

# Highly sensitive analysis of distillate products per ASTM Method D8110 using single quadrupole ICP-MS

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## Abstract

**Purpose:** The goal of this poster is to demonstrate the performance of an analytical method for routine analysis of crude oil, but also products such as naphtha, with different boiling ranges using single quadrupole ICP-MS following the guidelines provided in ASTM Method D8110 Standard Test Method for Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

**Methods:** An analytical method was developed with single quadrupole ICP-MS for elemental analysis of a range of typical petroleum samples with varying physical and chemical properties.

**Results:** Key figures of merit such as instrument detection limits (IDLs) and correlation coefficients ( $R^2$ ) were found to be meeting analytical requirements of ASTM Method. The accuracy of analytical method was found to be well within 80-120% for all analytes in all matrices. Long term robustness of system was monitored over 10 hours. The response of both internal standards readback was within 75-120% compared to first calibration blank analyzed at the beginning of long sequence.



Figure 1. Thermo Scientific™ iCAP™ MSX ICP-MS

## Introduction

Control of impurities in the petrochemical industry is an essential step to ensure the quality of the crude, intermediates, and finished products. In many laboratories, the analysis of crude, intermediates, and finished products, including light and middle distillates for trace elements, is accomplished using inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS). However, the regulations and specifications for content of elemental impurities are becoming more stringent, which enforces determination of these impurities at lower concentration levels. Due to its higher sensitivity and specificity, ICP-MS is becoming the technology of choice for laboratories. The American Society for Testing and Materials (ASTM) issues standard D8110 that outlines the specifications and test method for elemental analysis of distillate products by ICP-MS. Analysis of combustible organic samples like naphtha, vacuum gas oil (VGO), or aviation turbine fuel (ATF) using ICP-MS could be challenging compared to conventional aqueous samples mainly because unexpected and intermittent extinguishing of plasma as well as carbon deposition in the interface region extracting ions into the mass spectrometer. The direct introduction of volatile organics increases the plasma load due to their high vapor pressure, causes destabilization of plasma and results in poor sensitivity and precision of measurements. Carbon-based interference on key analytes, such as chromium or vanadium, cause additional concerns but can typically be overcome using kinetic energy discrimination (KED) on single quadrupole instruments, or other typical gases used in collision/reaction cells<sup>1</sup>. This poster discusses a complete workflow developed using the Thermo Scientific™ iCAP™ MSX ICP-MS (Figure 1) for the sensitive determination of elemental impurities in typical distillate samples including light naphtha, heavy naphtha, and crude oil samples.

## Materials and methods

### Sample Preparation

**Fuel oil/crude oil:** The oil sample was initially heated in a water bath to 40–60 ° C and mixed thoroughly to ensure the sample homogeneity. About 1 g of homogenized oil sample was then weighed accurately in a 50 mL volumetric flask followed by an approximate 100-fold dilution using PremiSolv™ as a diluent and addition of an internal standard. Additional dilutions (25-fold and 50-fold, respectively) were prepared to evaluate effect of varying sample concentration (difference in viscosity) on the analytical performance.

**Heavy naphtha (160–180 ° C boiling range):** Heavy naphtha was aspirated directly after addition of an internal standard.

**Light naphtha (40–60 ° C boiling range):** Light naphtha was diluted 10-fold using PremiSolv followed by the addition of the required amount of internal standards stock solution before aspiration into the ICP-MS.

