MICAP-OES 1000

Analysis of trace elements in diesel fuel with a N_2 ICP-OES system

Introduction

Diesel is fuel source that is commonly used in many transportation applications. It is most commonly a product of petroleum distillation, but numerous regions utilize fuel with blended addition from biodiesel sources. To ensure the quality of the fuel, there are numerous standardized tests performed. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) has been used recently to monitor trace elemental content of diesel and other fuels.

This note describes the use of the simultaneous MICAP OES-1000 N_2 ICP-OES system for routine analysis of diesel fuel following the procedures outlined in ASTM Method D5708, which is designed for analysis of both oils and fuels by ICP-OES. Analytical performance of the MICAP is presented to demonstrate accurate and stable performance during the analysis of diesel fuel samples.

Instrumentation

The ASTM standard test method D5708[1] includes two sample handling procedures: solvent-dilution and acid decomposition. In this work the solvent-dilution procedure (Test Method A) will be utilized. This requires the Radom Instruments MICAP-OES 1000 to be configured with an organic solvent introduction system. A double-pass cyclonic spray chamber and high-solids V-Groove nebulizer were connected to the standard one-piece torch for introduction of samples into the N_2 plasma.

Microwave energy in the MICAP is coupled into the Cerawave™ ring in a highly efficient process that creates the magnetic fields required to inductively couple energy into the robust N_2 plasma emission source. The 4 MP sCMOS camera simultaneously collects the emission lines from the high-resolution spectrometer.

Experimental Conditions

The analyses were performed on the simultaneous MICAP (Figure 1 utilizing the conditions listed in Table 1. Samples were introduced with an autosampler, with each analysis taking just under 2 minutes/sample.

The ICP-OES analysis conditions employed on the MICAP follow closely the procedures outlined in ASTM Method D5708[1] Determination of Ni, V, and Fe in Crude Oils and Residual Fuels, as well as several other ASTM Standard Methods.[2] Table 2 provides specifics on the analyte and internal standard Cobalt (Co) wavelengths used for this analysis.

Figure 1. MICAP-OES 1000 N_2 ICP-OES

Table 1. MICAP operational conditions

Parameter	Value
Torch	Quartz 1-piece, 1.5mm injector
Spray Chamber	Double pass cyclonic
Nebulizer	V-Groove glass
Sample Tubing	Solvaflex Blk/Blk (0.76 mm ID)
Drain Tubing	Solvaflex Blu/Yel (1.52 mm ID)
Rinse	PremiSolv™
Coolant Gas Flow	14 L/min
Auxiliary Gas Flow	0.4 L/min
Nebulizer Gas Flow	0.3 L/min
Peristaltic Pump	75 rpm
Plasma Viewing	Axial
Camera Exposure	4.5 sec (50 ms @ 90 reps)
# of Repeats	3

Table 2. Analyte and internal standard wavelengths

Analyte Wavelength (nm)	Internal Standard Wavelength (nm)
Ag 328.068	Co I 240.725
Al 396.152	
B 249.677	
Ba 585.368	Co II 238.892
Ca 422.673	Co I 240.725
Cd 266.501	Co II 238.892
Cr 428.973	Co I 240.725
Cu 324.754	
Fe 259.940	Co II 238.892
K 766.490	Co I 240.725
Mg 280.270	Co II 238.892
Mn 257.610	
Mo 281.615	
Na588.995	Co I 240.725
Ni 300.249	
P 213.618	
Pb 238.305	
Si 251.611	
Sn 283.998	
Tl 323.451	Co II 238.892
V 309.310	Co I 240.725
Zn 213.857	Co II 238.892

Table 3. Analytes and standard concentrations, in mg/Kg (ppm)

Analyte Wavelength (nm)	Low Std (mg/Kg)	High Std (mg/Kg)	QC Std (mg/Kg)
Ag 328.068	0.1	20	10
Al 396.152	1	20	10
B 249.677	1	50	10
Ba 585.368	1	50	10
Ca 422.673	1	50	10
Cd 226.501	1	50	10
Cr 428.973	1	50	10
Cu 324.754	0.1	50	10
Fe 259.940	1	50	10
K 766.490	5	20	10
Mg 280.270	0.1	20	10

Analyte Wavelength (nm)	Low Std (mg/Kg)	High Std (mg/Kg)	QC Std (mg/Kg)
Mn 257.610	0.1	20	10
Mo 281.615	1	50	10
Na 588.995	0.1	20	10
Ni 300.249	1	50	10
P 213.618	5	50	10
Pb 283.305	5	50	10
Si 251.611	0.1	50	10
Sn 283.998	1	50	10
Ti 323.451	0.1	50	10
V 309.310	1	20	10
Zn 213.857	0.1	10	10

Standard and Sample Preparation

The calibration standards, blanks, and samples were prepared in accordance with the protocols outlined in ASTM Method D5708[1]. Working standards were prepared by diluting oil-based stock standards (VHG, LGC Standards, Manchester, NH, USA) while maintaining the oil level with a Base Oil. Blanks and QC samples were prepared in the same manner.

