

Determination of Metals in Petroleum Fractions using MP-AES

Including a comparison of sample preparation methods



Authors

Laura Poirier¹, Jenny Nelson²,
Greg Gilleland², Steve Wall², Lidia
Berhane¹, and Francisco Lopez-
Linares¹

¹Chevron Energy Technology
Company, USA

²Agilent Technologies, Inc., USA

Introduction

The determination of carbon, hydrogen, nitrogen, sulfur, and metals in feedstocks is critical to decision making in oil refineries [1]. To analyze metals in heavy hydrocarbons, such as bitumen and heavy oil, each fraction is normally separated from the hydrocarbon matrix. This separation is achieved by converting each fraction into aqueous based samples using acid assisted digestion. Typically, nitric acid and hydrochloric acid combined with hydrogen peroxide are used to solubilize metals via an ashing and refluxing method or microwave digestion. Flame Atomic Absorption (FAAS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), and ICP-Mass Spectrometry (ICP-MS) are often used for the analysis [2–6]. Microwave Plasma Atomic Emission Spectrometry (MP-AES) can also analyze the digested samples [7]. MP-AES is attractive alternative technique for the application because of its relatively low operating costs and robustness.



The Agilent 4200 and 4210 MP-AES use magnetically coupled microwave energy to generate a robust and stable plasma using nitrogen gas. The N₂ can be extracted directly from air using the Agilent 4107 nitrogen generator or from a Dewar, allowing onsite testing in remote locations. Compared to FAAS and ICP techniques, MP-AES eliminates the need for expensive and flammable gases like acetylene and argon. This results in lower running costs, and safe, unattended operation. To aid in the processing of petroleum and other organic samples the MP-AES can be fitted with an External Gas Control Module (EGCM). The EGCM injects air into the plasma preventing the buildup of carbon in the torch. It also reduces the background emissions caused by carbon species during measurements.

ASTM D5708, ASTM D5863, and ASTM D7876 methods relate to the determination of metals such as iron, nickel, vanadium, and sodium in crude oils and residual fuels [8-10]. Each method allows sample preparation using wet ash digestion (WAD), direct dilution (DD) in an organic solvent, microwave (MW) assisted acid digestion, and AAS or ICP-OES as the detection technique.

MP-AES was used as an alternative detection technique for the elemental analysis of crude oils in a previous study [11]. The samples covered a wide range of American Petroleum Institute (API) gravity, nitrogen and sulfur (N&S) content, and density. The study showed that MP-AES was suitable for the measurement of samples prepared using DD.

In this work, iron, nickel, and vanadium were determined in crude oil residues diluted in *o*-xylene using an Agilent 4200 MP-AES. The Agilent 4210 MP-AES instrument can also be used for this application.

Samples and standards

Ten crude oil samples covering a wide range of API gravity, N&S content, and density were analyzed in this study. Each crude oil sample was diluted from 1:20 up to 1:200 in *o*-xylene (Fisher Scientific) by weight, based on the estimated metal concentrations. A matrix modifier (mineral oil, Fisher Scientific), a dispersant (Chevron Oronite, US), and scandium (Sc), as the internal standard (Conostan[®], SCP Science, Canada), were added to all standards, samples, and blanks. Compared to acid digestion, direct dilution reduces sample preparation time to a minimum, which is beneficial for laboratories that need to analyze high sample volumes. Direct dilution also reduces the possibility of analyte loss or contamination during sample preparation.

Calibration standards were prepared for V, Ca, Fe, Ni, Na, and Mo at 1, 2, 5, and 10 mg/kg. The standards were prepared by adding Conostan S21 standard by weight into pre-prepared *o*-xylene diluent. The *o*-xylene diluent containing a matrix modifier and Sc ISTD was run as the blank for the calibration.

