

Analysis of trace metallic impurities in hydrocarbon fuels by ICP-MS

Application note

Energy and Fuels

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Introduction

Hydrocarbon fuels include vehicle fuels such as gasoline and diesel as well as fuel oils for domestic and commercial heating and power generation. Since these solvents are obtained as early distillate fractions in hydrocarbon processing, concentrations of metallic impurities are generally low. Therefore, challenges of light to mid distillate fuel analysis are summarized as follows:

1. The light distillate fractions are highly volatile organic solvents, introduction of which can make it difficult to sustain the plasma.
2. Impurity concentrations are typically low (sub-ppm), so instrumentation with good detection limits is required.



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A procedure for analyzing lubricating oils with the Agilent 7700x was established and described in another application note [1], and in this work, a similar procedure was applied to fuel analysis. Commercial fuel samples were purchased from local vendors and analyzed. In order to validate the procedure, NIST Standard Reference Material (SRM) 1634c (residual fuel oil) was analyzed, although the main characteristics of SRM 1634c such as viscosity and volatility differ somewhat from those of commercial fuels.

Experimental

Instrument and analytical conditions

The instrument and the sample introduction configuration used was similar to the previous report [1]. The operating conditions also followed the described standard procedure. High energy helium collision mode was applied instead of normal helium collision mode in order to increase the sensitivity and allow the determination of metals at the lower levels found in fuels. The instrument and operating conditions used are listed in Tables 1 and 2.

Reagents

Oil-based, organometallic standards including S-21 21 element mix were obtained from CONOSTAN (Quebec, Canada). Kerosene was used as the diluent solvent (purchased from Kanto Chemicals, Japan). No further purification was applied to the kerosene.

Table 1. Instrument configuration

Parameter	Value
Instrument	Agilent 7700x ICP-MS
Sample introduction	Glass concentric nebulizer with 0.25 mm diameter and 700 mm length capillary tube Quartz torch with 1.5 mm bore injector
Sample uptake	Self aspiration
Interface	Platinum-tipped sampling cone and skimmer cone
Autosampler	Agilent I-AS

Sample preparation

After purchase, fuel oils were transferred into PFA bottles and stored at -30 °C. Samples were kept at room temperature for at least 30 min prior to analysis. 5 mL of sample was pipetted into a 50 mL volumetric flask and weighed precisely. 300 µL of yttrium 5 ppm (w/w in kerosene) was added to the flask. The flask was filled up to 50 mL and weighed. The dilution factor was calculated by weight.

Table 2. ICP-MS operating conditions

Cell Mode			H ₂	He
	Stabilization time	sec	5	30
Plasma				
	RF power	W	1600	
	Sampling depth	mm	8	
	Carrier gas	L/min	0.6	
Auxiliary Gas				
	20% O ₂ + 80% Ar	L/min	0.4	
	Spray chamber temp.	°C	-5	
Lens settings				
	Extract 1	V	0	
	Extract 2	V	-100	
	Omega bias	V	-55	
	Omega lens	V	6.3	
	Cell entrance	V	-40	
	Cell exit	V	-70	-150
	Deflect	V	-2.4	-70
	Plate bias	V	-60	-150
Cell				
	H ₂ flow	mL/min	6	
	He flow	mL/min		10
	Octopole bias	V	-20	-100
	Energy discrimination	V	5	10
Measurement				
	Integration time	sec	0.66 x 3 points	
	ISTD		Yttrium	

Calibration

5 ppm (w/w in kerosene) of Conostan S-21 pre-mixed standard was used as the stock standard. 0, 2, 10 and 50 ppb (w/w) solutions were obtained by serial dilution of this stock standard. Yttrium internal standard was added (w/w) into each working standard solution. Detection Limits (DLs) and Background Equivalent Concentrations (BECs) in kerosene were calculated from the calibration curves and are shown in Table 3.

Table 3. DL and BEC of elements in kerosene

	<i>m/z</i>	Mode	DL (ppb)	BEC (ppb)
B	10	H ₂	0.85	2.1
Na	23	H ₂	0.41	2.8
Mg	24	H ₂	0.59	0.66
Al	27	He	0.03	0.11
Ca	40	H ₂	0.42	0.68
Ca	44	H ₂	0.63	0.60
Ti	49	He	0.14	0.01
V	51	He	0.005	0.01
Cr	52	H ₂	0.045	0.16
Fe	54	H ₂	0.11	0.078
Mn	55	He	0.01	0.005
Ni	60	He	0.02	0.02
Cu	63	He	0.05	0.26
Zn	66	He	0.21	0.33
Zn	67	He	0.33	0.29
Mo	95	He	0.005	0.005
Ag	107	He	0.01	0.01
Cd	114	He	0.005	0.01
Sn	118	He	0.005	0.01
Ba	137	H ₂	0.018	0.008
Pb	208	He	0.005	0.01

Results and discussion

Analytical results of commercial fuel oils are shown in Table 4 (see next page). "Alcohol" is used as fuel for camping stoves and lamps and is a mixture of methanol, ethanol, and isopropyl alcohols.

The long term stability was examined over 7 hours for a diesel oil sample spiked with 10 ppb S-12 multi-element standard. Normalized concentrations after correction using the yttrium internal standard are shown in Figure 1 with RSD%.

