

Industrial

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

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## Keywords

Petroleum products, distillate, ASTM D8110, crude oil, naphtha, elemental analysis, ICP-MS, Process and Quality Control, iCAP MSX ICP-MS

## Goal

The goal of this application note is to demonstrate the performance of an analytical method for routine analysis of typical samples relevant to the petrochemical industry, including starting materials such as 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)*.

## Introduction

Control of impurities in the petrochemical industry is an essential step to ensure the quality of the crude, intermediates, and finished products. Metals such as nickel, vanadium, mercury, or lead are known as catalyst poisons that can affect product quality even at very low levels. Premature failures of catalysts can lead to interruptions in the production cycle, resulting in high costs.

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). ICP-OES is the most widely used technique for this purpose due to its high tolerance to different sample types,

and especially its higher tolerance to organic solvents. 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.

The high viscosity of petroleum and many of its derivatives make it difficult to analyze these samples directly by ICP-MS. Therefore, the aspiration of organic liquids into the plasma normally requires additional equipment or sample pre-treatment to maintain plasma stability, reduce carbon build-up, and minimize background interferences. 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 problems are primarily related to the fact that carbon is often not completely ionized in plasma due to its high ionization potential (11.3 eV), leading to its subsequent deposition on the interface.

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 application note discusses a complete workflow developed using the Thermo Scientific™ iCAP™ MSX ICP-MS for the sensitive determination of elemental impurities in typical distillate samples including light naphtha, heavy naphtha, and crude oil samples.

## Experimental

A major challenge when analyzing different types of petrochemical samples are the differences in vapor pressure and viscosity, ultimately leading to the need for a dedicated configuration of the sample introduction system. Whereas samples with high boiling points, such as crude oil or fuel oil, require heating of the sample introduction system components to remain fluid, samples with a lower boiling point (i.e., naphtha) require cooling of the spray chamber to avoid overloading the plasma and sudden extinction. The new design of the spray

chamber Peltier cooling system available on the iCAP MSX ICP-MS ensures efficient and consistent cooling of the spray chamber, maintaining stable temperature throughout analytical measurement which ultimately improves analytical stability. In addition, the newly designed sample introduction system allows independent connection of an additional flow of argon (for online sample dilution using AGD) and oxygen (for analysis of organic samples) to two different locations at the spray chamber elbow. This allows users to switch between aqueous and organic applications rapidly without additional instrument downtime.

## Sample preparation

With the objective of analyzing various sample types in a single batch, samples were prepared differently in each case.

**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. The same oil sample was diluted 25-fold and 50-fold using PremiSolv as diluent and analyzed during the larger analytical batch to evaluate effect of varying sample concentration (difference in viscosity) on the analytical performance. The behavior of internal standards while analyzing these differently diluted samples was the parameter under investigation in this test.

**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.

**Quality control (QC) sample:** An independently prepared solution containing 5 µg·L<sup>-1</sup> of all analytes typically present at trace levels and 50 µg·L<sup>-1</sup> of K (corresponding to standard 3 as per Table 1) in PremiSolv was used to verify the validity of the calibration curve and was analyzed following every 10 unknown samples throughout the measurement of a larger batch containing more than 200 samples.

**Table 1. Concentration of elements in calibration standard solutions (µg·L<sup>-1</sup>)**

Analytes	LL 1	LL 2	LL 3	LL 4	LL 5
B, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Hg, Pb	0.1	0.5	5	10	50
K	5	50	100		

**Calibration standards:** To analyze various elements in a single consolidated method, five different calibration standards were prepared gravimetrically using a serially diluted stock standard solution containing 1 mg·kg<sup>-1</sup> (w/w) of trace analytes and 10 mg·kg<sup>-1</sup> (w/w) of K. This stock solution was prepared using a certified oil-based multi-element standard and selected oil-based single element standards for elements including As, Se, Sb, Hg, and K. Subsequent calibration solutions were prepared volumetrically.

To improve accuracy and compensate for potentially occurring drift during a longer sequence, internal standardization has been applied. Yttrium and indium were spiked at a concentration of 10 µg·L<sup>-1</sup> to each blank, standard, or sample and used as internal standards in the experiment.

