**Author**

**Stan Smith**

**PerkinElmer, Inc.**
**Shelton, CT 06484 USA**

# Analysis of Vanadium, Nickel, Sodium, and Iron in Fuel Oils using Flame Atomic Absorption Spectrophotometry

## Introduction

Elemental analysis of fuel oil is an important step in quantifying its quality. Combustion of fuels containing metals can lead to the formation of low melting-point compounds that are corrosive to metal parts. The presence of certain metals, even at trace levels, can deactivate or foul catalysts used during the processing of the oil. ASTM® International publishes numerous test methods for the analysis of petroleum products, including fuel oils. ASTM® D5863-00a (2005), "Standard Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry", is an industry-standard method for the analysis of fuel oils. Due to its multi-element capabilities, inductively coupled plasma optical emission spectroscopy (ICP-OES) may be the preferred technique for petroleum analyses requiring many elements, however, flame atomic absorption spectrophotometry (FAAS) methods are still quite effective and rapid for smaller numbers of elements such as those required for fuel oil analyses. In addition, flame AA instrumentation is significantly more compact than ICP-OES instruments, costs a fraction of the price, and requires less operator training.

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## Experimental Conditions

### Instrumentation

The analysis of a National Institute for Standards and Technology® (NIST®) Standard Reference Material (SRM) fuel oil was performed using a PerkinElmer® PinAAcle™ 900T spectrometer (Figure 1) operated in the flame mode. A stainless steel nebulizer (Part Nos. Nebulizer: N3160143; End Cap: N3160102) was used along with a solvent-resistant Kalrez® o-ring (Part No. N9300065) in the burner chamber and a solvent-resistant drain assembly. Hollow cathode lamps (Part Nos. V: N3050186, Ni: N3050152, Na: N3050148, Fe: N3050126) were used for all analyses and an air-acetylene flame was used for all elements except vanadium which was analyzed with a nitrous oxide-acetylene flame (Burner Head Part No. N0400100). Optimized parameters for each element are listed in Table 1.



*Figure 1.* PerkinElmer PinAAcle 900T and quick change burner assembly with stainless steel nebulizer and air-acetylene burner head.

Default recommended conditions found in the WinLab32™ for AA software were used for most parameters (Table 1). When analyzing high BTU organic solvents, however, the sample flow rate must be reduced as typical hydrocarbon solvents will flow faster than aqueous samples and hydro-carbon solvents are themselves fuel for the flame. The sample rate of 2.25 mL/min for the kerosene solvent (approximately 3 times lower than the typical 7 mL/min for aqueous samples) generated a lean blue flame and met the sensitivity checks for each element. For vanadium, which used a nitrous oxide-acetylene flame, the acetylene flow rate was adjusted to a slightly lower flow rate (6.0 L/min) from the default value (7.5 L/min) to provide a more stable flame.

*Table 1.* **Optimized experimental conditions for the analysis of metals in fuel oil using the PinAAcle 900T spectrometer.**

| Analtye | Vanadium | Nickel | Sodium | Iron |
|---|---|---|---|---|
| Wavelength (nm) | 318.40 | 232.00 | 589.00 | 248.33 |
| Slit Width (nm) | 0.7 | 0.2 | 0.2 | 0.2 |
| Read Time (sec) | 3.0 | 3.0 | 3.0 | 3.0 |
| Oxidant | Nitrous Oxide | Air | Air | Air |
| Oxidant Flow (L/min) | 6.0 | 10.0 | 10.0 | 10.0 |
| Acetylene Flow (L/min) | 6.7 | 2.5 | 2.5 | 2.5 |
| Sample Uptake Rate (mL/min) | 2.25 | 2.25 | 2.25 | 2.25 |

### Standard and Sample Preparation

Per Test Method B of ASTM® D5863, the sample and standards were prepared by solvent dilution. The solvent used was V-SOLV™ from VHG Labs (Part No. N9308265), a refined kerosene-like solvent. This method recommends the preparation of the oil in solvent at either a 5% ratio or a 20% ratio, depending on the actual concentration of the elements. In this experiment, both ratios were run to encompass the range of concentrations in the NIST® SRM and to determine if there would be any bias between the two oil ratios.

Calibration standards were Multi-Element Metallo-Organic Standards (VHG labs) in 75 centistoke (cSt) hydrocarbon base oil. Three V23 standards at: 10 µg/g (Part No. N0776109), 50 µg/g (Part No. N0776104) and 500 µg/g (Part No. N0776106); along with a V21 standard at 100 µg/g (Part No. N9308306) were used. The standards contained 23 and 21 elements, respectively, including nickel (Ni), vanadium (V), sodium (Na), and iron (Fe). The blank was comprised of the 75 cSt hydrocarbon base oil (Part No. N0776103) diluted in solvent. Each of the three calibration stock standards (10, 50, and 500 µg/g) were diluted in V-SOLV™ to create calibration standards at 0.5, 2.5, and 10 mg/kg in both 5% and 20% total oil. The blank base oil was used to make up the difference, if necessary, between the calibration stock standard and the needed 5% or 20% oil. This calibration range was sufficient to address the observed concentration range of the fuel oil sample. The 100 µg/g standard was diluted in V-SOLV™ to produce a secondary source quality control (QC) sample at 5 mg/kg in both 5% and 20% total oil.

