Multi-element analysis of petroleum crude oils using an Agilent 7900 ICP-MS

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EWCPS 2017
Poster ID: 145

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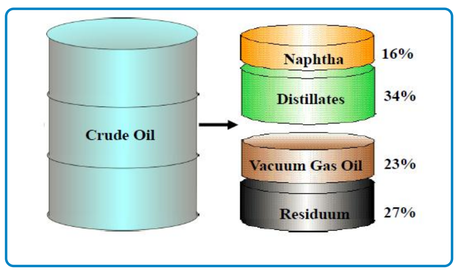
Introduction

In the petrochemical industry, certain analytes are known to impact the performance and value of the final product. Consequently, there are several ASTM methods on the elemental analysis of oils, lubricants and fuels. One example is standard test method ASTM D7111-15a for the determination of trace elements in middle distillate fuels which uses Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). This method is widely used in the industry, but as specifications for fuels become more stringent, some laboratories use a more sensitive analytical technique such as ICP-MS, which provides significantly lower detection limits than ICP-OES. To reflect this trend, the first ASTM ICP-MS method for petroleum has been balloted in D0203. This is likely to be followed by an ICP-MS method for petroleum crude oils.

This poster describes how the Agilent 7900 ICP-MS was used to analyze different types of crude oil samples following simple dilution in an organic solution containing *o*-xylene. The aim was to develop a method that is suitable for routine use in the petroleum refining industry, particularly in high sample volume facilities, where turnaround time is critical.



Experimental

Samples

A series of 18 petroleum crude oil samples were used in the study, as detailed in Table 1. The samples were divided into two categories according to properties including American Petroleum Institute (API) gravity, elemental composition, hydrocarbon (H/C) content, and density.

Sample Preparation

- The light set of crude petroleum oil samples and the multielement Conostan standard (10 elements at 2 mg/kg in crude oil) were prepared by taking an aliquot (~1 g) which was dissolved in (~9 g) of the *o*-xylene diluent.
- For the heavier samples, an aliquot and the amount of *o*-xylene diluent required varied in order to dilute the element with the highest concentration within the calibration range.
- Sample dilutions ranged from 1:10 to 1:600. All samples were shaken in a mechanical shaker for 30 mins to help the crude oil samples dissolve. The sample introduction system was rinsed using *o*-xylene between sample analysis.
- Multiple calibration standards ranging from 1 µg/kg to 1000 µg/kg were prepared for 23 target elements by weight using the Conostan S-21+K 10 mg/kg standard and *o*-xylene diluent. The diluent solution was used as the blank for calibration.
- The standard reference material (SRM) NIST 1634c Trace Elements in Fuel Oil (Gaithersburg, MD, USA) was used to validate the method for the following certified and reference elements: Ni, V, As and Se. NIST 1634c was diluted approximately 1:60 in the *o*-xylene diluent prior to analysis.

Table 1. Properties of the 18 crude oil samples analyzed in this study

	ICP-MS DIRECT DILUTION (ppmw)				Crude oil properties						
Sample	40Ca	56Fe	62Ni	51V	C (%)	H (%)	S (ppm)	N (ppm)	H/C	API @ 15.56 C/60F	Density (g/ml) @ 15.56 °C /60 F
S1	9.59	2.13	4.92	0.45	84.84	13.08	1123.00	1093.00	1.84	36.20	0.84
S2	5.12	2.46	4.83	4.83	85.90	13.31	5239.00	1078.00	1.85	35.40	0.85
S3	<LOQ	1.54	6.02	0.07	83.60	12.92	4910.00	336.00	1.84	31.40	0.87
S4	<LOQ	0.96	0.99	0.85	84.19	13.22	3886.00	310.30	1.87	41.40	0.82
S5	0.87	1.05	5.86	12.98	85.24	12.76	4204.00	651.90	1.78	32.60	0.86
S6	0.86	1.10	3.33	7.64	84.21	12.98	3129.00	513.60	1.84	33.10	0.86
S7	0.75	2.33	3.41	7.64	86.18	13.00	3350.00	499.60	1.80	33.60	0.86
S8	1.24	1.13	2.81	6.75	85.53	12.81	2741.00	497.90	1.78	33.10	0.86
S9	<LOQ	0.63	6.25	9.29	84.78	13.04	21000.00	508.00	1.83	35.00	0.85
S10	41.21	8.39	67.82	194.44	83.15	10.30	49100.00	4050.00	1.49	9.50	0.90
S11	8.22	4.39	32.83	41.96	85.52	11.23	18527.00	7580.00	1.58	13.50	0.95
S12	8.23	2.21	43.82	234.03	83.73	11.15	31980.00	3770.00	1.60	16.70	0.93
S13	8.94	2.14	39.09	209.30	84.64	11.32	23821.00	2430.00	1.60	19.50	0.94
S14	<LOQ	0.26	49.42	301.09	82.93	11.28	36809.00	3870.00	1.63	20.70	0.93
S15	<LOQ	0.40	18.68	47.89	84.63	11.32	38500.00	1360.00	1.60	23.50	0.91
S16	<LOQ	1.22	9.67	25.29	87.39	12.67	10490.00	1470.00	1.74	30.90	0.87
S17	9.59	2.13	4.92	0.45	84.84	13.08	1123.00	1093.00	1.85	36.20	0.84
S18	0.52	1.23	0.21	0.42	83.94	13.69	311.50	55.40	1.94	51.30	0.77