### Instrumentation

An iCAP MSX ICP-MS equipped with a 250 mL·min<sup>-1</sup> additional mass flow controller has been used in the study. The system was operated in conjunction with a Thermo Scientific™ iSC-65 Autosampler. The sample introduction system was configured for the analysis of organic samples using the components summarized in Table 2.

**Table 2. Instrument configuration of iCAP MSX ICP-MS used in the experiment**

Parameter	Value
Nebulizer	iCAP MX Series nebulizer
Interface cones	Pt-tipped sample and skimmer
Spray chamber	Cyclonic quartz
Injector	Quartz, 1.0 mm i.d.
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
AGD dilution	None
AGD flow, Argon (L·min <sup>-1</sup> )	NA
RF power (W)	1,550
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 3 V kinetic energy barrier)
Number of sweeps	5

To tackle the challenge of carbon deposition, a constant flow of pure oxygen was introduced into the spray chamber elbow using an additional mass flow controller. The completely redesigned sample introduction system of the iCAP MSX ICP-MS now allows introduction of additional gases independently from argon used for optional sample dilution through a dedicated port located at the spray chamber elbow. This is a significant advantage for laboratories that need to switch between aqueous and organic solvents, which is now possible without switching gas connections.

All 28 analytes including internal standards were measured in KED mode using pure helium as the only cell gas. The iCAP MSX ICP-MS was operated in Matrix mode, which is optimized to provide exceptional matrix tolerance robustness when analyzing challenging matrices. The instrument was fully tuned before analysis using the provided autotune sequence and using a tune solution prepared in same diluent (PremiSolv) to ensure that the instrument delivers optimum performance in terms of sensitivity and oxides formation. Notably, the oxide formation rate was maintained below 2% without compromising sensitivity despite the addition of oxygen in plasma as mentioned previously. The oxide formation rate was maintained substantially low as a result of optimized sampling depth, oxygen flow rate, and other critical parameters obtained during the autotuning of the instrument using a tune solution prepared in the same solvent.

To reduce the impact of high vapor pressure generated by organic solvents in plasma, and to enable the analysis of various sample types in a single sequence, the spray chamber was cooled to -5 °C. The instrument was also equipped with the PLUS torch, a geometrically identical replacement for the standard quartz torch, but which is manufactured from high performance ceramic materials. This torch offers superior durability and lifetime especially in conjunction with organic solvents, which create a much stronger UV emission in the plasma and can lead to quick devitrification and subsequent degradation of standard torches.

## Data processing and software

The data acquisition and processing were done using Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. Qtegra ISDS Software contains a variety of functions supporting the analyst in achieving comprehensive and accurate analysis of trace elements. This includes a fully automatic start-up and performance verification using the Get Ready function, as well as simplified set-up of methods inside Qtegra ISDS LabBooks and a full feature set for automated quality control included in the default installation.

Figure 1 illustrates the Get Ready functionality available in Qtegra ISDS Software. As can be seen, Get Ready supports the daily workflow of any analytical laboratory and enables users to perform the start-up and performance check of the ICP-MS

automatically, freeing their time for sample preparation and other laboratory-related work. This functionality supports the workflow and ensures instrument readiness for analysis without the need of any manual intervention from the analyst. It also offers full flexibility and allows for customization to include/exclude steps to comply with an internal standard operation procedure (SOP).

- Plasma ignition and warm-up using defined solution (Step 1).
- Autotune and performance check in desired measurement modes (Step 2).
- Switch instrument into desired measurement mode, typically KED (Step 3).

For detailed information on the Get Ready functionality, please refer to the product spotlight.<sup>2</sup>

