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From Crude to Fuels – Trace Metals Analysis by ICP-OES for ASTM D7691 and D7111

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Introduction

Understanding the metals content of crude oil and refined fuels are critical to assessing their value, determining refining workflows, and ensuring appropriate functionality during combustion. Some metals, like cobalt and vanadium, are naturally-occurring components of crude oil and may need to be removed during the refining process. Other elements, such as phosphorus, manganese, or iron may be added to the fuel to improve its properties. Regardless of their source, assessing a crude oil or a fuel for unwanted or intentionally added elemental constituents is a critical part of a quality control protocol.

To accomplish testing for trace metals in crude oils and fuels derived from them, laboratories typically adhere to standard test methods from organizations such as ASTM or UOP, among others. Here, we present trace metals data acquired using a Shimadzu ICPE-9820 in compliance with ASTM D7111 for middle distillates.

The ICPE-9820 is ideally suited for oil and fuels analysis. It allows for radial and axial viewing of its vertically-oriented plasma torch, enabling a wide dynamic range of detection. The vertical orientation of the torch minimizes the build-up of carbon-based soot, allowing for samples in organic solvent to be analyzed without the introduction of a stream of oxygen. Its vacuum-purged optical bench precludes the need for a constant bleed of gas and increases sensitivity in the deep ultraviolet range. The features of the ICPE-9820 ensure that it is a cost-effective and robust tool for oils and fuels analysis.

Experimental

Sample Preparation

Three petrochemical samples including commercial k-1 kerosene, diesel, and jet fuel were analyzed.

A two point calibration curve, as suggested by D7111-16, including blank (kerosene) and 2ppm calibration standard was used in this study. Calibration standards prepared by diluting the Conostan multi-elements standard in kerosene (Honeywell, Purum) on weight basis.

A quality control standard sample was prepared by spiking kerosene with 1 ppm of analysis elements. Yttrium was used as internal standard and all samples and standards contained 1 ppm Y. Standards and spike concentrations are listed in Table 1.

Table 1. Standards and spike concentrations

Calibration Standard	QC Standard	Samples spike concentration
2 ppm	1 ppm	1 ppm

Instrumentation

Different types of fuels were analyzed with a Shimadzu Dual view ICPE-9820 equipped with a special sample introduction kit for organic solvent including twister spray chamber, standard organic torch, and a conical nebulizer. Detailed operating conditions are listed in Table 2.

Table 2. Operating conditions of Shimadzu ICPE-9820

Parameter	Setting	Parameter	Setting
Radio Freq. Power	1.40 kW	Exposure Time	30 sec
Plasma Gas	20 L/min	Torch	Standard organic torch
Auxiliary Gas	1.4 L/min	Spray Chamber	Twister
Carrier Gas	0.4 L/min	Nebulizer	10UES

The ICPE-9820 is a vacuum spectrometer and unlike purge-type spectrometers, it does not need to be purged continuously with high purity argon or nitrogen gas. An industrial grade liquid argon dewar was used as a source of argon gas. It should be pointed out that research grade argon gas which is used at conventional ICP is not necessary for ICPE-9820.

Analytical elements, wavelength, detection limit and other method parameters are shown in Table 3.

The detection limit was calculated by multiplying the standard deviation of blank sample analysis by three. As shown in Table 3, for the majority of the elements, the method detection limit (MDL) fall within single digit ppb range.

Table 3. Analytical elements and their corresponding measurement parameters

Element	Wavelength (nm)	Plasma view	Detection Limit (ppb)	Exposure Time (sec)	Internal Standard	Repeat No.
Ag	328.068	Radial	3.7077	30	Y (371.030)	3
Al	396.153	Radial	49.1918	30	Y (371.030)	3
B	249.773	Radial	26.4746	30	Y (371.030)	3
Ba	233.527	Radial	2.7849	30	Y (371.030)	3
Ca	393.366	Radial	0.3107	30	Y (371.030)	3
Cd	214.438	Radial	4.4913	30	Y (371.030)	3
Cr	267.716	Radial	1.1099	30	Y (371.030)	3
Cu	324.754	Radial	18.1006	30	Y (371.030)	3
Fe	259.940	Radial	11.0234	30	Y (371.030)	3
Mg	279.553	Radial	0.183646	30	Y (371.030)	3
Mn	257.610	Radial	0.606123	30	Y (371.030)	3
Mo	202.030	Radial	13.6964	30	Y (371.030)	3
Ni	221.647	Radial	9.6235	30	Y (371.030)	3
Pb	220.353	Radial	247.5496	30	Y (371.030)	3
Sn	189.989	Radial	99.3484	30	Y (371.030)	3
Ti	334.941	Radial	3.3199	30	Y (371.030)	3
V	311.071	Radial	1.1177	30	Y (371.030)	3
Zn	213.856	Radial	2.3676	30	Y (371.030)	3

Results and Discussion

Table 4 shows the concentrations of elements in ppm in original samples and fortified samples for three different fuels as well as blank sample.

