Spectrophotometric Determination of Fe(III), V(V) and Cu(II) Using Some Hydroxamic Acid Derivatives

M.I. ROUSHDY, Y.M. ISSA*, S.M. EL-ZEIN and F.M.S. EL-DEEN HARB
Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.

New, simple, rapid and accurate methods for the spectro- photometric determination of Fe(III), V(V) and Cu(II) using N-benzoyl-N-phenylhydroxamic acid and four of its derivatives and N-furoyl-N-phenylhydroxamic acid are described. The optimum conditions favouring the formation of coloured complexes are extensively studied. The stoichiometric ratios of the formed complexes were 1 : 1, 1 : 3 (M : L) for Fe(III), 1 : 3 (M : L) for V(V) and 1 : 1, 1 : 2 (M : L) for Cu(II). The stability constants were determined applying spectrophotometric methods. Beer's law was found to be obeyed up to 4.48, 4.49 and 5.67 µg/mL for Fe(III)-(1a–1f), V(V)-(1a–1f), and Cu(II)-(1a–1f) complexes, respectively. The molar absorptivity, specific absorptivity, Sandell sensitivity and Ringbom optimum range are given. Spectrophotometric and direct titration methods using EDTA are suggested and the named hydroxamic acid derivatives as indicators. The applicability of using ligand (III) for the detrmination of Fe and V in crude oils has been evalutated.

INTRODUCTION

Hydroxamic acids are important reagents in analytical chemistry, and are widely used in the analysis of trace metals. Gupta and Sogan[1] described the use of N-acetyl-N-phenylhydroxylamine as a spectrophotometric reagent for iron at the pH range 1.8–3.5. Agrawal *et al.*[2] reported a spectrophotometric method for the micro determination of iron(III) using *p*-nitrobenzohydroxamic acid; the system obeys Beer's law over the range 1.4–30 µg iron/mL. Patel[3] studied Cu(II), Ni(II), Co(II) and Fe(III) chelates of Schiff base, N,N-isopropylene bis-(3-Br-2-OH, 5-Me-benzophenoneimine). A square planar structure for the bivalent metal complexes has been assigned on the basis of elemental analysis, magnetic moment and molecular weight. Richard *et al.*[4] compared the chelating properties of hydroxamic acid and N-methylhydroxamic acid with each other and with N-phenylhydroxamic acid. The extraction of 19 metal ions was studied as a function of pH for the N-methylhydroxamic acid resin.

Savartar and Joseph[5] reported that N-acetylsalicyloyl-N-phenylhydroxylamine, its halogen and methyl substituted derivatives were applied for the spectrophotometric determination of vanadium(V). In strong HCl solutions

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*Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt.

vanadium(V) forms 1 : 2 complex with these reagents which on extraction into chloroform shows maximum absorption at 530 nm.

The present investigation deals with the study of some N-phenylhydroxamic acid derivatives having the general formulae for the determination of Fe(III), V(V) and Cu(II) ions:

X	Y	
H	H	1a
Cl	H	1b
Cl	Cl	1c
NO$_2$	H	1d
OCH$_3$	H	1e

(1f)

EXPERIMENTAL
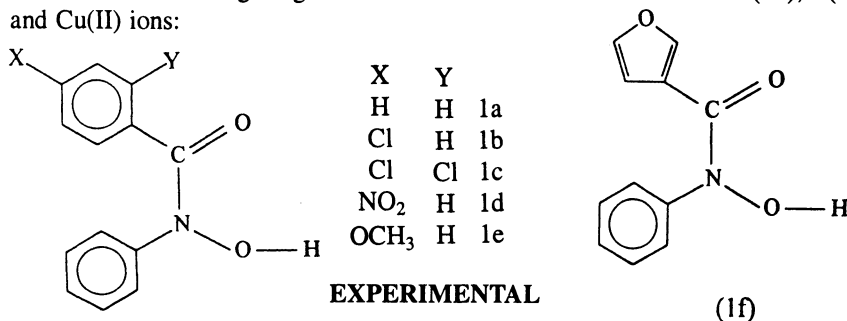
The water used in this investigation was always twice distilled from all glass equipment.

