Application Note
Energy and Chemicals

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ASTM D8322: Elemental Analysis of Crude Oil and Residual Fuels using MP-AES

Simple, streamlined, and safe analysis of petrochemical samples using an Agilent 4210 MP-AES

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Introduction

Trace elements can adversely affect both the refinery of petroleum into different products and the quality and value of those products (*1*). The most common problematic elements are Fe, V, and Ni but other elements such as Zn, Si, Al, Ca, Na, and K are also often present, typically at lower concentrations. Fe, Ni, and V and other trace elements (including Si, Al, K, and Zn) can poison catalysts in the refinery process or contribute to atmospheric emissions during the combustion of fuels. Monitoring Na and Ca in crude and residual fuel oils is important to ensure that efficient desalting of crude can be performed before distillation.

ASTM test method D8322-20 covers the determination of V, Ni, Ca, Na, Al, Si, Zn, and S in residual fuels and Fe, V, Ni, Ca, Na, K, and S in crude oils using MP-AES (*2*). Measuring the same elements previously required multiple ASTM methods and multiple techniques such as ICP-OES, flame AAS (FAAS), and X-ray spectrometry (*3*). D8322 streamlines the analysis using a single technique and extends the scope and elemental range of test methods D5708 and D5863 (*4, 5*), improving productivity. It uses simple 'dilute and shoot' method compared with other ASTM or Energy Institute IP test methods that use labor-intensive sample preparation such as ashing and fusion. Dilute and shoot reduces costs and improves productivity, as it requires less equipment, fewer reagents, and is easier and faster to do. It also reduces sources of error associated with sample ashing and fusion, improving the accuracy of the data.

Agilent MP-AES instruments use a nitrogen-based plasma as an atomization source rather than argon or acetylene required by ICP-OES and FAAS, respectively. The N_2 can be produced from air by an Agilent 4107 nitrogen generator, significantly reducing the costs and time associated with the supply and handling of gas bottles. MP-AES is often preferred over FAAS where lab-safety is important because it does not require flammable gases and can be used without close supervision, including for overnight runs. MP-AES with a N_2 generator can also be used in the field or remote areas where the petroleum industry operates.

The Agilent 4210 MP-AES is fully controlled using MP Expert software that guides operators through typical workflows using application-specific preset methods. The instruments are quick to startup, and the plug-and-play torch ensures reproducible performance, even between different operators. The instrument also includes diagnostic software so that analysts can check for any problems quickly, maximizing instrument uptime.

In this study, we report the average results obtained by three Agilent laboratories for the analysis of crude and residual fuel oil samples measured in accordance with the ASTM D8322-20 method.

Experimental

Instrumentation

All measurements were performed using three Agilent 4210 MP-AES instruments in three different laboratories. Depending on each lab's set up, the N_2 was supplied from an Agilent 4107 Nitrogen Generator, an in-house gas supply, or a combination of the two. Each MP-AES instrument was set up with an organics kit comprising an External Gas Control Module (EGCM), inert OneNeb Series 2 nebulizer, and a double-pass glass cyclonic spray chamber. The OneNeb nebulizer offers increased nebulization efficiency and a narrow distribution of small droplets. This performance allows the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, while maintaining excellent sensitivity. The EGCM injects air into the plasma preventing the build-up of carbon in the torch. The samples were introduced to the MP-AES using an Agilent SPS 4 autosampler. Instrument operating conditions are given in Table 1.

Table 1. MP-AES operating conditions.

Parameter	Setting
Read Time (s)	3 (10 for Sulfur)
Number of Replicate	3
Sample Uptake Delay (s)	60
Stabilization (s)	30
Rinse Time (s)	Approximately 60 s (depends on lab)
Pump Speed (rpm)	5
Sample Pump Tubing	*Orange/green (0.38 mm ID)
Internal Standard Tubing	*Orange/green (0.38 mm ID)
Waste Pump Tubing	*Blue/blue (1.65 mm ID)
Internal Standard	Yttrium
Background Correction	Auto
Air Injection Required	Yes

**Solvent-resistant tubing made from a fluoropolymer elastomer and synthetic rubber compound.*

ASTM D8322 method

Each laboratory used an MP Expert software method for ASTM D8322 that was provided by the authors. An MP Applet for the ASTM D8322 can be created within the MP Expert software, as shown in Figure 1. MP Expert Applet is a browser-based software interface that is suitable for routine operation of the 4210 MP-AES by users of all skill levels (*6*).