Experimental

Data Collection

7900 ICP-MS (Agilent)

Table 2. ICP-MS operating parameters

Instrument	Agilent 7900 ICP-MS
Acquisition mode(s)	No collision cell, Hydrogen and Helium cell modes
Sample introduction	Concentric Glass nebulizer with 0.89mm id Viton tubing Quartz torch with 1.0 mm bore injector Peltier Cooled quartz Scott double pass spray chamber
Sample uptake	Peristaltic pump at 0.04rps
Interface	Platinum sampling cone and skimmer cone

Parameter	Setting
RF power (W)	1550
Plasma gas flow rate (L/min)	15
Auxiliary gas flow rate (L/min)	0.9
Make up gas (L/min)	0.1
Carrier gas flow rate (L/min)	0.45
Optional O_2 gas flow rate (%)	10
Sampling depth (mm)	8
Spray chamber temperature (°C)	-2
Peri-pump speed rinse (rps)	0.5
Peri-pump speed analysis (rps)	0.04
Helium flow rate (mL/min)	3.4
Hydrogen flow rate (mL/min)	5

Agilent 7900 ICP-MS

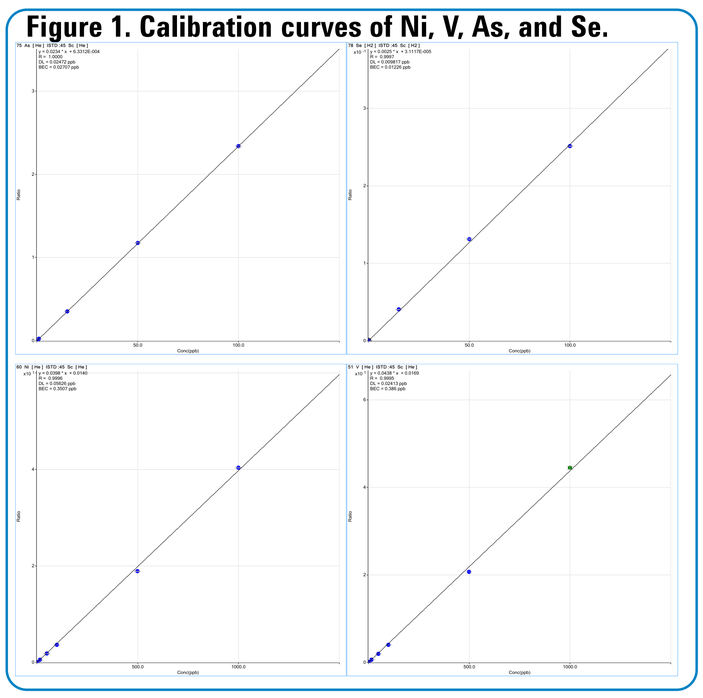
Data Analysis

- Since Ca, Fe, Ni, V, are the most abundant elements in crude oil, and are the most commonly studied elements within the industry, they were the focus of this study.

Results and Discussion

The calibration data shown in Table 2 is typical of the performance of the 7900 ICP-MS. Linear calibrations were obtained for all analytes as indicated by the calibration coefficients (>0.998 in all cases). Figure 1 shows representative calibration curves for Ni, V, As, and Se.

Figure 1. Calibration curves of Ni, V, As, and Se.



Detection limits

Typical instrument detection limits (IDLs) and background equivalent concentrations (BECs) for 23 elements are given in Table 3. The DLs were calculated from three times the standard deviation of 10 measurement results of the blank solution.

