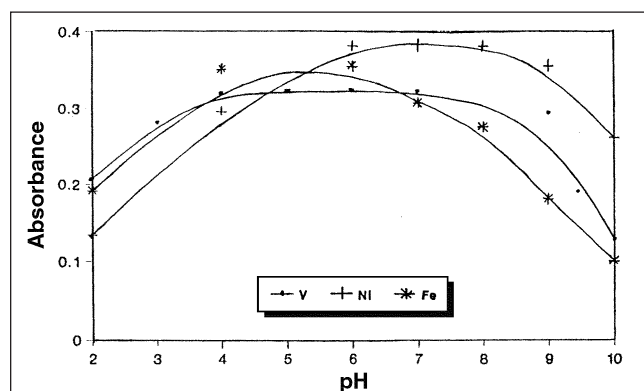


Figure 1. Effect of pH on the color development of metal–PAR chelates. Conditions: column, ODS (250 × 4.6 mm); solvent, MeOH–buffer (35:65); flow rate, 1 mL/min; detector, UV–vis, 510 nm, 0.04 AUFS.

was chosen, because it gave a maximum development of all three chelates and was also used in the eluent.

Selection of detection wavelength

To choose the wavelength for the detection of the eluted PAR chelates of V(V), Ni(II), and Fe(III), the absorption spectrum of each chelate was measured. The absorption maxima of the PAR chelates of V, Ni, and Fe were 540, 500, and 488 nm, respectively, and reagent blank and negligible absorption were at 480–550 nm. A wavelength of 510 nm was selected for detection, which gave good results for all the elements.

Effect of PAR concentration

For the complete development of the color, 5 µg of V(V) and 3 µg of Ni(II) or Fe(III) requires 0.2 mL and 0.3 mL of 0.1% PAR

Table I. Coefficients of Linear Regression Lines for the Calibration of Chromatographic Detector

Metal ion	V(V)	Ni (II)	Fe (III)
Concentration range (mg/L)	0.3–1.8	0.2–1.4	0.2–1.8
Slope, absorbance (L/mg)	0.0038	0.0095	0.0068
Intercept, absorbance	0.00072	–0.00002	–0.00088
Correlation coefficient	0.9929	0.9922	0.9987

Table II. Effect of Foreign Ions on the Determination of V(V), Ni(II) and Fe(III)

Foreign ion	Foreign ion maximum bearable concentration (ppm)		
	V(V)	Ni(II)	Fe(III)
Cu(II)	100.0	95.15	100.0
Co(II)	8.5	80.0	100.0
Cr(III)	60.0	45.0	80.5

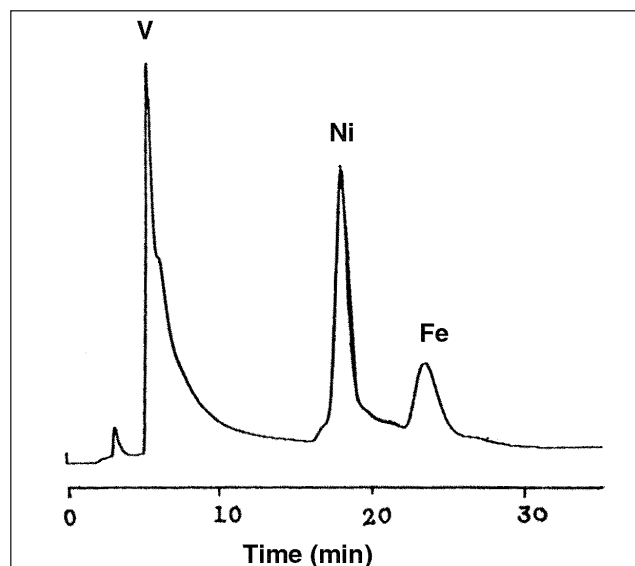


Figure 2. HPLC chromatograms of the PAR chelates of vanadium, nickel, and iron in a crude oil sample (Froozan).

solution, respectively. However, the optimum amount of the 0.1% PAR solution for the samples was decided to be 3mL.