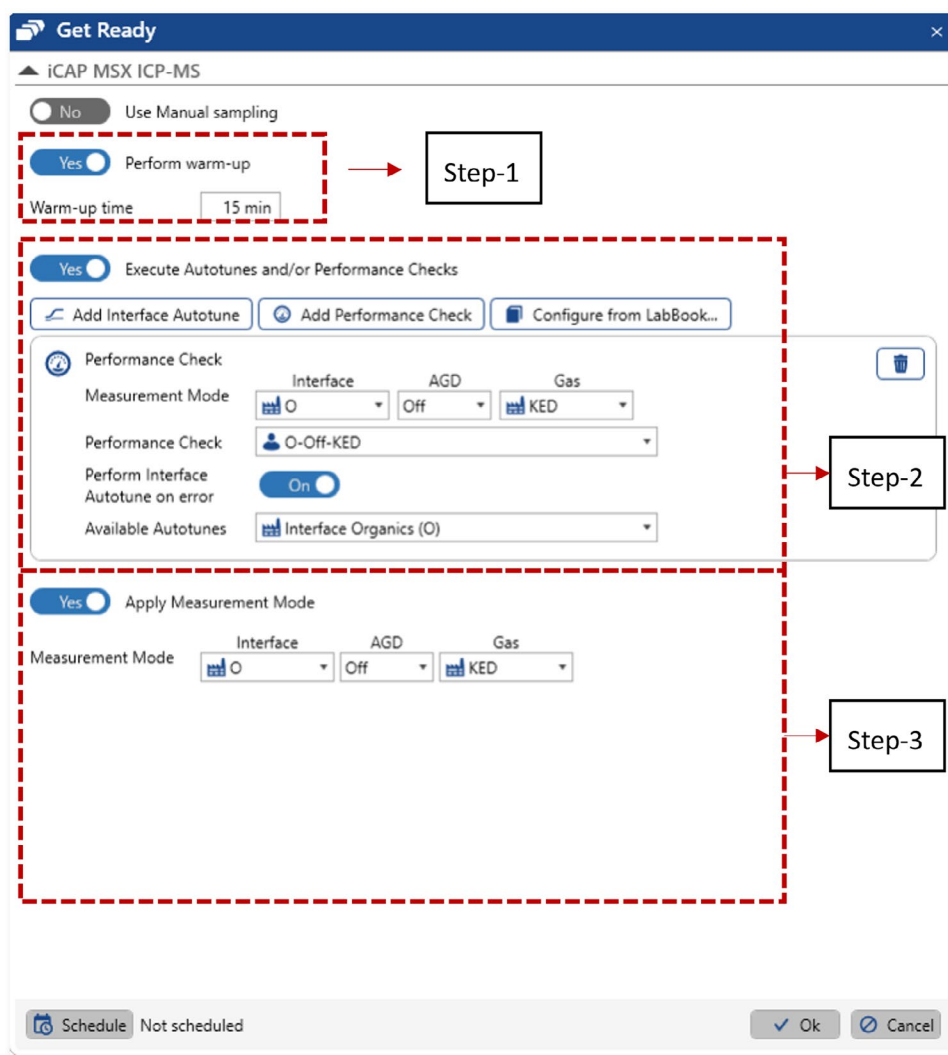


Figure 1. Overview of functionalities supported by the Get Ready feature

## Results and discussion

Considering the wide range of expected concentrations of various elements in different refinery products, the calibration standards were prepared to cover the concentration range between 0.1  $\mu\text{g}\cdot\text{L}^{-1}$  to 50  $\mu\text{g}\cdot\text{L}^{-1}$  for trace analytes and between 5 to 100  $\mu\text{g}\cdot\text{L}^{-1}$  for K using five individual standards. Analytical data obtained from the linearity study is presented in Table 3.

**Table 3. Correlation coefficients ( $R^2$ ) and instrument detection limits (IDLs) determined for all target analytes**

Element	$m/z$	$R^2$	IDL ( $\mu\text{g}\cdot\text{L}^{-1}$ )
Sodium (Na)	23	0.9987	55.6
Magnesium (Mg)	25	0.9976	1.99
Aluminium (Al)	27	0.9956	1.3
Potassium (K)	39	0.9980	0.74
Calcium (Ca)	42	0.9990	16
Titanium (Ti)	48	0.9999	0.01
Vanadium (v)	51	0.9998	0.003
Chromium (Cr)	52	0.9998	0.055
Manganese (Mn)	55	0.9990	0.046
Iron (Fe)	57	0.9997	0.107
Nickel (Ni)	60	0.9998	0.007
Copper (Cu)	63	0.9997	0.014
Zinc (Zn)	66	0.9950	0.394
Arsenic (As)	75	0.9996	0.019
Selenium (Se)	77	>0.9999	0.180
Molybdenum (Mo)	98	0.9994	0.004
Silver (Ag)	107	>0.9999	0.01
Cadmium (Cd)	111	0.9981	0.004
Tin (Sn)	118	0.9995	0.025
Antimony (Sb)	121	0.9995	0.0017
Barium (Ba)	137	0.9998	0.032
Mercury (Hg)	202	0.9993	0.014
Lead (Pb)	208	0.9995	0.009

