

Deep-UV Laser Ablation Technology [213 nm] Coupled with Plasma Quadrupole Mass Spectrometry for Rapid Determination of Nickel/Vanadium Ratios in Asphaltenes

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Abstract

Knowledge of nickel/vanadium (Ni/V) ratios in petroleum fuel is essential to source geochemical information and to limit catalytic poisoning and corrosive effects in chemical refining processes. However, these ratios have been found to vary widely and are affected by various factors, including the sulphur content of the petroleum feedstock. They are normally obtained by digesting and treating the feedstock in suitable acid or organic media followed by numerical analysis. Our research investigated a novel sample introduction technique for obtaining Ni/V ratios by ablating petrified asphaltene samples (following liquid nitrogen pre-treatment) with a 213 nm laser beam coupled to a hyphenated plasma mass spectroscopic system. Laser ablation is ideal for delving beneath the surface of a solid matrix to measure the composition of the substrate. Iterative scanning of the sample surface and subsequent depth-profiling was achieved at pre-determined surface points to depths of 50 μm at selected sub-surface intervals. Characteristic intensities originating from the metals of interest were measured. Laser results were compared with the 'digested' results obtained directly by ICP-MS. In the case of the digested crude oil samples, these ratios varied between 0.6 and 0.8. This was higher than corresponding literature values, which occurred within a range of 0.3-0.6. The laser ablation results for typical asphaltene samples showed that Ni/V ratios varied in the interval 0.2-0.8, which were considered to be elevated and in keeping with the elevated crude oil ratios. The digested asphaltenes also reflected higher ratios, suggesting the influence of sample inhomogeneity and nickel impurities. Factors affecting variations in this ratio are presented, and the advantages of a more stable ratio are discussed. The study is of definite interest to petroleum engineers, and has considerable scope for extended research.

Keywords: Mass spectrometry; ICP-MS; Nickel/vanadium ratios; Crude oil; Asphaltenes

Introduction

The thrust of this work concerns the development of a rapid laser technique [1,2] for deriving Ni/V ratios in solid asphaltene matrices. The traditional method for obtaining these ratios is solvent digestion [3], which is usually time-consuming and tedious. There is a need therefore, to obviate the lengthy procedure and save chemical resources. In the petroleum industry, the nickel/vanadium ratio is considered to be a popular 'damage control' parameter, especially in chemical refining processes [3]. These ratios are also employed by petroleum engineers to garner definite types of pre-historic geoscience information [4]. It has been shown in recent reports that these ratios tend to vary widely, from oil well to oil well, and from country to country. Recently, a paper by Chirinos [5] suggested that the [V/V+Ni] ratio could be considered a more reliable parameter to source information, especially for correlations in petroleum geoscience.

Petroleum feedstock in the form of crude oil and asphaltenes is generally associated with various types of rock formations, and trace metals embedded in the source rock find their way into the fluid petroleum. Asphaltenes represent a complex mixture of hydrocarbons that entrap trace metals within porphyrin matrices - of which nickel and vanadium are the most abundant. A research article by Pillay et al. [6] alludes to metal 'inclusions' or 'grain' formations in solid asphaltenes, which could result in significant fluctuations in Ni/V ratios at specific points in the solid asphaltene matrix. The object of this work was to explore some of the factors that affect the variation in these ratios and to determine whether the [V/V+Ni] parameter is a more stable one for use in the petroleum industry [5].

