MICAP-OES 1000

Direct analysis of trace elements in Middle Distillate Fuels with a compact N_2 ICP-OES system

Introduction

Middle distillates are a category of fuels produced from the distillation of crude oil. This includes products commonly referred to as diesel, marine diesel oil, kerosene and jet fuel. These colorless to light yellow fuels each differs slightly in their components based on the application. Elemental impurities present can impact critical properties such as combustion, corrosion, shelf life, and production of engine deposits. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is commonly utilized to monitor the trace elemental content of these various fuels.

This note describes the use of the simultaneous MICAP™ OES-1000 N_2 ICP-OES system for routine analysis of middle distillate fuels following the procedures outlined in ASTM Method D7111. Analytical performance of the MICAP is presented to demonstrate accurate and stable performance during the direct analysis of several fuel samples.

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Instrumentation

The ASTM standard test method D7111[1] covers the middle distillate products, which includes distillation fractions between 150 and 390 °C. The samples are analyzed directly against organometallic standards prepared in a kerosene solvent matrix. 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 source. The 4 MP sCMOS camera simultaneously collects the resulting 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 sample analysis taking approximately 3.5 minutes to complete.

The MICAP in this work was uniquely configured with air (rather than the standard N_2) as the nebulizer gas. This modification reduces the continuum background created by the combustion of carbon, resulting in significantly improved detection limits for several elements. Table 2 provides specifics on the analyte and Yttrium (Y) internal standard (I/S) wavelengths used for this analysis, as well as the detection limits obtained from 3x the standard deviation of 10 blank measurements.

Figure 1. MICAP-OES 1000 N_2 ICP-OES

Table 1. 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™
Stabilization Time	15 sec
Power	1000 W
Coolant Gas Flow	16 L/min N_2
Auxiliary Gas Flow	0.4 L/min N_2
Nebulizer Gas Flow	0.55 L/min Air
Peristaltic Pump	90 rpm
Plasma Viewing	Axial
Camera Exposure	30 sec (125 ms @ 240 exps)
# of Repeats	3

Table 2. Analyte wavelengths and fuel detection limits

Analyte Wavelength (nm)	Detection Limit (mg/Kg, ppm)
Ag 328.068	0.001
Al 396.152	0.007
B 249.677	0.022
Ba 585.368	0.018
Ca 393.366	0.0007
Cd 228.802	0.007
Cr 428.973	0.003
Cu 324.754	0.0007
Fe 259.940	0.006
K 766.490	0.020
Mg 279.553	0.0003
Mn 257.610	0.002
Mo 317.034	0.007
Na 588.995	0.002
Ni 300.249	0.016
P 213.618	0.380
Pb 283.305	0.035
Si 251.611	0.003
Sn 283.998	0.019
Ti 334.940	0.002
V 309.310	0.007
Zn 213.857	0.004
Y 371.029 (I/S)	-

Standard and Sample Preparation

The calibration standards, blanks, and samples were prepared in accordance with the protocols outlined in ASTM Method D7111. Working standards were prepared by diluting oil-based stock standards (VHG, LGC Standards, Manchester, NH, USA) in PremiSolv™ (Conostan, AnalytiChem, Bale-D'Urfe, QC, Canada) prepared by weight. The Yttrium (Y) internal standard was added at a final concentration of 3 mg/Kg (ppm). A blank and a 2 mg/Kg mixed standard were prepared for all the listed analytes. Additionally, a 5 mg/Kg Phosphorus (P) standard was also prepared to provide a higher P calibration range.

Three middle distillate samples were sourced locally. These included a diesel fuel, an off-road (agricultural) diesel fuel, and Jet A fuel sample. Each of the samples were also prepared with a known spike (1 mg/kg, except P spiked at 2 mg/Kg) to evaluate system performance. The Y internal standard was also added to each of these fuel samples.

Results

The MICAP was calibrated as described above and all wavelengths were viewed in the Radom Instruments Software (RIS) Profiles View to verify no spectral interferences existed and to set peak integration points. The emission lines utilized for quantitation were selected from numerous line options available. The simultaneous, full wavelength range data collection also provided the ability during method development to confirm accurate measurements across multiple emission lines for each analyte element.

Figure 2 provides example emission peaks for the analytes of Mg, Cu, and Ti. Note the clear baseline resolution between the Ti 334.903 and 334.940 nm emission lines, demonstrating the high resolving power of the spectrometer. This capability helps ensure the analyte peaks of interest are not impacted by nearby spectral interferences from other potential trace elemental components.

The middle distillate fuel results and analytical spike results are displayed in Table 3. The three samples show very little elemental contamination is present. The sample spike results show excellent recoveries, with the exception of Boron (B) - for which stability / volatility issues are often quite common.

Internal standard recovery values were consistently within ± 15%, indicating that the system response was very stable between the calibration standards and the samples.

