Direct multi-elemental analysis of crude oils using the Agilent 4200/4210 Microwave Plasma-Atomic Emission Spectrometer

Application note

Petrochemical, energy and fuels

Authors

Jenny Nelson[1], Greg Gilleland[1],
Laura Poirier[2], David Leong[2],
Paul Hajdu[2] and
Francisco Lopez-Linares[2]

1.Agilent Technologies, Inc., USA,

2. Petroleum and Material
Characterization Unit, Chevron
Energy Technology Co. USA

Verified for Agilent
4210 MP-AES

Introduction

Knowing the metal concentration of crude oil is vitally important to the petroleum industry at all stages of the product cycle. Metals are used to monitor crude migration within an oil reservoir; inform business opportunities; affect the efficiency of catalysts or render them inactive; as well as being integral to the final product quality and specification. Metals are also closely monitored to avoid environmental issues such as soil contamination from the decommissioning of petrochemical facilities and land reclamation.

Typically, techniques such as inductively coupled plasma-optical emission spectroscopy (ICP-OES), ICP-mass spectrometry (ICP-MS), flame atomic absorption (FAAS), X-ray fluorescence (XRF), and neutron activation analysis (NAA) are used in petroleum labs for the identification and quantification of elements in aqueous or organic samples. However, Microwave Plasma-Atomic Emission Spectroscopy (MP-AES) technology is a suitable alternative for this industry, and is increasingly used for the multi-element analysis of a wide range of sample types, including complex organic matrices. In addition, elemental analysis is often required in the field or remote areas where the petroleum industry operates, which can be challenging depending on the location. Agilent's 4200 MP-AES uses magnetically coupled microwave energy to generate a robust and stable plasma using nitrogen gas. The nitrogen needed for the plasma is extracted straight from air using the Agilent 4107 nitrogen generator or from a nitrogen Dewar. Compared to conventional flame AA and ICP techniques, MP-AES eliminates the need for expensive and flammable gases like acetylene and argon gas to sustain the atomization/ionization source, resulting in lower running costs and safe unattended operation.

There are several ASTM methods for the determination of elements in crude oil analysis. For example, ASTM D7691 specifies ICP-OES for the analysis of S, V, Fe and Ni in crude oil after dilution with an organic solvent. Both ASTM D5708 and D5863 specify acid digestion or direct dilution with an organic solvent for the determination of Ni, V and Fe by ICP-OES and Ni, V, Fe and Na by FAAS respectively.

This application note describes the analysis of V, Ca, Fe, Ni, and Na in 20 crude oil samples using the Agilent 4200 MP-AES following a simple 1:10 dilution in *o*-xylene. Results obtained using a combination of ICP-OES and ICP-MS are given for comparison purposes. This application is also applicable for Agilent's 4210 MP-AES instrument.

Experimental

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, double pass glass cyclonic spray chamber and solvent resistant sample tubing. An External Gas Control Module (EGCM) accessory was used to inject a flow of air into the plasma to prevent carbon deposits from building up in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and to reduce background emissions caused by carbon species in the plasma.

The instrument is controlled by the intuitive MP Expert software. The MP-AES features continuous wavelength coverage and MP Expert software automatically adds the recommended wavelength, nebulizer flow rate, and EGCM setting when elements are selected for simplified method development. The powerful Auto background correction mode easily handles any background emission arising from the organic matrix, making accurate corrections without any user intervention.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b.

Table 1a. Agilent 4200 MP-AES operating conditions.

Parameter	Value
EGCM setting	Low
Pump rate (RPM)	5
Sample tubing	Viton Organic black/black
Waste tubing	Viton Organic blue/blue
Read time (s)	3
Number of replicates	3
Sample uptake delay (s)	55
Stabilization delay (s)	10
Fast pump during uptake	Yes
Background correction	Auto

Table 1b. List of analytes with wavelength and nebulizer flow.