### Data Analysis

The data acquisition and processing were done using Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

Table1: Instrument parameters used on iCAP MSX ICP-MS

Parameter	Value
Nebulizer	iCAP MX Series nebulizer
Interface cones	Pt – tipped sample and skimmer
Spray chamber	Cyclonic quartz
Injector	Quartz, 1.0 mm ID
Torch	PLUS torch
Auxiliary Flow (L·min <sup>-1</sup> )	0.8
Cool Gas Flow (L·min <sup>-1</sup> )	14
Nebulizer Flow (L·min <sup>-1</sup> )	0.455
RF Power (W)	1550
Sampling depth (mm)	7
Number of Replicates	3
Spray Chamber Temp (° C)	-5
KED settings (gas flow rate in mL·min <sup>-1</sup> )	4.3 (with a 3V kinetic energy barrier)
Number of sweeps	5

## Results

Table 2. Analytes, m/z used, Correlation coefficients ( $R^2$ ) and instrument detection limits (IDLs) determined for all target analytes

Element	m/z	$R^2$	IDL ( $\mu\text{g L}^{-1}$ )	Element	m/z	$R^2$	IDL ( $\mu\text{g L}^{-1}$ )
Sodium (Na)	23	0.9987	55.6	Zinc (Zn)	66	0.9950	0.394
Magnesium (Mg)	25	0.9976	1.99	Arsenic (As)	75	0.9996	0.019
Aluminium (Al)	27	0.9956	1.3	Selenium (Se)	77	>0.9999	0.180
Potassium (K)	39	0.9985	0.74	Molybdenum (Mo)	98	0.9994	0.004
Calcium (Ca)	40	0.9993	16	Silver (Ag)	107	>0.9999	0.01
Titanium (Ti)	48	0.9999	0.01	Cadmium (Cd)	111	0.9981	0.004
Vanadium (v)	51	0.9998	0.003	Tin (Sn)	118	0.9995	0.025
Chromium (Cr)	52	0.9998	0.055	Antimony (Sb)	121	0.9995	0.0017
Manganese (Mn)	55	0.9990	0.046	Barium (Ba)	137	0.9998	0.032
Iron (Fe)	57	0.9997	0.107	Mercury (Hg)	202	0.9993	0.014
Nickel (Ni)	60	0.9998	0.007	Lead (Pb)	208	0.9995	0.009
Copper (Cu)	63	0.9997	0.014				

## Method accuracy and robustness

### Spike and recovery study

To test the accuracy and precision of the proposed method for the different sample types investigated in this study, a series of experiments were performed. The accuracy was determined using spike recovery testing in all sample types analyzed. The aliquots of light naphtha, heavy naphtha, and oil samples were spiked with analyte concentrations ( $5\text{ }\mu\text{g}\cdot\text{L}^{-1}$  of analytes except for K, which was spiked at  $50\text{ }\mu\text{g}\cdot\text{L}^{-1}$  concentration level). The results obtained from the study performed on light naphtha and 100-fold diluted oil sample are presented in Figure 2 and Figure 3, respectively. All values reported are as the average of three individual measurements of independent sample preparations. The accuracy values observed for all analytes in tested samples were found to be within the range of 80-120%. The results from light naphtha and oil samples are presented as they cover the entire range of typical samples with varying physical and chemical properties (viscosity, vapor pressure, and chemical composition). In the case of the oil sample, some of the analytes are omitted from the results because of their elevated apparent concentrations in unspiked sample, affecting recovery of those elements at specified spiked concentrations.

Figure 2. Results of spike recovery testing: % accuracy of various elements in light naphtha sample

