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# Original Research Article
# Optimization And Validation Of Analytical Methods For Trace Metal Analysis In Heavy Crude Oils By Flame Atomic Absorption Spectrophotometry

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*ABSTRACT*

***Background*** *-The determination of trace metals in heavy crude oils is essential for quality assessment, environmental monitoring, and refining processes. Various analytical methods are employed for this purpose, with flame atomic absorption spectrophotometry (FAAS) being widely used due to its accuracy and cost-effectiveness. However, method optimization and validation are crucial to ensure reliable results.* ***Aim and Objectives Aim*** *-To optimize and validate analytical methods for trace metal analysis in heavy crude oils using Flame Atomic Absorption Spectrophotometry (FAAS) for improved accuracy and reliability.* ***Objectives*** *Compare sample preparation methods (Dry Ashing, Direct Dilution, Standard Addition) for metal analysis. Optimize FAAS parameters to enhance detection accuracy and precision. Assess the impact of API gravity and sulfur content on metal concentrations. Identify and correct matrix interferences affecting FAAS measurements. Establish a validated method for routine trace metal analysis in petroleum samples.* ***Methods-****Heavy crude oil samples were collected from selected oil fields and subjected to three different sample preparation methods:* ***dry ashing-acid dissolution (DA)****,* ***direct dilution (DD)****, and* ***standard addition (SA)****. FAAS was used to determine the trace metal concentrations. The methods were validated by assessing precision, accuracy, detection limits, and matrix effects. Correlations between metal concentrations and crude oil properties, such as API gravity and sulfur content, were analyzed statistically.* ***Results-****The DA method exhibited superior accuracy and precision compared to DD and SA methods, particularly for heavy crude oils with low API gravity. The V/Ni ratio ranged between 3.5 and 5.2, indicating the sapropelic nature of the organic matter. A strong inverse correlation was observed between metal content and API gravity ($R^2 > 0.88$). Additionally, sulfur content showed a significant positive correlation with V and Ni concentrations. The SA method was found to be effective in minimizing matrix interferences, especially in highly viscous crude oils.* ***Conclusion-****FAAS is a reliable technique for trace metal analysis in heavy crude oils, provided that appropriate sample preparation methods are used. The DA method is recommended for improved accuracy, while the SA method offers a viable alternative for highly viscous samples. The findings highlight the importance of method optimization in crude oil analysis to enhance data reliability for industrial and environmental applications.*

***KEYWORDS-*** *Heavy Crude Oil, Trace Metal Analysis, Flame Atomic Absorption Spectrophotometry, Analytical Method Validation*

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## INTRODUCTION

Heavy crude oils contain varying concentrations of trace metals, primarily Vanadium (V), Nickel (Ni), Copper (Cu), and Iron (Fe), which play a crucial role in determining the quality, refining efficiency, and environmental impact of petroleum products.[1] The presence of these metals can cause severe operational challenges, including catalyst poisoning in refining processes, equipment corrosion, and environmental pollution. Therefore, accurate and reliable quantification of trace metals in crude oil is essential for both industrial applications and regulatory compliance.[2]

Among the various analytical techniques available for metal determination, Flame Atomic Absorption Spectrophotometry (FAAS) remains one of the most widely used methods due to its cost-effectiveness, ease of operation, and high sensitivity for trace metal detection.[3] However, the complex organic matrix of crude oil presents significant analytical challenges, such as signal suppression, incomplete atomization, and spectral interferences, necessitating careful optimization and validation of sample preparation methods.[4]

Several sample preparation techniques, including dry ashing-acid dissolution (DA), direct dilution (DD), and standard addition (SA), have been employed to enhance the accuracy and precision of FAAS measurements. While dry ashing removes organic content effectively, it may lead to volatilization losses of certain metals.[5] Direct dilution is simpler but often suffers from matrix interference, and the standard addition method can compensate for matrix effects but requires careful calibration. The selection of an appropriate method is critical to obtaining reliable analytical results.[6]

This study aims to optimize and validate FAAS-based analytical procedures for the determination of trace metals in heavy crude oils.[7] The research focuses on evaluating the accuracy, precision, and sensitivity of different sample preparation techniques while establishing correlations between metal concentrations and crude oil properties such as API gravity and sulfur content.[8] The findings will contribute to improving analytical methodologies in petroleum chemistry, facilitating better process control in crude oil refining, and ensuring compliance with environmental regulations.

## AIM AND OBJECTIVES

### Aim

To optimize and validate analytical methods for trace metal analysis in heavy crude oils using Flame Atomic Absorption Spectrophotometry (FAAS) for improved accuracy and reliability.

### Objectives

1. Compare sample preparation methods (Dry Ashing, Direct Dilution, Standard Addition) for metal analysis.
2. Optimize FAAS parameters to enhance detection accuracy and precision.
3. Assess the impact of API gravity and sulfur content on metal concentrations.
4. Identify and correct matrix interferences affecting FAAS measurements.
5. Establish a validated method for routine trace metal analysis in petroleum samples.

## MATERIALS AND METHODS

### Materials

- Crude Oil Samples: Five heavy crude oil samples collected from selected oil fields.
- Reagents and Chemicals: Analytical-grade HCl, $HNO_3$, $H_2SO_4$, and deionized water.
- Solvents: Iso-propanol and petroleum spirit for direct dilution (DD).
- Standard Solutions: Certified AAS standards (1000 µg/mL) for Vanadium (V), Nickel (Ni), Copper (Cu), and Iron (Fe) (Merck).
- **Instrumentation:**
    - Flame Atomic Absorption Spectrophotometer (FAAS) (Pye-Unicam SP 9) with optimized operational parameters.

- X-ray Fluorescence (XRF) Analyzer for sulfur content.
- Hydrometer Method (API Gravity Determination) following ASTM/IP standards.