As can be seen from Table 3, sufficiently low detection limits can be achieved using only helium as a collision cell gas and measuring all analytes in single KED mode. In some cases, use of pure hydrogen as a cell gas using hydrogen reaction mode can improve detection limits further if required (for example, for elements such as Ca, As, and Se). The iCAP MSX

ICP-MS can be equipped with one or two mass flow controllers connected to the QCell collision/reaction cell and thus offers the flexibility to use hydrogen, oxygen, and a mixture of reactive gases. Hydrogen typically allows for an improvement mainly for interferences based on argon polyatomics, and in some cases, such as selenium, the hydrogen can allow the use of a different and more abundant isotopes, leading to a higher sensitivity. In other cases, such as arsenic, the main interferences are more effectively removed using KED with helium.

However, addition of a second collision gas to the method requires a fill/flush cycle in the CRC, which leads to a slight increase in the method runtime of about 10 s. For high-throughput methods, it is often beneficial to analyze all elements using a single set of conditions, such as KED alone. The detailed comparison of analytical data obtained using hydrogen as a reactive gas against single helium KED mode is provided elsewhere.<sup>1</sup> Some interferences are not removable through KED using helium nor hydrogen. For sulfur, and especially its main isotope  $^{32}\text{S}$ , the use of oxygen ( $\text{O}_2$ ) is a promising alternative, removing the interference caused through the formation of  $^{16}\text{O}_2^+$  much more effectively and hence significantly improving detection limits. However, the use of these gases on a single quadrupole ICP-MS instrument would lead to the appearance of new interferences, as all ions of all elements in the sample can enter the cell and can potentially react with either reactive gas. The solution is the use of a triple quadrupole ICP-MS system, such as the Thermo Scientific™ iCAP™ MTX ICP-MS. Here, a third quadrupole mass filter situated axially in front of the CRC allows a pre-filtering of the ion beam. In this case, only the analyte and its interference can enter the CRC, while all ions of lower and higher mass are eliminated and cannot create new interference downstream of the mass spectrometer.

### Accuracy and precision

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  $\mu\text{g}\cdot\text{L}^{-1}$  of analytes except for K, which was spiked at 50  $\mu\text{g}\cdot\text{L}^{-1}$  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 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 un-spiked sample, affecting recovery of those elements at specified spiked concentrations.

### Stability study

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.

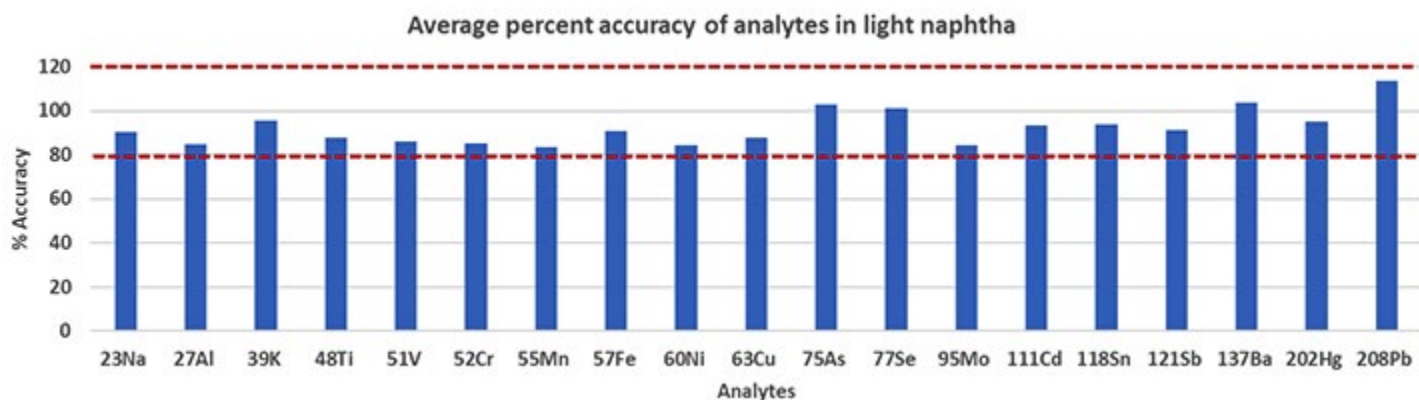


Figure 2. Results of spike recovery testing: % accuracy of various elements in light naphtha sample