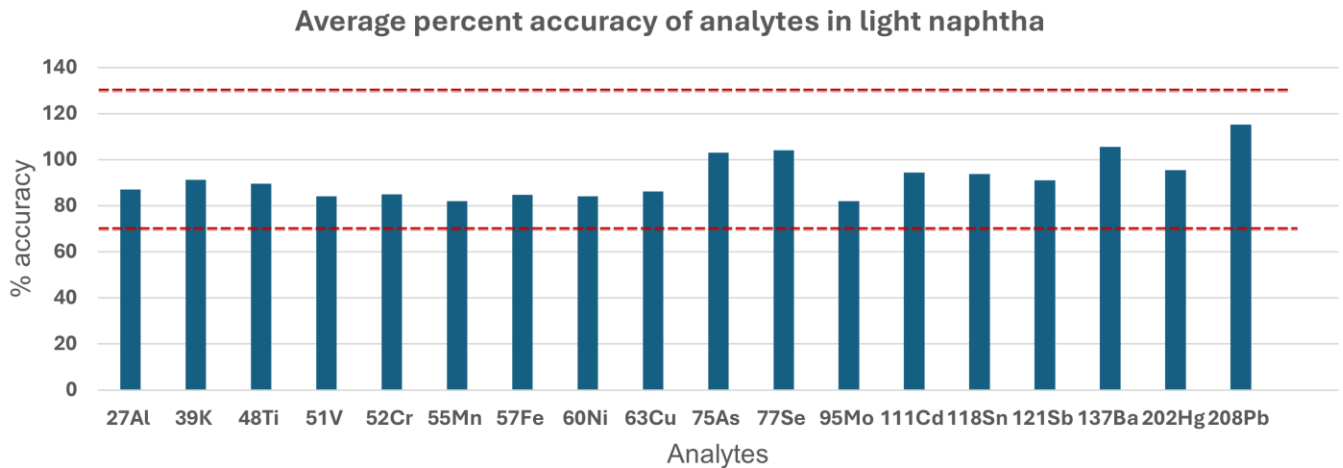
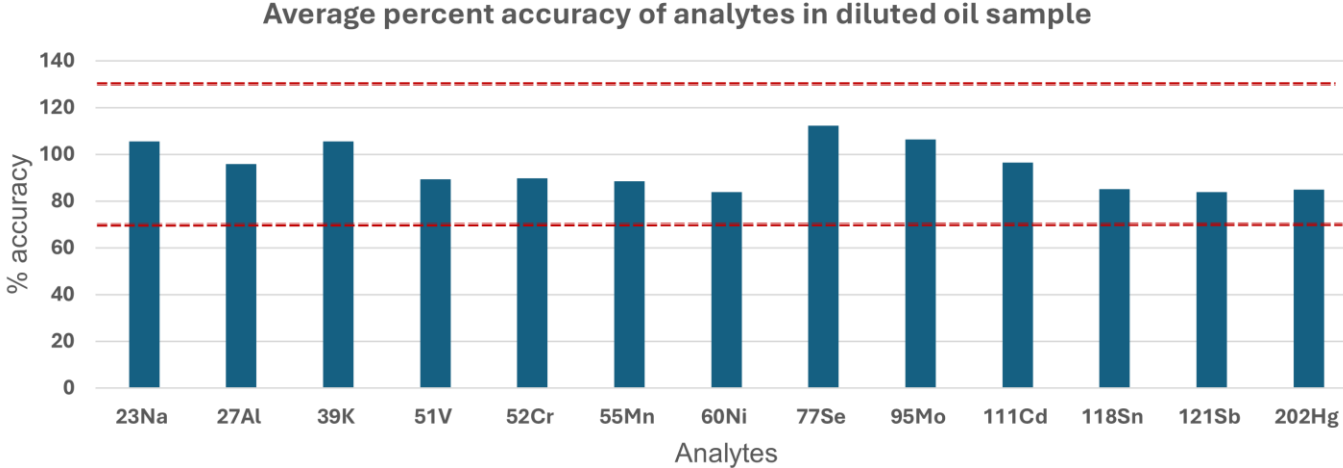


Figure 3. Results of spike recovery testing: % accuracy of various elements in crude oil sample