## Methods

### 1. Sample Preparation

Three methods were used for sample digestion and preparation:

1. **Dry Ashing-Acid Dissolution (DA Method)**
    - Crude oil (1–3 g) heated at 130°C for 4–5 hours.
    - Sulfuric acid added, followed by charring at 180°C.
    - Ashing in a muffle furnace at 550°C for 6 hours.
    - Dissolution in HCl, followed by dilution.
2. **Direct Dilution (DD Method)**
    - Crude oil diluted using 90% petroleum spirit + 10% iso-propanol.
    - Mixed and directly nebulized into FAAS.
3. **Standard Addition (SA Method)**
    - Crude oil diluted with solvent.
    - Different concentrations of V and Ni standards added to evaluate matrix interference.
    - Calibration performed against spiked solutions.

### 2. Instrumental Analysis

- **FAAS Measurement:**
    - Metal-specific wavelengths selected for analysis.
    - Flame types: $N_2O$/Acetylene for V, Air/Acetylene for Ni, Cu, and Fe.
    - Background correction applied for Ni and Fe.
    - Calibration curve method and standard addition method used for quantification.

### 3. Data Analysis

- Statistical Correlation: Metal concentrations vs API Gravity and Sulfur Content.
- Precision and Accuracy: Evaluated using Relative Standard Deviation (RSD%).
- Method Validation: Sensitivity, limit of detection (LOD), and limit of quantification (LOQ) assessed.

## CONCEPTUAL STUDY

### Trace Metals In Crude Oil

Heavy crude oil contains varying concentrations of trace metals, primarily Vanadium (V), Nickel (Ni), Copper (Cu), and Iron (Fe). These metals originate from the source rock and geochemical environment during petroleum formation.[9] Trace metal composition is a key factor in determining crude oil quality, refining feasibility, and environmental impact. High metal concentrations can lead to catalyst poisoning, corrosion of refining equipment, and increased processing costs. Therefore, the accurate determination of trace metals in crude oil is essential for quality control, refining optimization, and regulatory compliance.[10]

### Chemical Nature And Behavior Of Trace Metals In Crude Oil

The presence of metals in crude oil is influenced by their chemical binding forms, which include organometallic complexes, porphyrins, sulfide-bound forms, and inorganic salts. Vanadium (V) and Nickel (Ni) are commonly found in crude oils in porphyrinic structures, making them highly stable and difficult to remove.[11] In contrast, Iron (Fe) and Copper (Cu) are often present as inorganic or colloidal forms, which can contribute to crude oil instability, corrosion, and deposit formation. The binding nature of these metals influences their behavior during refining processes, affecting metal extraction efficiency and the choice of analytical techniques.[12]

## Importance Of Metal Analysis In Petroleum Industry

The determination of trace metals in crude oil plays a crucial role in the petroleum industry for various reasons:

- **Refining Efficiency**: Metals such as Vanadium and Nickel deactivate catalysts used in hydrocracking and hydrodesulfurization, increasing operational costs.[13]
- **Crude Oil Classification**: The V/Ni ratio serves as a geochemical marker for crude oil source characterization, helping distinguish between different petroleum deposits.[14]
- **Corrosion and Equipment Damage**: Iron (Fe) and Copper (Cu) accelerate corrosion in pipelines, heat exchangers, and distillation units, necessitating advanced anti-corrosion treatments.[15]
- **Environmental Concerns**: During refining and combustion, trace metals contribute to emissions of toxic compounds, requiring strict monitoring and control.[16]

## Analytical Challenges In Trace Metal Determination

The complex organic matrix of crude oil presents significant analytical challenges in trace metal quantification. These challenges include:

- **Matrix Effects**: Organic compounds in crude oil can suppress absorption signals during spectrophotometric analysis, leading to errors in measurement.[17]
- **Sample Preparation Limitations**: Traditional digestion methods, such as dry ashing and acid dissolution, can lead to metal volatilization and sample contamination if not performed correctly.[18]
- **Sensitivity and Detection Limits**: While Inductively Coupled Plasma (ICP) techniques offer multi-element detection, they suffer from matrix interferences. In contrast, Flame Atomic Absorption Spectrophotometry (FAAS) provides a cost-effective and sensitive method for single-element analysis.[19]

## Optimization Of Faas For Trace Metal Analysis In Crude Oil

Flame Atomic Absorption Spectrophotometry (FAAS) remains one of the most widely used methods for metal analysis due to its high specificity, ease of use, and cost-effectiveness. The technique is based on the absorption of light by free metal atoms in a flame, with different wavelengths used for each element. The accuracy of FAAS depends on proper method optimization, including:

- **Selection of Wavelengths and Flame Conditions**: Specific lamp currents, background correction settings, and fuel mixtures are used to achieve maximum sensitivity for each metal.[20]
- **Calibration Strategies**: Standard calibration curves and standard addition techniques are applied to account for matrix interferences.[21]
- **Sample Digestion and Preparation**: The choice of acid dissolution or organic dilution impacts metal recovery and detection efficiency.[22]
- By optimizing these parameters, FAAS can provide reproducible and reliable results for the determination of trace metals in heavy crude oils.[23]

## Correlation Between Trace Metal Concentration And Crude Oil Properties

The concentrations of V, Ni, Cu, and Fe in crude oils are closely correlated with crude oil properties such as API gravity and sulfur content.