Our work is an experimental study that uses the capability of deep-UV laser ablation (213 nm) to directly probe Ni/V ratios in solid asphaltenes. The laser ablation method refers to trace metal

determination by subjecting a solid sample to irradiation by a laser beam and subsequently directing the resulting vapour to a quadrupole ICP-MS instrument (Inductively Coupled Plasma Mass Spectrometry) for numerical analysis [7,8]. The technique is not easy to standardise mainly because most solid samples are highly inhomogeneous and, in addition, suitable certified reference standards (such as solid asphaltenes) are not easy to acquire. The diameter of the laser beam is of the order of micrometres, and the beam itself is not suitable for use on soft samples. A paper by Pillay et al. [9] describes the effect of 'splashing' during irradiation of soft samples, such as creams and gels. Some asphaltene samples are sufficiently coalesced and hard enough to withstand the impact of the laser without splashing effects. However, 'splashing' could occur (Figure 1) during analysis of asphaltenes and to prevent this phenomenon from occurring the sample could be solidified in liquid nitrogen prior to analysis. In a preliminary study we showed that this sample introduction technique is innovative and feasible [10]. Our research compares Ni/V ratios in asphaltenes (laser ablation) with values obtained by the traditional digestion method. It should be underscored that determination of Ni/V ratios in asphaltenes has been previously undertaken by other researchers in the field [5], but there is no record in the documented literature of direct quantification of this ratio in petrified asphaltene samples, subsequent

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Figure 1: Screen shot of 'splashing effects' in soft sample [9].

to liquid nitrogen-pre-treatment. From this perspective our research is novel and makes a definite contribution to fuel studies. Our work was extended to include Ni/V parameters in crude oil and compare them with published literature values.

Materials and Methods

Sample purification and handling

Two sample handling procedures were employed. The first procedure involved traditional digestion of the crude oil samples and derived asphaltene fractions. Crude oil samples (from different locations) were mixed with n-heptane and left to age for 3 days. This procedure was followed by Soxhlet reflux-distillation for six hours (Figure 2). Asphaltenes were subsequently precipitated from the crudes and purified by further refluxing to remove waxes and other undesirable impurities. The identity of the asphaltenes was established by density and solubility parameters. Sample purity was confirmed spectrophotometrically by observing UVVA resonances at 435 nm and 350 nm. Prior to ICP-MS analysis for trace nickel and vanadium the samples of crude and asphaltene derivatives were solubilised in concentrated aqueous acidic medium (69% HNO₃) in combination with hydrogen peroxide (30% H₂O₂) and subjected to microwave digestion. The resulting solutions were further diluted for analysis by plasma mass spectrometry. The second procedure was associated with direct laser ablation of asphaltenes. Samples of solid asphaltenes (abstracted by chemical means from crude oil) were immersed in liquid nitrogen, petrified, (Figure 3) and transferred to a special sample chamber for rapid laser irradiation. Depth-profiling of solidified asphaltenes, after liquid nitrogen immersion, represents the original feature of our study.

Instrumentation

Samples were analysed with a Perkin Elmer SCIEX DRC-e ICP-MS (Ontario, Canada) equipped with a New Wave UP213 Nd:YAG laser ablation system (Figure 4). Solid samples were irradiated in a specially designed sample chamber, 5 cm × 5 cm, and irradiated with a pulsed 213 nm laser beam operated at a repetition rate of 4 Hz and a beam energy level of 60%. Fluence was between 16 to 18 joules/cm². The beam scanned the sample surface and was conditioned to ablate successive depths of 5 μm at selected points to a final depth of 50 μm. The beam diameter was adjusted to 100 μm, and the laser gas flow was regulated to 0.80 L/min. Liquid samples were aspirated directly into the plasma and transported to the mass spectrometer. The instrument is fitted with a quadrupole mass selector to attain efficient mass separation. The technique is highly sensitive compared to other modern methods [11-15], and is capable of reaching lower detection limits of ng/L (sub-ppb levels). The analytical process underwent standard correction for background and matrix effects and certified standards were employed to establish instrumental performance and repeatability, which occurred within a standard deviation of 5% and was considered satisfactory.

