# An EPR-express method of determining the paramagnetic species in heavy crude oil and its residual fractions

**[1]C. S. Ajinomoh, [2]A. V. Fionov, [3]P. W. Igbagara and [1]O. R. Momoh**

*[1]Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria*
*[2]Department of Electrochemistry, Moscow State University, Moscow, Russia*
*[3]Department of Chemical Engineering, University of Uyo, Nigeria*

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## ABSTRACT

*Determining the concentration of vanadyl porphyrin in a sample of oil residue fractions above $360^oC$ is carried out by using two standards- the primary and the secondary. The primary standard used in the experiment consist of a sample of vanadium sulfate ($VOSO_4*H_2O$) of known concentration, for determining the content of vanadyl complex in the oil, and the secondary standard consist of carbonized sugar for determining the content of the free radicals in the oil samples. The absolute concentration of the paramagnetic species is based on the total content of the vanadyl porphyrin and by comparing it with the primary standard then dividing it by the concentration of the secondary standard and by the amplitude of rubin sample. The EPR spectral form, for the residue oil samples are found to be uniform for all (that is fro both treated or non- treated samples), except the variation in the $VO^{+2}$ concentration. The method further reveals that the $VO^{+2}$ ions are present in matrix with other micro element forming the paramagnetic species in the residue oil fraction and this is responsible for its EPR spectral broad line. Other method of determining the concentration of $VO^{+2}$ in oil i.e. method of atomic absorption spectroscopy is found to have a direct correlation with the method of EPR-spectroscopy by results.*

**Keywords:** vanadium complex, integration, residue fraction, samples, paramagnetic

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## INTRODUCTION

New approach of coping with of viscous asphatenic oil has advanced beyond obtaining the various fractional yields. At any stage of the refining processes the misery of the colloidal nature of resin asphatenic oil opens new direction for its study. In the monogram of [1] some conclusions were made based on homolytic theory of oil dispersed system that the stability of oil dispersed system is directly linked to the presence of free long life radicals; the shell of the colloidal system i.e the complex structural unit (CSU) represented by the radicals exhibit high spin-interacting potential; and changes or decrease in potential surrounding the shell layer, leads to regrouping of corresponding aromatic, naphthenic, paraffinic hydrocarbons.

The heteroatomic bonds by nature are similar to aromatics or non aromatic and poses high mobility and capable of repositioning at any part of the layer in the complex structure due to its low bond energy, and consequently due to its high spin-interacting potentials [1] during heating or solution of oil disperse system molecular collision, and

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consequently to destruction and formation of CSU. Major challenges in upgrading and refining asphaltenic oil are as a result of the behaviour of stable radical during heating and solution.

The presence of microelement in ODS has been a great interest to researchers in petroleum refining and technology. Such presence pose several consequences to refining operations and exploitation properties of oil products. In oil product trace amount of such metals are often found and the most predominant among all is nickel and vanadium. Among the last two the later has been characterised as the major dopant due to its stability in OWS at a high temperature[2].

Vanadium in OWS was found to occur in the farm of oxo-vanadyl phorphyrines, consisting of several homologous series which the most dominant is ethioporphyrin (Ethio) and deoxophylloerithroetio (WPEP).

The character of the oil dispersed system is synonym to its rheological properties and serves as a guid for its recovery from the well, transportation and refining processes.

In the work[3], that at the presence of heat, the association equilibrium of asphalten in OWS is distribed; like nise, the presence of polar solvent in the associative oil. The cater is reveal to linked with electron redistribution among the metalloporphyrins, thereby reducing the cohesive force of the miscelle molecules by donor acceptor interaction[4]. The miscelle polar solvent interaction is reversible process, and the cluster of asphattenes induce dipole under goes reorientation at polaricatim in the field of microwaves, through overcoming of charge transfer of the oxovadium central atom in the asphaltene oil in [5] was reported oil that there is significant decrease in the spin value for solvent possessing high dipole moment.