Figure 1. Applets created in MP Expert software.

Once an Applet has been created, it simplifies method setup by loading predefined analytical parameters such as analytes, wavelengths, background correction technique, and EGCM mode. It also ensures that operating conditions are quick to apply and are consistent from analyst-to-analyst. To ensure the accuracy and precision of the analysis of residual fuels and crude oils, the setting of the analyte nebulizer flow rate and EGCM are critical. Auto background correction was used for the application to resolve the element emission line from the organic matrix. The acquisition parameters used for the ASTM D8322 method are given in Table 2.

Table 2. MP-AES method acquisition parameters for the ASTM D8322 method.

Element	Wavelength (nm)	Nebulizer Flow Rate (L/min)	EGCM Air Injection Flow Rate	Background Correction
Iron	259.940	0.5	Medium	Auto
Vanadium	311.070	0.5	High	Auto
Nickel	341.476	0.5	High	Auto
Calcium	396.847	0.5	High	Auto
Sodium	588.995	0.5	High	Auto
Aluminum	396.152	0.5	High	Auto
Silicon	288.158	0.5	Medium	Auto
Zinc	213.857	0.5	Medium	Auto
Potassium	766.491	0.5	High	Auto
Sulfur	181.972	0.5	Low	Auto
Yttrium*	371.029	0.5	Medium	Auto

** Internal standard*

Reference materials and samples

Four National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) standard reference materials (SRMs) and two third-party RMs (Analytical Services, Inc., ASI, Houston, Texas, USA) were used to verify the method. NIST 1634c Trace Elements in Crude Oil and the third-party crude oil RM were used to validate the method for Ni, S, V, Ca, Na, K, and Fe in crude oil. NIST 2721 Crude Oil (Light-sour) and NIST 2722 (Heavy-sweet) were used to validate the method for S in crude oil. NIST 1619b Sulfur in Residual Fuel Oil and the third-party fuel oil RM were used to validate the method for Ni, S, V, Ca, Na, Fe, Zn, Si, and Al in fuel oil.

Fuel and crude oil samples were collected by ASI from various large oil companies that were participating in the ASTM interlaboratory study (ILS).

Standards and sample preparation

All calibration standards were prepared from Agilent A21+K multi-element organometallic standard. Working standards for V, Ni, Ca, Na, Al, Si, Zn, S, Fe, and K were prepared with final mass fractions of 0.1, 1.0, 10.0, 25.0, 50.0 and, 70 mg/kg. Working standards for sulfur were prepared at 40.0, 200.0, 500.0, 1000.0, and 2000.0 mg/kg from an Agilent single element standard.

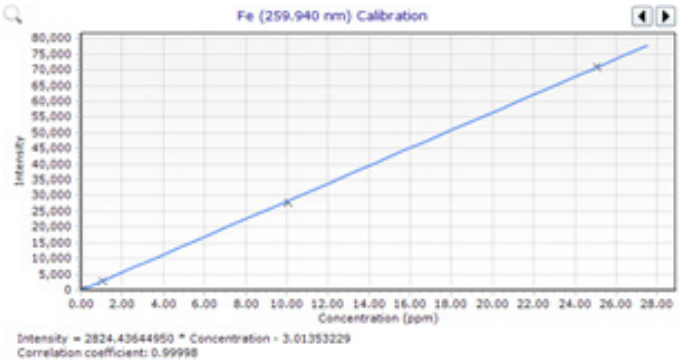
A blank calibration standard was used as the initial and continuing calibration blank (ICB and CCB). A 10 mg/kg multi-element standard was used as a Continuing Calibration Verification (CCV) solution for all elements except S, which was prepared at 1000 mg/kg. Yttrium, which was used as an internal standard (IS) at 20 mg/kg, was added to the sample line before the nebulizer using a mixing tee-connector. Standards, blanks, spikes, QCs, and IS were matrix matched to a constant viscosity with mineral oil (or 75 cts oil) and diluted with *o*-xylene to give a total oil concentration of 10% (w/w) in each solution.

