Spectrophotometric Method For The Determination Of Vanadium In Residue Crude Oil at Mulla-abdulla Gas Station

Mohammed Ghazi Abd-Alkareem
University of Tikrit-College of Pharmacy

Abstract

The subject of this research is to study the possibility of extraction and determination of vanadium (V) from the residue crude oil spectrophotometrically by using standard addition method.

Leaching method was used to extract vanadium from the residue by treating it with
[NaOH] solution which had highest selectivity for vanadium.

The effects of kind of media , solvent extraction , temperature and leaching time were studied the result show that vanadium could be successfully extracted from the esidue crude oil sample using [2.5]M NaOH solution at 80 ºC with leaching time of six hours .

Introduction

The most important metallic and nonmetallic elements found in the residue crude oil are(S,Ca,Mn,Fe,Co,Ni,V,Pb) with concentration varying as metals ranged between (0.1-1) ppm as (Mo,La,Pb,Ba,Mn,Zr,Sr), metals ranged between (1-10) ppm as (Sn,K,Mg,Al) and metals ranged between (10-100)ppm as (Na,Fe,V,Ni,Ca) [(1)] . The chemistry of Vanadium extends over oxidation state from (-1 to +5) where a large number of solid compounds is known[(2)] .
The most oxidation states are also found in aqueous solution .Vanadium has a very low and none accumulative toxicity recovery plants which can be operated in such a manner to ensure no air pollution result .The interest for industry metallurgy is being increased to find new methods for treating the poor ore and complex ore that be difficult to extraction the metals by using thermal methods which cause air pollution, high cost to extract the metals and need a high power and reduction agent [(1)] . According to the suggested methods, it is extracted by (hydrometallurgy) to treat the rich and poor ores by dissolving the ore containing metals in acidic or basic solution.

We prefer the Hydrometallurgy than the thermal method because of the low cost. It doesn't need high temperature and the air pollution is limited. In Iraq, the fuel oil is used in electric power stations to release off combustion gases which contain Vanadium that could constitute a good source of this metal [(1)] .Natural vanadium is a mixture of two isotopes 50 V (0.25%) and 51 V (99.75%) which are slight radioactive having along half-life . Seventeen other unstable isotopes are recognized .Extensive evidence proved that vanadium dust (usually the pentoxide) is severely irritating to the mucous membrane of the eyes, nose, throat, and respiratory tract. Exposure to vanadium which containing the dust can occur near the [(5)] Production sites of numerous vanadium compounds particularly (V_2O_5) and to a lesser extent the vanadates. Numerous exposures to vanadium compounds have occurred during the cleaning of oil fired burners, where the dust is generated from the residual oil ash of high vanadium content oil. Vanadium is present in all fuel oil, which remains in the residue after more volatile fractions has been distilled after combustion; it appears as pentoxide, which forms an acidic solution when mixed with water.[(5)]
Alaftan[(8)] has extracted vanadium (IV, V) by crown compounds, In this process the extraction complex with vanadium (V) $[VO_2L]SCN$ has formed From the industrial waste, Gupta, Mukhenjee [(9)] extracted vanadium (IV) as a metal or as a vanadium compounds like Sodium vanadate and ammonium vanadate by the precipitation method for these compounds using alkaline metals solutions.

Also Mohammed [(10)] has extracted vanadium (V) from the residual of the heavy oil burning using a polymer for the crown ether [PDB-18-C-6] where the complex [Na L Na_2 VO_2 Cl $_4$] was produced in a basic media Using the solutions (H_2SO_4, NaOH) Min Shing Shanglin [(11)] studied the dissolvation the residue of heavy oil burning in the electrical generation stations , the study showed that the best salvation for the vanadium was by NaOH [2M] during 2 hour and 30 °C . Where the extraction ratio was 80%. Alzobay [(12)] studied the effect of temperature and the concentration of [NaOH] and the time of salvation , the result have shown that the best salvation for vanadium was [2M] for NaOH solution and the time of salvation was 4 hour at 100 °C where the extraction ratio was 98% under these conditions. The purposes of this study is to study the media used in leaching process, the effect of concentration of solvent, the effect of temperature and the leaching time .

