

Determination of Vanadium in Crude Oil and Some Petroleum Products Spectrophotometrically

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ABSTRACT

Vanadium is undesired constituent found in crude oil and its products, where, it has many side effects in refineries, affects the catalyst activity and corrosion problems in plants. This paper offers analytical determination method of vanadium from crude oil and some petroleum products by extraction. The extraction was accomplished in 6 h at 80°C in basic media, followed by sample preparation, finally, spectrophotometric measurements at λ_{\max} of 395 nm.

The results showed various vanadium content of crude oil (31.25 – 223.75) ppm, fuel oil 210 ppm, kerosene 166.25 ppm, gasoline (285 – 287.5) ppm, lubricating engine oil (157.5 – 251.25) ppm and turbine oil (186.25 – 202.5) ppm.

KEY WORDS: Vanadium, Crude Oil, Turbine Oil, Diesel, Gasoline, Kerosene, Spectrophotometry.

1. INTRODUCTION

The existence of trace metals in crude oil and its products is important for exploration, production and refining processes. Also, it utilized elucidate the relationship between oil types obtained from reservoirs specific geological provinces (Elrich, 1985). The traces of heavy metal contents the traces of heavy metal contents directly correlation with light, middle and heavy crude oils (Barbooti, 2010). For heavy crude oil upgrading, the high metals levels makes the processing to be costly, either through the high cost of hydrogen addition or high yield loss (Reynolds, 2004). There the most common methods used to measure trace metals content in petroleum industry are: polarography (Bakirova, 1984), neutron activation (Chifang, 2005), high performance liquid chromatography HPLC (Tadayon, 1999), atomic absorption spectrophotometry AAS (Sebor, 1975), inductive coupled plasma ICP (Botto, 1987) and electrothermal vaporization (Saint'Pierre, 2002). AAS is the widely used method regarding to simplicity, cost of instrumentation requirements, precision, repeatability and reproducibility of flame method compare with the precision given by institute of petroleum (IP)288 method (Brandao, 2007; Kowalewska, 2007).

The purpose of this study is to estimate the vanadium concentration in crude oil, gasoline, diesel, kerosene, lubricating oil and turbine oil from Koya local market.

2. EXPERIMENTAL

Apparatus: A CECIL UV-visible CE7200 double beam Spectrophotometer, with 1cm matched quartz cells were used for absorbance measurements, hot plate magnetic stirrer (LabTech), sensitive balance (OHAUS), heating mantle (Isothermal) and extraction apparatus from Linetronic Technologies (Switzerland).

Chemicals: Sodium hydroxide (99.5% Scharlau), sodium tungstate (98% Fluka), Nitric acid (70% J.T.Baker). Phosphoric acid (Fluka) and ammonium solution (Hopkin & Williams) were used without further purification.

Standard Vanadium solution (1ppm): Dissolve 2.298 gm. of ammonium metavanadate NH_4VO_3 in water containing 5 ml. of concentrated nitric acid, and then, the contents diluted to one liter.

Procedure:

Extraction step: Five grams of sample weighed to a round bottom flask, 50 ml of sodium hydroxide solution added, the contents refluxed using extraction apparatus for 6h at 80°C. By using a separatory funnel, the lower layer separated, and then, diluted to 200 ml using distilled water.

Determination of λ_{\max} and construction of calibration curve:

Sample analysis: Into 150 ml beaker, take 10 ml of the above solution. Then 6 ml of vanadium standard solution, 0.8 ml of concentrated HNO_3 is added and the contents evaporated until 5 ml remain. 1.3 ml of 2:1 phosphoric acid was added, mix the solution by swirling and 1 ml of 0.2 M sodium tungstate are added, continue heating the solution in the beaker for at least 20 minutes. The beaker is cooled and the contents diluted to 25 ml. Measure the absorbance at 395 nm.

3. RESULTS AND DISCUSSION

Vanadium is a potentially dangerous chemical pollutant. The vanadium content in crude oil will vary according to the source of crude oil from (40 to 130) ppm, about (0.004 – 0.013) % by weight (Ortega, 2013; Qasim Mohammed, 2017).

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Vanadium exist mainly as vanadyl ion (VO^{2+}) in form of organometallic complexes with porphyrins (vanadyl porphyrins), which originated from the formation of crude oil.

In the porphyrin complexation, vanadium bonded by four nitrogen donor atoms, while, in the non-porphyrin compounds nitrogen, oxygen and sulfur can all act as donor atom such as in diketones, ketoimines, salicylaldimines, monothio and dithio-diketones, mono- and dithio-carbamates, etc. (Welz, 1999). The chemical structure of some typical vanadyl porphyrins and non-porphyrin complexes shown in Fig.1 (Barceloux, 1999).

Vanadium compounds cause corrosion problems derived from the combustion chamber of power plants and change in catalysts selectivity are typical problems (Pyrzynska, 2004).