The extends of free-stable redials (FSR) in oil and its products is determined through electron paramagnetic resound spectroscopy; EPR and the presence of the radical in a compound is known is paramagnetic compound (book on EPR). Among the paramagnetic species, the major is the vanadyl porhyrine complex $VO^{2+}$ which spectrum reveals a hyper-fine structure (HFS) from the vanadium atom (4+), and this consist of 8 component (representing spins of vanadium shell equal 7/2). When sample of oil product is freered or poses high viscosity, its EPR spectrum reveals axial anisotrophy of HFS, that is 8 lines, of respective parallel and perpendicular reientation. Beside that the g-factor of $VO^{2+}$ also reveals axial anistrophy [6,7]. Other forms of paramagnetic species, so called the free radicals and the EPR-spectrum is represented by a narsow line and g = 2.003. Though the nature of the radicals is not fully explained but was suggested that the radical enginated from the unpaised electrons in the condensed aromatic fragment of asphaltene molecules (eight = 0.2 – 0.3nm and diameter 0.7 – 1.5nm) [8].

At the same time, in most cases as in oil and its product reveals a large EPR bands of nasow lines representing high spin of metallic complexes, and also their origin is not well explained.

In this work, much attention is focused on the study of vanadylporphyrin complex sence its spectrum is easily interpreted, and according to [9], that it has practically four valency state. the grantitative analysis of vanadium content a practical value, since its presence in oil and its products, limit index of it refining processes, and also the exploitation characteristic of its product. According to [10] that considerable quantity of porphyries find its way into a fraction of initial boiling of around $300^0C$ due to its volatility at that temperature, and the vanadium component constitute corrosion of the reactor material.

However, as a result of various peculiar EPR methods of deterring vanadium contents several challenges are confronted, and efforts in tackling the present task various pathway are applied.

Also it has occurred that oils at room temperature tend to varied in visconsity as a result of variation in spin movement of the paramagnetic molecules of the sample and this leads to low precition of the EPR method of vanadium analysis by band intensity of separate line of isotropic spectrum. In standardizing the conditions for registration of spectrum, the samples is either freerea under nitrogen at $-196^0C$ (140) or heated to $12^0C$ in sealed ample for achieving isothropic spectrum [11]. As a standard, a known content of vanadium is used [12] or synthetic vanadium compound, of VO ($TCH_3CO)_2$ used as standard. The basic problem in quantitative analysis of vanadium complex by EPR method lies in accurate determination of the double integral, and which is further complicated by the width of the spectrum of the vanadyle complex, and base line disappearance.

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## MATERIALS AND METHODS

Quantity of bottom oil (residue fraction > $360^0$C) sample (0.0001-0.0002g)    is placed in a quarta tube of 0.5mm diameter, 8cm length. The sample is transfer into central resonator of rediospectrometer BRUKERELEXSYS E580 operating on x band (frequency 9.5GHZ).

Fall in signal of first spin echo is registered in the spectrometer ERUKER ELEXSYS 580 on x ban (ware length 3cm) by the aid of two sequential impulse amplitude 16nsec – 280nsec – 32 nsec at 200m temperature. The value of magnetic pole reaches maximinum the absorption curve of free radicals (max on the cone 13 (Ph.D thesis) fig (1) of first integral – radical cured fig 2). The induction –echo EPR spectrum is registered as the relationship of area under signal of spin-echo, obtained through serial of double implulse 40 nsec – 320 nsec – 80 nsec, from the value of magnetic pole, measured as ordinary ERP spectrum content of vanadium complex and free radicals are determined according to the formals

$$x = \frac{WI(X)/Cr(x)}{WI\frac{(Stad)}{Cr}(std)} [Std]$$

where $X_1$ number of spin of the sample

WI – value of double integral of EPR spectrum

Cr – Amplitude of spectrum of $2^{nd}$ standard (rubbin) recorded together with sample or with $1^{st}$ standard. primary standard as $VOSO_4$ $3H_2O$ was used for determining the concentration of vanadium, and carbonized sugar was used as standard for determining the concentration of free radicals   .

