Application Brief

Energy and Chemicals

Agilent

Trusted Answers

Analysis of Elements in Residual Fuels and Crude Oil by MP-AES

Simple sample preparation and streamlined analysis as per ASTM method D8322

The first ASTM accredited standard method for MP-AES

ASTM International develops and publishes standard test methods to ensure the quality and safety of products for consumers. In 2020, ASTM released method D8322-20 for 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 (*1*). Previously, measuring these elements required using multiple ASTM methods and multiple techniques such as ICP-OES, flame AAS (FAAS), and X-ray spectrometry (*2*). D8322 now streamlines the analysis using a single technique and simplifies sample preparation. It also extends the scope of test method D5708, which only applies to the determination of three elements, Ni, V, and Fe, in crude oils and residual fuels using ICP-OES.

Lower cost of ownership and improved safety

Trace element analysis is important in the petroleum industry, as some elements such as Fe, V, and Ni can adversely affect catalytic cracking, product yields, and product quality/value. A key advantage of MP-AES for petrochemical labs is its nitrogen-based plasma. The N_2 can be generated from air in the lab using an Agilent 4107 nitrogen generator. The local generation of the gas supply means that the operating costs of MP-AES are low, compared to the on-going supply costs of argon for ICP-OES or acetylene for FAAS. MP-AES is preferred over FAAS in many labs because it does not use flammable gases, improving safety and enabling unattended operation.

Developing a robust method for crude and fuel oils

Agilent developed the MP-AES method for the determination of multiple elements in different types of residual fuel and crude oil samples following simple dilution in *o*-xylene. The method's simple organic “dilute and shoot” sample preparation also makes it simpler than other ASTM or Energy Institute IP test methods. For example, ASTM D5184 and IP 501 require labor-intensive sample preparation such as sample ashing and fusion. The method was fully evaluated by ASTM in an interlaboratory study involving 12 laboratories before its approval.

The Agilent 4210 MP-AES instrument was equipped 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 EGCM injects air into the plasma preventing the build-up of carbon in the torch. An MP Applet for the ASTM D8322 can be created within the MP Expert software. The Applet simplifies method set up by predefining analytical parameters such as analytes, wavelengths, background correction technique and EGCM mode. It also ensures that operating conditions are quick to apply and consistent from analyst-to-analyst.

SRM and RM recoveries

Three NIST standard reference materials (SRMs) and two third-party reference materials (RMs) (Analytical Services, Inc., Texas, USA) were used to verify the method. All recoveries were within the reproducibility test described in ASTM D8332. The results demonstrate the accuracy of the ASTM D8322-20 method for MP-AES.

Repeatability of measurements

To check the ongoing validity of the calibration during the analysis of crude and residual fuel oil samples over an extended period, three CCV standards were analyzed after every 10 samples. The QC stability plot in Figure 1 shows the recovery of all elements to be within ±10% over approximately four hours. The results demonstrate the excellent robustness, stability, and precision of the 4210 MP-AES.

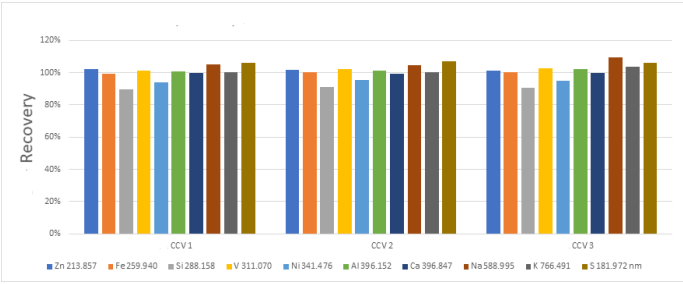

Figure 1. Recovery data for three QC samples measured every 10 samples for approximately four hours.

Table 1. Average recoveries of duplicate measurements done by three Agilent laboratories of multiple elements in NIST SRMs, a crude oil RM, a residual fuel oil RM. All recoveries were within the reproducibility test described in ASTM D8332.

	NIST1634c Trace Elements in Crude Oil		Third Party Crude Oil RM	
Element, Wavelength (nm)	Measured Value (mg/kg)	Recovery (%)	Measured Value (mg/kg)	Recovery (%)
Ni 341.476	17.25±1.7	98	5.05±0.5	101
S 181.972	20159±6250	101	1038±139	104
V 311.837	28.57±0.1	101	5.33±0.5	107
Ca 396.152			48.9±4.3	98
Na 588.995			49.6±8.3	99
K 766.491			45.8±1.0	92
Fe 259.940			23.6±1.1	94
	NIST 2721 Crude Oil (Light-sour)		NIST 2722 Crude Oil (Heavy-sweet)	
S 181.972	17101±556	108	2014±276	96
	Third Party Fuel Oil RM		NIST 1619b in Fuel oil	
Ni 341.476	10.66±1.1	107		
S 181.972	4940±639	99	7427±1641	107
V 311.837	10.31±1.7	103		
Ca 396.152	23.5±0.2	118		
Na 588.995	10.55±1.1	106		
Fe 259.940	6.26±0.2	104		
Zn 213.618	20.93±2.1	105		
Si 288.158	20.02±3.4	100		
Al 396.152	20.22±0.1	101		

References

1. Agilent ASTM D8322-20 https://www.astm.org/Standards/D8322.htm
2. Measuring Elements in Residual Fuels and Crude Oil per Method ASTM D8322, Agilent publication, 5994-2460EN
3. Agilent MP Expert software, Agilent publication 5990-8975EN

www.agilent.com/chem/4210mp-aes

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