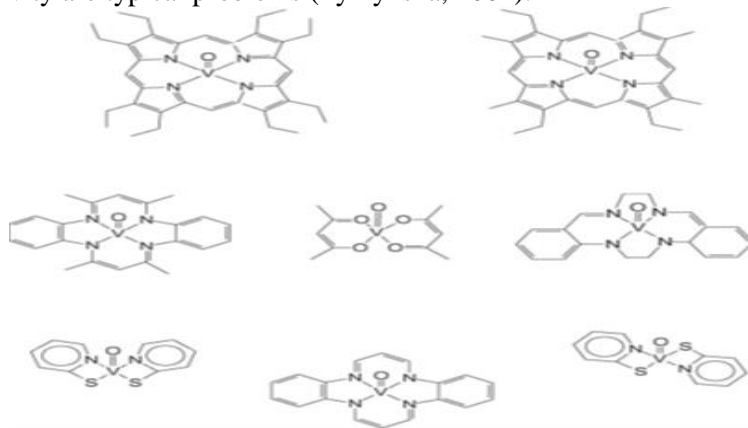


Figure.1. Chemical structures of typical vanadyl porphyrin and non-porphyrin complexes in crude oil

Absorption spectra: The maximum absorption takes place at 395 nm (figure.3) and being characteristic the green – yellowish complex, in contrast to the reagent blank. Therefore this wavelength was used in all measurements, to calculate the concentration of vanadium in all samples from calibration curve (figure.2).

The Effect of media: Basic medium is the optimum media for vanadium metal extraction. Because of the formation of tungstophospho - vanadic acid by adding phosphoric acid and sodium tungstate to the sample solution.

The extraction media: The extraction of Vanadium is increased with increasing the basicity of media, the suitable concentration of (NaOH) used is (2.5) M, due to the complex stability of extraction is increased in basic media.

Temperature of extraction: The optimum temperature on extraction Vanadium is 80°C. The mechanism of dissolving reaction needs a high temperature.

Time of extraction: The optimum time on extraction of Vanadium is 6 hr, it may be related to the formation of a complex of tungstophosphoric acid by increasing the time which causes increasing of determination of Vanadium because $(\text{V}_2\text{O}_6)^{-2}$ groups in the sample are substituted for some $(\text{W}_2\text{O}_7)^{-2}$ in complex tungstophosphoric acid and this process needs time (Oliveira, 2003).

The concentration of vanadium in all samples under study listed in table.1. The results show in most samples a high vanadium level, where the normal range of vanadium is (40 – 130) ppm (Ortega, 2013).

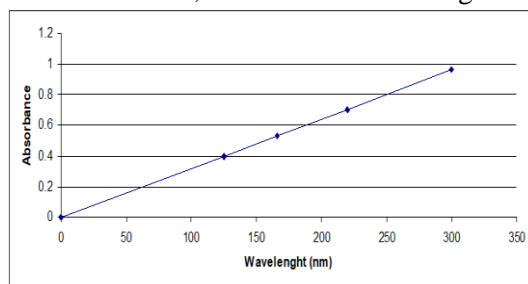


Figure.2. Calibration curve

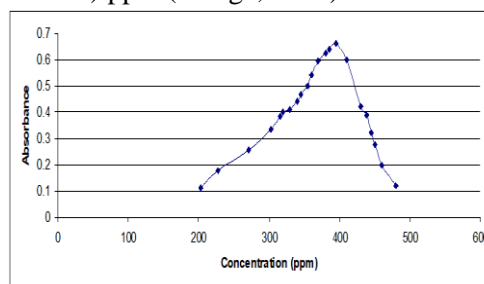


Figure.3. λ_{max} determination

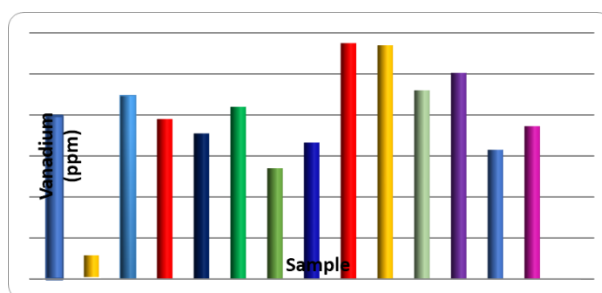


Figure.4. Flow chart of all results

Table.1. Concentration of Vanadium in the samples analyzed

No.	Sample	Vanadium (ppm)
1	Kurmalh (crude oil)	198.75
2	Taq Taq TT-15 (crude oil)	31.25
3	Kirkuk (crude oil)	223.75
4	Tawke (crude oil)	195
5	Ain zala (crude oil)	177.5
6	Fuel oil (bazian)	210
7	Diesel	135
8	Kerosine	166.25
9	Gasoline (bazian)	287.5
10	Gasoline (koya haibat sultan)	285
11	Magnum 15W-40 lubricating oil (virgin)	230
12	Magnum 15W-40 lubricating oil(used)	251.25
13	Arya oil SL Car X1 15W-40 (recycled)	157.5
14	Turbine oil (recycled)	186.25
15	Turbine oil (used)	202.5

4. CONCLUSION

Vanadium caused undesired side effects in the refining process, corrosion in oil-fired power plants and affects the catalyst activity. Spectrophotometrical determination based on extraction of vanadium from crude oil and some products achieved.

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