Table 3. ICP-MS performance data

Mass	Element	Tune Mode	R	DL, ppb	BEC, ppb
23	Na	H_2	0.999	1.743	26.667
23	Na	He	0.999	2.600	23.345
24	Mg	H_2	0.999	0.933	4.268
24	Mg	He	0.999	2.605	42.763
27	Al	H_2	1.000	3.351	31.582
27	Al	He	0.999	0.253	2.138
28	Si	H_2	1.000	1.484	15.537
31	P	He	1.000	3.319	24.785
39	K	H_2	0.999	1.635	6.395
39	K	He	0.998	2.125	21.778
40	Ca	H_2	1.000	2.969	3.526
43	Ca	H_2	1.000	6.984	6.423
44	Ca	H_2	1.000	0.645	7.259
47	Ti	He	1.000	0.066	0.026
51	V	He	0.998	0.023	0.073
52	Cr	H_2	1.000	0.119	1.152
52	Cr	He	0.999	0.087	1.968
55	Mn	He	1.000	0.095	0.821
56	Fe	H_2	1.000	0.985	95.665
56	Fe	He	0.999	1.242	93.355
57	Fe	He	1.000	7.800	107.258
60	Ni	He	1.000	0.032	0.141
62	Ni	He	1.000	0.126	0.163
63	Cu	He	1.000	0.068	0.542
65	Cu	He	0.999	0.068	0.504
66	Zn	He	1.000	0.085	1.270
68	Zn	He	1.000	0.087	1.214
75	As	He	1.000	0.009	0.015
78	Se	H_2	1.000	0.023	0.047
78	Se	He	1.000	0.140	0.105
80	Se	H_2	1.000	0.003	0.013
80	Se	He	1.000	2.203	15.651
82	Se	He	1.000	0.274	0.160
95	Mo	He	0.999	0.064	0.144
98	Mo	He	1.000	0.034	0.146
107	Ag	He	1.000	0.015	0.068
111	Cd	He	1.000	0.007	0.013
118	Sn	He	1.000	0.086	1.341
120	Sn	He	1.000	0.027	1.321
137	Ba	He	1.000	0.032	0.019
138	Ba	He	1.000	0.009	0.014
207	Pb	He	1.000	0.030	0.056
208	Pb	He	1.000	0.011	0.060

Results and Discussion

Certified reference values for V and Ni

- Nickel and vanadium are important elements in the assay of crude oils as they are usually present in the highest concentrations.
- As a performance check for the NIST certified elements Ni and V, the 7900 ICP-MS was used to analyze the diluted NIST 1634c standard a total of 18 times, with measurements taken on 6 separate days. The results in Table 3 show excellent recoveries for the certified elements V and Ni within + 10%, with good agreement between the results for ^{60}Ni and ^{62}Ni.

Reference values for As and Se

- Since there are only reference values available for As and Se in NIST 1643c, both elements were measured periodically over an extended period.. The long term performance check was based on a total of 147 separate measurements taken over the course of 12 months. The average recoveries for As and Se were also within ± 10%, as shown in Table 4. The statistical data for the study, shown in Table 5, confirms the excellent reproducibility of results for As and Se in the control sample over the year.

Table 4. Recoveries of V, Ni, As and Se in NIST SRM 1634c

Element and [cell gas mode]	Average of measured values taken on [a]18 times/6 separate days, [b]147 times/1 year (mg/kg)	Certified or *Reference value, mg/kg	Recovery, %
51 V [He]	[a]30720 ± 835	28190 ± 400	109
60 Ni [He]	[a]18897 ± 380	17540 ± 210	108
62 Ni [He]	[a]17544 ± 287	17540 ± 210	100
75 As [He]	[b]128.1 ± 5.3	142.6 ± 6.4*	90
78 Se [H_2]	[b]106.8± 5.8	102 ± 3.8*	105

Table 5. Repeatability data for As and Se in NIST SRM 1634c, based on 147 measurements over taken over a 1 year period

		As	Se
Repeatability variance	s(r)^2	2.117808219	0.400767123
Repeatability standard deviation	s(r)	1.455269123	0.633061706
Repeatability relative standard deviation	RSD(r)	1.082789526	0.603836041
Repeatability value = 2.8*s(r)	r	4.074753543	1.772572776

Quantitative results

Quantitative measurements of Ca, Fe, Ni and V in 18 crude oil samples by ICP-MS are shown in Table 6. The results show that the variation in concentration between the different samples is greatest for vanadium, from 0.07 to 301 ppm .

Table 6. Quantitative results for Ca, Fe, Ni and V in 18 crude oil samples by ICP-MS (all data ppmw)

Crude oil sample	^{40}Ca	^{56}Fe	^{62}Ni	^{51}V
S1	9.59	2.13	4.92	0.45
S2	5.12	2.46	4.83	4.83
S3	<LOQ	1.54	6.02	0.07
S4	<LOQ	0.96	0.99	0.85
S5	0.87	1.05	5.86	12.98
S6	0.86	1.10	3.33	7.64
S7	0.75	2.33	3.41	7.64
S8	1.24	1.13	2.81	6.75
S9	<LOQ	0.63	6.25	9.29
S10	41.21	8.39	67.82	194.44
S11	8.22	4.39	32.83	41.96
S12	8.23	2.21	43.82	234.03
S13	8.94	2.14	39.09	209.30
S14	<LOQ	0.26	49.42	301.09
S15	<LOQ	0.40	18.68	47.89
S16	<LOQ	1.22	9.67	25.29
S17	9.59	2.13	4.92	0.45
S18	0.52	1.23	0.21	0.42

Conclusions

The Agilent 7900 ICP-MS with ORS^4 is suitable for the direct multi-elemental analysis of crude oil samples following dilution in o-xylene. The high sensitivity of ICP-MS ensures significantly lower detection limits can be achieved for a wider range of elements compared to more traditional techniques, such as ICP-OES. Consequently, the industry is likely to receive an ASTM ICP-MS method for petroleum followed by one for petroleum crude oils.

References

[1] www.astm.org