The Analysis of Distillate Products Per ASTM D8110-17 Using the Agilent 7800 ICP-MS and Teledyne-Cetac MVX-7100µL Autosampler

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Introduction

In the petrochemical industry, certain analytes are known to impact the performance and value of the final product. In July 2017, ASTM issued their first test method for ICP-MS: ASTM D8110 – 17 Standard Test Method for Elemental Analysis of Distillate Products by ICP-MS. This test method describes the procedure for the determination of trace elements in light and middle distillate petroleum products using ICP-MS.

Objectives

- Analyze ASTM D8110-17 analytes (Al, Ca, Cu, Fe, K, Mg and Pb) by ICP-MS
- Achieve low detection limits, and good recoveries from analysis
- Address the safety and peri pump tubing issue with solvent analysis
  - Disadvantages of Peri Pump tubing for petroleum analysis is that many solvent resistant polymers are NOT significantly clean enough to achieve the best possible detection limits for some elements
  - A common problem with analysis of petroleum products is the ventilation requirements for o-xylene.

Approach

- Analyze samples using an Agilent 7800 ICP-MS coupled to a septum piercing, syringe driven autosampler, MVX-7100 µL workstation (Teledyne-Cetac)
- The MVX-7100 µL workstation is fully integrated into the Agilent Mass Hunter software. The MVX offers a metal-free and organic resistant liquid facing flow path for trace elemental applications. Septum piercing capabilities and no peristaltic pump tubing involved in sample introduction.

Experimental

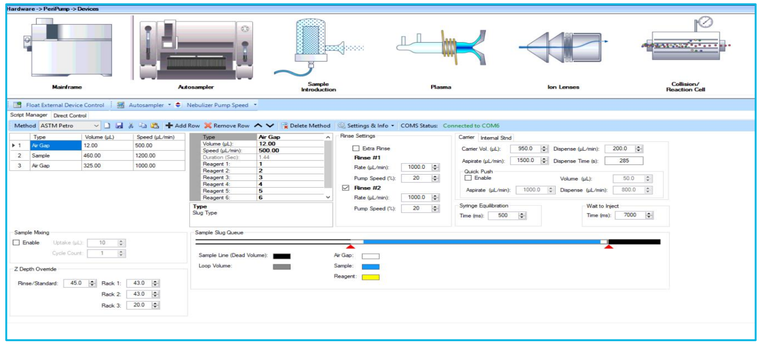
Samples

A series of 14 Petroleum samples were used in the study. Light and middle distillates (jet, diesel, Naphtha, and FCC feed).

Sample Preparation

- The petroleum oil samples were prepared by taking an aliquot (~1g) which was dissolved in (~9g) of the o-xylene diluent.
- All samples were shaken in a mechanical shaker for 30minutes to help the samples dissolve. The sample introduction system was rinsed with o-xylene between sample analysis.
- Multiple calibration standards ranging from 0.16ppb to500ppb were prepared for all elements by weight using the Agilent S21 + K 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 elements: Ni, and V. NIST 1634c was diluted approximately 1:100 in the o-xylene diluent prior to analysis.
- Samples were placed in 1.5mL septum capped vials for analysis.

Figure 1: MVX 7100 Autosampler Parameters



Data Collection

7800 ICP-MS (Agilent) with MVX 7100µL workstation (Teledyne-Cetac)

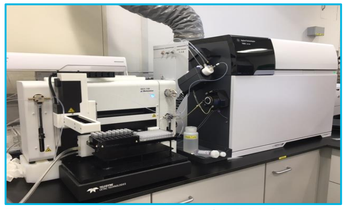


Figure 2: Agilent ICP-MS with MVX-7100

Instrument	Agilent 7800 ICP-MS
Acquisition mode(s)	Hydrogen and Helium cell modes
Sample Introduction	Micromist nebulizer
	Quartz torch with 1.00 mm injector
	Peltier Cooled quartz double pass spray chamber
Sample uptake - MVX 7100	500uL sample loop dispensing at 200uL/min
Interface	Platinum sampling and skimmer cone
Paramater	**Setting**
RF Power (W)	1550
Plasma gas flow rate (L/min)	15
Nebulizer gas flow rate (L/min)	0.37
Make up gas (L/min)	0.1
Optional O_2 gas flow rate (%)	21
Sampling depth (mm)	10
Spray chamber temperature (ºC)	-5
Helium flow rate (mL/min)	4.5
Hydrogen flow rate (mL/min)	5.5

Table 1: ICP-MS operating parameters

Results

The calibration data shown in Table 2 is typical of the performance of the 7800 ICP-MS. Linear Calibrations were obtained for all analytes as indicated by the calibration coefficients (>0.999 in all cases). Figure 3 shows the calibration curves for all analytes.