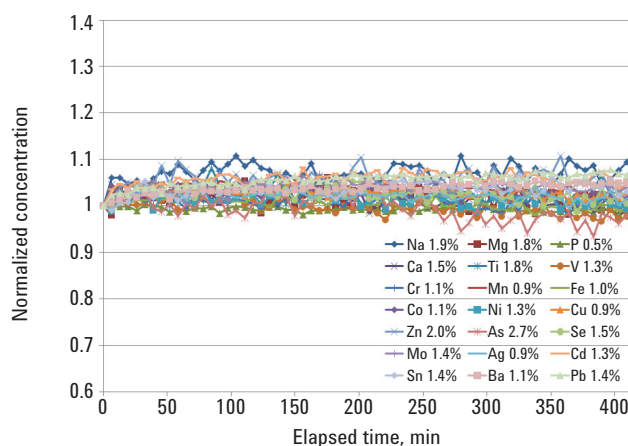


Figure 1. 7 hours long term stability test for 10 ppb multi-element spike in diesel oil

Table 4. Measured concentrations of metallic impurities in fuel oils ($\mu\text{g}/\text{kg}$, ppb)

		Kerosene*	Alcohol**	White gas A**	White gas B**	Diesel oil*	Regular gasoline*	High-octane gasoline*
¹⁰ B	H ₂	n. d.	920	16	25	1.5	5	n. d.
²³ Na	H ₂	n. d.	19	n. d.	25	4.1	n. d.	n. d.
²⁴ Mg	H ₂	n. d.	5.2	3.6	37	6.6	2.6	n. d.
²⁷ Al	He	0.4	8	n. d.	31	8.3	1.4	n. d.
⁴⁰ Ca	H ₂	0.3	6.4	3	42	10	11	0.3
⁴⁸ Ti	He	0.1	0.9	0.2	33	8.1	1.8	0.2
⁵¹ V	He	0.5	0.5	0.4	31	7.7	1.4	0.9
⁵² Cr	H ₂	0.1	1.8	1.3	37	8	1.9	0.3
⁵⁵ Mn	H ₂	0.3	2.6	1.3	36	8	2.2	0.4
⁵⁴ Fe	H ₂	1.2	41	0.6	39	8.9	10	0.6
⁵⁹ Co	He	0.2	1.1	0.1	0.9	0.3	0.2	0.4
⁶⁰ Ni	He	0.4	2	0.9	30	6.4	1.9	0.1
⁶³ Cu	He	2.1	14	4.8	41	7.4	2.8	0.5
⁶⁶ Zn	He	58	78	8.2	35	52	250	3.6
⁹⁵ Mo	He	0.1	0.6	0.2	31	6.9	1.5	0.3
¹⁰⁷ Ag	He	0.1	4.7	0.1	27	6.8	1.5	0.2
¹¹⁴ Cd***	He	0.1	12	0.5	30	6.4	1.5	0.3
¹¹⁸ Sn	He	n. d.	610	3.8	36	7.4	2	0.2
¹³⁸ Ba	H ₂	0.9	0.2	0.1	30	8.4	17	0.4
²⁰⁸ Pb	He	0.3	0.9	0.4	27	6.6	1.6	0.4

*Purchased from a gas station.

**Purchased from a camping equipment shop.

***Comparable performance was obtained with the Cd 111 isotope, which is the normal preferred isotope for Cd. However, in this application, since the levels of Sn are low in fuel oil/lubricating oil samples, we used the data from the more abundant Cd 114 isotope, which provided higher sensitivity and slightly improved DLs.

NIST SRM 1634c analysis

The NIST 1634c residual fuel oil has relatively high viscosity and low volatility compared with other fuel oils. To reduce the viscosity before sample preparation, the bottle with the NIST sample oil was immersed in a hot water bath at 70 °C for 10 minutes followed by ultrasonication of the bottle. Approximately 7 g of sample oil was transferred to a clean glass beaker, and approximately 60 g of kerosene was added to the beaker and ultrasonicated again until the sample completely dissolved. After dilution with kerosene and addition of yttrium internal standard, the final analytical sample was obtained. The dilution factor was calculated by weight. The analytical results are shown in Table 5.

Table 5. Analytical results of NIST SRM 1634c (mg/kg, ppm)

Element	Reference mg/kg	Result mg/kg
Na	37	37.7
V	28	28.0
Co	0.15	0.147
Ni	17	17.2
As	0.14	0.148
Se	0.10	0.102
Ba	1.8	1.87

Conclusions

The Agilent 7700x ICP-MS was used to analyze trace metallic impurities in a range of hydrocarbon fuel samples, demonstrating low BECs and mid-ppt level DLs. Excellent long-term stability (<2% SD over 7 hours) was achieved, and measured results for NIST 1634c Trace Elements in Fuel Oil were in good agreement with the certified values. Fuel samples ranging in viscosity and volatility from stove alcohol and gasoline to residual fuel oil were diluted into high purity kerosene and measured using a single ICP-MS analytical method and calibration.

References

1. Junichi Takahashi and Kei Kasahara, Analysis of metallic components in lubricating oils by ICP-MS, Agilent Application Note, 5991-3263EN.

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