To test recoveries of Ca, Fe, Na, Ni, Mo, and V, crude oil samples were spiked with 885 ppm of the S21 standard. Continuing calibration verification (CCV) standards were used to check the quality of calibrations. The CCV standard was diluted from the 885 ppm S21 standard (taken from a different lot number than the calibration standards) by weight of the diluent. The 885 mg/kg S21 standard was diluted to approximately 5 mg/kg (1:177), so the CCV would be at the midpoint of the calibration curve.

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES, with nitrogen supplied from an Agilent 4107 Nitrogen Generator. The sample introduction system consisted of a MicroMist nebulizer and double-pass glass cyclonic spray chamber. An External Gas Control Module (EGCM) accessory and an SPS 4 autosampler were also used.

The MP-AES was controlled using the intuitive MP Expert software, which recommends wavelengths for the selected elements, and automatically sets the nebulizer flow rate and EGCM settings. Auto background correction was used to resolve the element emission line from the organic matrix. Instrument operating conditions are given in Table 1.

Table 1. Agilent 4200 MP-AES operating conditions.

Parameter	Value
EGCM setting	High
Pump rate (RPM)	5
Sample tubing	Orange-white
Waste tubing	Blue-blue
Read time (s)	3
Number of replicates	3
Sample uptake delay (s)	55
Stabilization delay (s)	10
Fast pump during uptake	Yes
Rinse time (s)	60
Background correction	Auto

Results and Discussion

MDLs and LOQs

Method detection limits (MDLs) (3σ) and limits of quantification (LOQ) were calculated for Ca, Fe, Mo, Na, Ni, and V by measuring a blank solution (diluent containing a matrix modifier and internal standard) 10 times (10σ). The results are shown in Table 2.

The MDLs and LOQs show the efficiency of the MP-AES nitrogen plasma for the analysis of petrochemical residues following direct dilution with a solvent such as *o*-xylene.

Table 2. Method detection limits and the limit of quantification ($\mu\text{g}/\text{kg}$) with a blank solution using MP-AES.

Blank solution (MP-AES)	Na	Ca	V	Fe	Ni	Mo
	588.995 nm	396.847 nm	311.070 nm	259.940 nm	341.476 nm	313.259 nm
MDL	3.28	1.61	5.23	9.40	2.93	2.08
LOQ	10.95	5.37	17.44	93.97	9.78	6.94

Reprinted with permission from Laura Poirier et al, Energy Fuels, 2017, 31 (8), pp 7809–7815. Copyright (2017) American Chemical Society.

Quality Control test

Three Quality Control (QC) tests were performed. A CCV sample at the midpoint concentration of the calibration (5 mg/kg) was analyzed repeatedly. The S21 standard (885 mg/kg) was then analyzed. Finally, NIST 1634c Trace Elements in Fuel Oil was analyzed seven times for V

(28.19 mg/kg) and Ni (17.54 mg/kg) only. All recoveries were within $\pm 10\%$ ($\pm 12\%$ for V in S21), as shown in Table 3.

As already demonstrated for crude oil analysis using MP-AES [11], these results indicate that MP-AES can also be used as an alternative for residue analysis via direct dilution.

Table 3. QC average results of a CCV sample, S21 standard sample, and NIST 1634c Trace Elements in Fuel Oil CRM determined by MP-AES.

Element and wavelength (nm)	5 mg/kg (CCV)				885 mg/kg Standard				NIST 1643c (QC)			
	Mean conc mg/kg	SD	RSD (%)	Recovery (%)	Mean Conc mg/kg	SD	RSD (%)	Recovery (%)	Mean Conc mg/kg	SD	RSD (%)	Recovery (%)
Na 588.995	4.98	0.08	1.61	100	938.97	8.9	0.95	106	-	-	-	-
Ca 396.847	4.96	0.11	2.22	99	918.34	12.72	1.39	104	-	-	-	-
V 311.070	5.09	0.19	3.73	102	987.02	7.99	0.81	112	30.03	0.21	0.7	107
Fe 259.940	5.11	0.24	4.7	102	965.38	8.94	0.93	109	-	-	-	-
Ni 341.476	5.07	0.11	2.17	101	940.4	7.41	0.79	106	17.7	0.13	0.73	101
Mo 313.259	5.12	0.16	3.13	102	943.89	8.27	0.88	107	-	-	-	-