Preparation of the hydroxamic acid derivatives

The reagents were prepared as previously reported[6] through the reaction of the corresponding acid chloride with phenylhydroxylamine that was prepared by reduction of nitrobenzene. The results of the elemental analysis of the prepared hydroxamic acid derivatives (1a–1f) are in agreement with those required for $C_{13}H_{11}NO_2$, $C_{13}H_{10}NO_2Cl$, $C_{13}H_9NO_2Cl_2$, $C_{13}H_{10}N_2O_4$, $C_{14}H_{13}NO_3$ and $C_{11}H_9NO_3$, respectively.

0.01 M solutions of the reagents were prepared by dissolving the accurately weighed amount in the requisite volume of redistilled ethanol. 0.01 M solutions of $FeCl_3$, $CuCl_2 \cdot 2H_2O$ and NH_4VO_3 were prepared and standardized by recommended methods[7]. 0.001 M solutions were prepared by accurate dilution. 0.01 M solutions of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) were prepared by dissolving the accurately weighed amount in the requisite volume of redistilled water by warming. 0.5% (v/v) Triton X-100 (polyoxyethylene-*p*-tert-octylphenol) solution was prepared by diluting 0.5 mL of Triton X-100 to 100 mL with twice distilled water. Gelatin and gum arabic solutions (0.5%) were prepared by dissolving 0.5 g of each in warm water and the volume was diluted to 100 mL with redistilled water.

The buffers used were acetate buffers (HCl-sodium acetate)[8] and the modified Britton and Robinson universal series[8].

A Uvikon sp 860 spectrophotometer was used to obtain the absorbance values and absorption spectra. pH values were measured using a Chemtrix Model 62A pH-meter.

Procedures

Spectrophotometric determination of Fe(III), V(V) and Cu(II) using the prepared hydroxamic acid derivatives

To solutions containing 10.0–40.7, 15.4–36.3, 10.7–30.7, 12.0–33.1, 11.2–27.5

and 15.8–39.8 µg of Fe(III), 10.0–30.2, 10.0–25.1, 10.0–35.4, 10.8–30.1, 10.0–19.9 and 10.0–35.4 µg of V(V) and 11.2–31.6, 7.9–30.2, 14.1–35.4, 6.3–24.5, 3.1–31.6 and 7.0–24.5 µg of Cu(II) ion in case of 1a, 1b, 1c, 1d, 1e and 1f, respectively, 3.5 mL 10^{-3} M, 3 mL 10^{-3} M and 2.5 mL 10^{-3} M ligand solution in case of Fe(III), V(V) and Cu(II), respectively were added and completed to 10 mL with acetate buffer solutions of the recommended pH values (Table-1). The absorbances of the resulting solutions were measured at the optimum wavelength (Table-1), against a blank solution containing the same ingredients except the metal ion. Standard calibration curves were thus constructed.

Spectrophotometric determination of Fe(III) using the prepared reagents in presence of gelatin

The above procedure for Fe(III) complexes was carried out after the addition of 0.3 mL (0.5%) of gelatin solution (the amount found to give the maximum and constant absorbance).

The absorbance was measured at the recommended wavelengths against a blank solution containing the same ingredients except the metal ion. Standard calibration curves were constructed.

Spectrophotometric titration of Fe(III), V(V) and Cu(II) using the prepared ligands (1a–1f) as indicators

To 0.5–1.0 mL 10^{-3} M of Fe(III) and V(V) solutions (5×10^{-4} M in case of reagent 1c) and 4×10^{-4} M of Cu(II) solution, successive volumes of 10^{-3} M, 5×10^{-4} M and 4×10^{-4} M EDTA, respectively were added together with 1.5 or 3.0 mL 10^{-3} M indicator in case of Fe(III) and V(V) (5×10^{-4} M in case of indicator 1c) and 1.0 or 2.0 mL 4×10^{-4} M indicator in case of Cu(II). The solutions were then completed to 10 mL with the recommended buffer solution. The absorbances were measured at the recommended wavelengths (Table-1). The plots of absorbance-mL of EDTA are two straight lines intersecting at the end point.