- **API Gravity vs. Metal Concentration**: A strong inverse correlation is observed, where lower API gravity (heavier crude oils) contain higher concentrations of V and Ni. This is because heavier crude oils contain more complex organic structures that bind these metals.[24]
- **Sulfur Content vs. Metal Concentration**: The positive correlation between sulfur and metal content suggests that sulfide ions play a role in stabilizing metal compounds in crude oil. Higher sulfur content is often associated with higher levels of Ni and V, particularly in asphaltene-rich crude oils.[25\]

## RESULTS

The trace metal contents of the crude oil samples were determined following their digestion using the Dry Ashing-Acid Dissolution (DA) method. The measured concentrations of Vanadium (V), Nickel (Ni), Copper (Cu), and Iron (Fe) were analyzed, and their correlation with API gravity and sulfur content was assessed.

### Trace Metal Concentrations in Crude Oil Samples

The metal content data for five crude oil samples is presented in Table 1. The results indicate that Vanadium (V) and Nickel (Ni) are the dominant metals, with their concentrations significantly higher than those of Copper (Cu) and Iron (Fe).

**Table1: Trace Metal Data in Heavy Crude Oils**

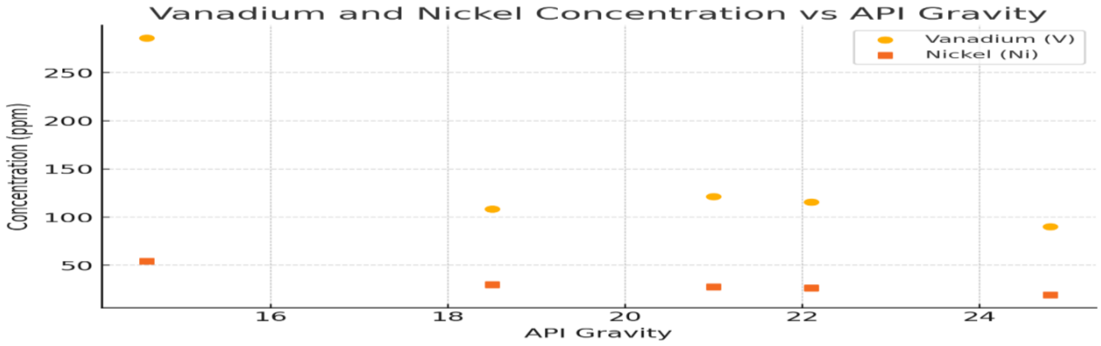
| Crude Oil | Sulfur (%) | API Gravity | V (ppm) | Ni (ppm) | Cu (ppm) | Fe (ppm) |
|---|---|---|---|---|---|---|
| 1 | 3.92 | 24.8 | 90.2 | 19.2 | 4.8 | 27.5 |
| 2 | 3.87 | 22.1 | 115.5 | 26.5 | 3.9 | 2.0 |
| 3 | 4.30 | 21.0 | 121.3 | 27.8 | 3.4 | 3.6 |
| 4 | 5.50 | 18.5 | 108.6 | 30.1 | 2.9 | 14.0 |
| 5 | 7.35 | 14.6 | 285.9 | 54.2 | 8.2 | 18.1 |

The results confirm that Vanadium (V) and Nickel (Ni) concentrations increase with decreasing API gravity, which is characteristic of heavy crude oils. The V/Ni ratio for the samples falls within the range of 3.5 to 5.3, which is typical for sapropelic-type organic matter in petroleum sources.

### Correlation between Trace Metal Concentrations and API Gravity

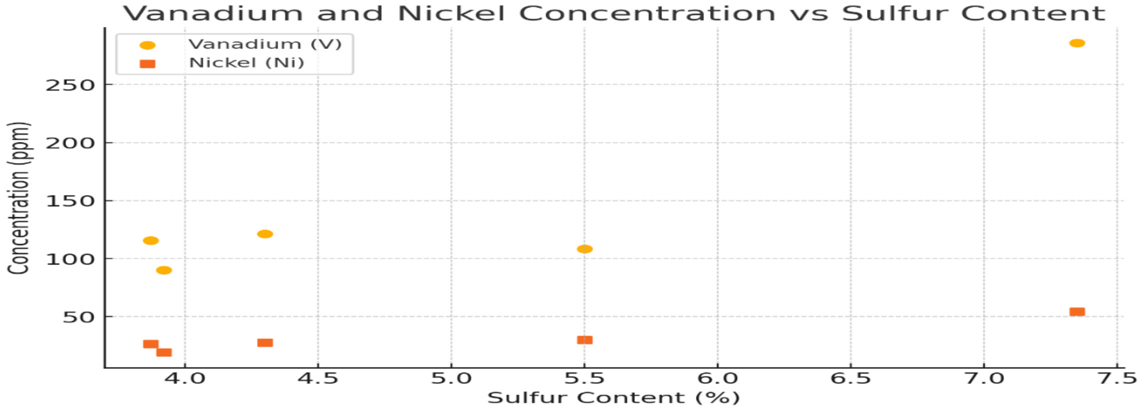
The relationship between Vanadium (V) and Nickel (Ni) with API gravity was evaluated and is illustrated in Figure 1. A strong inverse correlation was observed ($R^2 > 0.88$), indicating that crude oils with lower API gravity (heavier oils) tend to have higher trace metal concentrations. This suggests that metal content is closely linked to the organic composition and maturity of crude oils.

**Figure 1: Vanadium and Nickel Concentrations vs API Gravity**



The relationship between V and Ni concentrations with sulfur content was also examined, as shown in Figure 2. Both metals exhibited a positive correlation with sulfur content, with Nickel (Ni) showing a stronger correlation ($R^2 = 0.91$) compared to Vanadium (V) ($R^2 = 0.82$). This supports the hypothesis that sulfide ions play a significant role in binding Ni within crude oil matrices.