Experimental

Apparatus: A shimadzu UV-visible 160-Japan digital double beam recording Spectrophotometer, with 1cm matched quartz cells were used for absorbance measurements, hot plate magnetic stirrer (Stuart scientific) , balance (Sartorius) and oven (Isuzu , Japan).
Chemicals: Sodium hydroxide, Potassium chloride, sodium tungstate, Nitric acid (BDH). Hydrochloric acid and phosphoric acid (Riedel-Deheam) and ammonium Solution (Fluka) were used throughout .

Standard Vanadium solution **(1mg/ml)[(3)]**: Dissolve (2.298) gm of NH_4VO_3 in water containing (5) ml of concentrated ammonium solution , acidify the solution with (10) ml of concentrated (HNO_3) acid and dilute in a volumetric flask to one liter distill water.

The study of effects

1- Effect of kind of media: In each of (3) round bottom flasks of (500) ml a weight (5) gm from a sample of

crude oil. The sample is mixed with (50) ml of following solutions [1] M HCl, NaOH, KCl separately, then a reflux at (70) ˚C for (4) hr is made, and filtrated by using Couch crucible, the precipitate is washed by distilled water then the residue is dried, all above steps are repeated until reaching to constant weight from remaining matter to proof extraction of all metals found in residual. Finally, each solution is mixed respectively in volumetric flask (200) ml by using the same concentration of solution.

2- Effect of concentration of the [NaOH] solution: All the previous steps (1) are repeated except using solutions of NaOH [0.5, 1.0, 1.5, 2.0, 2.5, 3.0] M.

3- Effect of temperature: All the previous steps in (1, 2) are repeated except using [2.5] M from NaOH and change the temperature of a reflux as (40, 50, 60, 70, 80, 90) ºC.

4- **Effect of reflux time**: All the previous steps in (1, 2, 3) are repeated except the temperature at 80 ºC and the time is changed as following (2, 4, 6, 8, 10) hr.

Procedure [4]:

In five beakers (10) ml is added from a sample of residue, the following concentration from a standard solution is added [50] ppm, 0, 2, 4, 6, 8 ml to each beakers respectively. (16) Drops of concentrated nitric acid is added and the beaker is heated gently on a hot plate until a bout (5) ml of solution is remain. (25) Drops of 3:2 phosphoric acid are added, mixing the solution by swirling and (20) drops of (0.25) M sodium tungstate are added, continue heating the solution in the beaker for at least 20 minutes. The beaker is cooled and quantity transfer the solution to (25) ml volumetric flask dilute to the mark with distilled water. Measure the absorbance at (435) nm.

Results

Table (1) effect of kind of media

[1]M	V(v)ppm
NaOH	68.3
HCl	51.5
KCl	41.90

Table (2) effect of concentration of [NaOH] solution

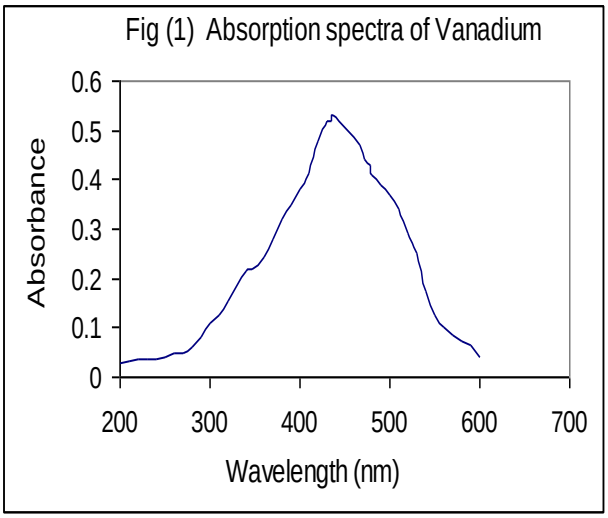
[NaOH]	V(v)ppm
0.5	62.3
1.0	68.3
1.5	71
2.0	86.7
2.5	107.1
3.0	94