Spectrophotometric determination of Fe and V in crude oils

The samples of oil (6.5 g) were wet-ashed, using concentrated sulphuric acid (3.5 mL sulphuric acid/g oil) and dissolved in 25 mL hydrochloric acid (1 : 1)[9]; then iron and vanadium in samples were determined using both flame atomic absorption-emission spectrophotometer, Model Spectro AA 20 Varian's. Iron and vanadium were determined by measurement of the atomic absorption at 248.3 nm using air-acetylene flame, and the atomic emission at 437.9 nm using nitrous oxide-acetylene flame respectively. Also iron and vanadium were determined spectrophotometrically using *o*-phenanthroline and phosphotungstate method, respectively. Iron was measured at 502 nm and vanadium at 404.8 nm according to the ASTMD 1068[10] and 1548[11]. Iron and vanadium were determined using the suggested method. The results are compared and discussed.

TABLE-1 OPTIMUM CONDITIONS AND CUMULATIVE DATA FOR SPECTROPHOTOMETRIC DETERMINATION OF Fe(III), V(V) AND Cu(II) IONS USING THE LIGANDS (1a–1f)

Complex	Colour	pH	λ_{max} (nm)	Beer's law linear range (µg/mL)	Ringbom linear range (µg/mL)	ε	a	S	s	r
Iron Complexes										
1a	Reddish brown	4.8	411	0.28–4.48	1.00–4.07	1.00×10^4	0.1780	0.0056	0.0126	0.9968
1b		5.2	436	0.28–3.92	1.54–3.63	0.50×10^4	0.0890	0.0112	0.0049	0.9985
1c		5.0	460	0.14–4.48	1.07–3.09	1.90×10^4	0.3390	0.0029	0.0078	0.9991
1d		5.2	428	0.14–3.92	1.20–3.31	0.73×10^4	0.1315	0.0076	0.0012	0.9999
1e		5.2	432	0.00–3.36	1.12–2.75	1.00×10^4	0.1785	0.0056	0.0099	0.9985
1f		5.0	452	0.10–4.48	1.58–3.98	0.70×10^4	0.1250	0.0080	0.0050	0.9986
Vanadium complexes										
1a	Reddish violet	2.3	440	0.00–3.57	1.00–3.02	0.84×10^4	0.1639	0.0061	0.0053	0.9992
1b		2.3	436	0.00–2.70	1.00–2.51	0.65×10^4	0.1280	0.0078	0.0086	0.9922
1c		2.3	430	0.27–3.85	1.00–3.54	1.30×10^4	0.2564	0.0039	0.0101	0.9969
1d		2.3	460	0.00–4.95	1.08–3.01	0.83×10^4	0.1620	0.0062	0.0075	0.9985
1e		2.3	444	0.27–3.85	1.00–1.99	0.74×10^4	0.1455	0.0068	0.0091	0.9995
1f		2.3	451	0.00–4.95	1.00–3.54	1.10×10^4	0.2127	0.0047	0.0071	0.9991
Copper complexes										
1a	Greenish yellow	2.3	330	0.46–5.04	1.12–3.16	2.30×10^4	0.3653	0.0027	0.0494	0.9912
1b		3.5	338	0.63–5.04	0.79–3.02	1.70×10^4	0.2702	0.0037	0.0294	0.9939
1c		3.0	312	0.94–5.67	1.41–3.54	1.00×10^4	0.1587	0.0063	0.0082	0.9984
1d		3.0	390	0.00–5.67	0.63–2.45	1.40×10^4	0.2222	0.0045	0.0126	0.9988
1e		2.3	321	0.15–4.41	0.31–3.16	1.50×10^4	0.2380	0.0042	0.0095	0.9992
1f		2.3	355	0.00–4.41	0.70–2.45	2.60×10^4	0.4132	0.0024	0.0419	0.9963