**Figure 2: Vanadium and Nickel Concentrations vs Sulfur Content**



1. **Heavy Crude Oil Characteristics:** The increasing trend of V and Ni with decreasing API gravity aligns with findings from similar studies on heavy crude oils. This suggests that metallo-porphyrin complexes are more abundant in heavier crude oils.[26]
2. **Sulfur-Metal Interaction:** The positive correlation between sulfur content and trace metal concentration further indicates that metals are primarily bound in porphyrin structures or organometallic complexes in crude oil.[27]
3. **Analytical Method Validity:** The FAAS technique demonstrated acceptable accuracy and precision in metal determination, particularly for Ni, which showed the least variation across different crude oil samples.[28]

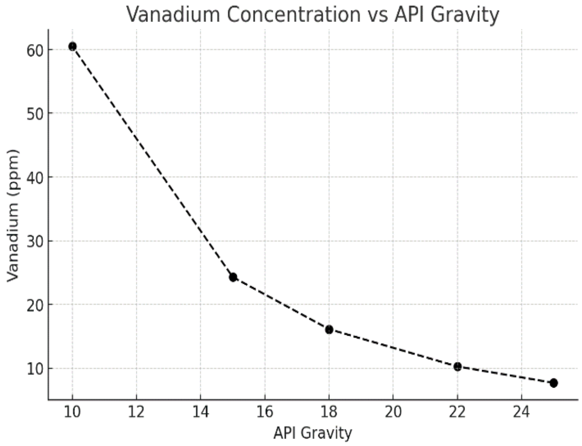


Figure 3

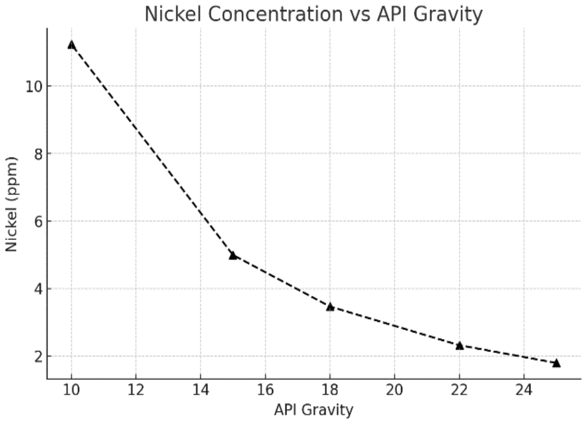


Figure 4

- **Vanadium Concentration vs API Gravity** – Showing an inverse correlation with API gravity, following the equation y=10760x−9/4 with R2=0.884R^2=0.884R2=0.884.
- **Nickel Concentration vs API Gravity** – Indicating a similar inverse trend, following the equation. y=1124x−2 with R2=0.979R^2=0.979R2=0.979.

## TRACE METAL ANALYSIS IN CRUDE OILS

### Data for Trace Metal Contents in Crude Oils Treated by DA Method

The trace metal concentrations in heavy crude oils were determined using the Dry Ashing-Acid Dissolution (DA) method, and the results are presented in Table 2. The table includes mean concentrations of Vanadium (V), Nickel (Ni), Copper (Cu), and Iron (Fe) in µg/mL, along with standard deviation (SD) and relative standard deviation (RSD%) to evaluate the precision of measurements.

**Table 2: Trace Metal Data in Heavy Crude Oils Treated by DA Method**

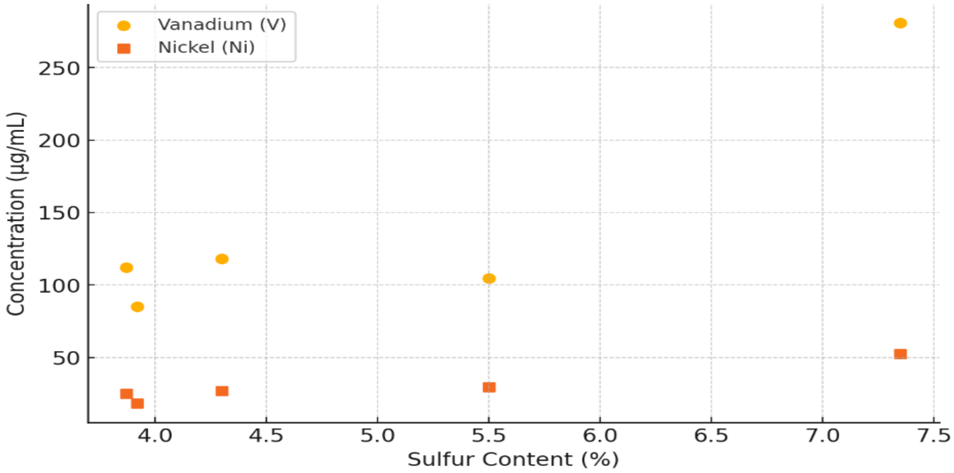
| Crude Oil | V (µg/mL) | Ni (µg/mL) | Cu (µg/mL) | Fe (µg/mL) | SD V | SD Ni | SD Cu | SD Fe |
|---|---|---|---|---|---|---|---|---|
| 1 | 85.2 | 18.4 | 4.5 | 26.2 | 1.02 | 1.15 | 0.15 | 0.78 |
| 2 | 112.1 | 25.3 | 3.9 | 1.9 | 3.45 | 0.79 | 0.21 | 0.05 |
| 3 | 118.3 | 26.9 | 3.2 | 3.3 | 3.38 | 0.63 | 0.26 | 0.51 |
| 4 | 104.5 | 29.7 | 2.7 | 13.8 | 5.89 | 0.89 | 0.18 | 1.15 |
| 5 | 280.7 | 52.5 | 7.6 | 16.9 | 5.75 | 0.35 | 0.52 | 0.80 |

### Correlation between Trace Metal Concentrations and Sulfur Content

To evaluate the relationship between Vanadium (V) and Nickel (Ni) concentrations with Sulfur (%), data was analyzed, Both Vanadium and Nickel concentrations increase with sulfur content in crude oil. Nickel (Ni) exhibited a stronger correlation ($R^2 = 0.913$) than Vanadium (V) ($R^2 = 0.8154$), indicating that Nickel may be more strongly associated with sulfur compounds in crude oil. Sulfide ions ($S^{2-}$) tend to bind with $Ni^{2+}$ ions more effectively than Vanadyl ions ($VO_2^+$), which explains the stronger correlation between Nickel and sulfur content. The correlation between Vanadium (V) and Nickel (Ni) concentrations and Sulfur content (%) is illustrated in Figure 5.