Element	Wavelength (nm)	Nebulizer Flow (L/min)
Ca	396.847	0.7
Fe	259.940	0.7
K	769.897	0.7
Na	588.995	0.7
Ni	341.476	0.7
V	311.070	0.7
Sc (internal standard)	335.372	0.7

Standards and samples

Twenty crude oil samples covering a wide range of American Petroleum Institute (API) gravity, nitrogen and sulfur (N&S) content, and density were analyzed in this study.

Each crude oil sample was diluted ~ 1:10 in *o*-xylene (Fisher Scientific) by weight. A matrix modifier of mineral oil (Fisher Scientific), a dispersant (Chevron Oronite) and scandium (Conostan®), as the internal standard were added to all standards, samples and blanks, to give a total oil concentration of 10% (w/w) in each solution. Sample dilution reduces sample preparation time to a minimum compared to acid digestion ensuring that a wide range of samples can be analyzed in a timely manner whilst minimizing analyte loss and contamination.

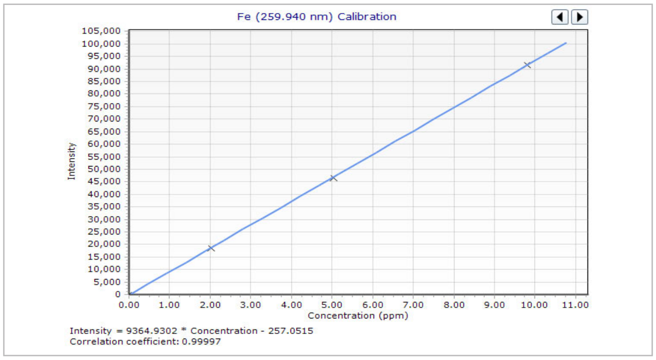
Calibration standards were prepared for V, Ca, Fe, Ni, Na, and K at the 0, 2, 5 and 10 ppm level by diluting by weight with Conostan® S-21+K standard into pre-prepared *o*-xylene diluent. The *o*-xylene diluent containing a matrix modifier and Scandium internal standard was run as the blank for the calibration.

To test recoveries of Ca, Fe, K, Na, Ni and V, crude oil samples were spiked with 885 ppm of Conostan® S-21+K standard.

Results and discussion

Working calibration range

The calibration curve for Fe is presented in Figure 1, highlighting the working range for the MP-AES. All correlation coefficients were greater than 0.999 (Table 2).



Intensity = 9364.9302 * Concentration - 257.0515
Correlation coefficient: 0.99997

Figure 1. Calibration curve for Fe 259.940 nm.

Table 2. Wavelength and working calibration concentration range.

Element & wavelength (nm)	Concentration range (ppm)	Correlation coefficient	Calibration Fit
Fe 259.940	0-10	0.9999	Linear
V 311.070	0-10	1.0000	Rational
Ni 341.476	0-10	0.9999	Rational
Ca 396.847	0-10	1.0000	Rational
Na 588.995	0-10	1.0000	Rational
K 769.897	0-10	0.9998	Rational

Method Detection Limit

Method detection limits (MDLs) (3σ) were calculated by measuring 10 consecutive blank readings. The MDLs (Table 3) demonstrate the ability of the Agilent 4200 MP-AES to provide excellent detection limits.

Table 3. Method detection limits (ppm) for Fe, V, Ni, Ca, Na and K.

Element & wavelength (nm)	MDL (ppm)
Fe 259.940	0.016
V 311.070	0.009
Ni 341.476	0.008
Ca 396.847	0.015
Na 588.995	0.022
K 769.897	0.190

QC spike recovery tests

To check the validity of the method, three separate Quality Control (QC) spike recovery tests were carried out. First, a Continuing Calibration Verification (CCV) sample at the midpoint concentration of the calibration (5 ppm) was analyzed 7 times, with a recovery within ±10% of the target values.

Secondly, a crude oil sample was spiked with S21+K at 885 ppm to validate the method at a high concentration level, with all recoveries within ±10%. Finally, a certified reference sample, NIST 1634c Trace Elements in Fuel Oil (NIST, Gaithersburg MD) was analyzed 7 times for vanadium (certified at 28.19 ppm) and nickel (certified value of 17.54 ppm) only, with recoveries within ±10%. A summary of the data is given in Table 4.