Petroleum fraction 1000 °F+ analysis

A variety of samples was analyzed by MP-AES to determine if the properties of the different feed samples would impact the plasma, causing a potential bias [7]. The samples included a vacuum residue, heavy oil crude, deasphalted crude oil containing different levels of sulfur (1.0 wt. % up to 5.5 wt. %), and nitrogen (200 mg/kg up to 14000 mg/kg).

The measured concentrations of the metals present in the residue samples are shown in Table 4. The results show how the metal concentrations differ among the samples. The samples were diluted 1:10 with the *o*-xylene diluent. When the concentration of any element was >100 mg/kg, the dilution

factor was increased from 1:20 up to 1:200 depending on the highest elemental concentration in the sample. The measurement standard deviations did not exceed 1.5 mg/kg. For this set of samples, all samples were analyzed using MP-AES.

However, it was not possible to quantify Na in samples S1, S2, S7, S8, and S10 because the dilution factor was too high (1:50-1:200). The Na injected concentration was too low to be quantified at the same time as the high-level of Ca, V, Fe, and Ni present in these samples. In some cases, applying a single dilution factor will not keep all elements within the effective calibration range.

Table 4. Measured concentrations of metals present in residue samples in mg/kg using MP-AES.

Solution label	Na 588.995 nm	Ca 396.847 nm	V 311.070 nm	Fe 259.940 nm	Ni 341.476 nm	Mo 313.259 nm
S1	<13.00	508.9	311.37	116.76	176.08	<8.21
S2	<43.20	40.90	995.46	<24.9	204.01	<27.00
S3	14.43	<2.05	166.29	16.79	63.13	<2.55
S4	14.67	<2.58	165.63	16.99	63.97	<3.21
S5	17.21	<2.09	180.22	14.67	70.73	<2.60
S6	9.44	<1.85	126.72	10.93	37.91	<2.31
S7	<2.15	<1.09	56.21	30.58	28.73	<1.35
S8	<12.4	<6.26	287.59	42.57	68.93	<7.79
S9	14.54	<5.80	406.58	16.22	147.02	18.58
S10	<28.20	<14.30	427.39	21.32	197.77	151.93
NIST 8505	<15.10	17.33	424.67	<8.74	50.66	<9.54

* Results are the mean of triplicate measurements with RSD lower than 10 % < indicates that the concentration was less than the method detection limit
Reprinted with permission from Laura Poirier et al, Energy Fuels, 2017, 31 (8), pp 7809–7815. Copyright (2017) American Chemical Society.

Comparison of sample preparation techniques

Previously, we reported the analysis of crude oil samples by MP-AES following dilution in an organic solvent [7, 11]. Due to the complex nature of the samples selected for this work, different solubility behavior and the potential presence of insoluble solids was anticipated. Therefore, the direct dilution (DD) method was compared to a conventional wet ash digestion (WAD) method for the most useful elements found in these samples: V, Fe, and Ni. Samples prepared by DD were measured by MP-AES and the samples prepared by WAD were measured by ICP-OES. The results are presented in Table 5.

Table 5. Sample preparation method and measured concentration of V, Fe, and Ni in mg/kg.

