

Analysis of inorganic impurities in lubricating oils by ICP-MS

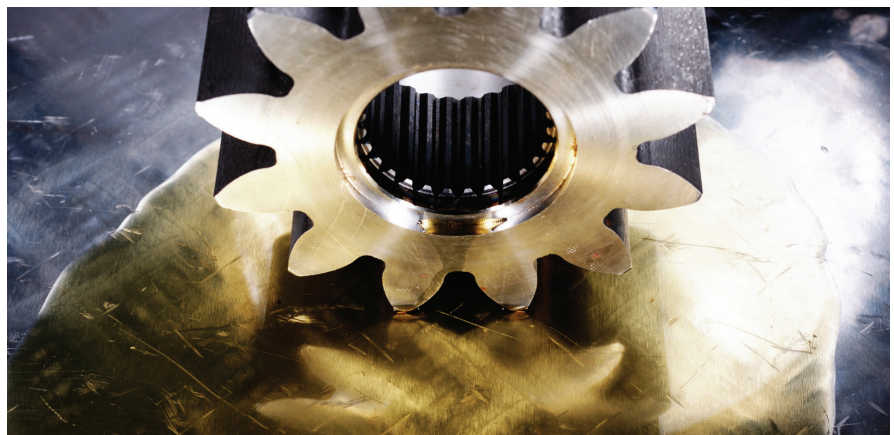
Application note

Energy and Fuels

Authors

Junichi Takahashi, Kei Kasahara

Agilent Technologies, Japan



Introduction

The most widely used techniques for monitoring metals in petrochemical products have been atomic absorption spectrometry (AAS), x-ray fluorescence spectrometry (XRF) and inductively coupled plasma optical emission spectrometry (ICP-OES) [1]. These techniques give sufficient detection limits for the common applications so, while the importance of metals in the products has not been ignored, not much attention has been given to updating analytical methods to take advantage of new technology such as ICP-MS. Official analytical methods issued by ASTM from 1991 to 2005 were based upon AAS [2,3,4] and ICP-OES [5,6]. Papers published during these years have mainly discussed sample preparation such as emulsification [7], solvent extraction [8], and so on with AAS or ICP-OES. Although the superior sensitivity of ICP-MS is well known and ICP-MS is



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accepted in a variety of industrial fields, ICP-MS has not been widely utilized for routine applications in the petrochemical industry. There are various reasons for this, including the fact that petroleum manufacturing and refining sites do not require the superior sensitivity offered by ICP-MS. Another factor is that the high purity organic reagents needed for ultratrace analysis are not commonly available in the commercial market. For example, metallic standards for oil analysis are manufactured by very few vendors. Although 72 elements can be determined by ICP-MS, the number of elements included in commercially available organic standards is around 30 at most. That number is sufficient for most existing methods, because the other elements are typically too low to be determined using ICP-OES.

Regardless of the detection mode, analysis of petroleum-based samples presents a significant challenge for ICP instrumentation. It is very difficult to sustain an ICP when introducing organic solvents, particularly volatile ones. For ICP analysis, a liquid sample is typically converted to an aerosol by a nebulizer; at the same time, a large amount of solvent vapor is created and transported to the ICP torch, even when a chilled spray chamber is used. Sample aerosol droplets and particles coming out of the central tube of the torch pass through the center of the plasma. However, organic vapor cannot do so because the high temperature argon plasma has a much higher viscosity than the low temperature organic vapor. If the linear velocity of the carrier gas is not high enough to penetrate the plasma, the vapor surrounds the plasma and, as a result, cuts off the electromagnetic coupling between the load coil and ICP. The use of a narrower bore injector such as 1.0 mm internal diameter increases the linear gas velocity and allows the sample aerosol to punch through the plasma, so enabling organic solvent introduction, but the sensitivity is reduced by approximately 30% compared to a typical injector used with aqueous samples. For analysis by ICP-MS, the high concentration of carbon matrix in the organic samples could also lead to soot deposits on

the sampling cone and torch. In order to avoid such deposits, ICP-MS requires the addition of O₂ to the carrier gas to decompose the carbon in the plasma. In order to ignite the ICP with O₂ gas present, a very robust radio frequency (RF) generator circuit is required. Successful analysis of petroleum samples using ICP-MS must overcome these challenges.

The all solid state RF generator for the Agilent 7700 Series ICP-MS is so robust that a 1.5 mm injector torch can be used to introduce most organic solvents. Moreover, the ignition of the ICP is possible with organic solvent and oxygen present. In this report, the analysis of lubricant oil using the Agilent 7700x ICP-MS is described.