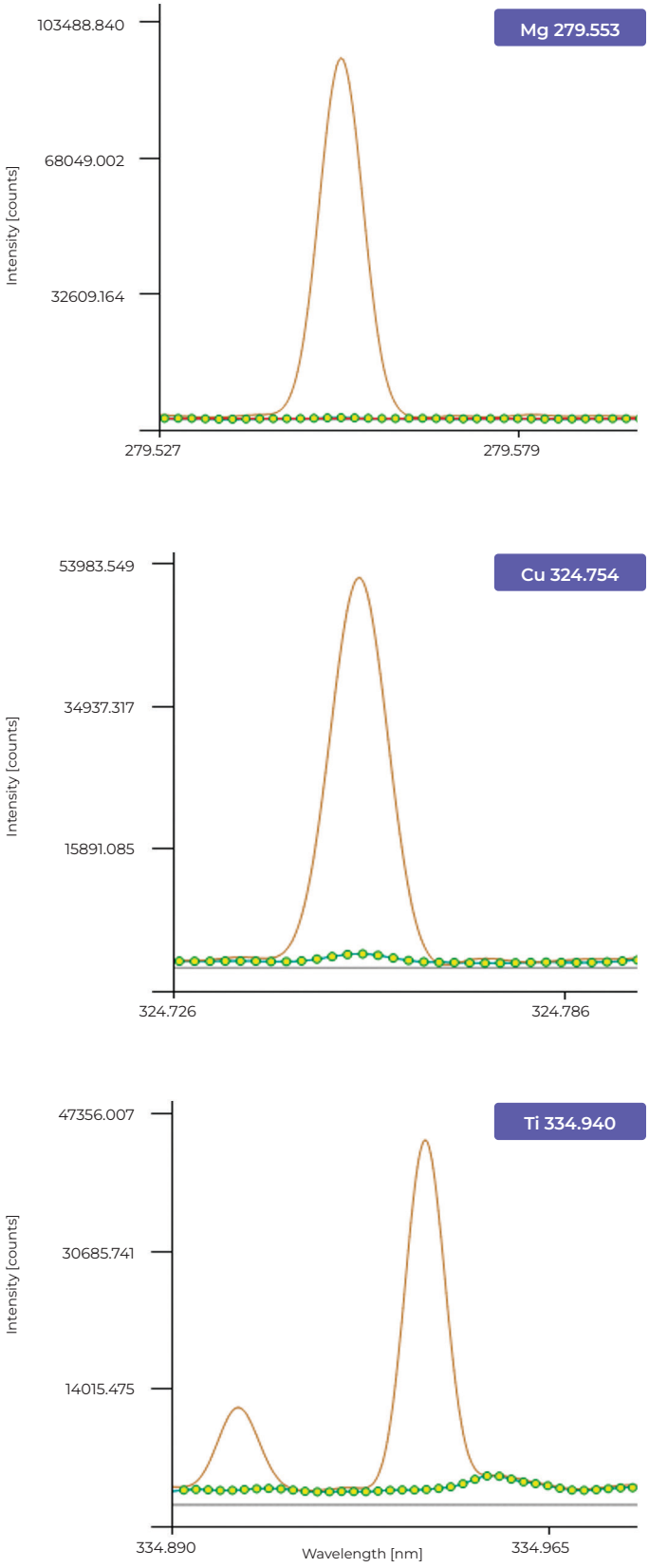

Figure 2. Profiles view of Mg, Cu & Ti emission lines in 1 mg/Kg spiked Jet A fuel. Sample emission lines displayed in brown with blank baseline indicated in green.

Table 3. Middle Distillate Fuel Analysis - sample and spike results (1 mg/Kg, P at 2 mg/Kg)

Analyte Wavelength (nm)	Diesel Fuel		Agricultural Diesel Fuel		Jet A Fuel	
	Conc. (mg/Kg)	Spike Recovery (%)	Conc. (mg/Kg)	Spike Recovery (%)	Conc. (mg/Kg)	Spike Recovery (%)
Ag 328.068	0.038	100	0.010	104	-0.004	97
Al 396.152	0.028	105	0.028	108	-0.041	102
B 249.772*	0.279	72	0.067	101	0.062	84
Ba 585.368	0.119	101	0.078	105	-0.308	102
Ca 393.366	0.006	111	0.008	114	0.015	110
Cd 228.802	0.012	100	0.008	102	-0.021	97
Cr 428.973	0.003	102	0.005	104	0.020	99
Cu 324.754	-0.001	101	-0.001	104	0.000	98
Fe 259.940	0.007	102	0.042	105	-0.004	104
K 766.490	-0.077	88	-0.044	87	0.116	95
Mg 279.553	0.001	102	0.003	104	0.002	103
Mn 257.610	0.011	101	0.010	103	-0.010	103
Mo 317.034	-0.014	102	-0.011	104	0.015	97
Na 588.995	0.018	95	0.012	97	-0.015	95
Ni 300.249	-0.004	106	-0.007	108	0.001	103
P 213.618	-0.076	106	1.646	115	0.123	88
Pb 283.305	0.031	106	0.056	104	0.017	96
Si 251.611	-0.002	100	0.062	99	0.024	97
Sn 283.998	0.021	104	0.027	106	0.008	100
Ti 334.940	-0.010	102	-0.010	104	0.001	104
V 309.310	-0.010	103	-0.007	105	0.017	103
Zn 213.857	0.033	101	0.030	103	0.012	100

** Boron demonstrated carryover at low levels, impacting spike recoveries*

Conclusions

The MICAP-OES 1000 N_2 ICP-OES demonstrated its capability for the direct analysis of middle distillate fuels in accordance with ASTM Standard Method D7111. No carbon deposition from the samples was observed on the MICAP torch throughout this application work, demonstrating a significant impact on productivity as no user maintenance is required to clean the torch and then restart the system. The excellent accuracy and this stability confirms MICAP's capability for routine analysis of these fuel samples.

References

1. ASTM D7111, Standard Test Method for Determination of Trace Elements in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), ASTM Intn, West Conshohocken, PA, 2025, www.astm.org

2. ASTM D5708, 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, 2025, www.astm.org

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