

Multi-element analysis of crude oil samples by ICP-MS

Application note

Energy and Fuels

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Introduction

The analysis of trace metals and other undesirable elemental components in crude oils prior to refining is of critical importance to the refining industry. Trace metals can act as catalyst poisons, shortening the life of expensive catalysts. Toxic elements such as mercury, arsenic, selenium and lead need to be controlled because of environmental and waste disposal concerns. Elements such as sulfur can form corrosive compounds that attack plant facilities and residual sulfur is responsible for the formation of SO_x emissions from burned fuels. Other elements such as sodium can form salts that deposit on refinery equipment surfaces. Furthermore, the actual refining process used is dependent on the crude oil characteristics. Due to the historical analytical requirements and available instrumentation in refinery laboratories, there are several ASTM methods for crude oil analysis.



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- ASTM D7691 is a multi-element method using ICP-OES after dilution with an organic solvent. Due to the limited sensitivity of ICP-OES the applicable elements are restricted to S, V, Fe and Ni.
- ASTM D5708 can be used for the determination of Ni, V and Fe by ICP-OES with acid digestion or after direct dilution with an organic solvent. Acid digestion is time consuming and subject to potential analyte loss or contamination during sample preparation.
- ASTM D5863 is intended for the determination of Ni, V, Fe and Na by FAAS with acid digestion or after direct dilution with an organic solvent. It is severely limited in detection limits by the relatively poor sensitivity of FAAS.

As a proposed alternative to the current ASTM methods based on either ICP-OES or FAAS, ICP-MS can provide significantly lower detection limits in crude oils, even after dilution in an organic solvent. Dilution with an organic solvent is simple and minimizes the possibility of analyte loss or contamination during sample preparation. This technique is robust enough for routine use in the refining industry.

Table 1. Tuning parameters

Agilent 7700x ICP-MS	ORS Mode			
	H ₂	He	Low He	No gas
RF power	1600 W			
Carrier gas flow rate	0.60 L/min			
Spray chamber temperature	-5.0 °C			
Extract 1	0.0 V			
Extract 2	-150.0 V			
Helium flow rate	0.0 L/min	5.0 L/min	4.0 L/min	0.0 L/min
Hydrogen flow rate	7.0 L/min	0.0 L/min		
Energy discrimination	4.0 V			5.0 V

Experimental

Instrumentation

An Agilent 7700x ICP-MS with I-AS autosampler was used. Samples were introduced using the standard quartz MicroMist concentric nebulizer using self-aspiration. The sample uptake rate was controlled by the sample tube inner diameter (i.d.), its length and the carrier gas flow rate. In this analysis, a 0.25 mm i.d. x 700 mm length tube was used. Under these conditions, the sample uptake rate was 0.2 mL/min. Carrier gas flow is shown along with other important tune parameters in Table 1.

A standard Peltier cooled quartz spray chamber was controlled at -5 °C to minimize the vapor pressure of the organic solvent. A 1.5 mm injector torch was used for stable sample introduction to the plasma. Platinum sampling and skimmer cones were used. 20% oxygen in Ar was added to the injector gas stream after the spray chamber to avoid carbon deposition on the sampling and skimmer cones. The peristaltic pump was used to drain the spray chamber.

In this method, the Octopole Reaction System (ORS³) cell was utilized to remove interfering polyatomic ions. Based on a detailed evaluation of cell parameters, helium mode (He mode), low flow helium mode (Low He), hydrogen mode (H₂ mode) and no gas mode (No Gas) were used for the analysis. ICP-MS acquisition parameters are shown in Table 2.

Table 2. ICP-MS acquisition parameters

Parameter	Value
Mode	Spectrum mode
Peak pattern	3 points/mass
Replicates	3
Sweeps/Replicate	20
Integration time	0.3 s/mass
Sample uptake stabilization	120 s
Rinse 1, o-xylene	30 s
Rinse 2, o-xylene	30 s

Standards and samples

All calibration standard solutions were prepared from Conostan (Quebec, Canada) oil analysis standard solutions. Because the Conostan organometallic standards contain sulfur, two separate sets of calibration standard solutions were prepared; one containing sulfur only and one containing a mixture of the other metals. The stock solutions included a 1000 ppm sulfur in mineral oil standard, a 100 ppm S-21 multi-element standard, a 100 ppm As, 100 ppm Se and a 100 ppm Hg standard. The standard solutions were diluted by weight with o-xylene (Kanto Chemical Co., Inc., Japan). Calibration standards were prepared in o-xylene at 0, 200, 500 and 1000 µg/kg for all elements except sulfur which was prepared separately at 0, 10, 25 and 50 mg/kg. Because of instability of boron in the calibration standards over multiple days, new standards are prepared fresh daily. Yttrium was added to all standards, samples and blanks as an internal standard at 500 µg/kg.

