Multi-Element Analysis of Petroleum Crude Oils using an Agilent 7900 ICP-MS

Application note

Energy and fuels

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Introduction

ASTM International develops and publishes voluntary consensus standards for materials, products, systems and services across a wide-range of industry sectors. The purpose of the 12000+ ASTM standard test methods is to improve product quality and safety for consumers and to facilitate market access and trade between businesses that adhere to the relevant standards [1].

In the petrochemical industry, certain elements are known to impact the performance and value of the final product, while others have detrimental effects on petroleum refining processes, as in the case of elements which can deactivate or poison catalysts. 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 using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). This method is widely used in the industry, but as specifications for the levels of trace elements in fuels become more stringent, some laboratories have migrated their analysis to the more sensitive technique of ICP-MS, which provides significantly lower detection limits than ICP-OES. To reflect this trend, the first ASTM ICP-MS method for trace element analysis in petroleum has been balloted in D0203. This is likely to be followed by an ICP-MS method for elemental analysis in petroleum crude oils.

This application note describes how the Agilent 7900 ICP-MS was used to analyze different types of crude oil samples following simple dilution in an organic solvent, *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

Standards

All calibration standard solutions were prepared from Conostan (Quebec, Canada) oil-base standards. The diluent comprised trace metal grade purity *o*-xylene (Fisher Scientific), a matrix modifier (made from mineral oil; Fisher Scientific), an in-house dispersant, and scandium and yttrium as internal standards, spiked at 0.1 mg/kg.

Multiple calibration standards ranging from 1 µg/kg to 1000 µg/kg were prepared for the target elements by weight from the 10 mg/kg Conostan S-21+K multi-element organometallic standard and *o*-xylene diluent. Separate calibration standards were prepared for As and Se from Conostan oil-based standards. 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 certified elements Ni and V and the reference elements As and Se. NIST 1634c was diluted approximately 1:60 in the *o*-xylene diluent prior to analysis.

Samples and sample preparation

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

The set of light crude petroleum oil samples and the multi-element Conostan standard (10 elements at 2 mg/kg in crude oil) were prepared by taking an aliquot of approximately 1 g, which was dissolved in approximately 9 g of the *o*-xylene diluent. For the heavier samples the sample aliquot and the amount of *o*-xylene diluent required was varied in order to dilute the analyte element with the highest concentration to 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 ensure that the crude oil samples were fully dissolved. The sample introduction system was rinsed using *o*-xylene between each sample analysis.

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

Instrumentation

An Agilent 7900 ICP-MS with an Agilent ASX-520 auto sampler was used. The crude oil solutions were delivered to the standard glass MicroMist concentric nebulizer through solvent-resistant peristaltic pump tubing with a diameter of 0.89 mm. Different pump speeds were used for rinsing and analyzing the sample, as shown in Table 2. The standard Peltier cooled quartz spray chamber was controlled at -2 °C to minimize the vapor pressure of the organic solvent. A plasma torch with a 1 mm injector was used for stable sample introduction to the plasma. The optional 5th gas mass flow controller was used to add oxygen (20% in Ar) to the injector gas stream after the spray chamber. O_2 addition serves to decompose the carbon matrix and thereby avoid carbon deposition on the interface cones. The more reactive plasma environment with O_2 addition requires the use of the more chemically-resistant optional Pt sampling and skimmer cones. The 7900 was also fitted with an organics drain kit.

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

Sample*	C (%)	H (%)	S (ppm)	N (ppm)	H/C	API gravity @ 15.56 °C/60 °F	Density (g/mL) @ 15.56 °C /60 °F
S1	84.84	13.08	1123	1093	1.84	36.20	0.8429
S2	85.90	13.31	5239	1078	1.85	35.40	0.8471
S3	83.60	12.92	4910	336	1.84	31.40	0.8685
S4	84.19	13.22	3886	310	1.87	41.40	0.8175
S5	85.24	12.76	4204	652	1.78	32.60	0.8616
S6	84.21	12.98	3350	500	1.84	33.60	0.8564
S7	86.18	13.00	2741	498	1.80	33.60	0.8569
S8	85.53	12.81	3129	514	1.78	33.10	0.8589
S9	84.78	13.04	21000	508	1.83	35.00	0.8512
S10	83.15	10.30	49100	4050	1.49	9.67	1.0030
S11	85.52	11.23	18527	7580	1.58	13.50	0.9740
S12	83.73	11.15	31980	3770	1.60	16.70	0.9532
S13	84.64	11.32	23821	2430	1.60	19.50	0.9364
S14	82.93	11.28	36809	3870	1.63	20.70	0.9286
S15	84.63	11.32	38500	1360	1.60	23.50	0.9121
S16	87.39	12.67	10490	1470	1.74	30.90	0.8702
S17	84.84	13.08	1123	1093	1.85	36.20	0.8429
S18	83.94	13.69	312	55.40	1.94	51.30	0.7733