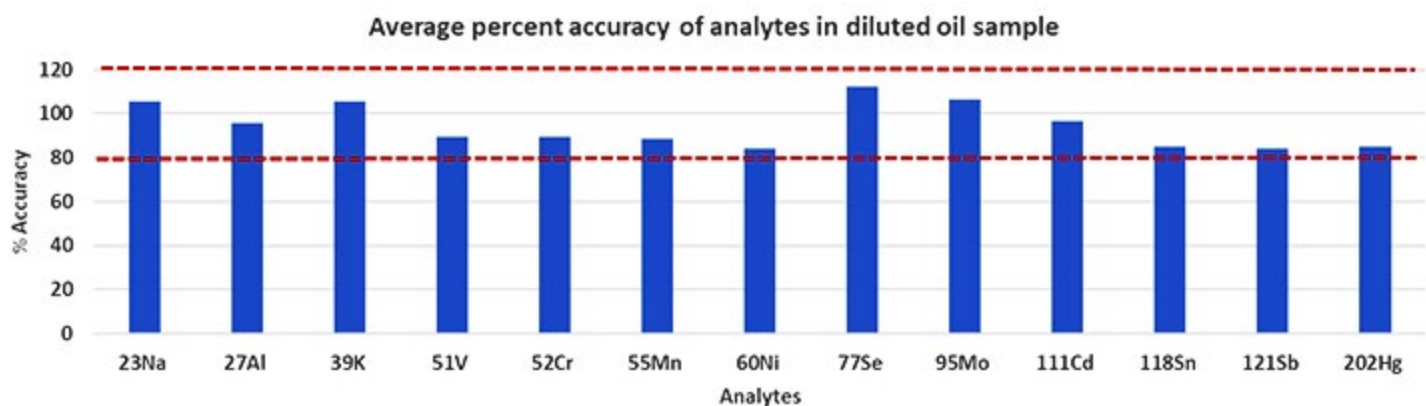


Figure 3. Results of spike recovery testing: % accuracy of various elements in crude oil sample

For the entire batch, the response of internal standards was monitored and indicated that the instrument set-up was stable. Figure 4 shows the signal of both internal standards used in the study and analyzed using KED mode. 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.

Additionally, QC samples were analyzed every 10 samples to check the accuracy of analysis over the entire analytical run. Figure 5 shows average percent accuracy calculated for all analytes in the quality control (QC) sample analyzed periodically over 10 hours of the long analytical batch. The average percent accuracy for all analytes was found to be within the range of 80–120% with relative standard deviation of less than 5%, which strongly suggests that the data acquired over an extended period is accurate and precise.