ASTM D7691 (Standard Test Method for Multielement Analysis of Crude Oils Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)) recommends that a suitable solvent is selected based on the solubility of the sample being investigated. Since any variation in viscosity of the diluted solution would affect the sample flow when using self-aspiration, a higher (20x) dilution factor was applied. Prior to sample preparation, a solubility test and blank test were performed. From these results, o-xylene was selected as the solvent for this analysis.

A series of crude oil samples of various types including pitch asphalt were procured. 0.5 g of each crude oil sample was diluted 20 times with o-xylene up to 10 g. The rinse solution used to flush the sample introduction system between samples was o-xylene.

The rinse method was setup to automatically move the autosampler probe to two separate rinse vials, to give a two-step rinse.

Procedure

The plasma was ignited in organic mode while aspirating isopropanol (IPA). Tuning and optimization of plasma parameters, lens parameters and ORS parameters was performed by aspirating a 1 ppb tuning solution prepared from an inorganic standard diluted in IPA.

External calibration curves were acquired from the standard solutions, followed by the analysis of the diluted sample solutions. Measured values were corrected for wt/wt dilution factors to obtain the concentration in the original crude oil sample. Target elements analyzed were B, Na, Mg, Al, Si, P, S, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Ba, Hg and Pb.

Results and discussion

Calibration

Figure 1 shows representative calibration curves obtained under optimized conditions. Figure 1a shows the calibration curves for the elements S, V, Fe and Ni, which until now have usually been measured by ICP-OES, since these concentrations are generally high enough. The remaining calibration curves for the lower level elements (typically present at below the limit of detection for ICP-OES) are presented in Figure 1b. In all cases, linear calibration curves were obtained. While several elements can suffer from potential polyatomic interferences arising from the organic solvent, sample matrix and plasma gases (Ar, N, O), these calibration curves demonstrate that the 7700 method effectively removed the potential interferences on all these analytes.