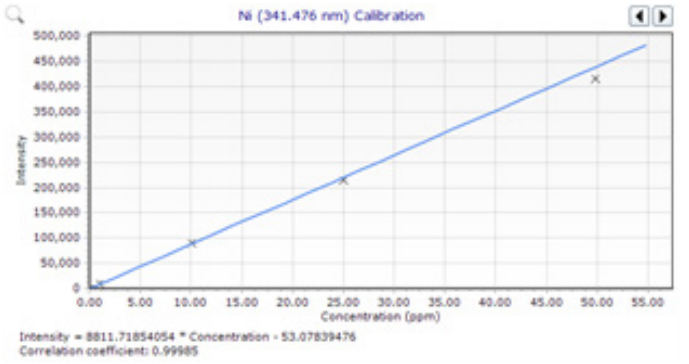
The residual fuel and crude oils covering a wide range of API gravity and density were analyzed in this study. The samples were prepared according to the ASTM D8322 method. The samples were all diluted from 1:10 up to 1:20 in *o*-xylene by weight. The more viscous samples that did not readily flow at room temperature were heated in a hot block at 60 °C and shaken before being weighed and diluted with *o*-xylene. ASI also prepared all the solutions used for the spike recovery test at the concentrations given in Table 4.

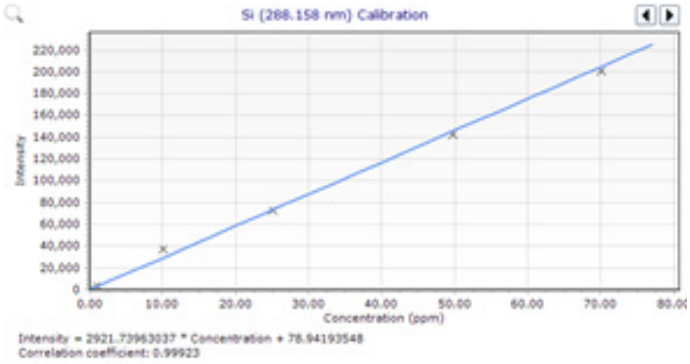
Results and discussion

Calibration

Figure 2 shows representative calibration curves for Fe, Ni, Si, and V obtained from the analysis of the standard solutions under optimized conditions. Linear calibration curves were obtained for all elements.







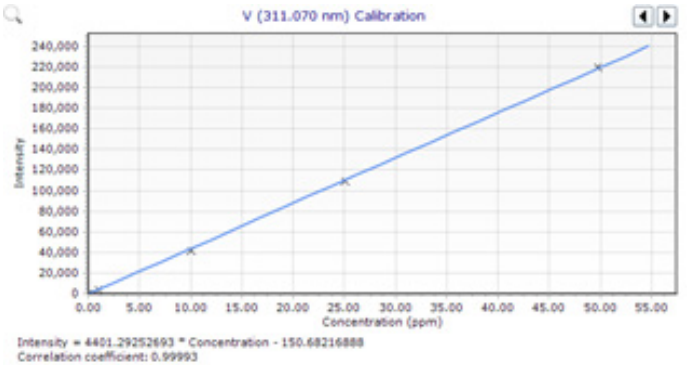


Figure 2. Calibration curves for Fe, Ni, Si, and V.

Quality control

To check the ongoing validity of the calibration during the analysis of crude and residual fuel oil samples over four days, three CCV standards were analyzed after every 10 samples. In accordance with the ASTM ILS guidance, the MP-AES was calibrated at the beginning of every day. The QC stability plot in Figure 3 shows the recovery of all elements to be within ±20%. The results demonstrate the excellent robustness, stability, and precision of the 4210 MP-AES over four days. ASTM D8322 does not specify acceptance criteria for the recovery of elements in the QC samples, allowing labs to set their own limits.

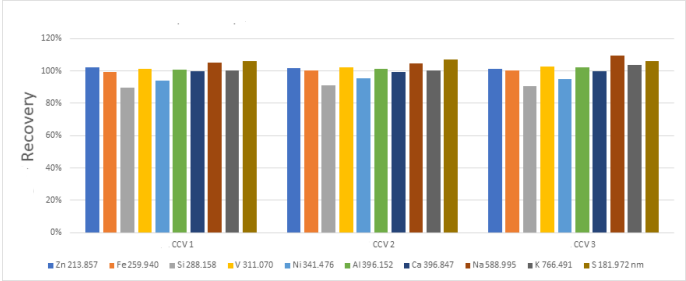


Figure 3. Recovery data for three QC samples measured every 10 samples for approximately four hours.