Results and Discussion

Variation in Ni/V ratios

From previous reports by other authors [5,16] it has come to light that Ni/V ratios in petroleum feedstock fluctuate appreciably across regions, and even within an oil-producing region there can be significant inconsistencies. To obtain a deeper understanding of these variations, Ni/V ratios were extracted from the published literature for similar oils from different regions, plotted, and the scatter of the data studied. Figure 5 represents a plot of Ni/V ratios for Abu Dhabi crude oil, Russian crude and Venezuelan crude [3,5,16]. It is clear from the plot that distinct clusters exist within a group of oils (encircled). Venezuelan crude reflects ratios in two widely separated knots: one occurring between 0.05-0.10; and the other between 0.20-0.25. This width in separation is significant and reflects the extent of the variations encountered in this parameter. For the Russian oils the Ni/V ratios are clustered around the 0.10 mark, but outliers can reach close to 0.30-demonstrating again that the inconsistencies in these ratios are wide. In the case of the Abu Dhabi oils, the data span a broad range from about 0.30 to 0.60, confirming the extensive scatter in this ratio. A prominent feature of Figure 5 is that the Ni/V parameters derived for the Abu Dhabi oils are comparatively elevated. This could be due to differences in the source rock and geological formations associated with the petroleum feedstock. Abu Dhabi asphaltenes will, therefore, be expected to have corresponding elevated Ni/V ratios.

Depth-Profiling/plasma mass spectrometry

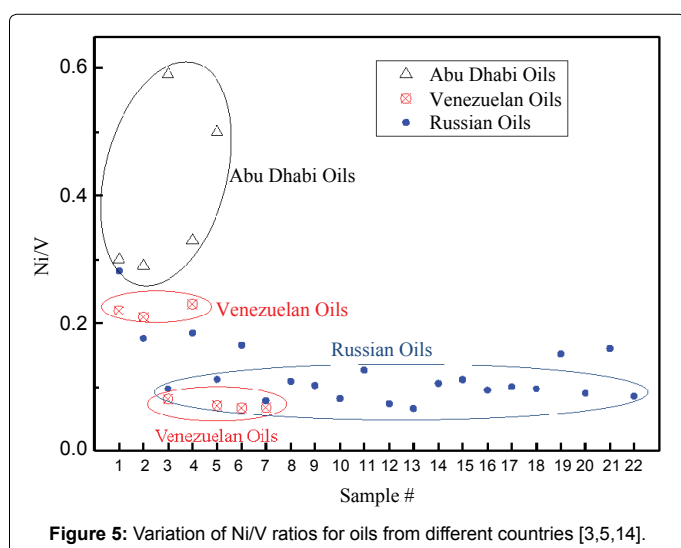
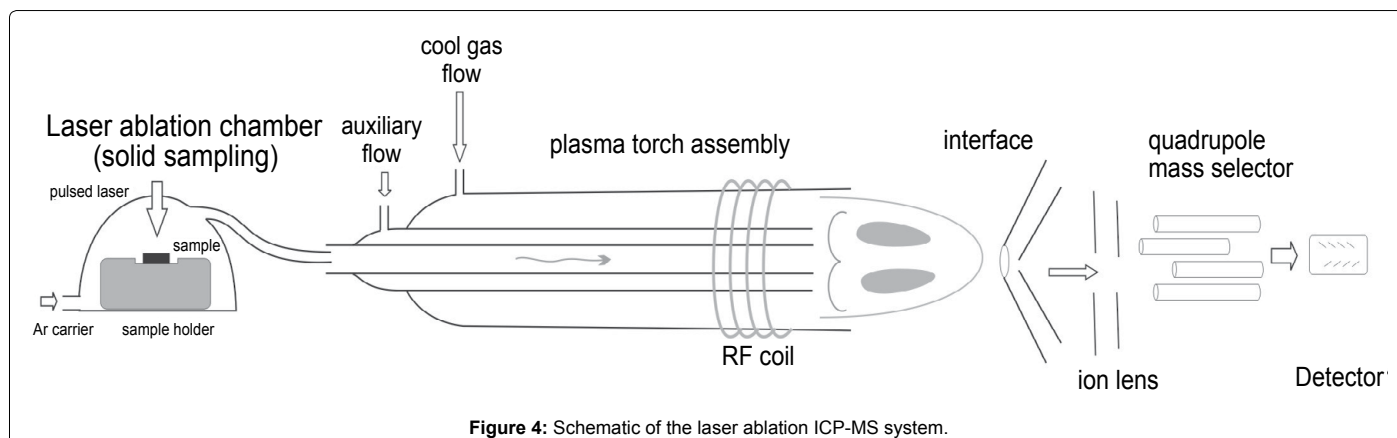
Depth-profiling [17] is a unique approach that provides information with pinpoint accuracy beneath the surface of a sample by 'drilling' to different depths with a high-powered laser beam. This, coupled with iterative surface scanning by the beam, provides elemental profiles spatially and in sample strata. The impact of the beam on a spot on the sample surface converts the material at the spot into a vapour, which