Experimental

Equipment

An Agilent 7700x ICP-MS was used with a standard glass concentric nebulizer, quartz spray chamber and connector tube. Sample uptake was by self aspiration, using a 70 cm long sample capillary tube with 0.25 mm internal diameter. The instrument's peristaltic pump was used only for draining the spray chamber, using solvent resistant peristaltic pump tubing. The optional platinum (Pt) tipped sampling cone and skimmer cone were used, as the plasma with O₂ addition is much more reactive and would quickly degrade the standard nickel cones. An Agilent I-AS autosampler was used to automate sample introduction over a long sequence.

Standards and samples

All metallic standards were prepared from Conostan Oil Analysis Standards. Conostan S-21 pre-mixed standard containing 21 metals at 100 ppm was used as the stock standard and by serial dilution of S-21, a working standard solution with the same concentration for each metal was easily obtained. This is very convenient for trace and ultratrace analysis, but when concentrations of some elements are significantly higher than others, S-21 must be modified. In order to determine minor and ultratrace elements simultaneously, single element standards were mixed with S-21. A yttrium standard

blended in blank oil was used as the internal standard. Analytical grade O-xylene or kerosene (from Kanto Chemicals, Japan) was used as the blank solvent for dilution of the oil samples. Lubricating oil samples were purchased from various suppliers.

Procedure

The plasma was ignited while aspirating iso-propyl alcohol (IPA). A 1 ppb tuning solution, prepared by diluting SPEX mixed inorganic standard in IPA, was used for the optimization of plasma and ion lens parameters. In Table 1, the major operating parameters used in this experiment are shown. Most lens parameters were optimized using the auto-tuning function of the instrument. Hydrogen reaction and helium collision modes were used and, apart from the cell gas and flow rate, the operating parameters were identical in all modes.

Table 1. ICP-MS operating parameters

Mode			H ₂	He	LoHe
	Stabilization time	sec	5	30	30
Plasma					
	RF power	W		1600	
	Sampling depth	mm		8	
	Carrier gas	L/min		0.6*	
	Makeup gas	L/min		0	
	Option gas**	L/min		0.4	
	Spray chamber temp	°C		-5	
Lenses					
	Extract 1	V		0	
	Extract 2	V		-135	
	Cell entrance	V		-30	
	Cell exit	V		-60	
	Octopole bias	V		-20	
	Q-pole bias	V		-16	
Cell Gas					
	H ₂ flow	mL/min	7	0	0
	He flow	mL/min	0	5	4

*Kerosene uptake was 70 µL/min using self aspiration.

**20% oxygen balanced with 80% argon was used.

Approximately 2 g of each oil sample was taken, weighed precisely and dissolved in kerosene (w/w). The final dilution factor should be 100 or lower. Samples were analyzed using an external calibration method with 300 ppb yttrium as the internal standard. Yttrium was added manually to each sample solution (w/w) prior to analysis. An example calibration set is shown in Table 2.

Table 2. Target concentrations of calibration standards

	Unit	CALBLK	CALSTD1	CALSTD2	CALSTD3	CALSTD4
Na	ppm	0	0.005	0.02	0.1	0.5
Mg	ppm	0	0.5	2	10	50
P	ppm	0	0.5	2	10	50
Ca	ppm	0	2	8	40	200
Zn	ppm	0	0.5	2	10	50
Mo	ppm	0	0.1	0.4	2	10
Al	ppb	0	0.2	0.8	4	20
Fe	ppb	0	0.2	0.8	4	20
Cd	ppb	0	0.2	0.8	4	20
Ti	ppb	0	0.2	0.8	4	20
V	ppb	0	0.2	0.8	4	20
Cr	ppb	0	0.2	0.8	4	20
Mn	ppb	0	0.2	0.8	4	20
Ni	ppb	0	0.2	0.8	4	20
Cu	ppb	0	0.2	0.8	4	20
Ag	ppb	0	0.2	0.8	4	20
Sn	ppb	0	0.2	0.8	4	20
Ba	ppb	0	0.2	0.8	4	20
Pb	ppb	0	0.2	0.8	4	20

Results and discussion

Selection of diluent solvent

Xylene is frequently used as a diluent solvent of oil samples, and particularly some crude oil samples are dissolved most easily in xylene. However, considering the stability of metallic standards at concentrations as low as 1 ppb, xylene is not always the best choice for the diluent solvent. Therefore, the analytical results of NIST SRM 1848 were compared between xylene and kerosene, which is available with low trace element impurity levels. Table 3 does not show any significant differences in quantitative results so, in this experiment, kerosene was chosen as the diluent solvent for lubricating oils.

