The Determination of Vanadium and Nickel in Heavy Oil by ICP-MS

Application Note

Petrochemical

Katsuo Mizobuchi

Abstract

This application note describes the determination of vanadium and nickel in heavy oil. The 4500 ICP-MS is capable of analyzing hydrocarbons, such as vacuum gas oil and naphtha, by dilution with xylenes or other appropriate solvents. V and Ni were studied because they can cause the deterioration of catalysts during the refining process. A standard reference oil diluted in xylenes was used to make calibration curves that the samples were quantitated from. The measured concentrations are in good agreement with concentrations determined by a dry ashing and digestion procedure that takes about 17 hours.

Agilent Technologies
Innovating the HP Way

Introduction

The determination of metal impurities in petroleum products is of interest to the petroleum industry as many metals can cause the deterioration of catalysts. Premature failures of catalysts can easily cost millions of dollars, in addition to the production of out-of-spec-product which must be disposed of. Nickel and vanadium are the classic examples of trace elements that can cause catalyst breakdown. Because the processes used are continuous, a rapid and precise method of determining the amount of these metals in incoming raw material is crucial.

The 4500 ICP-MS has several features that make the direct analysis of hydrocarbons based possible. The 4500 ICP-MS is typically operated at a sample uptake rate of 0.4 mL/min, which is less than one third the sample uptake rate of other systems. In combination with a Peltier cooled spray chamber, the low flow rate leads to decreased sample loading in the plasma. The plasma therefore is more stable and carbon deposition on the interface is significantly reduced. Any carbon that is formed is easily removed by the addition of oxygen to the sample stream. The 4500 ICP-MS is equipped with an auxiliary mass flow controller for a second blend gas (oxygen) to be added directly to the spray chamber.

Instrumentation

The ICP-MS system used was a standard 4500 ICP-MS. The sample introduction system consisted of a concentric nebulizer (self-aspiration), quartz spray chamber, a one-piece quartz torch and platinum interface cones.

Operating parameters for the 4500 ICP-MS are given in Table 1. The spray chamber temperature was held at 2 deg C to decrease the sample loading into the plasma. Platinum interface cones are used to increase the lifetime of the cones when adding oxygen to the sample stream. Nickel interface cones can also be used but will quickly degrade in the presence of excess oxygen. While a concentric nebulizer was used for the following work, the Agilent cross flow nebulizer can also be used.

Sample Preparation

Two sample preparation methods for hydrocarbons were performed. One was simply a 100 times dilution with xylenes. The other was digestion by dry ashing, which takes about 17 hours. The final step of the ashing procedure was to dissolve the residual material in 1% nitric acid.

A standard reference material of heavy oil supplied by the Petrochemical Association (Tokyo, Japan) was used to make the calibration curves for the dilution sample preparation method. The oil standard which contains known concentrations of V (107 ppm) and Ni (37 ppm) in heavy oil base was diluted in xylenes to appropriate concentration for analysis as follows:

Plasma gas flow rate	16.0 L/min
Aux. gas flow rate	1.0 L/min
Carrier gas flow rate	1.1 L/min
Blend gas (oxygen) flow rate	96 mL/min
RF Power	1590 W
Nebulizer	Concentric type
Spray chamber	Pyrex, double pass
Spray chamber temp	2 deg C
ICP torch injector	Quartz, 2.5 mm
Sample uptake rate	0.1 mL/min
Sampler cone	Platinum
Skimmer cone	Platinum
Sampling depth	15 mm
Points/mass	3
Integration time/mass	1 sec
Total acquisition time/replicate	3.8 sec
Replicates	5
Total acquisition time/sample	18.8 sec

Table 1.
4500 ICP-MS Operating Parameters

1) xylenes only (blank)

2) 100 times dilution
of standard heavy oil
(V:1.07 ppm, Ni:0.37 ppm)

3) 50 times dilution
of standard heavy oil
(V:2.14 ppm, Ni:0.74 ppm)

4) 33 times dilution
of standard heavy oil
(V:3.24 ppm, Ni:1.12 ppm)

Aqueous standard solutions (in 1% HNO_3) were used for the digested sample analysis.