Table 4. QC spike recovery results of a CCV sample, S21 + K spiked crude oil sample and NIST 1634c Trace Elements in Fuel Oil CRM.

	Element and wavelength (nm)					
	Fe 259.940	V 311.070	Ni 341.476	Ca 396.847	Na 588.995	K 769.897
5 ppm CCV sample (mean, n=7)	4.83	4.94	4.96	5.03	4.94	5.04
% Recovery	**97**	**99**	**99**	**101**	**99**	**101**
885 ppm S-21+K spiked sample (mean, n=7)	862.9	894.4	876.5	853.0	834.9	940.9
Certified value (ppm)	885.0	885.0	885.0	885.0	885.0	885.0
% Recovery	**98**	**101**	**99**	**96**	**94**	**106**
NIST 1634c CRM (mean, n=7)	-	30.95	18.03	-	-	-
Certified value (ppm)	-	28.19	17.54	-	-	-
% Recovery	-	**110**	**103**	-	-	-

Spike recoveries of a crude oil sample

Accuracy of the method was checked by spiking a crude oil sample in triplicate with S21 +K at 79.89 ppm for all analytes. The spike recovery results are shown in Table 5. For all analytes, recoveries were within the ±10% range of the target values. The results demonstrate the ability of the 4200 MP-AES to analyze Fe, V, Ni, Ca, and K spikes accurately.

Table 5. Results of 79.89 ppm concentration spike recovery test in a crude oil sample.

	Element and wavelength (nm)					
	Fe 259.940	V 311.070	Ni 341.476	Ca 396.847	Na 588.995	K 769.897
Average (ppm)	74.24	78.23	75.82	76.45	72.43	75.60
Spiked conc. (ppm)	76.89	76.89	76.89	76.89	76.89	76.89
% Recovery	**97**	**102**	**99**	**99**	**94**	**98**

Analysis of crude oil samples

The developed method for MP-AES was applied to the determination of Fe, V, Ni, Ca and Na in 20 crude oil samples. Displayed, in Tables 6a and 6b, are the results for three of the crude oil samples; S1, S10 and S20. The results presented show that the concentration level of each element varies between the different oil samples. Sample "S20" was analyzed in duplicate, with good agreement between the 2 sets of results.

Table 6a. Measured concentrations of metallic impurities in crude oil samples S1, S10 and S20 (ppm).

Sample	Fe 259.940 (nm)	SD	V 311.070 (nm)	SD	Ni 341.476 (nm)	SD
S1	0.46	0.13	13.86	0.03	9.51	0.05
S10	9.65	0.57	0.13	0.03	0.87	0.03
S20	130.99	1.05	87.48	0.21	68.08	0.18
*S20b	130.81	0.86	87.08	0.32	68.15	0.06

Table 6b. Measured concentrations of metallic impurities in crude oil samples S1, S10 and S20 (ppm).

Sample	Ca 396.847 nm	SD	Na 588.995 nm	SD
S1	<LOD	-	<LOD	-
S10	5.05	0.33	5.99	0.39
S20	58.29	0.27	26.59	0.41
*S20b	59.43	0.62	25.89	0.22

* Duplicate sample of S20

<LOD indicates the result was below the limit of detection

Comparative results with ICP-MS/ICP-OES

Quantitative measurements of Ni, V, Fe and Ca in the 20 crude oil samples by MP-AES were in good agreement with the data obtained using a combination of ICP-OES and ICP-MS, showing good correlation between techniques (Figure 2).