During the duration of registering the sample (number of points in the specks, scale of turing of the magnetic pole, power rating of the microwave radiation, temperature are kept constant.

Some challenges are encountered during determination of the double integral of vanadium complex since in the EPR spectrum are encounter are wide range of lines which may be originated from other paramagnetic species and this forms the bases of the method to reduce the error as a result of the base line.
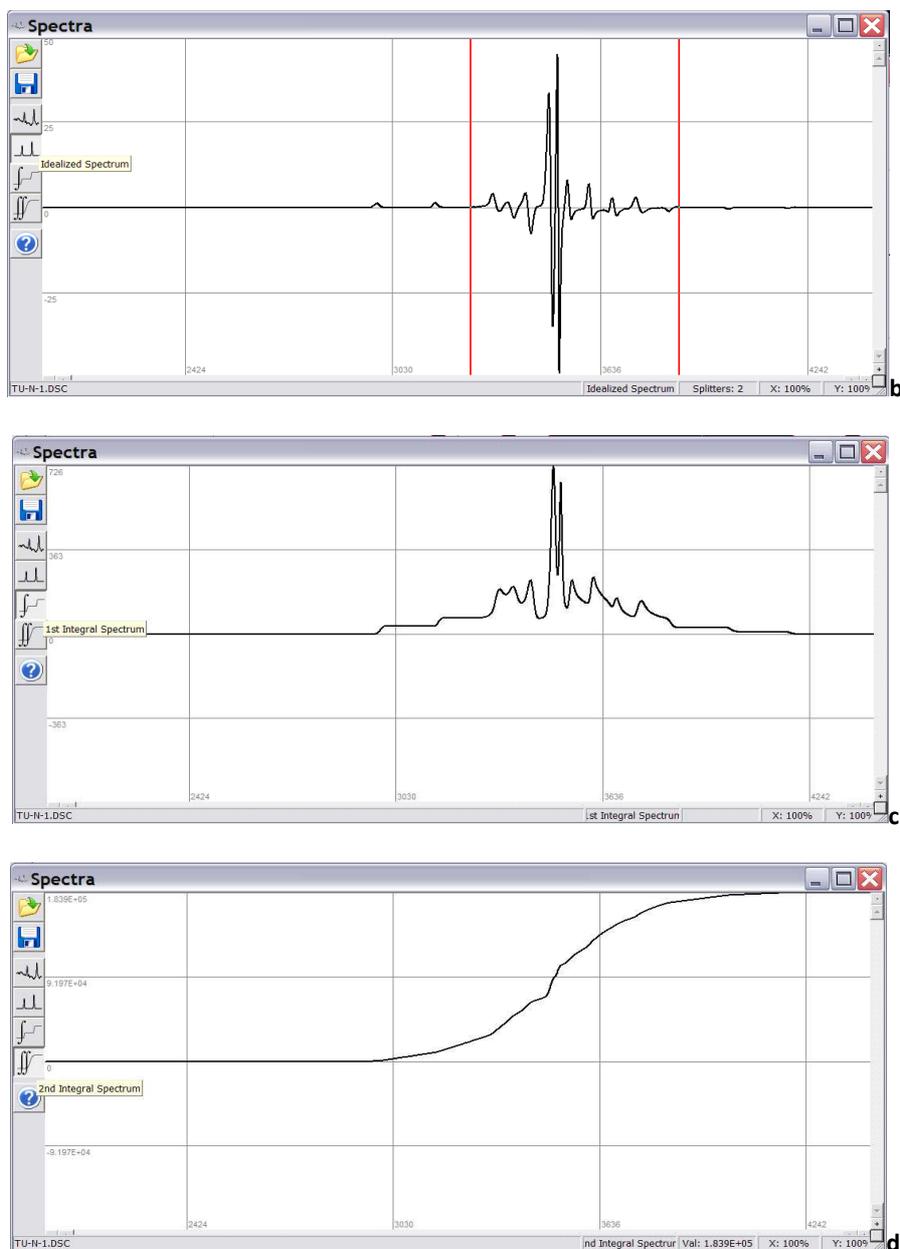
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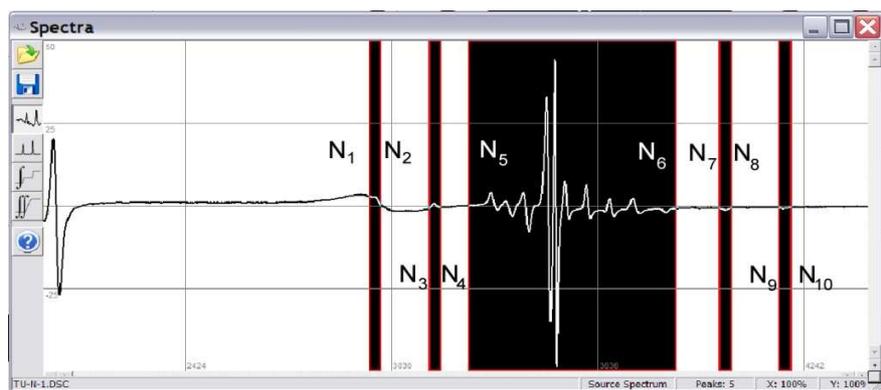