All of the target elements are below the detection limit for the blank sample (unspiked kerosene), which is expected. The 1-K commercial kerosene contains small amount of Aluminum. Jet Fuel contains Cadmium and Zinc addition to Aluminum. Diesel sample contains more elements including Calcium, Cadmium, Iron, Magnesium, Nickel, and Zinc.

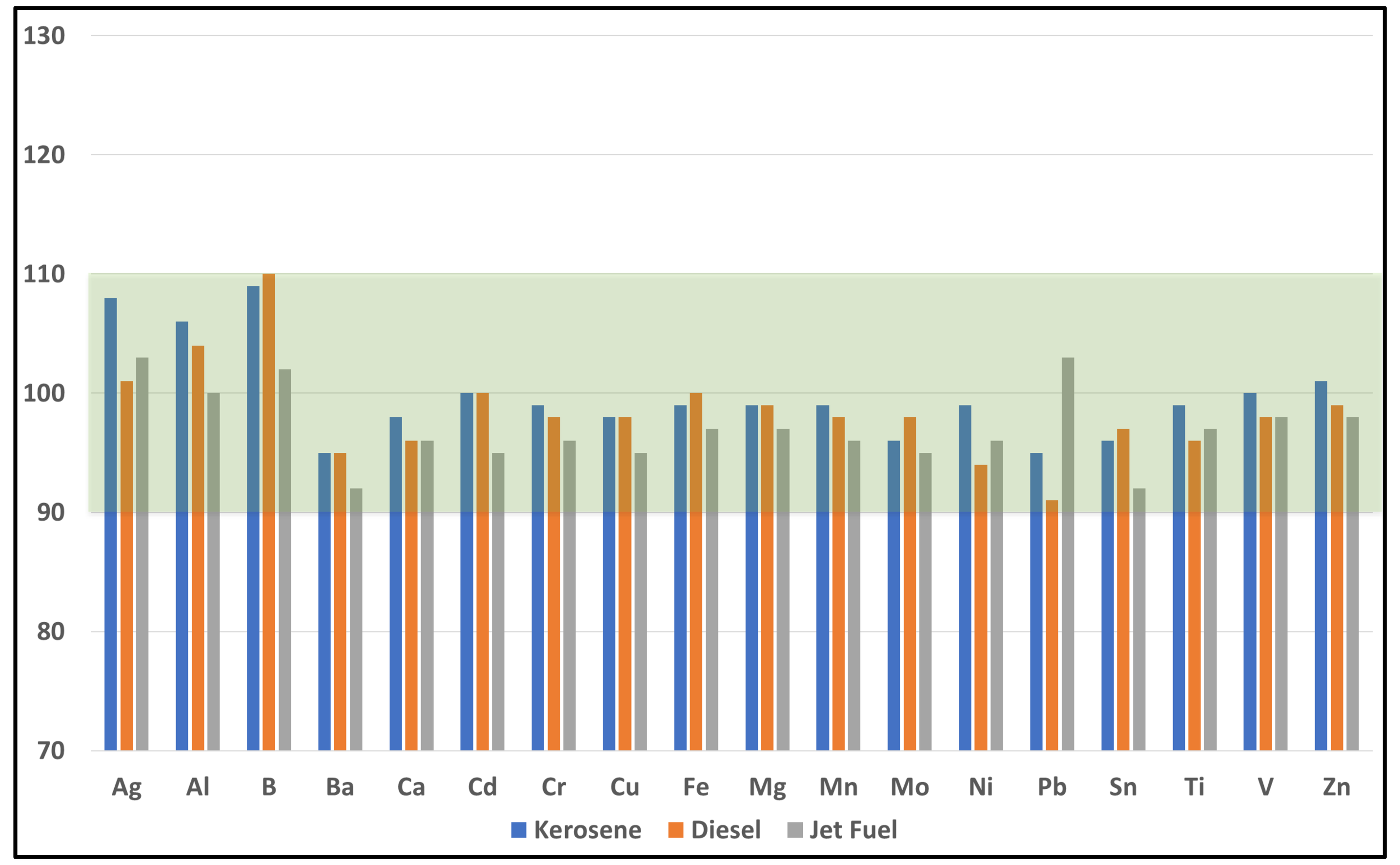
To validate the method, investigation on the recoveries of spiked pure kerosene (QC standard) and 3 types of samples (fuels) were performed using Shimadzu ICPE-9820. All the obtained recoveries were within the acceptable range of 90 to 110% of the spiked values as shown in Table 4.