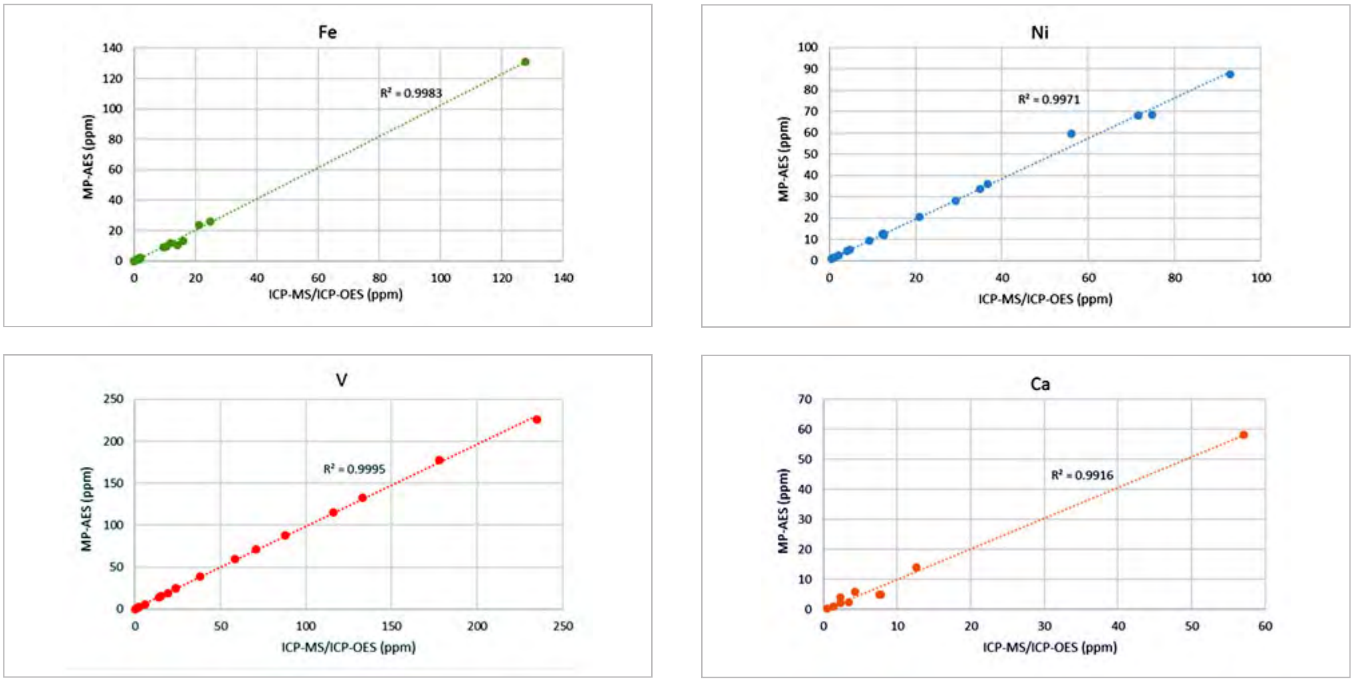


Figure 2. Comparison of measured values for Ni, V, Fe and Ca in crude oil samples obtained using a combination of ICP-MS & ICP-OES and MP-AES, including correlation coefficients.

Conclusions

The Agilent 4200 MP-AES fitted with the EGCM accessory was used successfully for the analysis of 20 crude oil samples following a simple 10x dilution in *o*-xylene, comparatively to preparation methods and procedures as defined in ASTM D7691.

Excellent detection limits and spike recoveries were achieved for Ni, V, Fe, Ca, Na and K in this difficult matrix.

The recoveries obtained from the analysis of the three QC test materials were within ±10% of the actual/certified values. A wide-API range of crude oil samples was evaluated and the MP-AES results compared well with measured values obtained by ICP-OES or ICP-MS.

The 4200's use of a nitrogen-based plasma eliminates the need for hazardous gases such as acetylene, ensuring a significant reduction in running costs associated with ongoing gas supply and greatly improving laboratory safety for unattended operation.

Productivity is further improved with the new generation of MP Expert software that facilitates simultaneous auto background correction and a series of ease-of-use features, including application-specific software applets plus plug-and-play hardware, that simplify method development and torch alignment, with minimal training.

Reference

J. Nelson, G. Gilleland, L. Poirier, D. Leong, P. Hajdu,and F. Lopez-Linares, Elemental Analysis of Crude Oils Using Microwave Plasma Atomic Emission Spectroscopy, *Energy & Fuels,* 2015, 29 (9), 5587–5594.

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

Published September 1 2016
Publication number: 5991-7104EN

Agilent Technologies