ε: Molar absorpitivity (L mol^{-1} cm^{-1})
a: Specific absorptivity (mg^{-1} cm^{-1})
S: Sandell sensitivity (µg cm^{-2})
s: Standard deviation
r: Correlation coefficient

RESULTS AND DISCUSSION

The absorption spectra of Fe(III), V(V) and Cu(II) with the reagents (1a–1f) were investigated at different pH values; representative graph is shown in Fig. 1. The optimum pH values and buffer constituents for developing Fe(III), V(V) and Cu(II) complexes with the ligands (1a–1f) are listed in Table-1. The absorption spectra of the ligand solutions (curve a), complex solutions (curve b) both against buffer as blank and the complex solutions against the ligand as blank (curve c) are represented in Fig. 2. The maximum absorbance of the complexes is thus obtained (Table-1) and used for further measurements.
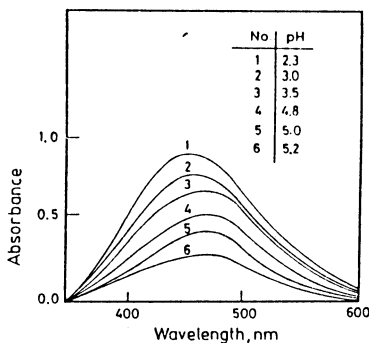

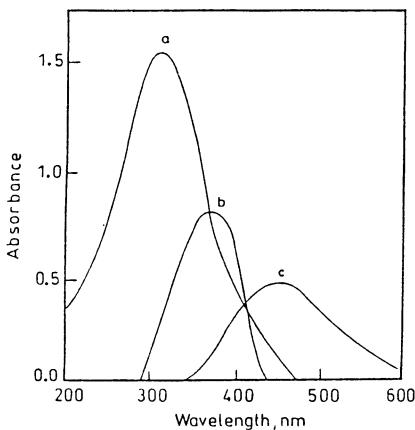Fig. 1.   Absorption spectrum of V-1e complex in acetate buffer solution of varying pH values.

Fig. 2. Absorption spectrum of V-1e complex in acetate buffer pH 2.3: a $= 1 \times 10^{-4}$ M(1e), b $= 1 \times 10^{-4}$ M(1e), V-1e vs. ligand + buffer, c $= 1 \times 10^{-4}$ M(1e), V-1e vs. ligand

The effects of time, temperature and order of addition on the formation of these complexes were studied in detail. The colour intensity of the complexes increases within 2 min and then remains stable for more than 24 h. It was found that raising the temperature up to 50°C has no effect on the absorption spectra of

the complexes formed. The sequence ligand-metal-buffer was the best sequence for formation of the complexes in all cases.

The effect of addition of surfactants on the formation of the above mentioned complexes was studied. It was found that only the Fe(III) complexes were sensitized by the addition of surfactants; enhancement of the absorbance was obtained in the presence of gelatin. Table-2 illustrates the effect of the different types of surfactants on the formation of Fe(III)-(1a–1f) complexes. The best sensitizer showing enhancement of the coslour reaction was gelatin; other used sensitizers show no detectable effect.