Solution Label	DD-MP-AES			WAD-ICP-OES		
	V 311.070 nm	Fe 259.940 nm	Ni 341.476 nm	V 309.31 nm	Fe 238.20 nm	Ni 231.60 nm
S1	311.37	116.76	176.08	289.00	117.00	166.00
S2	995.46	<24.90	204.01	884.00	17.60	203.00
S3	166.29	16.79	63.13	156.00	32.10	64.90
S4	165.63	16.99	63.97	156.00	32.40	64.90
S5	180.22	14.67	70.73	168.00	27.00	72.00
S6	126.72	10.93	37.91	120.00	18.50	39.80
S7	56.21	30.58	28.73	89.40	169.00	45.30
S8	287.59	42.57	68.93	262.00	61.80	66.00
S9	406.58	16.22	147.02	335.00	25.30	145.00
S10	427.39	21.32	197.77	383.00	29.50	187.00
NIST 8505	424.67	<8.74	50.66	386.00	6.49	51.37

Reprinted with permission from Laura Poirier et al, Energy Fuels, 2017, 31 (8), pp 7809–7815. Copyright (2017) American Chemical Society.

In most cases, the DD results correlate well with the WAD results for V and Ni, while there is greater variability in the Fe results. The DD/WAD ratios for Ni and V span from 1.00 up to 1.14, which implies that DD can be used as an alternative to WAD for analyzing these metals in a residue. Solid microparticulate minerals containing Fe could be present in the heavy oil fractions and deposits [1], contributing to the low bias for this metal. Fe is reportedly the dominant element present in such minerals [12]. If this particulate was not adequately dispersed in the organic solvent, lower results would be expected in comparison with an acid digestion method.

V and Ni are the most common elements in petroleum fractions. They also tend to be present at a higher concentration in the heaviest and non-distillable fractions, such as residues, resins, and asphaltenes [13]. Additionally, they are the two most important elements measured in a crude oil assay. Assays are carried out to determine if a crude oil feedstock is suitable for a particular petroleum refinery [14]. Figure 1 presents a comparison of ratios between the sample methods evaluated (DD and WAD) for V and Ni.

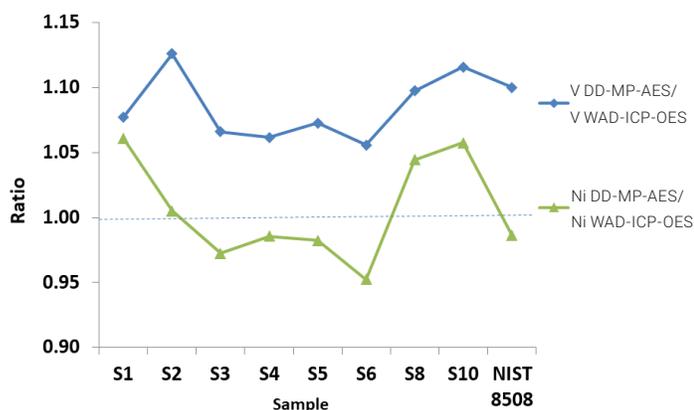


Figure 1. Comparison of sample preparation methods and detection techniques for vanadium and nickel.

Conclusions

Vanadium, nickel, and iron can be analyzed in residue samples following direct dilution in an organic solvent, in combination with measurement using MP-AES. While V and Ni are not sensitive to the sample preparation method, Fe recovery using the direct dilution method is often biased low because microparticles of iron may not distribute well into organic solutions. For Fe, better results are obtained using wet ash digestion.

A comparison of sample preparation techniques showed good agreement for Ni and V in samples prepared using wet ash digestion and direct dilution. The samples were measured by ICP-OES and MP-AES, respectively. Direct dilution is convenient for laboratories that need to analyze large numbers of samples. It eliminates the need for time consuming acid digestion processes and reduces the possibility of analyte loss or contamination during sample preparation.

The Agilent 4200/4210 MP-AES represents a low-cost alternative technique for the analysis of petrochemical sample types. When fitted with a nitrogen generator, the technique can be safely used in remote areas or field locations.