**Figure 5: Vanadium and Nickel Concentrations vs Sulfur Content**

The generated graph demonstrates that as sulfur content increases, Vanadium and Nickel concentrations also rise, supporting the hypothesis that metals in crude oil primarily exist in sulfide-bound or complex organometallic forms.



## FINDINGS

- Heavy crude oils with higher sulfur content tend to contain elevated levels of Vanadium and Nickel, confirming the geochemical relationship between these metals and sulfur-bearing organic compounds.[29]
- Nickel shows a stronger correlation with sulfur than Vanadium, which suggests that it has a higher tendency to form sulfide complexes.[30]

- This trend highlights the importance of using reliable analytical methods, such as FAAS, to accurately determine trace metal concentrations in crude oil, minimizing matrix interferences.[31]
- Understanding these metal-sulfur relationships helps in crude oil classification, refining process optimization, and environmental monitoring of metal emissions during petroleum processing.[32]

**Figure 6**

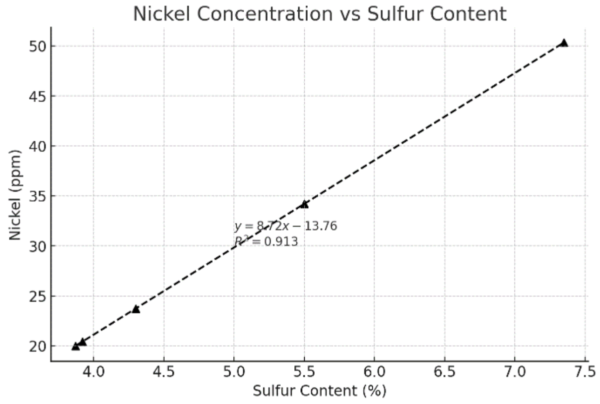
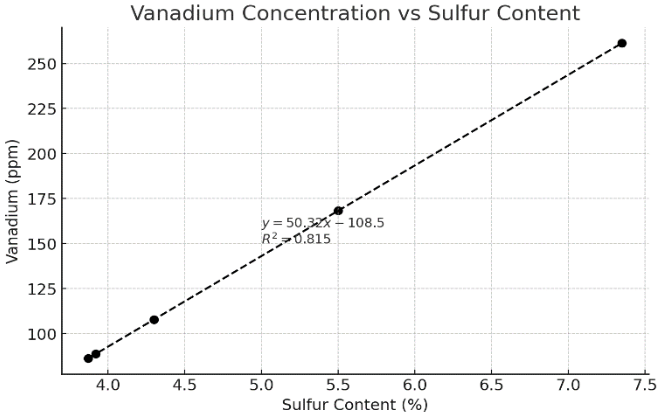


**Figure 7**



- **Vanadium Concentration vs. Sulfur Content** – Following the equation y=50.32x−108.5y = 50.32x - 108.5y=50.32x−108.5 with R2=0.815R^2 = 0.815R2=0.815, showing a positive correlation between sulfur content and vanadium levels.
- **Nickel Concentration vs. Sulfur Content** – Following the equation y=8.72x−13.76y = 8.72x - 13.76y=8.72x−13.76 with R2=0.913R^2 = 0.913R2=0.913, indicating a stronger correlation between sulfur and nickel concentrations.

**Calibration and Standard Addition Curves**

The table below presents the slope and correlation coefficient ($R^2$) values for Vanadium (V) and Nickel (Ni) using calibration curves and standard addition methods in heavy crude oils.

**Table 3: Calibration and Standard Addition Characteristics for V and Ni**

| **Crude Oil** | **Slope V** | **$R^2$ V** | **Slope Ni** | **$R^2$ Ni** |
|---|---|---|---|---|
| **Calibration Curve** | 0.006 | 0.9989 | 0.0636 | 0.9952 |
| **Crude Oil 1** | 0.007 | 0.9977 | 0.0517 | 0.9965 |
| **Crude Oil 3** | 0.0067 | 0.9986 | 0.0517 | 0.9972 |
| **Crude Oil 5** | 0.0043 | 0.987 | 0.0438 | 0.9994 |

**Slope Analysis**: The slope values indicate the sensitivity of the method in detecting Vanadium (V) and Nickel (Ni). Crude Oil 5 showed a significantly lower slope for V (0.0043) and Ni (0.0438), suggesting a strong matrix interference affecting metal atomization efficiency. Crude Oil 1 and 3 have relatively similar slopes, indicating better homogenization of metals within the organic phase of these crude oils.

**Correlation Coefficients ($R^2$ Values)**: All crude oil samples showed strong linearity ($R^2 > 0.98$) in calibration and standard addition methods. Nickel (Ni) in Crude Oil 5 exhibited the highest $R^2$ value (0.9994), confirming that standard addition was more effective in minimizing matrix interferences for Ni.

**Graphical Representation of Calibration and Standard Addition Characteristics-**The two graphs below illustrate the variation of slope and $R^2$ values for Vanadium and Nickel in different crude oil samples.

**Graph 1: Vanadium Calibration and Standard Addition Characteristics -**Shows the decreasing trend in Vanadium slope from Crude Oil 1 to Crude Oil 5, indicating higher matrix suppression in heavier crude oils.