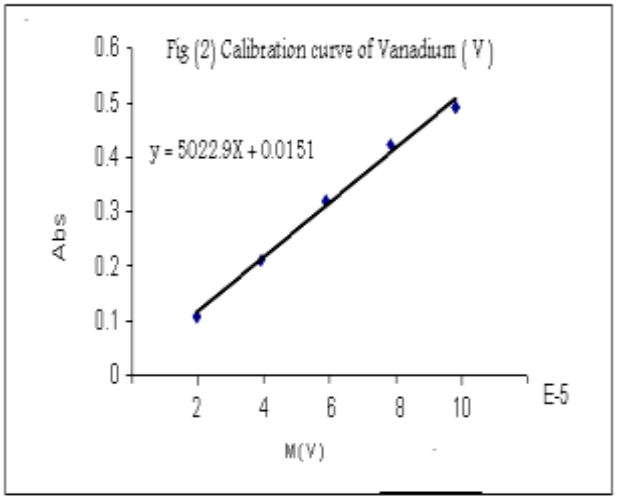
Table (3) effect of temperature

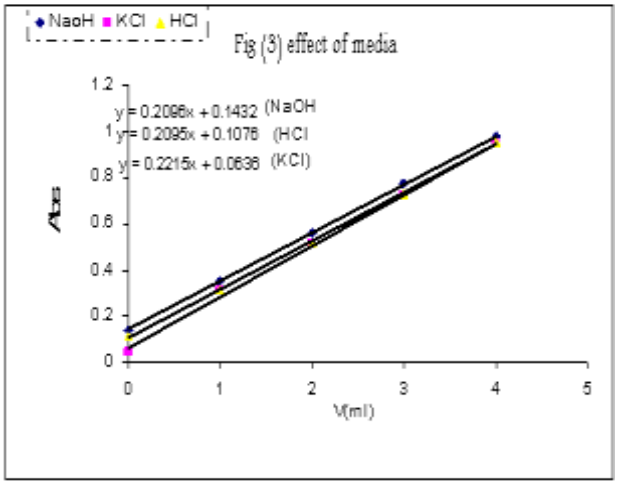
Temperature (˚C)	V(v)ppm
40	81.7
50	93.7
60	103
70	107.8
80	121.8
90	113.07