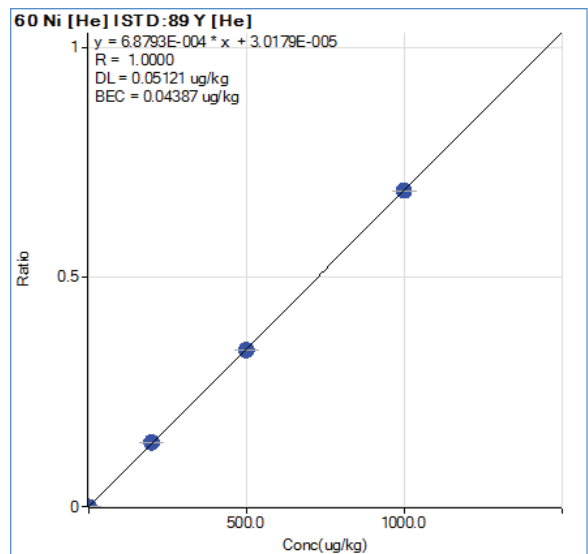
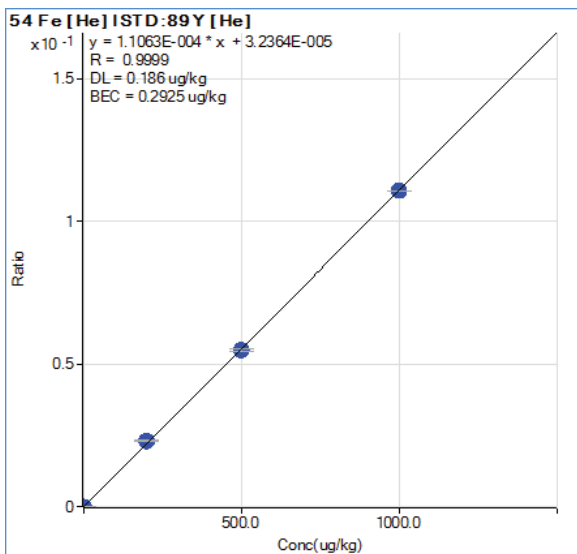
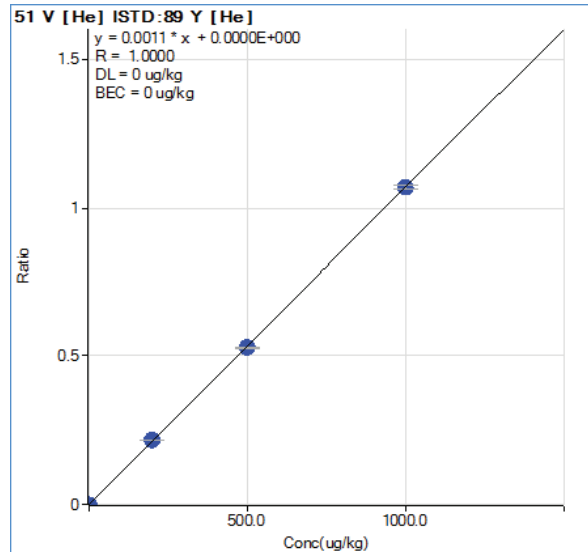
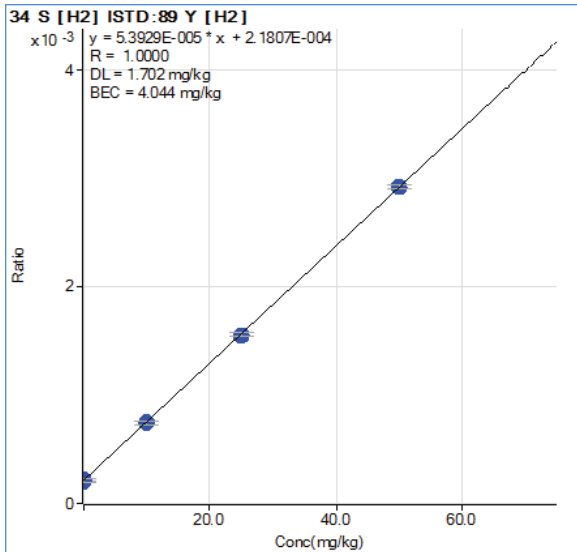


Figure 1a. Calibration curves of S, V, Fe and Ni. These elements are often measured by ICP-OES