TABLE-2
EFFECT OF SOME SURFACTANTS AND PROTECTIVE COLLOIDS ON THE
SPECTRAL CHARACTERISTICS OF Fe-(1a–1f) COMPLEXES

Surfactant of protective colloid	Fe-1a		Fe-1b		Fe-1c		Fe-1d		Fe-1e		Fe-1f	
	λ_{max} (nm)	$\varepsilon \times 10^{-4}$	λ_{max} (nm)	$\varepsilon \times 10^{-4}$	λ_{max} (nm)	$\varepsilon \times 10^{-4}$	λ_{max} (nm)	$\varepsilon \times 10^{-4}$	λ_{max} (nm)	$\varepsilon \times 10^{-4}$	λ_{max} (nm)	$\varepsilon \times 10^{-4}$
Without	411	1.00	436	0.50	460	1.90	428	0.73	432	1.00	452	0.70
SDS	418	1.05	444	0.51	470	1.91	430	0.76	436	1.10	458	0.71
CTAB	420	1.05	444	0.59	472	1.92	430	0.76	437	1.19	457	0.72
Triton X-100	420	1.00	443	0.59	469	1.92	435	0.79	433	0.85	459	0.77
Gum arabic	420	1.07	440	0.59	467	1.93	435	0.75	436	0.81	460	0.76
Gelatin	411	1.30	436	0.70	460	3.00	428	1.00	432	2.00	452	1.60

ε: Molar absorptivity (L mol^{-1} cm^{-1}).

Effect of gelatin concentration on the absorbance of the Fe(III)-(1a–1f) complexes

The influence of gelatin concentration on the absorbance of Fe-(1a–1f) complexes was investigated using 0.02–0.80 mL 10^{-3} M of Fe(III) solution and 2.5 mL 10^{-3} M ligand at the optimum pH (Table-1). The gelatin concentration ranged between 0.1 and 1.0% by volume. The results revealed a maximum absorbance in the presence of 0.015% as a final concentration. 0.3 mL 0.5% gelatin solution is the amount which was found to give maximum and constant absorbance.

Nature and composition of the complexes: The stoichiometry of the formed complexes was studied using standard spectrophotometric methods such as the molar ratio[12] and continuous variation[12] methods. The results indicate the formation of 1 : 1, 1 : 3 (M : L) for Fe(III)-(1a–1f) complexes; 1 : 3 (M : L) for V(V)-(1a–1f) complexes and 1 : 1, 1 : 2 (M : L) for Cu(II)-(1a–1f) complexes.

Stability constants of the complexes: The overall formation constants (β_n) of the metal ion complexes with ligands (1a–1f) were calculated using the data of the molar ratio[12] and continuous variation[12] methods, applying the relation:

$$\beta_n = \frac{A/A_m}{(1 - A/A_m)^{n+1}(C_L)^n n^2}$$

where: A = Absorbance at ligand concentration C_L

       A_m = Maximum absorbance at full colour development

       n = Stoichiometric ratio of the complex

The results listed in Table-3 show that the complexes are fairly stable as indicated by high values of the log stability constants. The effect of substituents (X) was investigated by plotting log β_n values vs. Hammett substitution constants (σx)[13] (Fig. 3). The linear plot was statistically analyzed applying the least squares method[14] and the results are recorded in Table-4. The slope (ρ) is negative indicating that electron withdrawing groups decrease the pKa values, *i.e.*, increase the ionization constants of the ligands and the stability constants of the complexes. The correlation coefficient (r) values are high enough to reflect the inductive effect of the substituents. The intercept (c) values go along with the experimental values (Table-3). The standard deviation (s) values are low confirming the linear relation.

TABLE-3
THE OVERALL STABILITY CONSTANTS OF METAL
COMPLEXES OF LIGANDS (1a–1f)