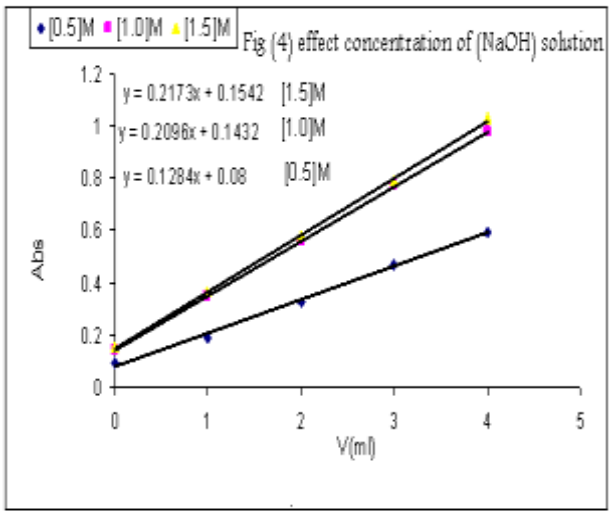
Table (4) effect of time

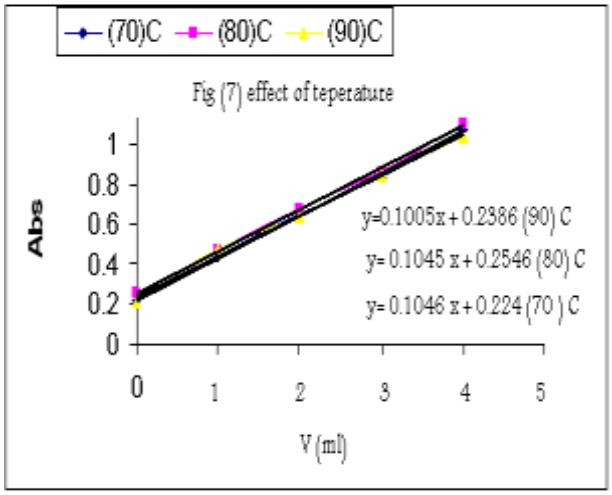
Time (hr)	V(v)ppm
2	100.7
4	121.8
6	133.6
8	134.1