Table 3. Example of analysis of NIST Standard Reference Material 1848 (Lubricating Oil Additive Package)

	Kerosene	Xylene	Certified Value % (uncertainty)
Calcium	0.36	0.36	0.359 (0.011)
Magnesium	0.78	0.83	0.821 (0.038)
Phosphorus	0.78	0.88	0.788 (0.028)
Zinc	0.87	0.93	0.873 (0.022)

Detection Limit (DL) and Background Equivalent Concentration (BEC)

DLs and BECs calculated from the calibration curve are shown in Table 4. As expected, the figures of merit obtained by ICP-MS were significantly lower than is achievable using ICP-OES, by around 1 or 2 orders of magnitude for both DL and BEC. These values are impressive despite the significant contribution from the elemental impurities present in the diluent solvent. In order to simplify the analytical procedure, commercial reagents were used without further purification.

Table 4. 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	LoHe	0.096	0.092
P	31	He	58	95
Ca	40	H ₂	0.42	0.68
Ca	44	H ₂	0.63	0.60
Ti	49	LoHe	0.14	0.036
V	51	He	0.013	0.004
Cr	52	H ₂	0.045	0.016
Fe	54	H ₂	0.11	0.078
Mn	55	He	0.031	0.008
Ni	60	He	0.045	0.037
Cu	63	He	0.06	0.17
Zn	66	He	0.12	0.14
Zn	67	He	0.47	0.20
Mo	95	He	0.087	0.11
Mo	97	He	0.049	0.096
Ag	107	He	0.012	0.01
Cd	114	He	0.015	0.008
Sn	118	He	0.064	0.062
Ba	137	H ₂	0.018	0.008
Pb	208	He	0.015	0.03

Recovery test

In order to validate the analytical method proposed here, a recovery test was carried out. A partially synthetic oil sample was diluted and spiked. The results are shown in Table 5. Recoveries for P and Ca were adversely affected by the low concentration of the spikes compared to the unspiked concentrations.

Table 5. Spike recovery test

	Concentration spiked	Measured		Recovery rate (%)
		Unspiked	Spiked	
B	50 ppb	4.3	47	85
Na	0.1 ppm	0.023	0.12	99
Mg	10 ppm	0.11	10	101
Al	4 ppb	17	21	107
P	10 ppm	25	36	116
Ca	10 ppm	32	44	121
Ti	4 ppb	4.9	8.7	97
V	4 ppb	1.9	5.8	96
Cr	4 ppb	0.64	5.6	123
Mn	4 ppb	4.4	8.8	108
Fe	4 ppb	1.9	6	103
Ni	4 ppb	1.2	5.5	107
Cu	4 ppb	0.098	4.5	109
Zn	10 ppm	29	39	101
Mo	2 ppm	3.3	5.4	108
Ag	4 ppb	0.029	4.6	113
Cd	4 ppb	3.2	7.5	107
Sn	4 ppb	0	3.9	101
Ba	4 ppb	0.97	5.4	111
Pb	4 ppb	7.2	11	99

Analysis of commercial lubricating oils

From an evaluation of the full mass spectra, it was clear that the concentration variation between elements was significant. Some elements must be determined at relatively high concentrations, while others are present at very low concentrations. The proposed calibration strategy was sufficient to cover this range after a dilution factor of 100. The analytical results for minor and trace elements are shown in Table 6 and ultratrace elements are shown in Table 7.

Long term stability

An oil sample spiked with 19 elements was measured for 5 hours to assess long-term signal stability. Considering the most difficult case, a 10 times diluted oil sample (partially synthetic oil) was used. 100 ppb S-21 standard was spiked into the sample and the spiked concentrations were monitored. The normalized concentrations were plotted in Figure 1 with RSD%. Considering the very low dilution factor (high matrix level), excellent stability was obtained.