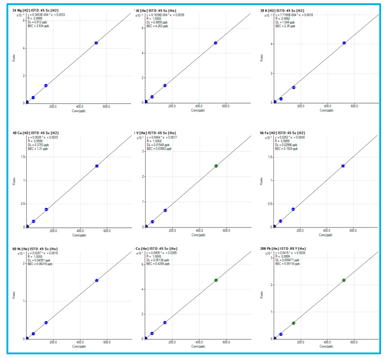


Figure 3 : Calibration Curves

Detection Limits

Typical instrument detection limits (IDLs) and background equivalent concentrations (BECs) are given in Table X. The DLs were calculated from three times the standard deviation of 10 measurements of the blank.

Mass	Element	Tune Mode	R	DL, ppb	BEC
24	Mg	H2	1.000	0.912	3.934
27	Al	He	1.000	0.986	4.263
39	K	H2	0.999	0.629	3.379
40	Ca	H2	1.000	0.375	1.310
51	V	He	1.000	0.015	0.036
56	Fe	H2	1.000	0.030	0.193
60	Ni	He	1.000	0.041	0.063
63	Cu	He	1.000	0.030	0.196
208	Pb	He	1.000	0.009	0.091

Table 2: 7800 ICP-MS Performance Data

Results and Discussion

Certified Reference Values for V and Ni

As a performance check for the NIST certified elements Ni and V, the 7800 ICP-MS was used to analyze the diluted NIST 1643c standard a total of 9 times throughout the analysis. The results in Table X show excellent recoveries for the certified elements V and Ni within +/- 10%.

Element	Average measured values (mg/kg)	Certified value (mg/kg)	Recovery
51 V	26148 ± 376	28190 ± 400	92.8%
60 Ni	16748 ± 287	17540 ± 210	95.5%

Table 3: Recoveries of V and Ni in NIST SRM 1634c

QC Results

A second source standard, Conostan S-21, was analyzed a total of 9 times throughout the analysis to ensure accuracy. The second source QC was prepared to 51.14 PPB. Low standard deviations with good recoveries show accuracy and precision in the analysis. As K was not present in the second source standard a CCV at 145.88ppb was analyzed 3 times throughout the run. Results showed excellent recoveries for all elements.

	Second Source QC*		CCV**	
Analyte	Average measured values (PPB)	Recovery	Average measured values (PPB)	Recovery
24 Mg	49.7 ± 1.3	96.5%	159.1	109.0%
27 Al	51.9 ±1.3	100.9%	159.9	109.6%
39 K	NA	NA	140.9	96.6%
39 K	NA	NA	149.0	102.1%
40 Ca	49.7 ± 1.8	96.5%	162.4	111.3%
51 V	45.2 ± 0.4	87.9%	145.0	99.4%
56 Fe	49.9 ± 0.7	97.0%	150.3	103.0%
56 Fe	48.6 ± 0.2	94.4%	145.1	99.5%
60 Ni	47.0 ± 0.8	91.3%	148.5	101.8%
63 Cu	46.6 ± 0.7	90.6%	157.0	107.6%
208 Pb	45.4 ± 0.5	88.3%	147.0	100.7%

Table 4: QC Recoveries
*Second Source QC analyzed a total of 9 times and does not contain K
**CCV analyzed 3 times

Quantitative Results

All results were in expected concentration ranges for each of the sample types (Table 5). Samples were also run in a separate lab on an Agilent ICP-MS and results confirmed the results obtained on the MVX-71000 connected to the 7800 Agilent ICP-MS.

Sample Name	24 Mg	27 Al	39 K	40 Ca	51 V	56 Fe	60 Ni	63 Cu
M1	< LOQ	< LOQ	< LOQ	54.0	2.2	31.7	6.8	11.9
M2	31.4	< LOQ	< LOQ	38.7	1.0	3.5	2.4	8.2
M3	22.0	< LOQ	< LOQ	47.5	< LOQ	5.1	< LOQ	2.7
M4	36.6	< LOQ	< LOQ	24.0	54.1	14.9	16.8	5.4
M5	< LOQ	36.1	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
M6	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	3.0
M7	< LOQ	< LOQ	< LOQ	30.6	< LOQ	58.5	< LOQ	3.3
A1	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	14.5	6.8	16.7
A2	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	3.4
A3	50.2	< LOQ	< LOQ	76.9	10.1	28.6	5.9	5.4
A4	< LOQ	< LOQ	64.4	49.2	0.6	11.6	< LOQ	3.7
A5	< LOQ	40.2	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
A6	< LOQ	< LOQ	< LOQ	47.3	0.5	6.4	< LOQ	3.6
A7	< LOQ	< LOQ	< LOQ	13.1	< LOQ	7.8	< LOQ	1.6

Table 5: Quantitative sample results (PPB)

Conclusions

The Agilent 7800 ICP-MS is suitable for the multi-analysis of petroleum samples per ASTM D8110-17. The high sensitivity of ICP-MS ensures lower detection limits can be achieved for a wider range of elements compared to other techniques such as ICP-OES. The MVX 7100µL autosampler provided reproducible results while allowing lower sample consumption, septum piercing capabilities, and no peri-pump tubing required.

References

ASTM D8110-17 www.astm.org