Ligand	Metal	log β_n					
		1 : 1		1 : 2		1 : 3	
		MR	CV	MR	CV	MR	CV
1a	Fe	5.21	5.41			12.00	11.92
	V					11.55	11.65
	Cu	7.00	6.80	11.11	11.21		
1b	Fe	5.02	5.12			11.01	11.21
	V					10.99	10.87
	Cu	5.80	5.82	10.51	10.32		
1c	Fe	4.91	4.91			10.61	10.83
	V					11.52	11.49
	Cu	5.50	5.31	10.21	10.02		
1d	Fe	4.52	4.62			9.92	9.91
	V					11.06	11.09
	Cu	5.33	5.11	9.61	9.71		
1e	Fe	7.01	7.12			13.01	13.21
	V					12.20	11.99
	Cu	8.01	8.09	11.81	11.89		
1f	Fe	5.23	5.52			11.53	11.31
	V					11.43	11.34
	Cu	6.01	6.09	10.81	10.91		
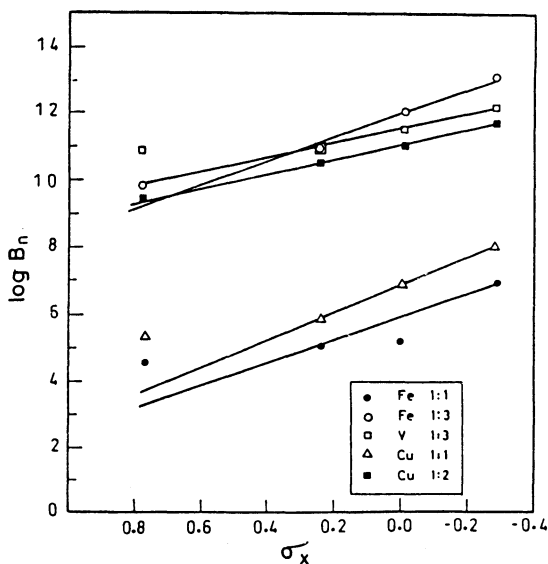
Fig. 3.   log β_n *vs.* σ_x plot for 1a–1f with Fe, Cu and V

TABLE-4

REGRESSION ANALYSIS

Mathematical value	log β_1		log β_2	log β_3	
	Fe	Cu	Cu	Fe	V
Slope (ρ)	–2.0959	–2.5234	–2.0727	–2.9084	–1.0255
Correlation coefficient (r)	0.7389	0.8675	0.9831	0.9757	0.6709
Standard deviation (s)	0.6807	0.5389	0.1484	0.2507	0.3925
Intercept (c)	5.8927	7.0018	11.0255	12.0481	11.1434

Effect of foreign ions: In case of Fe(III)-(1a–1f) complexes (22.4 µg/10 mL) and V(V)-(1a–1f) complexes (15.3 µg/10 mL) up to 30 folds of Na^+, K^+, Zn^+, Mg^{2+}, Cu^{2+}, CH_3COO^- and NO_3^- do not interfere; also vanadium and iron do not interfere in the determination of each other. EDTA and oxalate interfere.

In case of Cu(II)-(1a–1f) complexes (18.9 µg Cu^{2+}/10 mL) up to 20 folds of Na^+, K^+, Zn^{2+}, Mg^{2+}, V(V), Fe(III), CH_3COO^- and NO_3^- do not interfere; on the other hand, EDTA and oxalate seriously interfere.

Validity of Beer's law: The micro determination of Fe(III), V(V) and Cu(II) ions spectrophotometrically was carried out. Beer's law was verified and found to be satisfactorily obeyed up to 4.48, 4.95 and 5.67 µg/mL of Fe(III), V(V) and Cu(II) complexes, respectively. The molar absorptivity (ε)[12], specific absorpitivity (a)[15] and Sandell sensitivity (s)[16] values were calculated and listed in Table-1. It is clear that 1c, 1e and 1f are the most sensitive ligands for Fe, V and Cu respectively.