Effect of temperature and stability

The colored chelates of V(V), Ni(II), and Fe(III) with PAR were readily formed at ambient temperature. The mixture with V(V) and Ni(II) should be kept for at least 15 min, and that with Fe(III) should be kept for at least 20 min for constant absorbance to be reached. High temperatures had a negligible effect on the absorbance of the V(V)-PAR chelate. The detector response to freshly prepared and aged standard solutions of the metal chelates was similar for periods up to 2 h. Concentration values for Ni(II), V(V), and Fe(III) chelates remained constant.

Chromatogram and calibration graphs

The retention times of the PAR chelates of vanadium, nickel, and iron were 6.29, 17.40, and 24.81 min, respectively, at a flow rate of 1.0mL/min. The slopes and intercepts of the calibration graphs for the simultaneous determination of V, Ni, and Fe calculated by linear regression analysis of the peak height

(absorbance) versus metal concentration data are summarized in Table I. The detection limits (at a signal-to-noise ratio of 31 and AUFS = 0.005) were 0.9 ng for V, 0.4 ng for Ni, and 0.7 ng for Fe. Relative standard deviations calculated from 5 replicate analyses of a solution containing 0.6 mg/L each of V, Ni, and Fe were 1.1, 2.8, and 1.3%, respectively.

Effect of foreign ions

The effect of Co(II), Cu(II), and Cr(III) (as the most abundant metals after V, Ni, and Fe in crude oil) was examined (Table II). When present in concentrations comparable to Ni(II) and Fe(III), the metal ions examined for interference had no effect on the determination of V, Ni, and Fe. Co(II) caused a serious interference in the determination of V(V). Therefore, before the HPLC method is applied to actual samples, this interfering ion must be masked or removed by extraction.

Sample analysis

The separation of metal ions in the crude oil sample is shown on Figure 2. The results obtained by HPLC analysis with various extraction methods and the ashing method are compared with results of the same samples obtained by AAS analysis. The analytical results, summarized in Tables III-V, show good agreement between HPLC and AAS methods.

Conclusion

The simultaneous speciation of vanadium, nickel, and iron ions was accomplished by reversed-phase HPLC on an ODS column. The proposed method requires minimum sample pre-treatment steps, and the color developing step requires only approximately 20 min at ambient temperature, so a heating step is not necessary. After chelation with PAR, V(V)-PAR, Ni(II)-PAR, and Fe(III)-PAR were well separated with relatively good resolution within 25 min.

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Metal	Extraction with pyridine-water-toluene		Wet ashing	
	HPLC	AAS	HPLC	AAS
Vanadium (ppm)	30.2	—*	30.5	31.0
Nickel (ppm)	11.5	12.0	9.2	9.6
Iron (ppm)	4.3	4.6	3.2	3.4

* Because the prepared solutions are so diluted by extraction methods, it was impossible to determine vanadium by AAS.

Metal	Extraction with					
	Extraction with methanol-toluene		pyridine-water-toluene		Wet ashing	
	HPLC	AAS	HPLC	AAS	HPLC	AAS
Vanadium (ppm)	50.7	—*	53.5	—*	53.1	54.0
Nickel (ppm)	12.9	13.4	16.8	17.0	14.6	15.0
Iron (ppm)	5.2	5.4	5.3	5.6	4.5	4.8

* Because the prepared solutions are so diluted by extraction methods, it was impossible to determine vanadium by AAS.

Metal	Column chromatography		Wet ashing	
	HPLC	AAS	HPLC	AAS
Vanadium (ppm)	248.5	—*	250.7	252.3
Nickel (ppm)	68.2	70.0	68.9	71.7
Iron (ppm)	33.5	35.5	30.1	32.4

* Because the prepared solutions are so diluted by extraction methods, it was impossible to determine vanadium by AAS.

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