* S1-S9 (API gravity >30°) represent light crude oils samples with element concentrations <15 mg/kg. S10-S18 include all types of crudes with API gravity from 9° up to 51°.

The 7900 ICP-MS features a fourth-generation collision/reaction cell, the ORS^4, which includes a standard He mode cell gas line for removal of common polyatomic interferences on most elements. The optional H_2 cell gas line was used for this application, as H_2 mode gives superior removal of the intense plasma- or matrix-based polyatomic overlaps on certain elements, notably Mg (*m/z* 24 – C_2 interference), Si (*m/z* 28 – CO/N_2), Ca (*m/z* 40 – Ar), Fe (*m/z* 56 – ArO) and Se (*m/z* 78 & 80 – Ar_2). Instrument operating parameters are given in Table 2.

Table 2. ICP-MS operating parameters

Parameter	Setting
RF power (W)	1550
Make up gas (L/min)	0.1
Carrier gas flow rate (L/min)	0.45
Option gas (O_2:Ar – 20:80) flow rate (%)	10
Sampling depth (mm)	8
Spray chamber temperature (°C)	-2
Peri-pump speed during rinse (rps)	0.5
Peri-pump speed during acquisition (rps)	0.04
Helium mode cell gas flow rate (mL/min)	3.4
Hydrogen mode cell gas flow rate (mL/min)	5

Results and discussion

Calibration

The calibration data shown in Table 3 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 V, Ni, As, and Se.