Results

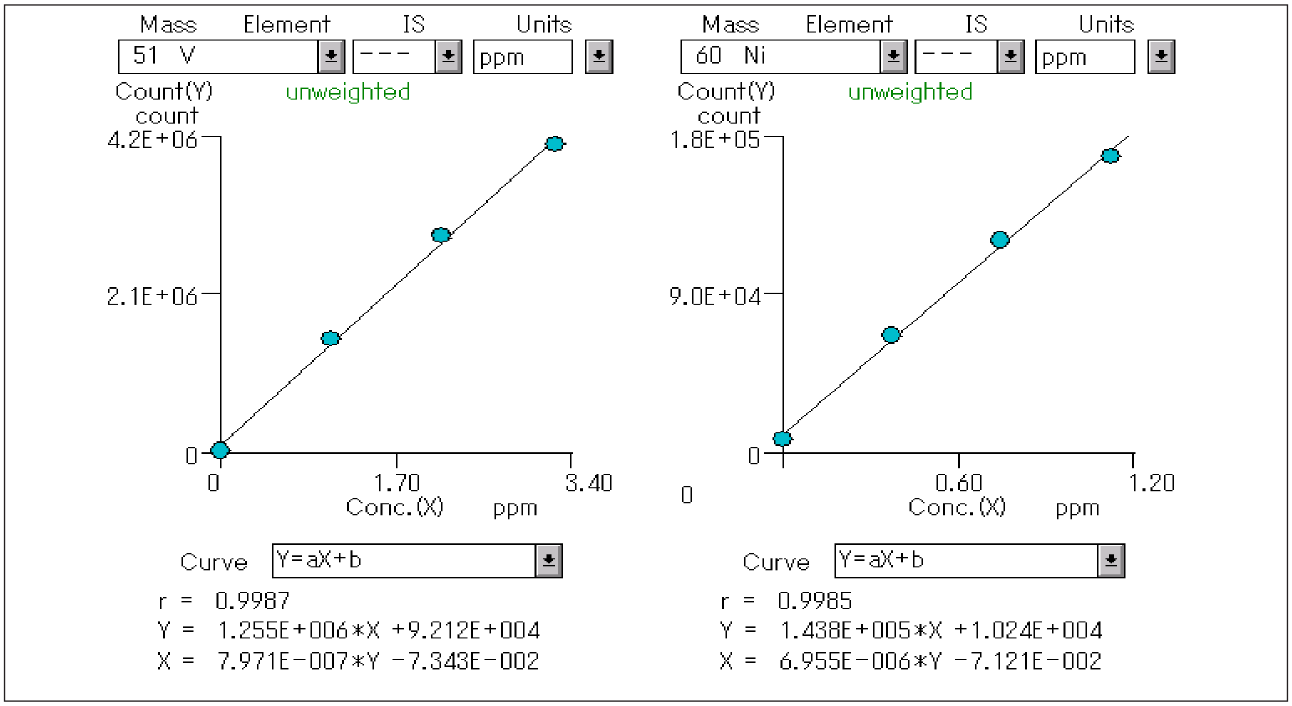
The xylenes based calibration curves for V and Ni showed good linearity with a linear correlation coefficient of r=0.99 or better (shown in Fig.1).

The quantitative results for V (m/z=51) and Ni (m/z= 60) are shown in Table 2. There is excellent agreement between the simple dilution method and the dry ashing method. The precision of both methods is also very good. For 5 replicate analysis the RSD is less than 0.6%. These values demonstrate that the 4500 ICP-MS can analyze these sample types directly following simple dilution, and that instrument stability does not suffer when switching to an organic matrix.

Conclusion

The analysis of hydrocarbon samples can be performed by dilution in the appropriate solvent. The ability to run organic solvents allows for rapid and convenient analysis.

For most organic solvents the detection limits are limited by inorganic contaminants in solvent used. ICP-MS possesses superior detection power for petrochemical samples when compared to ICP-OES, allowing the analyst to meet future requirements for trace metal analysis in oils.



```
r =  0.9987
Y =  1.255E+006*X +9.212E+004
X =  7.971E-007*Y -7.343E-002
```

```
r =  0.9985
Y =  1.438E+005*X +1.024E+004
X =  6.955E-006*Y -7.121E-002
```

Figure1
Calibration Curves for V and Ni

Element	m/z	Diluted sample (ppm)	RSD (%) n=5	Digested sample (ppm)	RSD (%) n=5
V	51	1.56	0.56	1.57	0.67
Ni	60	0.42	0.58	0.41	1.4

Table 2
Quantitative Results

Visit our website at
http:/www.agilent.com/chem/icpms

Printed 4/2000
Publication number 5966-3068E

Agilent Technologies
Innovating the HP Way