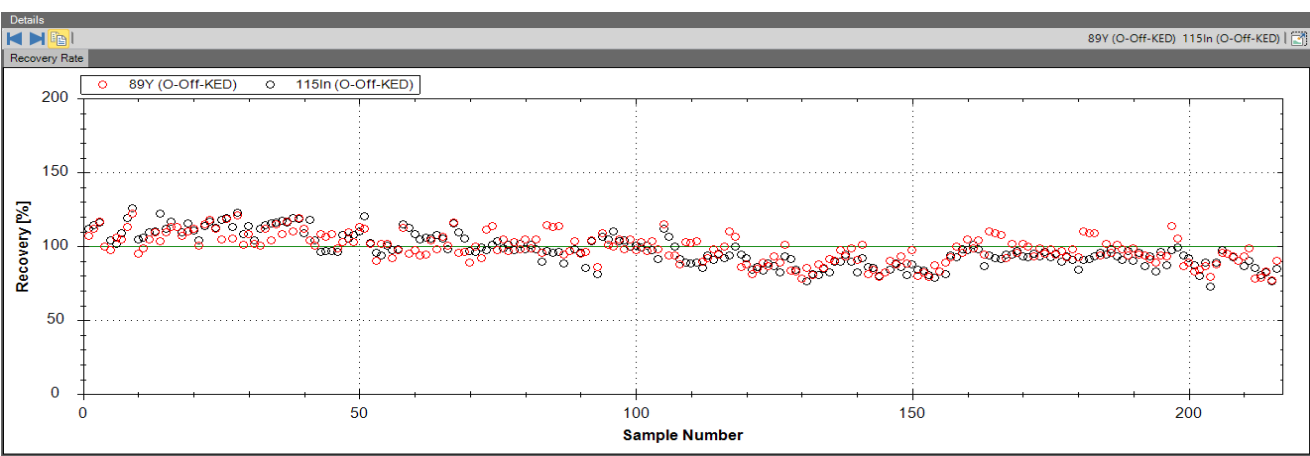


### Long-term instrument robustness

Since crude, intermediates, and final product have vastly different physicochemical properties, the need for often dedicated instrument configurations and methods for each of the sample types is a challenge for laboratories in the petrochemical industry. To assess the stability of the system (including sample introduction system, plasma generation, and interference removal), a large sample batch containing all types of samples was scheduled for analysis.

The batch contained a mixed sequence of petroleum products including crude oil, light naphtha, and heavy naphtha samples and was analyzed continuously over a period of 10 hours. In accordance with the sample preparation section above, the crude oil samples and light naphtha were diluted using PremiSolv to reduce the impact of the different viscosities, whereas heavy naphtha was run undiluted. Different dilution factors ranging from 25-fold to 100-fold were used for oil sample preparation to check for potential matrix effects affecting the sample introduction system and the plasma response. For the entire batch, the response of internal standards was monitored and indicated that the instrument set-up was stable. In this case, the internal standards read back in the range between 75% and 120% of their initial values, indicating that the proposed method is suitable for longer batch analysis containing a variety of sample types.

Figure 4. Response of the internal standards during a larger sample batch containing all sample types investigated in this study



## Conclusions

The results obtained from the experiments described in this application note demonstrate the following:

- The proposed method and instrument set-up for elemental analysis of different petroleum products using the iCAP MSX ICP-MS represents a viable solution for laboratories performing oil and refinery product testing.
- The combination of the sample introduction system together with a uniquely robust plasma generation system and a powerful CRC allows for sensitive analysis and comprehensive interference removal for all elements commonly analyzed in the industry.
- The use of KED with helium provided effective for removal of polyatomic interferences commonly observed in such challenging matrices, as was demonstrated by the detection limits and blank equivalent concentrations (BECs) achieved.
- The method therefore allows the accurate and precise determination of a total of 28 elements in different kinds of distillate products, as was demonstrated by the results obtained in the spike recovery test.
- If needed, other reactive gases can be used in a multi-mode analysis performed during a single aspiration of a sample, including alternative cell gases such as hydrogen. Thanks to the fast gas switching in the QCell CRC, the added time for switching cell gases is often negligible for the overall analysis time per sample.
- The novel design of the sample introduction system of the iCAP MSX ICP-MS allows to easily switch between oxygen addition and the use of argon gas dilution without the need to change gas connections.

## References

- Thermo Fisher Scientific Application Note 44465: [Addressing the challenges of routine determination of elemental impurities in refinery products using a robust ICP-MS approach](#)

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