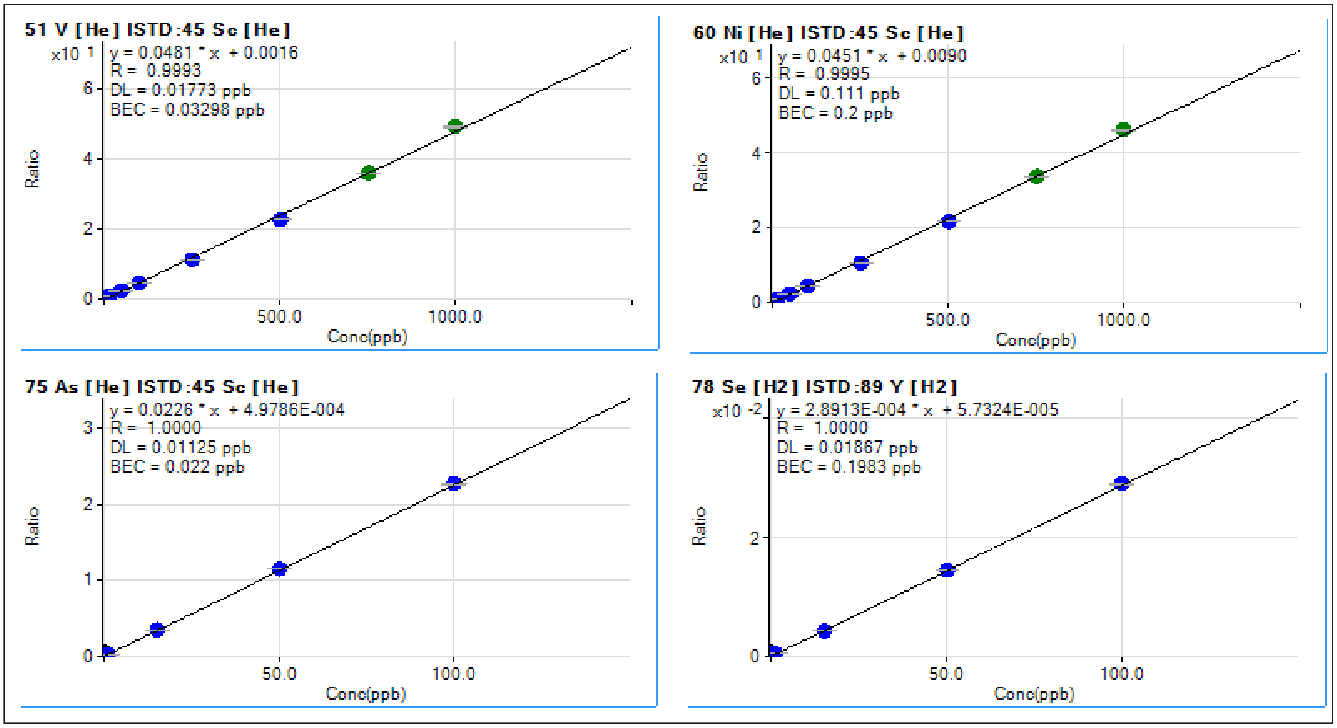


Figure 1. Calibration curves of V, Ni, As, and Se

Detection limits

Typical limits of detection (LODs) and background equivalent concentrations (BECs) for 23 elements are given in Table 3. The LODs were calculated from three times the standard deviation of 7 measurement results of the blank solution.

Table 3. ICP-MS performance data

Mass	Element	Tune Mode	R	LOD µg/kg	BEC µg/kg
23	Na	He	0.999	1.64	26.67
24	Mg	H_2	0.999	0.23	4.27
27	Al	He	0.999	0.48	2.14
28	Si	H_2	1.000	1.19	15.54
31	P	He	1.000	1.42	24.79
39	K	H_2	0.999	0.26	6.40
40	Ca	H_2	1.000	0.21	3.53
47	Ti	He	1.000	0.04	0.03
51	V	He	0.998	0.01	0.07
52	Cr	He	0.999	0.08	1.97
55	Mn	He	1.000	0.02	0.82
56	Fe	H_2	1.000	0.02	95.67
60	Ni	He	1.000	0.03	0.14
62	Ni	He	1.000	0.06	0.16
63	Cu	He	1.000	0.02	0.54
65	Cu	He	0.999	0.02	0.50
66	Zn	He	1.000	0.05	1.27
68	Zn	He	1.000	0.08	1.21
75	As	He	1.000	0.01	0.02
78	Se	H_2	1.000	0.09	0.05
80	Se	H_2	1.000	0.07	0.01
95	Mo	He	0.999	0.01	0.15
98	Mo	He	1.000	0.03	0.07
107	Ag	He	1.000	0.01	0.01
111	Cd	He	1.000	4.52	1.34
118	Sn	He	1.000	4.65	1.32
120	Sn	He	1.000	0.03	0.02
137	Ba	He	1.000	0.02	0.01
138	Ba	He	1.000	0.01	0.06
207	Pb	He	1.000	0.01	0.06
208	Pb	He	1.000	0.01	0.06

The relatively high BECs and LODs for Fe, Zn, Cd and Sn are probably due to contamination, most likely from the mineral oil component of the matrix modifier used in the blank.

Recovery of certified reference elements V and Ni

NIST 1634c has certified values for vanadium and nickel, which are important elements in the assay of crude oils as they are usually present in the highest concentrations. Both elements can adversely affect catalyst activity and product yields during the refinery process and vanadium compounds can cause refractory damage in furnaces [1]. As a performance check for the ability of the 7900 ICP-MS to provide consistent, accurate determination of these important elements, V and Ni were measured a total of 18 times in the diluted NIST 1634c standard, with measurements spread over 6 separate days.

The results in Table 4 show excellent recoveries within 10% of the certified values for both elements. It is also apparent that there was good agreement between the Ni results calculated independently using the different isotopes, ^{60}Ni and ^{62}Ni. This illustrates one of the key advantages of helium cell mode on the 7900 ICP-MS, where a single set of cell conditions can address all common polyatomic interferences, giving access to secondary or qualifier isotopes which can be used to confirm the result measured using the primary isotope.