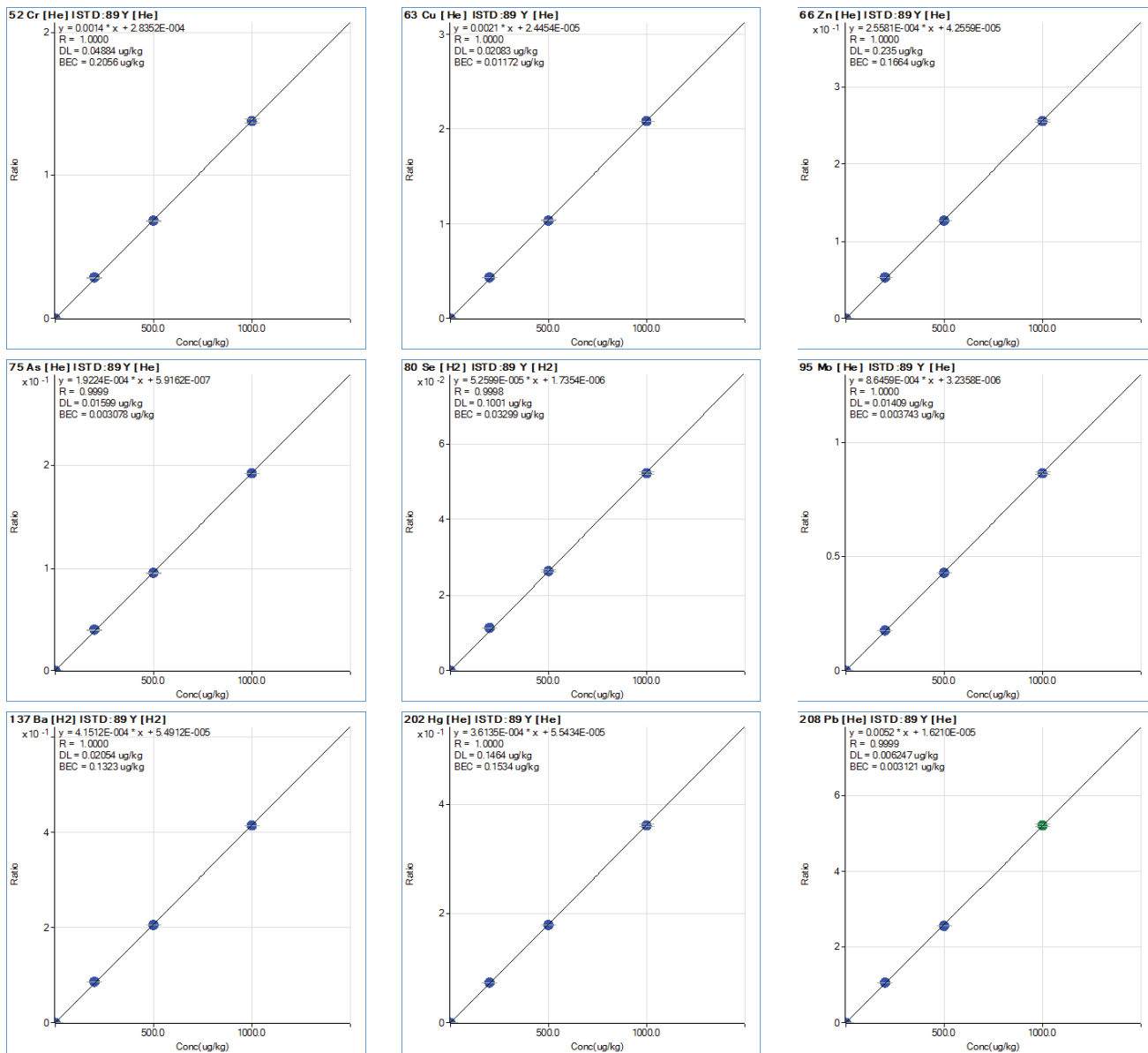


Figure 1b. Calibration curves of Cr, Cu, Zn, As, Se, Mo, Ba, Hg and Pb. These elements are difficult to analyze by ICP-OES due to low concentration in crude oil

Detection limits

Detection limits were calculated from three times the standard deviation of nine measurement results of the blank solution. The determined detection limits for all analytes are summarized in Table 3. Detection limits for both the 20-fold diluted and raw sample material (undiluted) are shown. The detection limits are in general more than an order of magnitude lower than those currently available using ICP-OES according to ASTM D7691-11 Multielement Analysis of Crude Oils Using Inductively Coupled Plasma Atomic Emission Spectrometry, which provides typical DLs for several elements.

Sample results

Quantitative measurements of trace elements in 22 crude oil samples by ICP-MS yielded results in good agreement with the data obtained using conventional techniques.

Spike recovery test

A spike recovery test was conducted in replicate using one of the crude oil samples. Sulfur and other elements were tested separately for the reasons described previously. In the case of sulfur, a 100 ppm S spike was added. In the case of the other elements, a mixed spike containing 200 ppb of each analyte was added. Table 4 shows that the spike recoveries were consistently good for all analyte elements.

Table 3. Analyte elements, ORS mode, calibration range, and detection limits in 20x diluted samples and raw crude samples. ICP-OES method detection limits specified in ASTM D7691-11 Multielement Analysis of Crude Oils Using ICP-AES are reported for comparison purposes.