The recoveries for the different samples were also displayed in Figure 1 and acceptable range of ±10% was highlighted with green color. Most of relative standard deviations (RSD) are also below 5, further validating the methodology and the accuracy.

Table 4. Concentrations of elements in ppm in original samples and fortified samples for three different fuels and blank sample as well as recovery yields in percent

		Ag	Al	B	Ba	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
Blank (Kerosene)	Mean value	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	RSD (n = 3)	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Fortified blank (QC Standard)	Mean value	0.979	1.02	0.964	0.970	0.986	0.984	0.983	0.913	0.979	0.986	0.974	0.978	0.977	0.938	0.915	0.983	0.982	0.973
	RSD (n = 3)	0.21	1.19	0.71	0.19	1.09	0.38	0.40	0.33	0.28	1.01	0.08	1.38	0.53	2.91	0.88	0.36	0.08	0.07
Recovery (%)		98	102	96	97	99	98	98	91	98	99	97	98	98	94	92	98	98	97
1-K commercial Kerosene	Mean value	n.d.	0.0927	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	RSD (n = 3)	---	11.61	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Fortified Kerosene	Mean value	1.08	1.15	1.09	0.95	0.982	0.998	0.992	0.983	0.994	0.99	0.989	0.963	0.986	0.948	0.960	0.993	1.00	1.01
	RSD (n = 3)	0.1	0.91	0.36	0.31	0.67	0.36	0.23	0.12	0.33	0.63	0.21	0.90	0.57	3.41	4.71	0.39	0.35	0.48
Recovery (%)		108	106	109	95	98	100	99	98	99	99	99	96	99	95	96	99	100	101
Diesel	Mean value	n.d.	n.d.	n.d.	n.d.	0.0202	0.0138	n.d.	n.d.	0.0247	0.0049	n.d.	n.d.	0.0881	n.d.	n.d.	n.d.	n.d.	0.0567
	RSD (n = 3)	---	---	---	---	7.36	2.22	---	---	3.2	2.95	---	---	7.94	---	---	---	---	3.67
Fortified Diesel	Mean value	1.01	1.04	1.10	0.95	0.978	1.01	0.985	0.977	1.02	0.991	0.981	0.984	1.03	0.910	0.965	0.958	0.984	1.05
	RSD (n = 3)	0.25	2.49	0.59	0.28	0.22	0.05	0.65	0.72	0.14	0.42	0.08	2.33	0.41	8.96	3.61	0.31	0.26	0.61
Recovery (%)		101	104	110	95	96	100	98	98	100	99	98	98	94	91	97	96	98	99
Jet Fuel	Mean value	n.d.	0.115	n.d.	n.d.	n.d.	0.0088	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.501
	RSD (n = 3)	---	4.73	---	---		3.86	---	---	---	---	---	---	---	---	---	---	---	0.54
Fortified Jet Fuel	Mean value	1.03	1.11	1.02	0.923	0.961	0.963	0.959	0.952	0.974	0.967	0.964	0.947	0.956	1.03	0.924	0.974	0.979	1.48
	RSD (n = 3)	1.49	4.02	1.84	1.48	1.7	1.55	1.43	2.22	1.71	1.22	1.54	0.86	1.24	4.35	2.80	1.48	1.43	1.21
Recovery (%)		103	100	102	92	96	95	96	95	97	97	96	95	96	103	92	97	98	98

Figure 1. Recovery for Kerosene, Diesel, and Jet Fuel samples



Conclusions

The metal content of refined fuels can be analyzed with the Shimadzu ICPE-9820 to ensure appropriate functionality during combustion and determining refining workflows according to ASTM D7111-16 method. The CCD detector with one million pixels is capable of simultaneous recording of all wavelengths.

Three petrochemical samples including commercial k-1 kerosene, diesel, and jet fuel were successfully analyzed and the method was validated. The obtained recovery were in the acceptable range between 90 to 110%.

The Shimadzu ICPE-9820 in conjunction with an organic sample introduction kit and ICPE solution software provides excellent sensitivity, precision, accuracy, tolerance and fast time response to meet and exceed compliance with regulations on heavy metals in refined fuels.

References

1. Roseli Martins de Souza, Luiz Gustavo Leocadio, Carmem Lucia P. da Silveira, ICP OES Simultaneous Determination of Ca, Cu, Fe, Mg, Mn, Na, and P in Biodiesel by Axial and Radial Inductively Coupled Plasma-Optical Emission Spectrometry, Analytical Letters, 41:9, 1615-1622 (2008).

2. Andrea Ulrich, Adrian Wichser, Analysis of additive metals in fuel and emission aerosols of diesel vehicles with and without particle traps. Analytical and Bioanalytical Chemistry, 377, 71–81 (2003).