Figure 2: Soxhlet distillation set-up of asphaltene sample.



Figure 3: Liquid nitrogen pre-treatment.



is transported to the plasma torch, where it is atomised, ionised and conveyed to the mass spectrometer. The laser ablation results (Ni/V vs. depth) for typical asphaltene samples that were petrified in liquid nitrogen appear in Figure 6. It is evident from the plots that the scatter of the ratios is significant and generally extends from about 0.20 to 0.80. The regression lines shown on the plots are very rough approximations of the average distribution of the data, but clearly cannot be used as appropriate criteria to gauge the level of scatter. No clear pattern emerges from these data and the overall spread suggests that the samples themselves are highly inhomogeneous, which corroborates the report by Pillay et al. [6], namely that, at microscopic levels solid asphaltenes tend to be 'grainy' and metals could agglomerate at certain points within the asphaltene matrix. This point is further borne out by the fact that several data points in the plots in Figure 6 occur in small groups or clusters, which could represent close formations of such metal complexes.

For purposes of comparison, digested solutions of the corresponding asphaltenes were aspirated into the ICP-MS core and analysed for total nickel and vanadium. The experimental results obtained from the digested asphaltene samples are presented in Table 1. These results are elevated compared to the laser ablation data in Figure 6. This is expected as the digested sample would produce an overall result derived from the accumulation of points in Figure 6. As depicted in Table 1 the Ni/V ratios from the asphaltene solutions range between 1.2-1.6. Both the Venezuelan and Russian asphaltenes produce Ni/V

ratios between 0.10-0.30. In comparison our results show appreciable elevation, in keeping with the higher Ni/V parameters in our crudes (Figure 5). Pillay et al. [6] further point out that nickel 'hotspots' occur in asphaltenes implying that there could be other factors at play that influence the elevated nature of these ratios.

Sulphur/nickel effects

A report in 1999 in the British Corrosion Journal by Smith [18] stated that to minimise corrosion the interior casing of pipelines in Abu Dhabi was coated with nickel-chrome alloy. Clearly, the crude oil that constantly washes against such a casing would leach nickel out of it, thus elevating the nickel content in the crude through contamination. An earlier report in 1990 by Barwise [16] stated that there is a direct correlation between the sulphur content of Abu Dhabi crudes and corresponding vanadium levels, demonstrating that as the sulphur content increases so do the vanadium concentrations.

These reports purport that there are two major factors at play that could influence the variation of Ni/V ratios. One is the 'sulphur effect' and the other is potential nickel contamination. These two factors work against each other and, judging from the elevated Ni/V ratios for digested crude oil in Table 1, it would seem that the 'sulphur effect' is outweighed by a more pronounced 'nickel effect'. Whether or not nickel and vanadium concentrate in equivalent proportions in the asphaltene fraction is not known at this stage, and could be the subject of future study. In a report by Elhameed et al. [19] it is stated that the