Recoveries of certified elements in crude oil and fuel RMs

Fe, V, and Ni are important elements in the assay of crude oil as they are usually present at the highest concentrations, and they can adversely affect catalytic cracking, product yields, and product quality/value. Ni, S, V, Ca, Na, K, and Fe were measured in the crude oil RMs and Ni, S, V, Ca, Na, Fe, Zn, Si, and Al were measured in a fuel oil RM in each lab over four days. The results in Table 3 show excellent recoveries within ±10% of the certified values or information values for all elements, apart from Ca in the fuel oil RM. Ca was within ±20% of the reproducibility test described in the ASTM D8322. The data demonstrates the accuracy, reproducibility, and reliability of the method.

Table 3. Average recoveries for results from three Agilent laboratories of multiple elements in NIST SRM, a crude oil RM, and a residual fuel oil RM. All recoveries are within the reproducibility test criteria described in ASTM D8322.

Crude Oil						
	NIST 1634c			Third-Party Crude Oil RM		
Element and Wavelength (nm)	Measured Value (mg/kg)	Certified Value (mg/kg)	Recovery (%)	Measured Value (mg/kg)	Certified Value (mg/kg)	Recovery (%)
Ni 341.476	17.25±1.7	17.54	98	5.05±0.5	5.00	101
S 181.972	20159±6250	20000[IV]	101	1038±139	1000	104
V 311.837	28.57±0.1	28.19	101	5.33±0.5	5.00	107
Ca 396.152				48.9±4.3	50.00	98
Na 588.995				49.6±8.3	50.00	99
K 766.491				45.8±1.0	50.00	92
Fe 259.940				23.62±1.1	25.00	94
	NIST 2721 Crude Oil (Light-Sour)			NIST 2722 (Heavy-Sweet)		
S 181.972	17101±556	15832	108	2015 ± 276	2103.70	96
Residual Oil						
	Third-Party Fuel Oil RM			NIST 1619b		
Element and Wavelength (nm)	Measured Value (mg/kg)	Certified Value (mg/kg)	Recovery (%)	Measured Value (mg/kg)	Certified Value (mg/kg)	Recovery (%)
Ni 341.476	10.66±1.1	10.00	107			
S 181.972	4940±631.9	5000	99	7427±1641	6960.0	107
V 311.837	10.31±1.7	10.00	103			
Ca 396.152	23.51±0.2	20.00	118			
Na 588.995	10.55±1.1	10.00	106			
Fe 259.940	6.26±0.2	6.00	104			
Zn 213.618	20.93±2.1	20.00	105			
Si 288.158	20.02±3.4	20.00	100			
Al 396.152	20.22±0.1	20.00	101			
IV=Information value						

Spike recovery test

The average of the spike recovery results for multiple elements in four crude oil and five residual fuel samples obtained by the three labs are shown in Table 4. All recoveries were all within ±20% of the reproducibility test described in ASTM D8322. The recovery data demonstrates the accuracy of the method for the analysis of Fe, V, Ca, Na, K, and S in crude oils and V, Ni, Ca, Na, Al, Si, Zn, and S in residual fuels by MP-AES.

Table 4. Average spike recovery results for duplicate measurements of elements in crude oil and in residual fuel samples measured using MP-AES in three labs over four days, n=6.

Crude Oil									
	Spiked Sample-D			Spiked Sample-K			Spiked Sample-N		
Element and Wave-length (nm)	Measured Value (mg/kg)	Spiked Value (mg/kg)	Recovery (%)	Measured Value (mg/kg)	Spiked Value (mg/kg)	Recovery (%)	Measured Value (mg/kg)	Spiked Value (mg/kg)	Recovery (%)
S 181.972	20997±1303	20000	105	2236±308.9	2610.0	86			
V 311.837				3.27±0.2	3.67	89			
Ca 396.152							3.83±2.0	3.50	110
Na 588.995							100.9±13.8	100.0	101
K 766.491	11.73±0.8	12.00	98	24.51±4.2	25.00	98	64.71±8.9	70.00	92
Fe 259.940							138.1±8.6	150.0	92
Residual Oil									
	Spiked Sample-D			Spiked Sample-H			Spiked Sample-L		
Ni 341.476	0.48±0.0	0.40	119	51.12±1.6	50.00	102	70.65±4.1	70.00	101
S 181.972							12627±1690	12000	105
V 311.837	29.23±4.1	30.00	97	247.13±7.6	250.0	99	376.4±3.8	400.0	94
Ca 396.152	66.45±2.3	70.00	95				93.99±8.1	100.0	94
Na 588.995				75.21±1.7	70.82	106	45.56±1.1	40.00	114
Zn 213.618	1.98±0.2	2.00	99				102.2±1.6	100.0	102
Si 288.158	49.04±2.5	45.00	109	156.3±19.7	158.9	98	243.9±19.2	250.0	98
Al 396.152	3.71±0.0	3.30	113	94.12±2.8	90.00	105	148.5±5.2	150.0	99