All standards and samples were diluted in PremiSolv™ (Conostan, AnalytiChem, Bale-D'Urfe, QC, Canada) prepared by weight, with the Cobalt (Co) internal standard also included at this time. A quality control sample (Conostan) was also analyzed to provide an external check for calibration accuracy. Table 3 provides the concentration levels of the standards and QC sample. The diesel fuel samples were sourced from a local supplier then diluted 1:10 (w/w).

Results

The MICAP was calibrated as described above and all wavelengths were viewed in Radom Instruments Software (RIS) Profiles View to ensure no spectral interferences and to set peak integration points. Figure 2 provides example peaks for elements Ni, V, & Fe.

A detection limit study was performed by analyzing ten blanks and detection limits (DL) were calculated by multiplying the standard deviation by 3. The DL values obtained are shown in Table 4. These values are presented on the basis of the actual diesel samples (reflecting the 10x dilution). The diesel fuel results, analytical spikes (at 10 mg/Kg), and external QC Check Std (10 mg/Kg) obtained are also provided in Table 4. Quality controls analyzed at the beginning and end of the analysis (10 mg/Kg) all recovered within ± 5%.

Conclusions

The MICAP-OES 1000 N_2 ICP-OES demonstrated its capability for the analysis of diesel fuels in accordance with ASTM Standard Method D5708. No carbon deposition from the samples was observed on the MICAP torch throughout this application work. The excellent accuracy and stability shown confirms its capability for this challenging sample matrix.