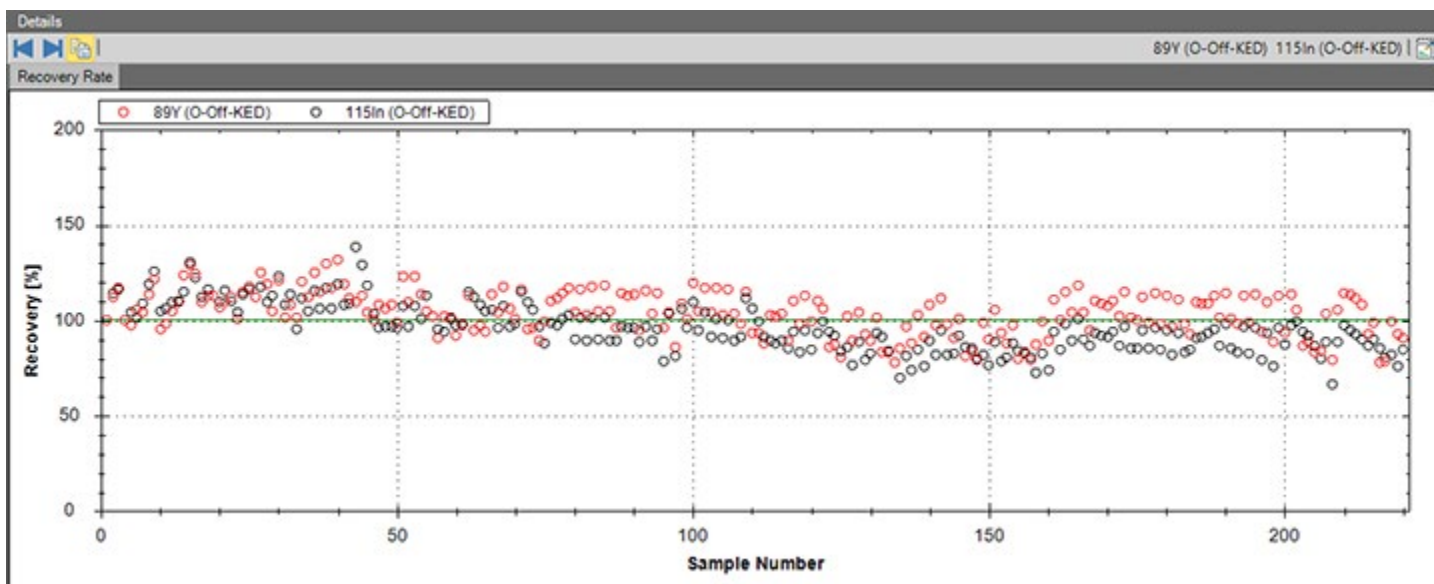


Figure 4. Response of the internal standards during a larger sample batch containing all sample types investigated in this study

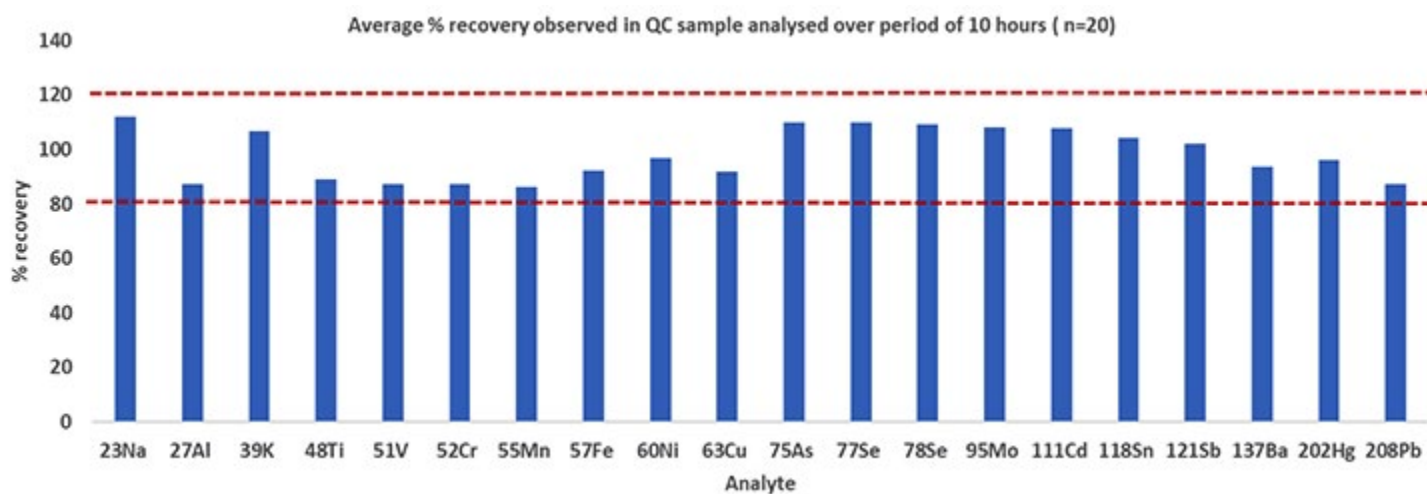


Figure 5. Comparison of % accuracy for QC standards: initial and final (after 10 hours)

## 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. A common sample preparation method encompassing simple dilution of any products with either higher viscosity or lower boiling point in PremiSolv offers complete flexibility for the analysis of a variety of based petroleum sample matrices.
- 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.

Taken together, the results obtained demonstrate that the proposed analytical method can be used in routine laboratories to achieve high-throughput, robust, and reliable analytical results with minimum downtime of the system.

## References

1. Thermo Fisher Scientific Application Note 44465: [Addressing the challenges of routine determination of elemental impurities in refinery products using a robust ICP-MS approach](#)
2. Thermo Fisher Scientific Product Spotlight 002910: Thermo Scientific iCAP MX Series ICP-MS: Fully automatic start up and performance verification

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