Sample#	Ni/V crude oil	[V/V+Ni] crude oil
1	0.69	0.59
2	0.66	0.60
3	0.60	0.63
4	0.84	0.54
5	0.82	0.55
Mean ± SD	0.72 ± 14.4%	0.58 ± 6.4%
Sample#	Ni/V asphaltenes	[V/V+Ni] asphaltenes
1	1.22	0.45
2	1.24	0.45
3	1.54	0.39
4	1.24	0.45
5	1.41	0.42
6	1.58	0.39
7	1.31	0.43
Mean ± SD	1.36 ± 11.0%	0.43 ± 6.3%

Table 1: Ni/V and [V/V+Ni] ratios for digested crudes and asphaltenes. Asphaltene samples 1, 2 and 5 are derived directly from corresponding crude oil samples.

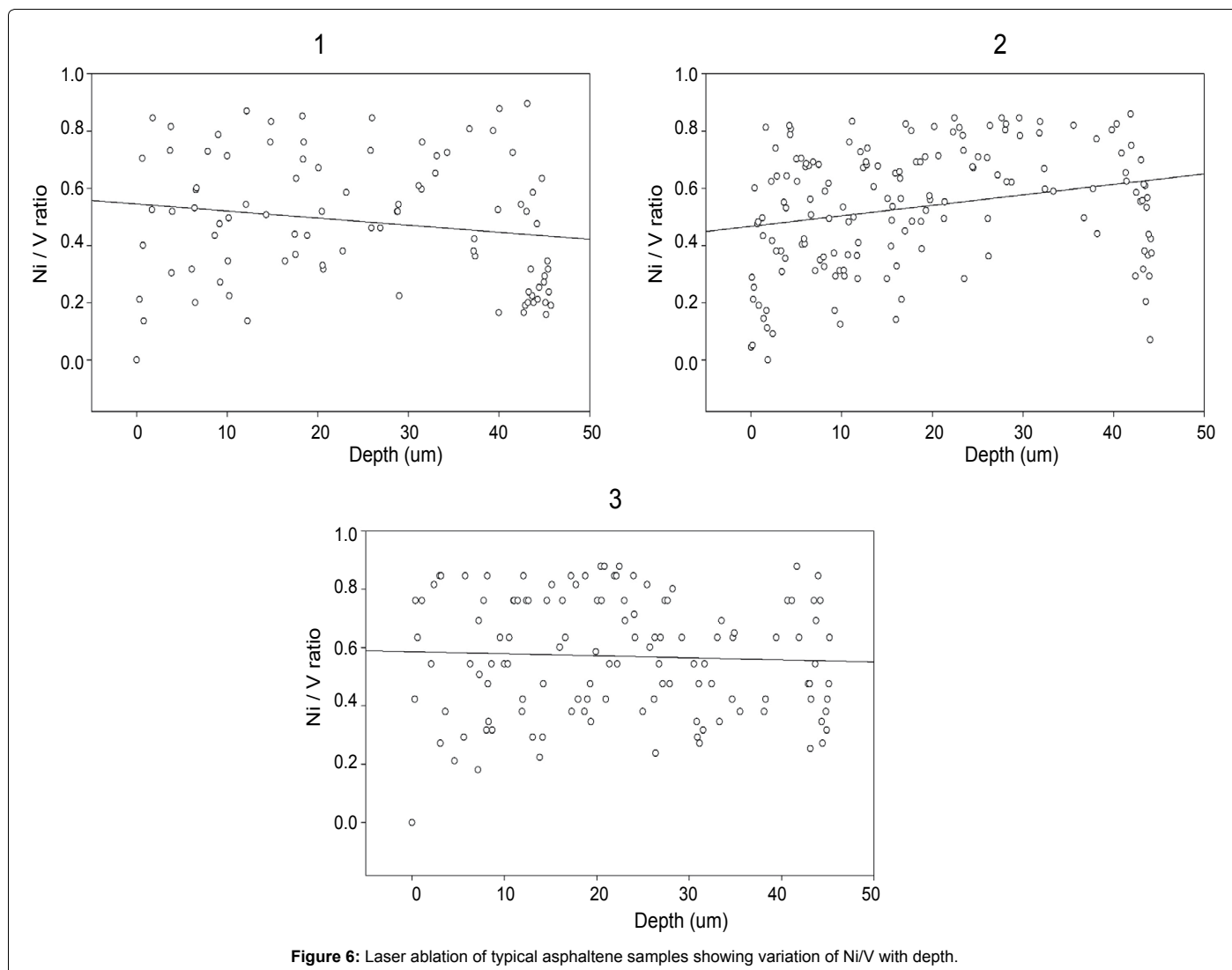


Figure 6: Laser ablation of typical asphaltene samples showing variation of Ni/V with depth.

mechanism of metal transfer from crude oil to asphaltene fraction is not at all clear, implying that certain metals could form unusually high conglomerates in the asphaltene phase (as supported by Pillay et al.) [6]. This suggests that a third factor could affect the variation in Ni/V data, namely that, the process of metal separation is disproportionate and favours some metals over others - thus nickel could concentrate to a marked extent in the asphaltene fraction.

Impact of the study

The question to ask is: How reliable are these Ni/V ratios in predicting chemical disruption in oil refining and in forecasting geoscientific correlations? It was pointed out earlier that if reinforced nickel tubing is used to case pipelines, the crude oil that flows through these conduits could be 'awash' with trace nickel, which could ultimately lead to elevated Ni/V ratios. This implies significant deviations in these parameters and necessitates regular determination of these ratios to predict the level of damage in refining processes. The suggestion by Pillay et al. [6] that asphaltenes are inherently widely inhomogeneous and contain 'hotspots' of metal inclusions [6] leads to the inference that Ni/V ratios are expected to vary widely from region to region and even within an oil-producing country - as is generally the case. Although it is known that sulphur has a direct effect on vanadium, the exact role of

sulphur and its scientific mechanism with vanadium is not clear, and could be the subject of an extended study.