**Fig 2.14 stages of integrating EPR spectrum of vanadium complex VO$^{+2}$ in  heavy oil residue fraction above >360$^o$C. a-shaded region prior to integration, b- correction of the base line, c- first integration, d-second integration**

Determining the value of double integral for vanadium complex.

The initial EPR spectrum consist of massive number, and can be represented as a(N), where a – ordinate value, and N- number of point, which changes from Y to N = 4096. Integration is carried out in several steps (fig 2.14)

In the first step of the spectrum was divided into 5 zone (fig 2.14a), respectively first ($M_1 = +7/2$) and second ($M_1 = +5/2$) parallel component of hyper fine structure (hfs) from shell the central region of the spectrum, and also seventh ($M_1 - -5/2$ and eight ($M_1 = -7/2$) parallel component of HFS.

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Respectively are represent $N_1$ and $N_2$ for initial and final point of first region ($M_1 = +7/2$), $N_3$ and N4 – for second region ($M_1 = +5/2$), $N_5$ and $N_6$ third or (central spectral region), $N_7$ and $N_8$ – for fourth ($M_1 = -5/2$), $N_9$ and $N_{10}$ for fifty region ($M_1 = -7/2$).

second stage – by carrying out correcting of base line in the initial spectrum (fig 2.14b) the corrected spectrum is represented as b(N). Then the algorithm of correction is presented in the following form:

Third step – calculate the integral of the EPR spectral curve (fig 2.14c) and this is represented by c(N). the algorithm of the calculation of integral is describe as follows:
fourth step (fig 2.14d) calculate the value of double integral of the spectrum according to the formula

$$WI = \sum_{i=i}^{i=N_{max}} c(i)$$

The obtained value of W1 represent the total spectrum of vanadium complex and free radicals.

calculation for the double integral for free radicals WI ® is carried out as follows: represent $N_{R1}$ and $N_{R2}$ – as the initial and final point of the spectral region of the free radicals.

a9N) – the ordinate, N – number of point from $N_{R1}$ to $N_{R2}$.

base line correction is represented as b(N)

By the where NE[$N_{R1}$, $N_{R2}$]

later expression other the base-line correction of EPR absorption c($N_{R1}$)$^2$O, c($N_{R2}$) = O then the repeated integration gives the value of double integral for free radicals:

$$WI(R) = \sum_{i=R_2}^{i=R_2} c(N)$$

hence the value for vanadyl complex double integral is obtained as follows:

WI ($VO^{2+}$) = WI – DI (R)

where WI is the double integral for primary and secondary standard (respectively $VOSO_43H_2O$ and carbonized singar), carried out also according the algorithm above. Fig 2.15 illustrated the spectral form of vanadium sulfate at various stages of its transformation.