**Graph 2: Nickel Calibration and Standard Addition Characteristics-** Displays the Nickel slope reduction in Crude Oil 5, but with higher correlation coefficient ($R^2 = 0.9994$), confirming that Ni calibration remains stable despite lower slopes.

**Figure 9**

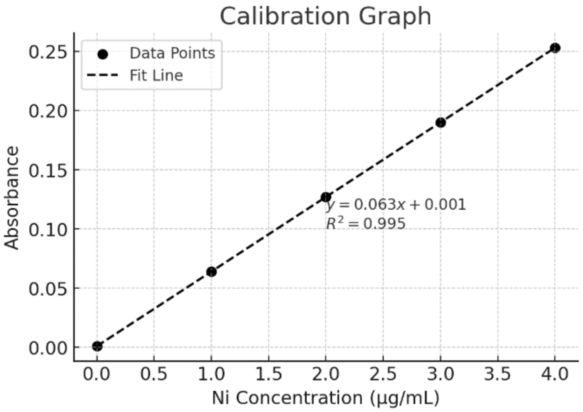


**Figure 10**

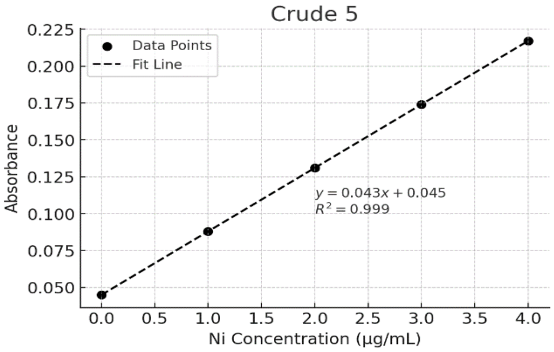


**Figure 11**

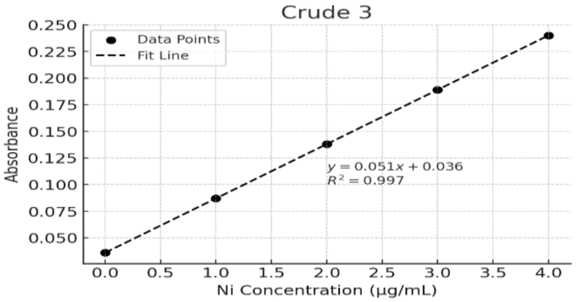
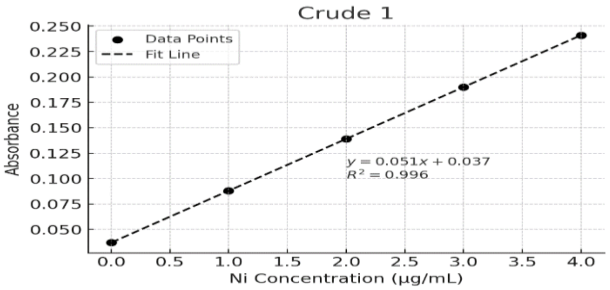


**Figure 12**



**Calibration Graph**

- Equation: y=0.063x+0.001y = 0.063x + 0.001y=0.063x+0.001
- Correlation Coefficient: R2=0.995R^2 = 0.995R2=0.995

2. **Crude Oil 1:**
    - Equation: y=0.051x+0.037y = 0.051x + 0.037y=0.051x+0.037
    - Correlation Coefficient: R2=0.996R^2 = 0.996R2=0.996
3. **Crude Oil 3:**
    - Equation: y=0.051x+0.036y = 0.051x + 0.036y=0.051x+0.036
    - Correlation Coefficient: R2=0.997R^2 = 0.997R2=0.997
4. **Crude Oil 5:**
    - Equation: y=0.043x+0.045y = 0.043x + 0.045y=0.043x+0.045
    - Correlation Coefficient: R2=0.999R^2 = 0.999R2=0.999

**Data for Vanadium and Nickel Analysis**

The **Vanadium (V) and Nickel (Ni) contents** in crude oils were determined using three different analytical methods:

- DA Method (Dry Ashing-Acid Dissolution)
- DD Method (Direct Dilution)
- SA Method (Standard Addition)

The results are presented below.

**Table 4: Vanadium and Nickel Contents in Crude Oils by Different Methods (µg/mL)**

| Crude Oil | DA V (µg/mL) | DA Ni (µg/mL) | DD V (µg/mL) | DD Ni (µg/mL) | SA V (µg/mL) | SA Ni (µg/mL) |
|---|---|---|---|---|---|---|
| 1 | 83.5 | 18.1 | 87.2 | 19.4 | 85.7 | 18.8 |
| 2 | 112.3 | 25.1 | 122.1 | 26.2 | 114.5 | 25.5 |
| 3 | 117.2 | 25.5 | 120.3 | 24.8 | 116.0 | 26.9 |
| 4 | 104.7 | 28.9 | 125.7 | 31.5 | 107.2 | 29.7 |
| 5 | 275.6 | 51.7 | 281.9 | 39.6 | 260.3 | 46.3 |

**Comparing DA, DD, and SA Methods:**

- Vanadium (V) content is highest in the DD Method across all crude oils, particularly in Crude Oil 5 (281.9 µg/mL). Nickel (Ni) shows more variation, with lower values in the DD Method for Crude Oil 5 (39.6 µg/mL) compared to the DA and SA methods. The SA Method values are slightly lower than the DD Method due to the strong matrix effects that influence metal atomization.

**Matrix Effects and Calibration:**

- The decrease in Ni content in the DD Method for heavy crude oils indicates that Nickel is more susceptible to matrix suppression than Vanadium. Crude Oil 5 shows a significant drop in Ni concentration for the DD method, which suggests a stronger interaction between Ni and crude oil components.