According to the report by Chirinos et al. [5], the $[V/V+Ni]$ ratio is more reliable for geochemical purposes. The parameter $[V/V+Ni]=[V]/\{[V]+[Ni]\}$, which represents the concentration of vanadium divided by the sum of the concentrations of vanadium and nickel. Table 1 shows $[V/V+Ni]$ for our study for digested crude oil and asphaltenes. Clearly, from the calculated standard deviations in the table, the results are quite consistent: varying from 0.55 to 0.63 for crude oil; and from about 0.40 to 0.45 for asphaltenes. Evidently, this new ratio is more uniform and minimises the fluctuations encountered in the use of the Ni/V (or V/Ni) ratio, and tends to correct for any undesirable effects that could dramatically influence these latter ratios. It would seem that the $[V/V+Ni]$ parameter is a more stable one - also independent of API gravity of the oil - and could be considered for routine implementation. Application of the $[V/V+Ni]$ ratio to the data points in Figure 6 indicates that it varies from about 0.20 to 0.40. Thus, with laser beam technology $[V/V+Ni]$ ratios that fall within this interval could be implemented to characterise Abu Dhabi asphaltenes. The prospect of using other ratios such as As^{3+}/As^{5+} , Bi/Th or Th/U also exists - as proposed by Elhameed et al. [19-21].

Conclusion

Our research has clearly demonstrated that laser depth-profiling of Ni/V (or V/Ni) in petrified asphaltenes, after liquid nitrogen pre-treatment, is a novel approach towards determination of this parameter. Evidently, these ratios tend to vary widely, and are affected by various factors and therefore, may not be a reliable parameter for making predictions that relate to chemical refining processes or geochemical phenomena. However, the [V/V+Ni] ratio tends to be a more stable parameter and could be implemented for purposes of characterising crudes and asphaltenes. Other ratios proposed by the same authors: As³⁺/As⁵⁺, Bi/Th and Th/U could also be useful for practical applications in asphaltene studies.

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