



## Determination of Ni and V in Bitumen by Simple Sample Preparation by Emulsion

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### 1 Introduction

The analysis of organometallics samples using an ICP-AES is not a simple proposition as digestion of the sample or dissolution in an adequate solvent is required. Digestion is a lengthy process and loss of analytes and contamination are severe problems. The dissolution method however requires an aromatic solvent, resulting in specific analysis conditions and special pump tubing, which are not easy problems for a typical laboratory to overcome.

This Application Note presents the preparation, characterization and optimization of bitumen after emulsion in water.

### 2 Principle

#### 2.1 Technique used

The elemental analysis of solutions was undertaken by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

#### 2.2 Wavelength choice

The choice of the wavelength in a given matrix can be made using the "profile" function, or by using Win-IMAGE, which is rapid semi-quantitative analysis mode using multiple wavelengths. The principle is the same in either case: record the scans of analytes at low concentration, and of the matrix. By superimposing the spectra, we see possible interferences.

#### 2.3 Limits of detection estimation

The limits of detection are calculated using the following formula:

$$\text{LOD} = k \times \text{BEC} \times \text{RSD}_0$$

With:

LOD = limits of detection,

$k=3$  for the normal 3-sigma values,

BEC = Background equivalent concentration,

$\text{RSD}_0$  = relative standard deviation of the blank.

To calculate the LOD, a calibration curve is constructed using two points, 0 ppm and 5 ppm, or some concentration where the calibration is linear; this gives the BEC. The  $\text{RSD}_0$  is evaluated by running the blank ten times.

### 3 Sample preparation

The emulsion used is an oil/water emulsion. It is made of two phases, xylene and distilled water, and of a surfactant (Triton X® 100). The emulsion was maintained by a magnetic stirrer.

1.5 g of bitumen was weighed into a 100 mL beaker and dissolved in 5 mL of xylene. The dissolution was accelerated by using an ultrasonic bath. After complete dissolution, 2 mL of Triton X® was added drop by drop with continuous



magnetic agitation. Add in the same manner, 25 mL of distilled water.

Put the emulsion in a 100 mL flask, rinse several times the beaker with distilled water, complete with water at 100 mL.

The emulsion is well prepared when no adherence occurs on the beaker walls.

The standards are prepared in the same manner and by adding V and Ni.

## 4 Instrument specification

The work was done on a JY 24/124/2000. The specifications of this instrument are listed Table 1.

**Table 1: Specification of spectrometer**

| Parameters                | Specifications |
|---------------------------|----------------|
| Mounting                  | Czerny-Turner  |
| Focal length              | 0.64 m         |
| Thermoregulation          | Yes            |
| Nitrogen purge            | Yes            |
| Grating number of grooves | 2400 gr/mm     |
| 1st order resolution      | 0.025 nm       |
| 2nd order resolution      | 0.012 nm       |
| Order                     | 2nd order      |

## 5 Operating conditions

The operating conditions are listed Table 2 below.

**Table 2: Operating conditions**

| Parameter              | Condition             |
|------------------------|-----------------------|
| RF Generator power     | 1200 W                |
| Plasma gas flowrate    | 18 L/min              |
| Auxiliary gas flowrate | 0.6 L/min             |
| Sheath gas flowrate    | 0.4 L/min             |
| Nebulizer flowrate     | 1.4 bars              |
| Sample uptake          | 1.2 mL/min            |
| Type of nebulizer      | Concentric (TR-50-C3) |
| Type of spray chamber  | Scott                 |
| Argon humidifier       | No                    |
| Injector tube diameter | 3.0 mm                |

## 6 Wavelength selection and analytical conditions

The line with the highest sensitivity was used for analysis of each element, as there were no problems with interferences. The analysis conditions were the same for all elements.

**Table 3: Analysis conditions**

| Element      | Slits $\mu\text{m}$ | Analysis Mode | Integration Time (sec) |
|--------------|---------------------|---------------|------------------------|
| All elements | 30 x 50             | Gaussian      | 0.6                    |

The use of the TR-50-C3, the argon humidifier and the large internal diameter (ID) of the injector tube enabled trouble free analysis, even with high dissolved salts. The larger ID injector tube also ensures a minimization of interferences. Due to the high dissolved salts, an initial conditioning of the spray chamber is advisable for maximum stability. It is imperative to use matched standards or standards additions due to the viscosity of the solutions.

## 7 Discussion

### 7.1 Intensity

The intensities of Ni and V in the emulsion was compared with those obtained for solutions in water.