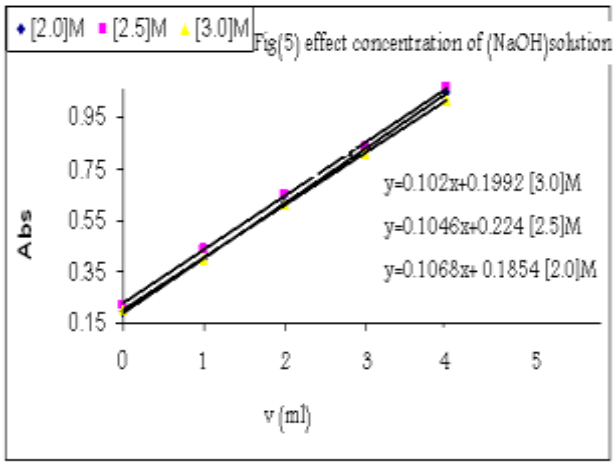


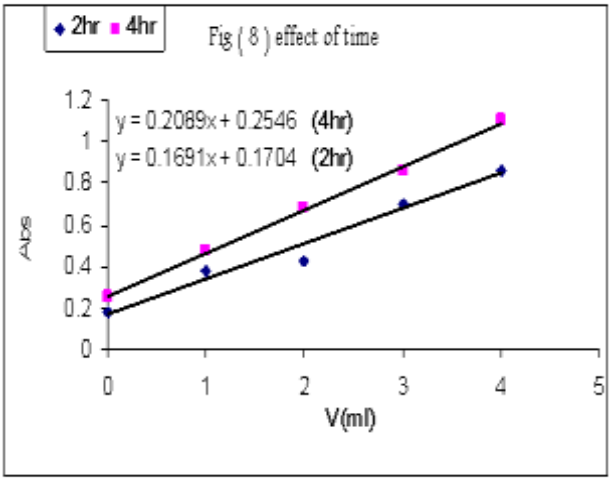


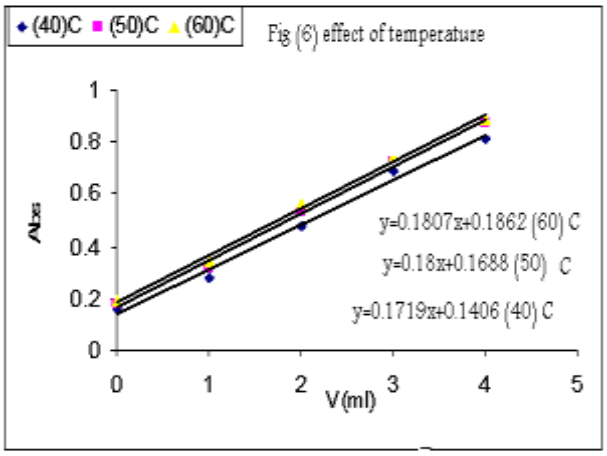


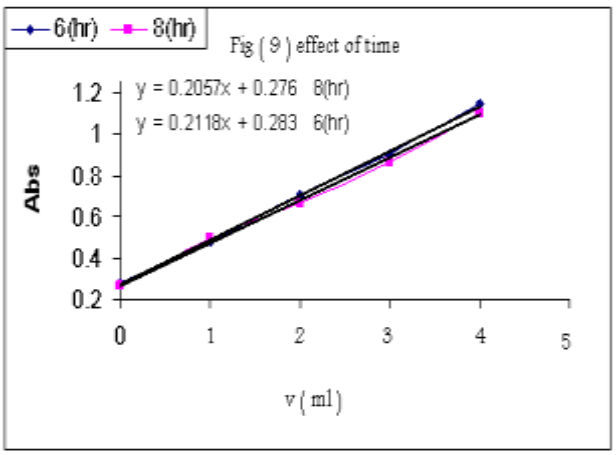

[0.5]M [1.0]M [1.5]M
Fig (4) effect concentration of (NaOH) solution
y = 0.2173x + 0.1542 [1.5]M
y = 0.2096x + 0.1432 [1.0]M
y = 0.1284x + 0.08 [0.5]M
Abs
V(ml)


(70)C (80)C (90)C
Fig (7) effect of teperature
y=0.1005x + 0.2386 (90) C
y= 0.1045 x + 0.2546 (80) C
y= 0.1046 x + 0.224 (70) C
Abs
V (ml)


[2.0]M [2.5]M [3.0]M
Fig(5) effect concentration of (NaOH)solution
y=0.102x+0.1992 [3.0]M
y=0.1046x+0.224 [2.5]M
y=0.1068x+ 0.1854 [2.0]M
Abs
v (ml)


2hr 4hr
Fig (8) effect of time
y = 0.2089x + 0.2546 (4hr)
y = 0.1691x + 0.1704 (2hr)
Abs
V(ml)


(40)C (50)C (60)C
Fig (6) effect of temperature
y=0.1807x+0.1862 (60) C
y=0.18x+0.1688 (50) C
y=0.1719x+0.1406 (40) C
Abs
V(ml)


6(hr) 8(hr)
Fig (9) effect of time
y = 0.2057x + 0.276 8(hr)
y = 0.2118x + 0.283 6(hr)
Abs
v (ml)

Discussion

Absorption spectra: When vanadium ion (V) was treated according to the procedure mention above in fig (1). The maximum absorption occurs at 435 nm and being characteristic the green –yellowish complex , in contrast to the reagent blank. Therefore this wavelength was used in all subsequent measurements

.

The Effect of media: Figure (3) and table (1) shows that the basic media is the most suitable media to determine the Vanadium metal .Because of Determining Vanadium is based on this method of the heteropoly tungstophospho-Vandic acid formed by adding phosphoric acid and sodium tungstate to the sample solution which contains vanadium as $(V_2O_6)^{-2}$ groups is substituted for some $(W_2O_7)^{-2}$ groups in tungstophosphoric acid molecules as the reaction [3] .

$H_7[P(W_2O_7)_6]+ n\ V_2O_6^{-2} \rightarrow H_7[P(W_2O_7)_{6-n}(V_2O_6)_n]+ n\ W_2O_6^{-2}$

and perhaps the reaction between tungstophosphovandic acid and sodium hydroxide has produced stable salts as the reaction [7] .

$H_7[P(W_2O_7)_{6-n}(V_2O_6)_n] + 7NaOH \rightarrow Na_7[P(W_2O_7)_{6-n}(V_2O_6)_n] + 7H_2O.$

The Effect of concentration of solvent: Figures (4,5) and table (2) show the extraction of Vanadium is increased with increasing the concentration of [NaOH] till reaching (2.5)M, of the solvent concentration. Perhaps the complex stability of extraction is increased in basic media. [6]

The Effect of temperature: Figures (6, 7) and table (3) show that the optimum temperature on extraction Vanadium is (80)˚C because there are some factors whaich effect on leaching a surface area , granule volume , speed motion and temperature. Therefore, average of dissolving is increased with the increasing of the temperature because the kinetic of dissolving reaction needs spreading the solvent from dissolving liquid to solid surface, then spreading the solvent from the porous layer to a new metal surface and these steps need a high temperature [7].