Quantitative results

Quantitative results for various elements in crude oil and residual fuel samples measured over four days by MP-AES are shown in Tables 5 and 6 respectively. All measured values have been corrected for the wt/wt dilution factors to obtain the concentration in the original sample. The results show some variation in concentration for each element between the different samples. The greatest difference was for V, which ranged from 1 to over 360 ppm in both the crude oil and residual oil samples.

Table 5. Average quantitative results for six elements in crude oil samples measured using MP-AES in three labs in duplicate over four days. All data mg/kg.

Crude Oil	API	Fe	V	Ni	Ca	Na	S	K
Sample A	21	2.08	283.0	58.89	ND	ND	37858	3.38
Sample B	40.2	0.95	1.59	0.81	ND	0.65	1893	1.18
Sample C	50.4	0.98	0.71	ND	ND	1.07	1198	1.45
Sample D	41.6	31.77	0.92	0.54	2.81	17.21	1479	2.27
Sample E	44.6	4.00	2.09	0.82	1.33	2.40	2132	1.69
Sample F	27.8	26.67	102.3	21.81	12.43	90.79	22277	6.20
Sample G	21	12.12	303.8	56.77	4.21	3.42	29648	6.97
Sample H	40.2	67.41	34.48	10.35	103.5	6.46	1628	7.91
Sample I	50.4	6.83	7.59	99.84	64.77	11.82	991.7	21.73
Sample J	41.6	4.28	0.28	1.00	29.77	61.93	1310.6	34.25
Sample K	44.6	173.5	383.5	1.87	ND	3.09	1686	3.65
Sample L	30	23.14	4.74	5.05	48.92	53.89	1038	45.81
Sample M	Unknown	26.55	20.89	17.73	8.85	29.45	24145	5.98
Sample N	27.8	2.42	118.9	31.20	ND	0.40	27779	1.60

ND = below valid test range.

Table 6. Average quantitative results for nine elements in residual fuel samples measured using MP-AES by three labs in duplicate over four days. All data reported as mg/kg.

Fuel Oil	Fe	V	Ni	Ca	Na	Al	Si	Zn	S
Sample A	2.69	4.81	1.41	0.64	0.81	2.65	3.00	ND	5574
Sample B	1.95	1.74	0.49	0.75	0.87	ND	5.14	4.05	10420
Sample C	3.63	17.87	5.41	0.86	1.23	9.02	5.97	0.11	7142
Sample D	2.11	ND	ND	ND	4.17	ND	ND	0.18	3121
Sample E	2.95	ND	0.27	1.46	11.71	1.37	2.35	ND	3359
Sample F	6.84	11.28	11.73	23.54	10.55	14.69	15.70	20.93	4940
Sample G	1.52	364.9	104.9	95.04	98.39	120.0	211.6	106.9	2002
Sample H	2.33	ND	2.78	50.59	74.56	50.81	153.3	72.68	1878
Sample I	2.20	ND	1.11	3.32	5.84	47.55	99.45	10.57	1243
Sample J	1.63	6.03	0.97	12.28	6.90	2.89	6.58	1.08	2377
Sample K	7.25	159.5	44.03	1.68	7.61	9.92	19.87	ND	33222

ND = below valid test range.

Conclusion

The publication of the first ASTM D8322-20 method for MP-AES provides the petroleum industry with a viable technique for the direct analysis of complex samples. D8322-20 relates to the quantification of V, Ni, Ca, Na, Al, Si, Zn, and S in residual fuels and Fe, V, Ni, Ca, Na, K, and S in crude oils following dilution in *o*-xylene. Previously, measuring these elements required using multiple ASTM methods and multiple techniques. D8322 streamlines the analysis using a single technique and simplifies sample preparation, ensuring greater productivity and more accurate results.

Excellent accuracy was demonstrated with good recoveries for certified elements in various crude and fuel reference materials, and good spike recoveries of actual samples. A QC stability test over four days showed the excellent robustness, stability, and precision of the 4210 MP-AES, with no need to recalibrate.

The simplicity, accuracy, and reproducibility of the method, plus the low running costs and safety of MP-AES make it suitable for routine use in the petroleum industry.

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