Ringbom optimum range: For more accurate spectrophotometric analysis Ringbom plot has been drawn (Fig. 4) from which the Ringbom[17, 18] optimum range for analysis was determined and listed in Table-1.
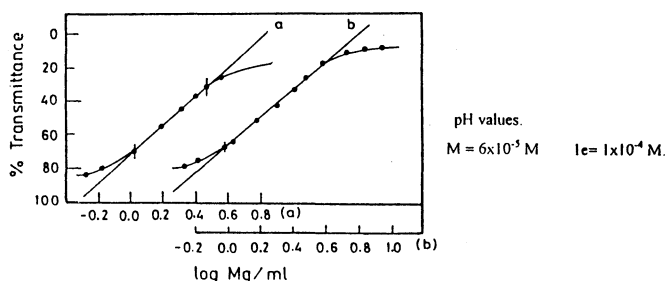
Fig. 4.   Ringbom plot for V-1d(a) and V-1f(b) complexes

Spectrophotometric titration of Fe(III), V(V) and Cu(II) with EDTA using the prepared ligands as indicators

The application of the prepared ligands (1a–1f) as indicators for the spectrophotometric titration of Fe(III), V(V) and Cu(II) ions with EDTA has been ascertained (Table-5). With the aid of these ligands up to 5.58, 5.09 and 6.35

TABLE-5

RESULTS OF SPECTROPHOTOMETRIC TITRATION OF Fe, V AND Cu WITH EDTA USING THE PREPARED LIGANDS (1a–1f) AS INDICATORS

Element	Taken mg/10 mL	Recovery % (error)					
		1a	1b	1c	1d	1e	1f
Fe	27.92	99.60	99.92	99.53	99.57	100.10	100.03
		0.40	0.08	0.47	0.47	10.10	0.03
	55.83	99.80	99.94	99.76	99.83	100.05	100.01
		0.20	0.06	0.24	0.24	0.05	0.01
V	25.47	99.73	99.84	99.68	99.73	99.80	99.76
		0.27	0.16	0.32	0.27	0.20	0.24
	50.94	99.90	99.94	99.88	99.92	99.94	99.92
		0.10	0.06	0.12	0.08	0.06	0.08
Cu	12.71	99.84	99.74	99.77	99.77	99.81	99.87
		0.16	0.26	0.23	0.23	0.19	0.13
	25.42	99.92	99.96	99.95	99.93	99.92	99.95
		0.08	0.04	0.05	0.07	0.08	0.05

TABLE-6

DETERMINATION OF Fe AND V IN SOME CRUDE OILS

Sample	μg Fe/g oil					μg V/g oil				
	Certified			Recom. method	Standard deviation	Certified			Recom. method	Standard deviation
	FAA[1]	MA[3]	Average			FAE[2]	MA[3]	Average		
Sample A	8.36	9.89	9.12	9.01	0.0100	27.19	25.61	26.40	26.01	0.010
Sample B	8.69	8.00	8.35	8.21	0.1159	6.69	6.53	6.61	6.50	0.125

Sample A = July; Sample B = Razzak
[1] = Flame atomic absorption spectrophotometry
[2] = Flame atomic emission spectrophotometry
[3] = Molecular absorption (visible) spectrophotometry

μg/mL of Fe(III), V(V) and Cu(II) respectively can be determined with fair accuracy and precision while 0.12–1.2 μg Fe/mL can be determined by the thiocyanate indicator[6].

Application of the method: The applicability of this method to the determination of Fe and V in crude oil has been evaluated using ligand 1c which is considered to be the most sensitive one in case of Fe and V (Table-5). The results obtained by the recommended method are in good agreement with the certified values (Table-6).

Conclusion

The above results indicate that the present methods are highly sensitive, accurate and rapid for the determination of Fe(III), V(V) and Cu(II). The sensitivity for the ligands in case of Fe, V and Cu decrease according to the order 1c > 1a = 1e > 1d > 1f > 1b, 1c > 1f > 1a > 1d > 1e > 1b and 1f > 1a > 1b > 1e > 1d > 1c, respectively. The addition of gelatin enhances the absorbance of Fe(III)-(1a–1f) complexes. The molar absorpitivities (ε) of these complexes are increased by 30% in case of 1a and 100% in case of 1e on addition of gelatin. The method can be applied successfully for the determination of iron and vanadium in petroleum crude oil.

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