**Table 4: Intensities**

|                | Intensities (counts) Ni | Intensities (counts) V |
|----------------|-------------------------|------------------------|
| Aqueous medium | 5359.1                  | 404.66                 |
| Emulsion       | 9952.4                  | 854.07                 |

It was noted that the intensities improved when analyzing the emulsion. This is probably due to the addition of surface agent, which decreases the surface tension and facilitates the flow of the liquid and thus the nebulization.



### 7.3.2 Analysis of 4 known bitumen samples

Four bitumen samples, which had been previously analyzed to provide a known sample, were evaluated. The samples were measured after three different preparations, with the concentrations given in the table the mean value of 5 measurements.

**Table 7: Ni results**

| Bitumen | Obtained values | Ni ( $\lambda = 231.605$ nm), ppm |                 |                    |
|---------|-----------------|-----------------------------------|-----------------|--------------------|
|         |                 | Mean                              | SHRP values [1] | BISHARA values [2] |
| AAA-1   | 81.9            | 78.2 $\pm$ 2.9                    | 86.0 $\pm$ 2.2  | 75.0 $\pm$ 1.2     |
|         | 77.8            |                                   |                 |                    |
|         | 74.8            |                                   |                 |                    |
| AAB-1   | 60.1            | 56.8 $\pm$ 2.5                    | 57.0 $\pm$ 2.8  | 47.7 $\pm$ 2.15    |
|         | 54.2            |                                   |                 |                    |
|         | 56.1            |                                   |                 |                    |
| AAD-1   | 133.8           | 141.2 $\pm$ 6.2                   | 141.3 $\pm$ 9.7 | 123.4 $\pm$ 4.7    |
|         | 148.9           |                                   |                 |                    |
|         | 141.0           |                                   |                 |                    |
| AAK-1   | 138.7           | 134.1 $\pm$ 3.9                   | 141.0 $\pm$ 7.9 | 118.9 $\pm$ 2.6    |
|         | 134.4           |                                   |                 |                    |
|         | 129.1           |                                   |                 |                    |

**Table 8: V results**

| Bitumen | Obtained values | V ( $\lambda = 290.882$ nm), ppm |                   |                    |
|---------|-----------------|----------------------------------|-------------------|--------------------|
|         |                 | Mean                             | SHRP values [1]   | BISHARA values [2] |
| AAA-1   | 169.7           | 160.1 $\pm$ 7.1                  | 173.7 $\pm$ 2.9   | 170.0 $\pm$ 1.5    |
|         | 157.7           |                                  |                   |                    |
|         | 152.9           |                                  |                   |                    |
| AAB-1   | 227.6           | 220.0 $\pm$ 13.0                 | 222.0 $\pm$ 9.9   | 206.5 $\pm$ 7.6    |
|         | 230.7           |                                  |                   |                    |
|         | 201.8           |                                  |                   |                    |
| AAD-1   | 297.6           | 311.4 $\pm$ 10.4                 | 307.7 $\pm$ 12.3  | 295.7 $\pm$ 5.4    |
|         | 322.7           |                                  |                   |                    |
|         | 314.0           |                                  |                   |                    |
| AAK-1   | 1590.3          | 1511.1 $\pm$ 68.6                | 1498.0 $\pm$ 58.3 | 1373.3 $\pm$ 19.4  |
|         | 1520.0          |                                  |                   |                    |
|         | 1422.9          |                                  |                   |                    |



## 7.2 Limits of Detection

The limits of detection were calculated following the formula in paragraph 2.3 and given in the following table in µg/g in the solution.

**Table 5: Limits of detection**

| Element | Limits of Detection |
|---------|---------------------|
| Ni      | 4.4 ppb             |
| V       | 12 ppb              |

## 7.3 Method validation

### 7.3.1 Standard addition method

The concentration of one sample was determined by standard addition and by direct calibration. Below is the comparison of results for Ni and V obtained by the two methods. We can see that no significant differences were obtained.

**Table 6: Bitumen results**

| Bitumen (mg/kg)          | Ni    | V      |
|--------------------------|-------|--------|
| Standard addition method | 43.19 | 396.80 |
| Direct calibration       | 9.33  | 408.72 |

From these results, we can see that the percent variation of the results obtained in this set of analyses are very similar across the range of concentrations, 50 to 150 ppm for Ni and 170 to 1500 ppm for V. The coefficient of variation is around 3.8 % for Ni and 4.5 % for V. The results were found to be in agreement with those already determined.

## 8 Summary

The analysis of V and Ni in bitumen enabled identification of the origin of the raw product. The preparation by emulsion is simple and it permits to use a classical ICP configuration (nebulizer, spray chamber, pump tubing).

## 9 References

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