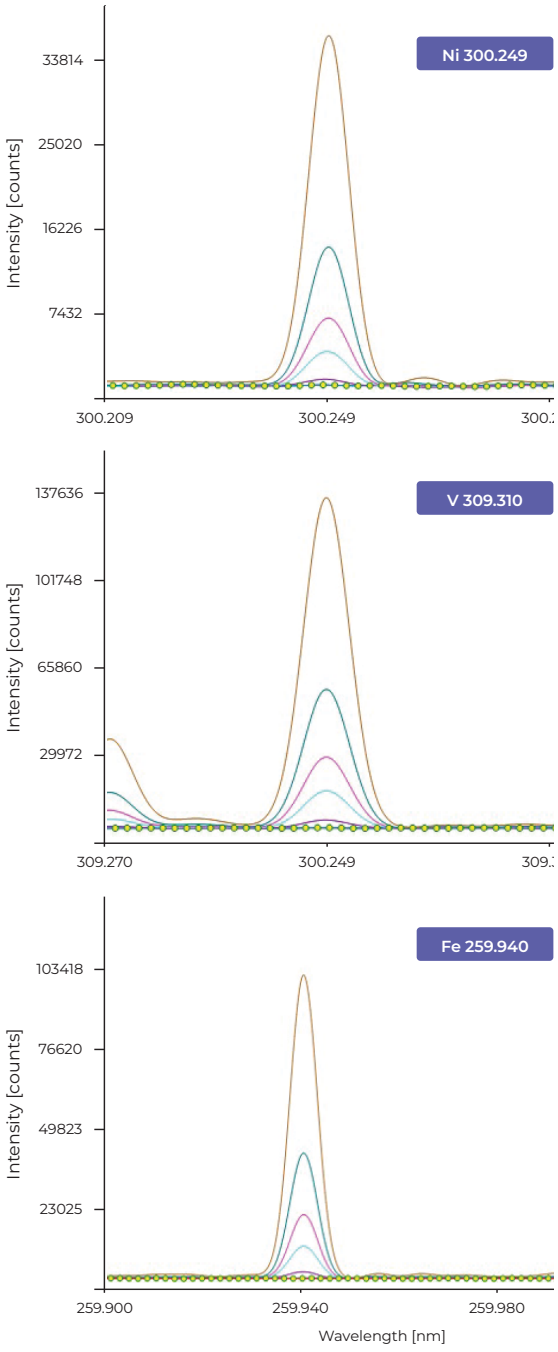

Figure 2. Example analyte peaks for Ni, V, and Fe

Table 4. Diesel Fuel Analysis Results

Analyte Wavelength (nm)	DL in Fuel (mg/Kg)	External QC Std (% Rec)	Fuel 1 (mg/Kg)	Fuel 1 Spike (% Rec)	Fuel 2 (mg/Kg)	Fuel 2 Spike (% Rec)
Ag 328.068	0.20	102	0.11	100	0.10	100
Al 396.152	1.18	101	0.22	96	0.27	98
B 249.677	1.20	105	0.46	98	0.50	102
Ba 585.368	1.76	98	-0.12	95	-0.02	96
Ca 422.673	0.85	103	0.07	103	-0.02	104
Cd 226.501	1.33	105	0.01	101	0.03	104
Cr 428.973	0.51	101	0.12	101	0.10	101
Cu 324.754	0.09	101	0.12	101	0.10	101
Fe 259.940	0.50	100	0.08	99	0.08	99
K 766.490	5.68	106	1.06	93	1.12	97
Mg 280.270	0.07	98	0.12	99	0.09	99
Mn 257.610	0.08	95	0.11	99	0.08	99
Mo 281.615	1.14	99	0.03	97	0.16	98
Na 588.995	0.20	107	0.09	104	0.07	104
Ni 300.249	2.16	98	0.14	99	0.06	99
P 213.618	15.7	102	1.19	98	-0.05	98
Pb 283.305	2.32	102	0.07	99	0.06	100
Si 251.611	0.33	97	0.12	99	0.11	99
Sn 283.998	1.58	101	0.14	102	0.10	100
Ti 323.451	0.09	103	0.13	100	0.10	100
V 309.310	0.34	93	0.09	97	0.06	97
Zn 213.857	0.67	100	0.15	99	0.15	101

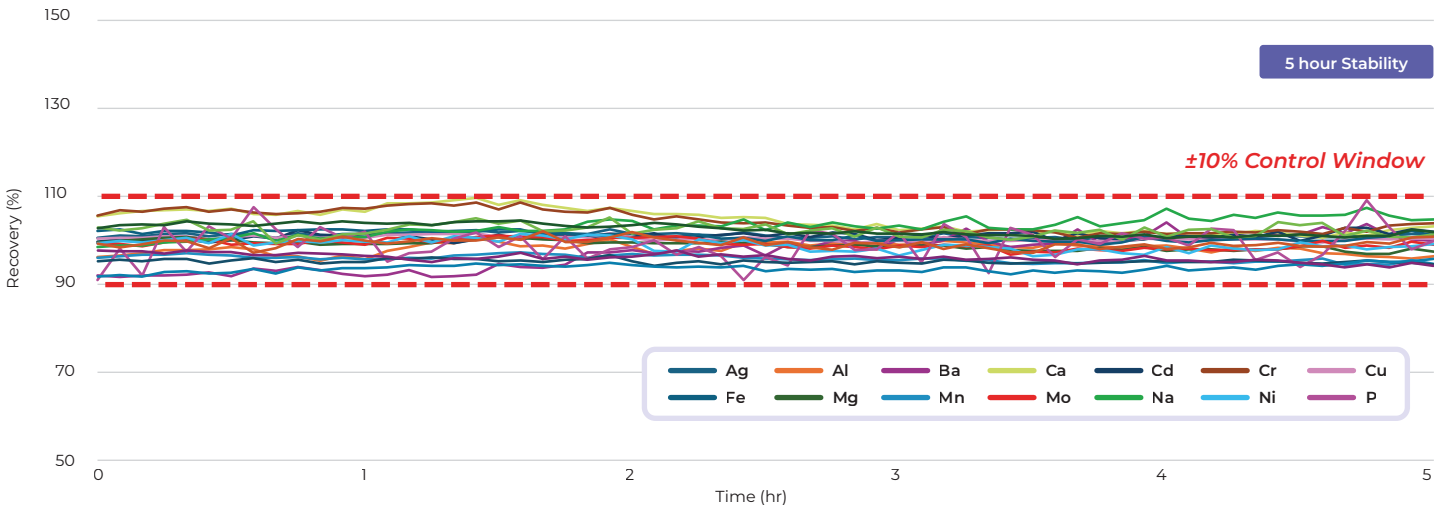

Figure 3. Long term diesel fuel stability. Sample spiked with 10 mg/Kg measured every 5 minutes over 5 hrs. Boron suffered stability issues and Potassium spike level too low, so both were excluded.

References

1. ASTM D5708-15, Standard Test Method for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry, ASTM Intn, West Conshohocken, PA, 2024, www.astm.org

2. ASTM D7111-16, Standard Test Method for Determination of Trace Metals in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), ASTM Intn, West Conshohocken, PA, 2024, www.astm.org

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