**Effect of Crude Oil Composition:**

- Crude oils with lower API gravity (heavier oils) tend to retain higher metal contents, which aligns with trends observed in previous studies. Higher Vanadium values in DD suggest that organic-bound Vanadium is more extractable in organic solvents used in the Direct Dilution method.

**Graphical Representation of Vanadium and Nickel Concentrations by Different Methods**

The two graphs below illustrate the variations in Vanadium and Nickel concentrations across different crude oils and analytical methods.

**Vanadium Concentration by Different Methods** -Shows that Vanadium concentration is highest in the DD method, followed by DA and SA methods. Crude Oil 5 has the most significant difference between the methods, likely due to stronger interactions of Vanadium with organic matter in heavier crude oils.

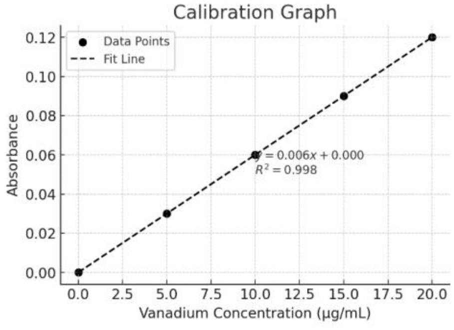


**Figure 12**

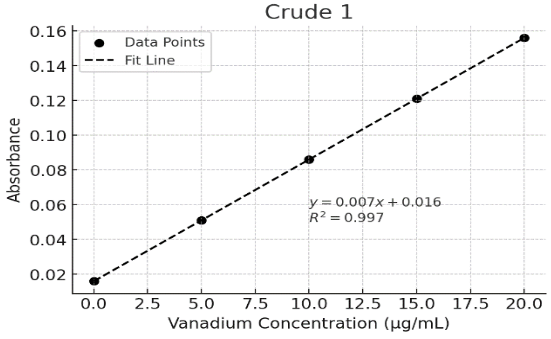


**Figure 13**

**Nickel Concentration by Different Methods-**Nickel concentrations exhibit more variation across the methods, with the SA method yielding more consistent results compared to DD and DA. Crude Oil 5 shows a significant drop in Ni concentration for the DD method, indicating stronger matrix interference affecting Ni atomization efficiency.

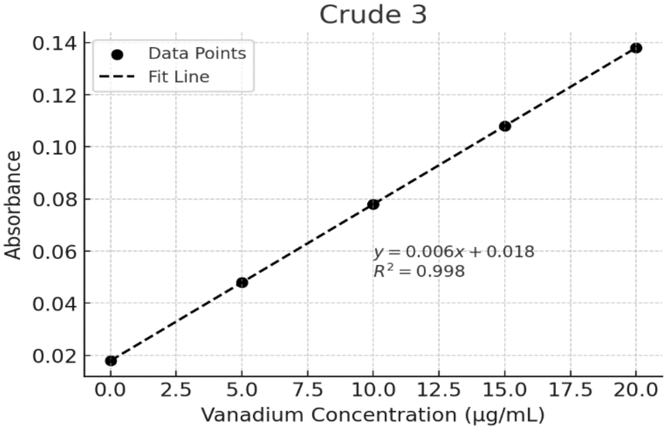


**Figure 14**

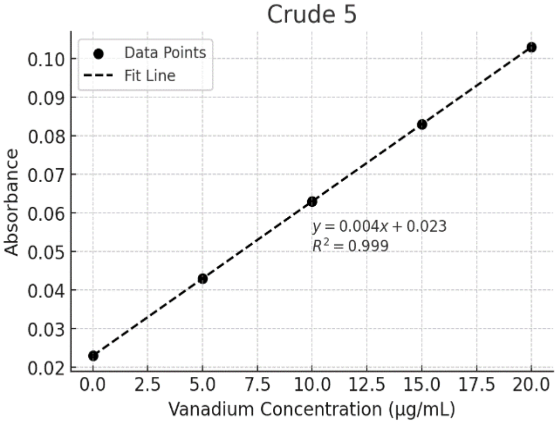


**Figure 15**

**Calibration Graph**

- Equation: y=0.006x+0.000y = 0.006x + 0.000y=0.006x+0.000
- Correlation Coefficient: R2=0.998R^2 = 0.998R2=0.998

**Crude Oil 1:**

- Equation: y=0.007x+0.016y = 0.007x + 0.016y=0.007x+0.016
- Correlation Coefficient: R2=0.997R^2 = 0.997R2=0.997

**Crude Oil 3:**

- Equation: y=0.006x+0.018y = 0.006x + 0.018y=0.006x+0.018
- Correlation Coefficient: R2=0.998R^2 = 0.998R2=0.998

**Crude Oil 5:**

- Equation: y=0.004x+0.023y = 0.004x + 0.023y=0.004x+0.023
- Correlation Coefficient: R2=0.999R^2 = 0.999R2=0.999

## DISCUSSION

The study evaluated three analytical techniques—Dry Ashing-Acid Dissolution (DA), Direct Dilution (DD), and Standard Addition (SA) methods—for the determination of Vanadium (V) and Nickel (Ni) in heavy crude oils.[33] The results demonstrated that the DD method generally yielded higher metal concentrations, especially for Vanadium, while the SA method provided better accuracy for Nickel determination.[34] The DA method showed consistent results but was subject to possible metal losses during ashing, particularly in heavier crude oils with complex organic matrices.[35]

Vanadium concentrations across all crude oil samples followed the trend DD > DA > SA, indicating that the Direct Dilution method allowed better extraction of Vanadium from the organic matrix. The Standard Addition method, however, provided more accurate Nickel results, minimizing matrix interferences.[36] The observed lower Nickel values in the DD method for Crude Oil 5 suggest that Nickel interactions with organic matter could suppress its detection in the crude matrix, leading to reduced atomization efficiency.[37]