<i>m/z</i> Element	Cell mode	Calibration range	DL in 20x diluted sample ($\mu\text{g}/\text{kg}$)	DL in raw sample ($\mu\text{g}/\text{kg}$)	ICP-OES MDL (for comparison) ($\mu\text{g}/\text{kg}$)
10 B	No Gas	0–1000 $\mu\text{g}/\text{kg}$	0.68	14	1000
23 Na	H ₂	0–1000 $\mu\text{g}/\text{kg}$	0.79	16	N/A
24 Mg	H ₂	0–1000 $\mu\text{g}/\text{kg}$	0.32	6.4	1000
27 Al	Low He	0–1000 $\mu\text{g}/\text{kg}$	0.035	0.70	1000
28 Si	H ₂	0–1000 $\mu\text{g}/\text{kg}$	3.2	64	4000
31 P	Low He	0–1000 $\mu\text{g}/\text{kg}$	13	260	1000
34 S	H ₂	0–50 mg/kg	1.2	23	N/A
40 Ca	H ₂	0–1000 $\mu\text{g}/\text{kg}$	0.22	4.5	100
49 Ti	Low He	0–1000 $\mu\text{g}/\text{kg}$	0.029	0.58	N/A
51 V	He	0–1000 $\mu\text{g}/\text{kg}$	0.0034	0.068	N/A
52 Cr	He	0–1000 $\mu\text{g}/\text{kg}$	0.036	0.72	100
55 Mn	He	0–1000 $\mu\text{g}/\text{kg}$	0.0085	0.17	100
54 Fe	He	0–1000 $\mu\text{g}/\text{kg}$	0.19	3.8	N/A
60 Ni	He	0–1000 $\mu\text{g}/\text{kg}$	0.036	0.72	N/A
63 Cu	He	0–1000 $\mu\text{g}/\text{kg}$	0.012	0.25	100
66 Zn	He	0–1000 $\mu\text{g}/\text{kg}$	0.041	0.83	500
75 As	He	0–1000 $\mu\text{g}/\text{kg}$	0.013	0.26	N/A
80 Se	H ₂	0–1000 $\mu\text{g}/\text{kg}$	0.046	0.91	N/A
95 Mo	He	0–1000 $\mu\text{g}/\text{kg}$	0.0075	0.15	200
107 Ag	He	0–1000 $\mu\text{g}/\text{kg}$	0.012	0.24	N/A
111 Cd	He	0–1000 $\mu\text{g}/\text{kg}$	0.0089	0.18	N/A
118 Sn	H ₂	0–1000 $\mu\text{g}/\text{kg}$	0.0055	0.11	N/A
137 Ba	H ₂	0–1000 $\mu\text{g}/\text{kg}$	0.069	1.4	200
202 Hg	He	0–1000 $\mu\text{g}/\text{kg}$	0.40	8.0	N/A
208 Pb	He	0–1000 $\mu\text{g}/\text{kg}$	0.0020	0.040	1400

Table 4. Spike recoveries in representative crude samples

<i>m/z</i> Element	Mode	Unit	Spike conc	Replicate 1 measured values			Replicate 2 measured values		
				Unspiked	Spiked	Recovery (%)	Unspiked	Spiked	Recovery (%)
10 B	No Gas	µg/kg	200	318.9	550.5	116	316.1	547.0	115
23 Na	H ₂	µg/kg	200	-0.9	159.0	80	-0.7	158.9	80
24 Mg	H ₂	µg/kg	200	0.2	186.7	93	0.0	185.6	93
27 Al	Low He	µg/kg	200	0.2	199.1	99	0.3	197.2	98
28 Si	H ₂	µg/kg	200	4.5	191.0	93	8.2	194.7	93
31 P	Low He	µg/kg	200	9.8	207.2	99	11.2	194.3	92
34 S	H ₂	mg/kg	100	11.5	119.7	108	11.0	120.3	109
40 Ca	H ₂	µg/kg	200	-0.1	189.1	95	-0.1	187.1	94
49 Ti	Low He	µg/kg	200	1.8	198.7	98	1.7	203.4	101
51 V	He	µg/kg	200	253.9	459.2	103	256.5	465.1	104
52 Cr	He	µg/kg	200	0.3	201.0	100	0.3	202.5	101
55 Mn	He	µg/kg	200	0.0	194.8	97	0.0	195.0	97
54 Fe	He	µg/kg	200	2.7	206.6	102	2.6	207.0	102
60 Ni	He	µg/kg	200	95.7	299.5	102	96.2	303.0	103
63 Cu	He	µg/kg	200	0.9	205.7	102	0.7	206.9	103
66 Zn	He	µg/kg	200	0.8	183.2	91	0.9	183.1	91
75 As	He	µg/kg	200	0.2	197.7	99	0.3	195.6	98
80 Se	H ₂	µg/kg	200	0.9	198.0	99	0.9	198.2	99
95 Mo	He	µg/kg	200	6.3	213.0	103	6.3	214.2	104
107 Ag	He	µg/kg	200	0.1	207.5	104	0.0	208.4	104
111 Cd	He	µg/kg	200	0.0	195.1	98	0.0	196.9	98
118 Sn	H ₂	µg/kg	200	0.0	202.4	101	0.0	202.5	101
137 Ba	H ₂	µg/kg	200	0.0	204.0	102	0.0	203.0	101
202 Hg	He	µg/kg	200	0.7	207.2	103	0.6	207.0	103
208 Pb	He	µg/kg	200	0.0	176.8	88	0.0	177.0	88