More Information

Laura Poirier, Jenny Nelson, Greg Gilleland, Steve Wall, Lidia Berhane, and Francisco Lopez Linares, Comparison of Preparation Methods for the Determination of Metals in Petroleum Fractions (1000 °F+) by Microwave Plasma Atomic Emission Spectroscopy, *Energy Fuels*, **2017**, 31 (8), pp 7809–7815. DOI: 10.1021/acs.energyfuels.7b00654.

References

1. K. H. Altgelt, M. M. Boduszynski, *Composition and Analysis of Heavy Petroleum Fractions*, Marcel Dekker: New York, 1994, Chapter 2, 19-40
2. C. Hardaway, J. Sneddon, J. N. Beck, Determination of Metals in Crude Oil by Atomic Spectroscopy, *Analytical Letters*, **2004**, 37, 2881–2899.
3. R. A. Kishore Nadkarni, J. D. Hwang, L. Young, Multielement Analysis of Crude Oils Using Inductively Coupled Plasma-Atomic Emission Spectrometry, *Journal of ASTM International*, **2011**, 8, Paper ID JAI103837
4. R. Sanchez, J. L. Todoli, C-P. Lienemann, J. M. Mermet, Determination of trace elements in petroleum products by inductively coupled plasma techniques: a critical review. *Spectrochimica Acta*, Part B: Atomic Spectroscopy, **2013**, 88, 104–126
5. P. A. Mello, J. S. F. Pereira, M. F. Mesko, J. S. Barin, E. M. M. Flores, Sample preparation methods for subsequent determination of metals and non-metals in crude oils – A review. *Analytica Chimica Acta*, **2012**, 756, 15–36
6. L. Poirier, J. Nelson D. Leong, L. Berhane, P. Hajdu, F. Lopez-Linares, Application of ICP-MS and ICP-OES on the Determination of Nickel, Vanadium, Iron, and Calcium in Petroleum Crude Oils via Direct Dilution. *Energy Fuels*, **2016**, 30 (5), pp 3783–3790
7. L. Poirier, J. Nelson, G. Gilleland, S. Wall, L. Berhane, and F. Lopez Linares, Comparison of Preparation Methods for the Determination of Metals in Petroleum Fractions (1000 °F+) by Microwave Plasma Atomic Emission Spectroscopy, *Energy Fuels*, **2017**, 31 (8), 7809–7815
8. Standard Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry, ASTM D5708-12e1; ASTM International: West Conshohocken, PA, USA, 2012
9. Standard Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry. ASTM D5863; ASTM International: West Conshohocken, PA, USA, 2012
10. Standard Practice for Practice for Sample Decomposition Using Microwave Heating (With or Without Prior Ashing) for Atomic Spectroscopic Elemental Determination in Petroleum Products and Lubricants. ASTM D7876 – 13. ASTM International: West Conshohocken, PA, USA, 2013

11. J. Nelson, G. Gilleland, L. Poirier, D. Leong, P. Hajdu, F. Lopez-Linares, Elemental Analysis of Crude Oils Using Microwave Plasma-Atomic Emission Spectroscopy, *Energy Fuels*, 29, **2015**, 5587–5594
12. L. Carbognani, M. Orea, M. Fonseca, Complex Nature of Separated Solid Phases from Crude Oils, *Energy Fuels*, 13, **1999**, 351–358
13. T. F. Yen, The role of trace metal in petroleum. Ann Arbor Science Publisher Inc. 1975, Chapter 1, 1-30
14. H. N. Giles, Crude Oils. The significance of Test for Petroleum Products, Salvatore J. Rand, editor. ASTM Manual Series: MNL 1, Seventh Edition, ASTM International, 2014, West Conshohocken, PA. Chapter 5, 51-62

Verified for Agilent
4210 MP-AES



Results presented in this document were obtained using the 4200 instrument, but performance is also verified for the 4210 MP-AES

www.agilent.com/chem

This information is subject to change without notice.

© Agilent Technologies, Inc. 2018
Printed in the USA, March 21, 2018
5991-9122EN