The content of vanadium complex is determine through the route: by comparing their double integral, then divided by the amplitude of rubbin spectrum; and for double integral of absolute standard (vanadium sulfate $VOSO_4. 3H_2O$), also divided if by rubbin amplitude

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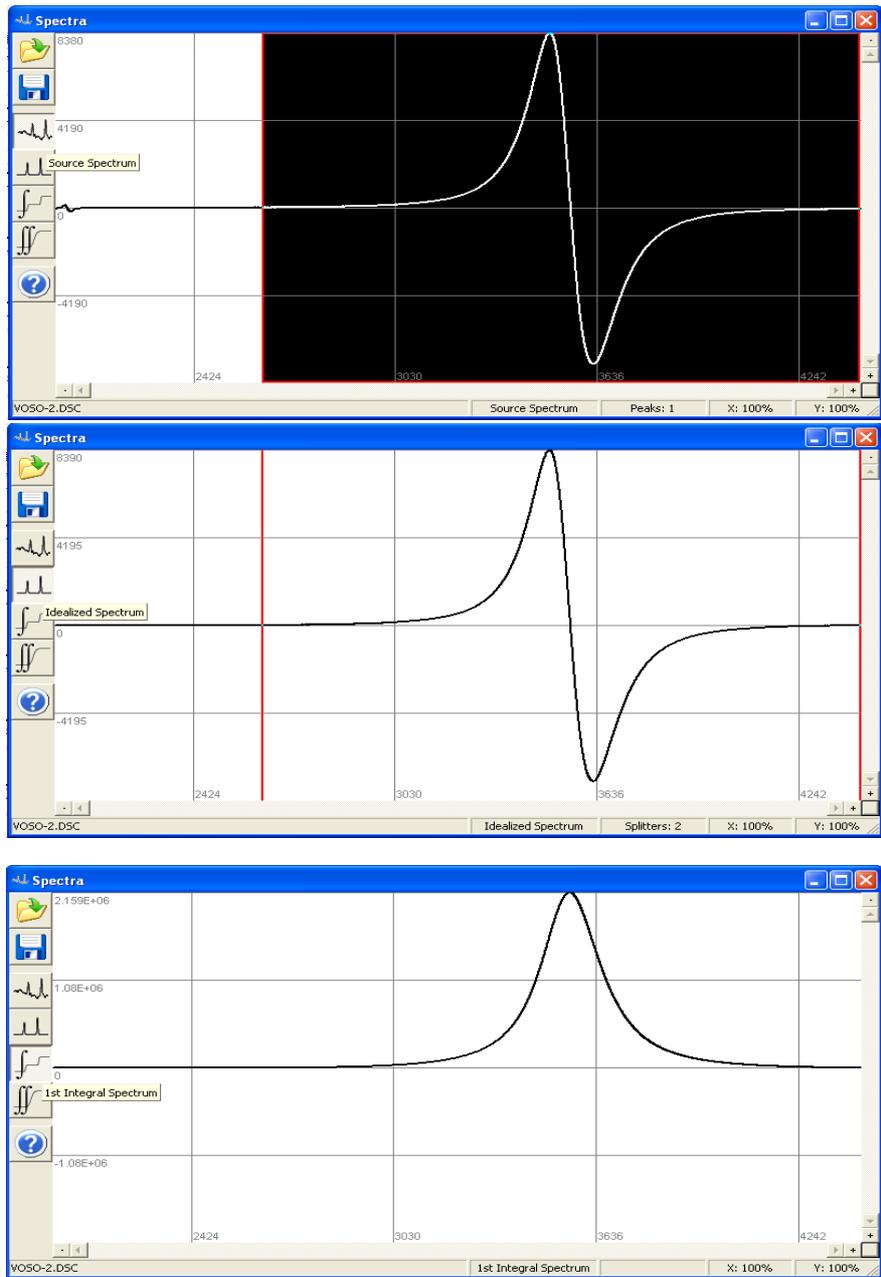