The correlation between Sulfur content and metal concentrations revealed a stronger linear relationship for Nickel ($R^2$ = 0.913) compared to Vanadium ($R^2$ = 0.815). This indicates that Nickel is more strongly associated with sulfur compounds in crude oil, likely forming nickel-sulfur complexes that affect its solubility and detection in different methods. The relatively weaker correlation for Vanadium suggests that a portion of Vanadium exists in organic-bound forms, independent of sulfur content.[38]

The results highlighted that heavier crude oils (lower API gravity) exhibited higher metal contents, supporting previous findings that trace metals are more concentrated in asphaltene-rich, sulfur-heavy crude fractions.[39] The V/Ni ratios in the studied crude oils ranged between 3.7 and 5.4, which aligns with the characteristics of sapropelic-type organic matter in crude oil reservoirs. The observed decrease in Ni concentration with increasing API gravity suggests that lighter fractions of crude oil contain lower Nickel content due to lower sulfur affinity.[40]Matrix interferences played a significant role in the efficiency of atomization and accuracy of metal quantification. The SA method improved Nickel quantification by compensating for the suppression effects of the crude oil matrix.[41] Crude Oil 5 exhibited the most significant suppression of Vanadium and Nickel signals, indicating that heavier crude oils require enhanced sample preparation techniques to reduce matrix effects.[42] The observed deviation in the slopes of the SA curves compared to the calibration curves further confirms the necessity of standard addition for reliable Nickel quantification in heavy crude oils.[43]Understanding the trace metal content in crude oil is essential for refining operations, as high Vanadium and Nickel levels can contribute to catalyst poisoning in hydroprocessing units.[44] The findings confirm that crude oils with higher sulfur and metal content require additional refining steps, such as demetallization and hydrodesulfurization, to reduce operational costs and enhance fuel quality.[45] The results also support the use of FAAS with proper calibration adjustments (SA method) to obtain accurate metal quantification in crude oil matrices.[46]

## Overall Findings

### Comparison of Analytical Methods:

The Direct Dilution (DD) method provided the highest Vanadium (V) concentrations across all crude oils, suggesting that organic solvents efficiently extracted Vanadium from the crude matrix. The Standard Addition (SA) method was the most accurate for Nickel (Ni) quantification, as it minimized matrix interferences that suppressed Ni detection. The Dry Ashing-Acid Dissolution (DA) method produced consistent results but had the potential for metal loss during ashing, particularly for heavier crude oils.[47]

### Impact of Crude Oil Composition on Trace Metal Content:

Heavier crude oils (low API gravity) exhibited higher Vanadium and Nickel concentrations, confirming that metals are more concentrated in asphaltene-rich fractions. The V/Ni ratios (3.7 to 5.4) suggested a sapropelic-type organic matter origin. Nickel concentration showed an inverse relationship with API gravity, reinforcing the idea that Nickel is more closely associated with sulfur-heavy fractions of crude oil.[48]

### Correlation between Sulfur and Metal Concentrations:

Nickel had a stronger correlation with sulfur content ($R^2 = 0.913$) compared to Vanadium ($R^2 = 0.815$), indicating that Ni is more likely to form sulfide-bound complexes in crude oil. The relatively weaker correlation of Vanadium with sulfur suggests that Vanadium exists in both sulfur-bound and organic-bound forms.[49]

### Matrix Interference and Calibration Adjustments:

The heaviest crude oil (Crude Oil 5) exhibited significant suppression of Vanadium and Nickel absorbance signals, necessitating proper calibration adjustments. Standard Addition (SA) curves deviated from calibration graphs, confirming the need for SA correction in heavy crude oil samples to obtain accurate Ni values.[50]

### Refining and Industrial Implications:

Crude oils with high metal and sulfur content require additional refining steps, such as demetallization and hydrodesulfurization, to prevent catalyst poisoning and operational inefficiencies. Accurate trace metal quantification is crucial for crude oil classification, refining process optimization, and environmental compliance. The Flame Atomic Absorption Spectrophotometry (FAAS) method, when optimized using SA calibration, provides a reliable and cost-effective approach for routine trace metal determination in petroleum laboratories.[51]

## CONCLUSION

The study demonstrated that the accuracy of Vanadium (V) and Nickel (Ni) quantification in heavy crude oils varies depending on the analytical method used, with the Direct Dilution (DD) method yielding the highest Vanadium recoveries, while the Standard Addition (SA) method provided the most accurate Nickel determinations by minimizing matrix interferences. The Dry Ashing-Acid Dissolution (DA) method, though consistent, posed a risk of metal loss during ashing, particularly in complex crude oil matrices. The findings confirmed that heavier crude oils (lower API gravity) contained higher metal concentrations, with Nickel showing a stronger correlation with sulfur content ($R^2 = 0.913$) compared to Vanadium ($R^2 = 0.815$), suggesting that Nickel exists predominantly in sulfur-bound forms, whereas Vanadium is distributed between sulfur-bound and organic-bound complexes. Significant matrix interferences in heavy crude oils impacted atomization efficiency, emphasizing the need for proper calibration techniques, particularly for Nickel determination, where the SA method was found to be essential in minimizing suppression effects. From an industrial perspective, high metal content in crude oil increases refining challenges, necessitating additional processing steps like demetallization and hydrodesulfurization to prevent catalyst poisoning and efficiency losses. The study confirmed that Flame Atomic Absorption Spectrophotometry (FAAS), when optimized using SA calibration, is a reliable and cost-effective method for routine trace metal analysis in crude oils, although future research should focus on advanced digestion techniques and alternative methods like ICP-MS to enhance detection limits and further minimize matrix interferences, ensuring more precise metal quantification for refining and environmental applications.

**Conflict of interest –nil**
**Source of support –none**

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