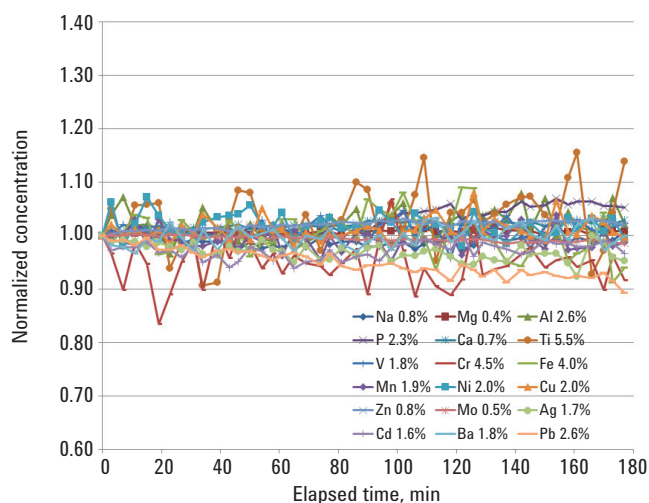


Figure 1. Long term stability of spiked elements in 10 times diluted oil sample

Table 6. Concentration of minor and trace elements measured in a series of commercial lubricating oils (mg/kg, ppm)

		²³ Na	²⁴ Mg	²⁷ Al	³¹ P	⁴⁴ Ca	⁵⁴ Fe	⁶⁶ Zn	⁹⁷ Mo	¹¹⁴ Cd
A	Mineral	1.4	11	0.75	1100	3000	0.23	1100	110	0.096
B	Mineral	2.6	20	1.1	1900	5100	0.42	1700	200	0.17
C	Mineral	1.9	18	1.1	1100	2900	0.33	1100	960	0.78
D	Partially synthetic	0.21	2	0.11	5.4	360	0.042	13	1.3	0.0013
E	Partially synthetic	0.51	1800	0.6	1800	1200	0.33	1900	2.1	0.0048
F	Mineral	2.2	30	0.14	690	1600	0.16	750	0.11	0.0051
G	Mineral	9	1100	1.6	1300	1400	0.84	1400	0.051	0.022
H	Mineral	2.3	7.8	0.39	780	2000	0.2	870	230	0.19
I	Partially synthetic	0.99	13	0.22	780	2200	0.17	840	78	0.069
J	Mineral	0.13	8.4	0.69	780	2100	0.09	870	81	0.075
K	Synthetic	0.96	9	0.29	750	2100	0.16	810	78	0.075
L	Partially synthetic	0.9	3.6	0.54	810	1100	0.16	990	110	0.11
M	Mineral	0.69	720	0.48	780	1200	0.21	870	81	0.075
N	Partially synthetic	0.99	8.4	0.39	780	2200	0.17	840	81	0.072
O	Partially synthetic	0.96	7.5	0.39	720	2100	0.15	780	78	0.069

Table 7. Concentration of ultratrace elements measured in a series of commercial lubricating oils (µg/kg, ppb)

		⁴⁹ Ti	⁵¹ V	⁵² Cr	⁵⁵ Mn	⁶⁰ Ni	⁶³ Cu	¹⁰⁷ Ag	¹¹⁸ Sn	¹³⁷ Ba	²⁰⁸ Pb
A	Mineral	39	63	51	130	29	5.1	n.d.	5.1	11	19
B	Mineral	51	100	66	210	45	9.3	n.d.	5.1	20	30
C	Mineral	81	54	21	75	26	6	0.45	7.5	10	19
D	Partially synthetic	8.7	5.7	2.6	12	2.7	n.d.	n.d.	n.d.	1.5	4.5
E	Partially synthetic	220	51	45	170	150	6.3	0.81	n.d.	17	33
F	Mineral	45	17	16	66	36	45	1.1	2.5	6600	75
G	Mineral	84	120	48	570	90	20	1.7	6.6	9.9	99
H	Mineral	27	9.3	33	93	54	8.7	n.d.	3.9	17	20
I	Partially synthetic	120	12	29	87	21	3.6	n.d.	1.8	9.6	14
J	Mineral	39	19	17	60	39	6	n.d.	n.d.	11	14
K	Synthetic	480	8.7	27	87	17	3.6	n.d.	n.d.	8.4	14
L	Partially synthetic	150	63	20	63	36	3.9	n.d.	n.d.	33	240
M	Mineral	39	42	20	81	24	3	n.d.	33	4.2	9
N	Partially synthetic	24	39	30	87	21	2.7	n.d.	n.d.	10	11
O	Partially synthetic	21	33	33	84	23	3	n.d.	n.d.	7.2	9.3

Conclusions

By applying ICP-MS to the analysis of metals in lubricating oils, the concentration range of detectable elements could be significantly extended compared to ICP-OES, namely from 0.5 ppb to 5000 ppm. From the standpoints of robustness and stability as well as sensitivity, ICP-MS has demonstrated significantly better performance than either ICP-OES or AAS.

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