Long term stability

Long term stability was tested using an unspiked composite of 20 diluted samples. The composite sample was analyzed as an unknown sample repeatedly for more than 8 hours. Figure 2 demonstrates excellent stability for S, V, Fe, Ni and Mo results, as evidenced by the low %RSDs (S - 2.3%, V - 0.7%, Fe - 2.2%, Ni - 0.8% and Mo - 1.9%). The other target elements were also analyzed in this sequence but many of these elements' concentrations were too low to evaluate long term stability. During the sequence, two CCV solutions were analyzed after every 9 crude oil samples. The two CCVs contained 20 ppm sulfur in o-xylene and 200 ppb of other analytes in o-xylene, respectively. Figure 3 shows the stability of these two CCV solutions.

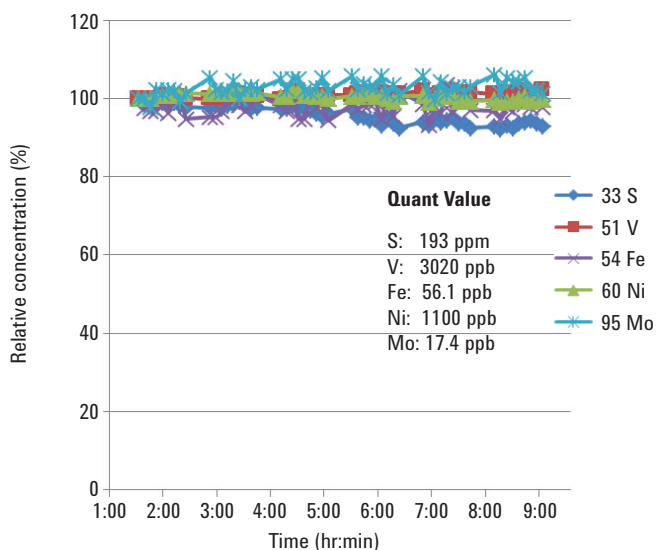


Figure 2. Long term stability of unspiked combined crude oil sample analysis

Conclusions

Direct analysis of crude oil samples by ICP-MS after 20x dilution in o-xylene is simple and reliable and provides superior detection limits for a wide range of elements, compared to existing ASTM methods.

The Octopole Reaction System (ORS³) and multi-tune (multiple cell gas modes) capability of the Agilent 7700x ICP-MS provides an efficient method to reduce interferences for all analytes. Determined results agreed well with reported values obtained using traditional ASTM methods. Limits of detection for most elements are more than one order lower than are possible using traditional techniques and excellent long term stability was obtained over 8 hours.

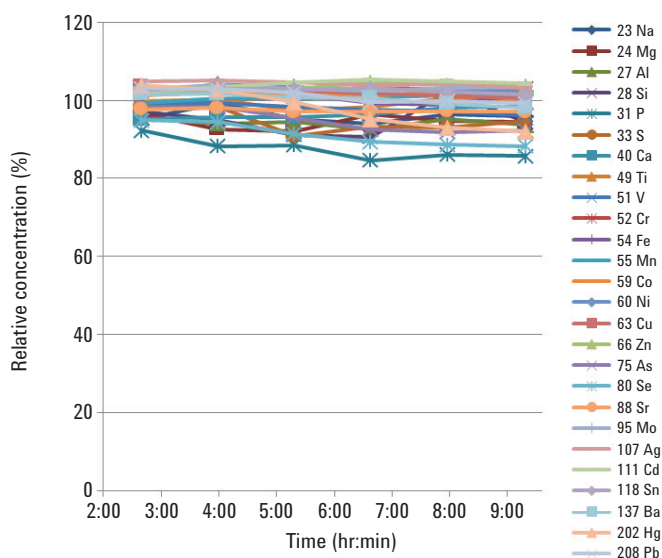


Figure 3. Long term CCV results. Two CCV solutions were analyzed. 1) 20 ppm sulfur in o-xylene. 2) 200 ppb other elements in o-xylene. This plot represents 8 hours stability from 2 hr 30 min to 10 hr 30 min.

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