The effect of time: Figures (8, 9) and the table (4) show that the optimum time on extraction Vanadium is (6) hr may increase the amount of complex tungstophosphoric acid by increasing the time which causes increasing of determination of Vanadium because $(V_2O_6)^{-2}$ groups in the sample are substituted for some $(W_2O_7)^{-2}$ in complex tungstophosphoric acid and this process needs time [7].

Statistical

Detection limit: The detection limit obtained for the aqueous solutions was 1 mg/l for Vanadium ion to various levels as the following. Table (5) the (D.L) for vanadium ion. *Accuracy and precision* The Accuracy and precision method were checked by measuring vanadium ion (V) at three different concentration the results are shown in table (5)

Accuracy of Method			**Precision of Method RSD)(**		
%٩٥	%٩٩	%٩٩,٩	♀Abs of 1.96×10^{-5} M	♀Abs of 5.88×10^{-5} M	Abs of 9.81×10^{-5} M
1.22×10^{-3}	1.77×10^{-3}	2.66×10^{-3}	0.106.	0.318	0.530
			0.105	0.318	0.531
			0.105	0.317	0.530
			0.317%	0.105%	0.063%

References

1- H. Al-ane M Sc Thesis Technological University of Baghdad (2001).

2- F.Cotton and Willkinson (Advance Inorganic chemistry) jons Wiley and sons inc (1971).

3- Zygmunt Marczenko "Spetrophotoetric Determination of elements" jons Wiley and sons inc (1976)

4-(ASTM)UOP Method 391-1981.

5-David R.Lide (Handbook of Chemistry and Physics) 78th edition 1998.

٦- إبراهيم محمود ،نوال عزت ١٩٩٠(استخلاص المعادن اللاحديدية).

٧- وليد عاصم ١٩٩٧(مدخل إلى الصناعات التعدينية).

٨- العفتان . يوسف ساجت. رسالة ماجستير مقدمة إلى كلية التربية – ابن الهيثم – جامعة بغداد (استخلاص الفناديوم الرباعي والخماسي بوساطة الايثرات التاجية) ، (١٩٩٦) .

٩-T.K. Mukherjee , C.K. Gupta " Hightemp . Materials and Process" vol. 11 no 1-4(1993) P.189-206.

10-M . Ghaze M. Sc Thesis College of Education University of Tikrit (2003) .

11-Shang lin min shing "Study of the extraction of Vanadium and Nickel in Oil Fired fly ash" Hydrometallurgy (1998) P.163-176.

١٢- الزوبعي ، خالد مخلف (دراسة عن إذابة واستخلاص الفناديوم من مخلفات حرق الوقود الثقيل) رسالة ماجستير إلى جامعة بغداد (١٩٩٩).

تقدير الفناديوم بطريقة طيفية في مخلفات النفط الثقيل في محطة ملا عبدالله الغازية

محمد غازي عبدالكريم

كلية الصيدلة، جامعة تكريت، تكريت، العراق

الخلاصة

تم في هذا البحث دراسة امكانية استخلاص وتقدير الفناديوم من مخلفات حرق الوقود الثقيل بواسطة استخدام طريقة الاضافة القياسية. تم دراسة تاثير نوع وسط الاذابة ، تركيز المذيب ، درجة الحرارة ، وزمن الاذابة ووجدت ان الظروف المثلى كانت كالاتي:-

- محلول هيدروكسيد الصوديوم كوسط للاذابة .
- تركيز المحلول المثالي (2.5) مولاري .
- درجة الحرارة المثلى ٨٠ درجة مئوية .
- زمن الاذابة المثالي ٦ ساعات