The fuel oil analyzed was NIST® Standard Reference Material 1634c Trace Elements in Fuel Oil. The NIST® SRM included certified values for V and Ni and a noncertified value for Na. As no value was provided for Fe, a 3.62 mg/kg Fe matrix spike was prepared from a 5000 µg/g stock organometallic standard (VHG labs) for the NIST® sample.

In the analysis of aqueous samples for sodium and vanadium, it is common to add 0.1% alkali salt such as KCl or LiCl to all standards and samples to act as an ionization suppressant. The high concentration of salt helps to control the ionization effects in the flame and prevent bias in the results. ASTM® D5863 does not call for the addition of an alkali salt, but a third set of calibration samples and NIST® SRM were prepared at 20% oil as stated above, but with the addition of 250 mg/kg of Li (5000 µg/g, Conostan S21 Organometallic Standard in Hydrocarbon Base Oil) to determine if vanadium results would improve with the presence of an ionization suppressant. It is difficult to spike significantly higher than this without affecting the total oil percentage due to the concentration of the stock organometallic standards.

The instrument was optimized for the four elements prior to analysis and the conditions are provided in Table 1. The analytical sequence for each of the four elements was to calibrate the instrument, analyze the blank and 5 mg/kg QC sample, analyze the NIST® SRM and matrix spike where applicable, and re-analyze the blank and QC sample.

## Results and Discussion

### NIST® and Spike Recoveries

Efficacy of the method was established by favorable comparison of the obtained results to the certified values provided with the NIST® SRM (Tables 2-3). Certified values were provided for V and Ni and a noncertified value was provided for Na. No reference value was provided for Fe, and instead, a matrix spike was performed to demonstrate efficacy. The NIST® SRM was prepared at the 5% oil ratio and spiked with 3.62 mg/kg of Fe. The spike concentration was mid range for the calibration curve and approximately four times greater than the observed (diluted) sample concentration (0.79 mg/kg) at 5% oil. The observed concentration of iron was 4.44 mg/kg in the spiked aliquot for a recovery of 101%. While this does not specifically demonstrate the accuracy of the results, it does provide support.

*Table 2.* **Recoveries of trace elements in NIST® SRM 1634c using a 5% oil solution (mg/kg).**

| Replicate | Iron | Nickel | Sodium | Vanadium |
|---|---|---|---|---|
| 1 | 15.2 | 18.0 | 35.0 | 28.8 |
| 2 | 15.4 | 18.2 | 34.4 | 30.4 |
| 3 | 15.4 | 18.0 | 35.2 | 28.8 |
| Mean | 15.3 | 18.1 | 34.9 | 29.3 |
| Standard Deviation | 0.12 | 0.14 | 0.42 | 0.92 |
| Certified Value | N/A | 17.54 ± 0.21 | 37 | 28.19 ± 0.40 |
| % Recovery | N/A | 103 | 94.2 | 104 |

*The uncertainty limits of the certified values are at a 95% confidence level.*

*Table 3.* **Recoveries of trace elements in NIST® SRM 1634c using a 20% oil solution (mg/kg).**

| Replicate | Iron | Nickel | Vanadium | Vanadium w/Li* |
|---|---|---|---|---|
| 1 | 15.6 | 17.5 | 26.5 | 29.9 |
| 2 | 15.5 | 17.7 | 26.7 | 29.7 |
| 3 | 15.5 | 17.7 | 26.7 | 29.7 |
| Mean | 15.5 | 17.6 | 26.7 | 29.7 |
| Standard Deviation | 0.029 | 0.13 | 0.12 | 0.17 |
| % Recovery | N/A | 101 | 94.5 | 106 |

*250 mg/kg Li ionization suppressant*

As can be seen by comparing the vanadium results between Tables 2 and 3, the lithium ionization suppressant had no significant effect on the results. These results support the conclusion that although an ionization suppressant is needed for aqueous samples, it is not necessary for organics and is consistent with the ASTM® method.

### Characteristic Concentration

The analytical conditions were modified from the typical aqueous conditions to accommodate the matrix being comprised of oil and solvent. However, the characteristic concentration for each of the four elements was similar to the recommended values provided in the WinLab32 for AA software for aqueous conditions (Table 4 – Page 4). Published data for the characteristic concentrations in organic solutions was not available. However, considering the differences in the rate of sample introduction and the relative stability of aqueous and organic solutions, the characteristic concentrations for the two different matrices should be similar.