Recovery of uncertified reference elements As and Se

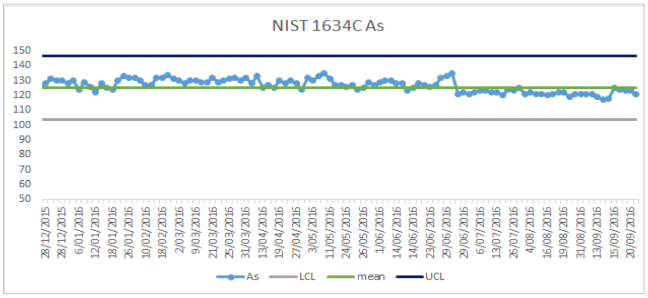
NIST 1643c also has uncertified reference values for As and Se. Both of these elements were measured repeatedly over an extended period in order to create quality control charts for the laboratory, as shown in Figure 2. The long-term performance check was based on a total of 147 separate measurements taken over the course of 12 months. Both charts show some variability within the upper and lower control limits but, overall, the reproducibility of results for As and Se in the control sample is very good. The average recoveries for As and Se were also within $\underline{+}$10% of the reference concentrations, 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 conc. & SD (mg/kg)	Certified (C) or Reference (R) value (mg/kg)	Recovery (%)
51 V [He]	[a]30720 ± 835	28190 ± 400 C	109
60 Ni [He]	[a]18897 ± 380	17540 ± 210 C	108
62 Ni [He]	[a]17544 ± 287	17540 ± 210 C	100
75 As [He]	[b]128.1 ± 5.3	142.6 ± 6.4 R	90
78 Se [H_2]	[b]106.8 ± 5.8	102 ± 3.8 R	105

[a] Calculated from 18 separate measurements taken on 6 separate days

[b] Calculated from 147 separate measurements taken over 12 months



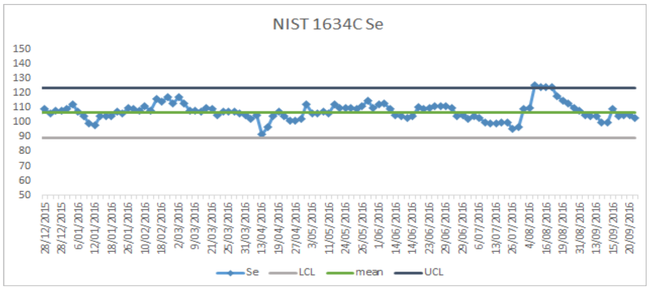


Figure 2. Quality control charts for As (top) and Se (bottom) based on a total of 147 separate measurements of NIST 1634c taken over 12 months

Table 5. Repeatability data (mg/kg) for As and Se in NIST SRM 1634c, based on 147 measurements taken over 12 months

		As	Se
Repeatability variance	$\sigma(r)^2$	2.118	0.401
Repeatability standard deviation	$\sigma(r)$	1.455	0.633
Repeatability relative standard deviation, %	RSD(r)	1.083	0.604
Repeatability value = 2.8 x σ(r)	r	4.075	1.773

Quantitative results

Quantitative results for Ca, Fe, Ni and V in 18 crude oil samples measured using the Agilent 7900 ICP-MS are shown in Table 6. The results show large variations in concentration for these critical elements between the different samples, with the greatest variation being observed for vanadium, ranging from 0.07 to 301 ppm.

Table 6. Quantitative results for Ca, Fe, Ni and V in 18 crude oil samples measured using ICP-MS (all data mg/kg)

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

*Limit of Quantitation (LOQ) was calculated from 10 measurements of a blank solution (diluent containing oil matrix and internal standard).

Conclusions

The Agilent 7900 ICP-MS with ORS^4 collision/reaction cell (CRC) was used for the direct multi-elemental analysis of crude oil samples following dilution in *o*-xylene. The efficient, frequency-matching rf generator of the Agilent 7900 provides a robust and stable plasma, facilitating reliable, accurate analysis of organic samples over an extended analytical period. Interferences on all analytes were reduced using He or H_2 cell gas mode. Fast gas switching in the ORS^4 allows the use of multiple gases in a single acquisition, without significant impact on acquisition time. The high sensitivity of the 7900 ICP-MS, combined with its low background and simple spectra in organic matrices, ensured that significantly lower detection limits were achieved for a wider range of elements compared to more traditional techniques, such as ICP-OES.

The method delivered excellent accuracy for certified and reference elements in NIST 1634c Trace Elements in Fuel Oil, with measurements taken on separate days over an extended period. The reproducibility of the methodology makes it suitable for routine use in the petroleum refining industry, increasing the likelihood that ASTM will issue an ICP-MS method for petroleum. It is anticipated that this will be followed by a further ASTM method for trace elements in petroleum crude oils.

Reference

1. ASTM International, www.astm.org

www.agilent.com/chem

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