**Fig. 2.15. Stages of integration of EPR spectrum of vanadium sulfate crystal (VOSO$_4$*3H$_2$O). a- shaded area prior to integration-correction of the base line, c- first integration, d- second integration.**

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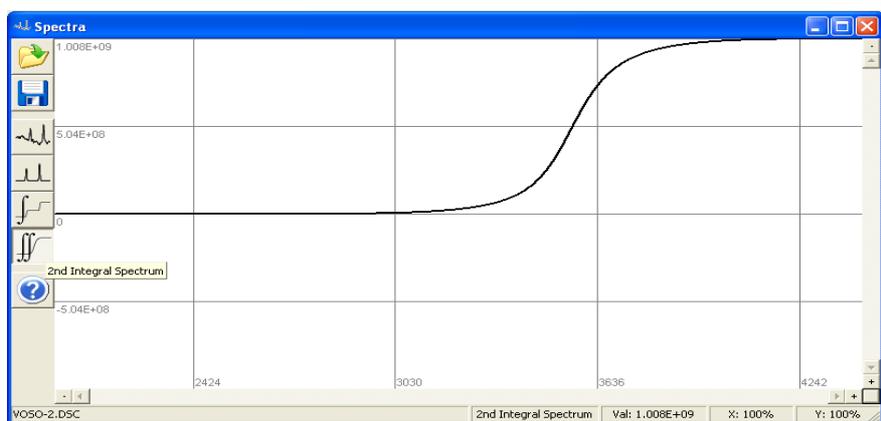
## RESULTS AND DISCUSSION

The EPR spectral form for bottom oil NORSI and KIRISHI oil was found to be similar irrespective of their differences in origin. The magnetic resonance parameter obtained A$_{11}$ = 156.5 x 10$^{-4}$cm$^{-1}$; A$_1$ = 54.4 x 10$^{-4}$cm$^{-1}$; g$_{11}$ = 1.961; g$_1$ = 1.985, which is still around around the boundary of literature value for vanadyl porhyrrain derived from oil (134). The sample was further treated with ozone (Ajini…) and was revealedthat the apart from changes in concentration of VO$^{2+}$, the spectral form remain the same.

Also was realised that the viscons sample, VO$^{2+}$ spectrum is totally anisotropic and there arise no more need for its heating or freezing as a standard for registering the spectrum, and this simplifies and précised the procedure in table 2.4 illustrated the results for determing vanadium content according to the developed method and by atomic-absorption method.

| Sample No | Vanadium Content, PPM | |
|---|---|---|
| | Atomic Absorption Method | EPR Method |
| 1 | 109 | 168 |
| 2 | 88 | 182 |
| 3 | 93 | 188 |
| 4 | 99 | 182 |
| 5 | 86 | 160 |
| 6 | 102 | 177 |
| 7 | 88 | 162 |
| 8 | 101 | 213 |
| 9 | 98 | 187 |

The presented table shows that the vanadium content in oil residue, as determined by EPR spectrum, is practically double that by atomic absorption method. The factor of such increase in value can be attributed to the presence of other metalorganic compound, possessing paramagnetic properties.

In general, the obtained data, and the various methods involve in the VO$^{2+}$ determination shows a good correlations. Hence the developed method can be recommended for VO$^{2+}$ determination.

## CONCLUSION

- Application of double standards facilitate the precision of obtained VO$^{2+}$ concentration EPR.

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- The spectral form of the $VO^{2+}$ samples are identical despite the differences in pretreatment with ozore.
- The method. Beside the $VO^{2+}$ also reveals that there is trace of other paramagnetic species which amount to the broad hypertive bands.
- Also that the result of the method has direct correlation with other method of analysis such as atomic absorption spectroscopy.

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