**Table 4.** Characteristic concentrations for the analysis of metals in fuel oil. Reference values are for aqueous solutions (mg/kg).

| Analyte | Aqueous Reference Value | % Oil | | |
|---|---|---|---|---|
| | | 5 | 20 | 20 w/Li |
| Iron | 0.1 | 0.12 | 0.13 | N/A |
| Nickel | 0.14 | 0.16 | 0.19 | N/A |
| Sodium | 0.012 | 0.032 | N/A | N/A |
| Vanadium | 1.9 | 0.67 | 0.77 | 0.79 |

### Calibration and Method Detection Limits

The calibration range used for all elements at both the 5% and 20% dilution ratios was similar to that recommended in ASTM® D5863 and also appropriate for the NIST® SRM. All correlation coefficients were calculated with a non-linear through zero calibration equation and were greater than 0.999. All calibration curves were verified with the secondary source standard and returned recoveries of no more than ±5% of the prepared value (i.e., 5 mg/kg). Examples of two calibration curves are shown in Figures 2 and 3.
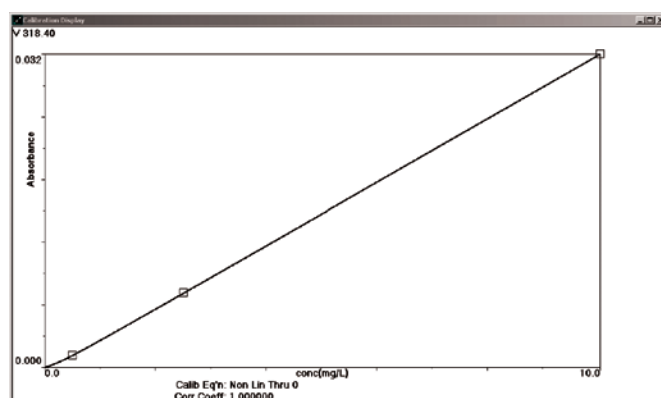
*Figure 2.* Calibration curve for the detection of vanadium in 20% oil using FAAS.

In addition to the NIST® results comparison, the method detection limits were estimated by repetitive analysis of the 0.5 mg/kg calibration standard (Table 6). This standard was analyzed 7 times and the resultant standard deviation was multiplied by the Student's t-value for 6 degrees of freedom and 99% confidence limits (3.143).

The percentage of oil did not appear to have any significant effect on the method detection limit (MDL) results. The more concentrated 20% oil solutions have slightly poorer MDLs than that of the 5% solutions. Considering the complex matrix in these sample solutions, these MDLs are a very good indication that the instrument performs normally. Better performance can be achieved, when desired, by additional optimization of the operating parameters and maintaining the cleanliness of the sample introduction system.
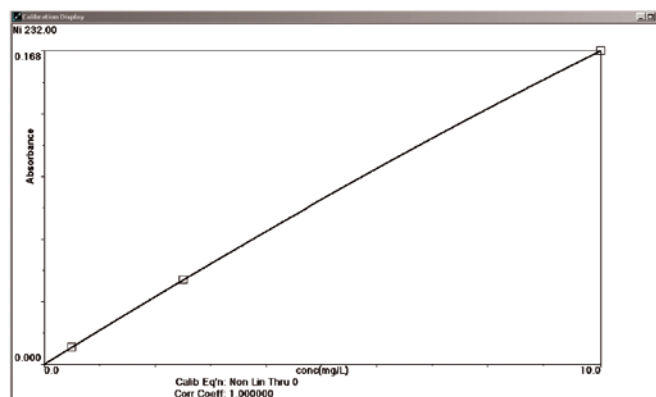
*Figure 3.* Calibration curve for the detection of nickel in 5% oil using FAAS.

The calculated MDL results clearly demonstrate that this method is more than adequate for the analysis of fuel oils and has excellent sensitivity.

**Table 6.** MDL reported in mg/kg in varying oil content for the analysis of metals in fuel oil by FAAS.

| Analyte | % Oil | Std Dev | MDL |
|---|---|---|---|
| Iron | 5 | 0.0034 | 0.011 |
| | 20 | 0.0086 | 0.027 |
| Nickel | 5 | 0.0079 | 0.025 |
| | 20 | 0.0089 | 0.028 |
| Sodium | 5 | 0.0039 | 0.012 |
| Vanadium | 5 | 0.033 | 0.10 |
| | 20 (w/Li) | 0.034 | 0.11 |

### Conclusions

While ICP-OES and ICP-MS instrumentation may receive more attention when it comes to metals analyses, FAAS is a viable option particularly in the petroleum industry. There are no less than 12 active ASTM® test methods available for the analysis of petroleum products by AA techniques. FAAS instrumentation offers rapid sample analysis, accuracy and precision, simple operation, a small instrument footprint, and all for a fraction of the price of the ICP instruments.

The PinAAcle 900T spectrometer is an excellent choice for petroleum product analyses and can be used with the ASTM® test methods. Very few and simple, optional modifications are suggested to handle the organic matrix. Excellent accuracy has been demonstrated with a fuel oil SRM. The quick-change spray chamber allows for fast and simple conversion from aqueous to organic samples. The WinLab32 for AA software and its automated features simplify analyses, freeing up more of the analyst's time. The PinAAcle 900F (flame only model) may also be used for this analysis.

## References

1. ASTM® Standard D5863, 2000a, "Standard Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry," ASTM® International, West Conshohocken, PA, 2005, DOI: 10.1520/D5863-00AR05, www.astm.org.

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