Challenge

Analysis of trace elements in highly volatile organics with high robustness, high resolution, and high sensitivity.

Solution

High-resolution ICP-OES with a high-resolution optical system, highest sensitivity, and matrix tolerance to achieve lowest detection limits for trace element determination in volatile organic samples.

Determination of Silicon and Other Trace Elements in Light Naphtha Feedstocks by HR ICP-OES

Introduction

Low-boiling naphtha (sometimes referred to as light or straight-run naphtha) is a petroleum fraction composed predominantly of pentane and hexane derivatives as well as smaller amounts of higher molecular weight hydrocarbon derivatives. It is used in the petroleum industry for gasoline formulation and in the petrochemical industry for producing a wide range of chemical products such as ethylene, propylene, and p-xylene. The monitoring of trace element contents in naphtha is important for a number of reasons. Some traces (e.g., vanadium) can cause corrosion problems, while the presence of specific elements can have unfavorable effects on the cracking process. In particular, the determination of silicon in petroleum products became relevant due to its poisonous effect on hydrogenation catalysts, but also on sensors in car catalysts. In fact, silicon species are adsorbed at the surface of the catalyst, thus decreasing its activity with a great economic impact. Therefore, monitoring potential silicon and other trace impurities in incoming goods, process intermediates, and final products down to the low µg/kg range is of great importance to refineries. This explains why the analysis is subject of many regulations, such as ASTM D7111, UOP 296 (withdrawn), UOP 796, and specification EN 228.

Volatile organic compounds (VOC) such as naphtha are among the most challenging samples to analyze using ICP techniques. For specification analysis in the low µg/kg range, ICP-MS is often the method of choice as conventional ICP-OES instruments lack sensitivity due to the necessity of sample dilution and the occurrence of spectral interferences. Typical analytical challenges are the poor short-term and long-term stability due to the high volatility of the samples and the high risk of soot formation caused by the high carbon content of the samples. Furthermore, the carbon-based emission complicates the spectra recorded and bears the risk of severe spectral interferences.

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Conventional ICP-OES instrumentation is forced to use less sensitive lines for many analytes, since interferences on primary lines cannot be resolved properly.
Here we present the application advantages for trace element determination in light naphtha samples originating from an ICP-OES instrument with high-resolution (HR)

optics (2 pm @ 200 nm), intelligent torch design, superior sensitivity, and high plasma robustness. Additionally, the benefits of the implementation of powerful software tools (ABC, CSI) for background correction and correction of spectral interferences are demonstrated.

Materials and Methods

Samples and reagents

Six light (straight-run) naphtha samples with different sulfur content were submitted to analysis for trace element impurities determination. The following chemicals were used for the preparation of standards, blanks, QC samples, and samples:

- 1,000 mg/kg yttrium organometallic standard (Conostan®, 20 cSt)
- 885 mg/kg multi-element organometallic standard (Conostan®, S21+K, 20 cSt)
- 100 mg/kg multi-element organometallic standard (Conostan®, S21+K, 20 cSt)
- 1,000 mg/kg antimony standard (Conostan®, 20 cSt)
- 100 mg/kg arsenic standard (Conostan®, 20 cSt)
- 100 mg/kg mercury standard (Conostan®, 20 cSt)
- 100 mg/kg selenium standard (Conostan®, 20 cSt)
- 1,000 mg/kg sulfur organic standard (Conostan®, 20 cSt)
- Kerosene (Sigma Aldrich, reagent grade)
- Hexane (Merck, LC grade)

Samples preparation

5.00 g of the sample were accurately (± 1 mg) weighed into a HDPE plastic container and diluted with 5.00 g kerosene. The quantification was based on an external calibration using concentrations as described in table 1. For this purpose, calibration standards were prepared from organometallic single and multi-element standards. Therefore, the required amount of standard was accurately weighed, and kerosene was added to bring the solution mass to a nominal 5.00 g. In the last step hexane was added to fill up to a total mass of 10.00 g. For the blank, 5.00 g of kerosene and 5.00 g of hexane were mixed. The test solution for determining the instrument's long-term stability was prepared by spiking a 1:1 mixture of hexane and kerosene with single and multi-element standards resulting in the following final analyte concentrations: 0.1 mg/kg (As, Hg, Sb, Se, Zr), 10 mg/kg (S), 1.0 mg/kg (Si and the rest of the element list).

For the internal standard stock solution, 4.00 g of the yttrium organometallic standard were accurately weighed into a HDPE plastic container. Kerosene was added to bring the solution mass to a nominal 20.00 g to give a final concentration of 200 mg/kg. Finally, blank, sample and standard solutions were spiked with 100 µL of internal standard stock solution.
The method of standard addition was also performed for selected elements by doping the diluent (dilution factor: 2, diluent: kerosene) with appropriate standard concentrations using an organometallic multi-element standard (Conostan®, S21+K, 100 mg/kg). The blank value was obtained by diluting 5.00 g of hexane with 5.00 g of kerosene.

Calibration

Calibration levels for each element were chosen based on expected concentration range. At least two calibration standards were used for each element as described in table 1.

Table 1: Concentration of calibration standards

Standard	Concentration [mg/kg]							
	B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Sn, Ti, V, Zn	Al, P, Pb, Si	As	Hg	S	Sb	Se	Zr
Calibration 0	0	0	0	0	0	0	0	0
Standard 1	0.0102	0.0102	0.0273	0.0261	-	0.0319	0.0291	0.0303
Standard 2	0.1012	0.1012	0.0537	0.0506	-	0.0626	0.0551	0.0566
Standard 3	-	1.125	-	-	-	-	-	-
Standard 4	-	9.947	-	-	-	-	-	-
Standard 5	-	-	-	-	52.11	-	-	-
Standard 6	-	-	-	-	250.1	-	-	-
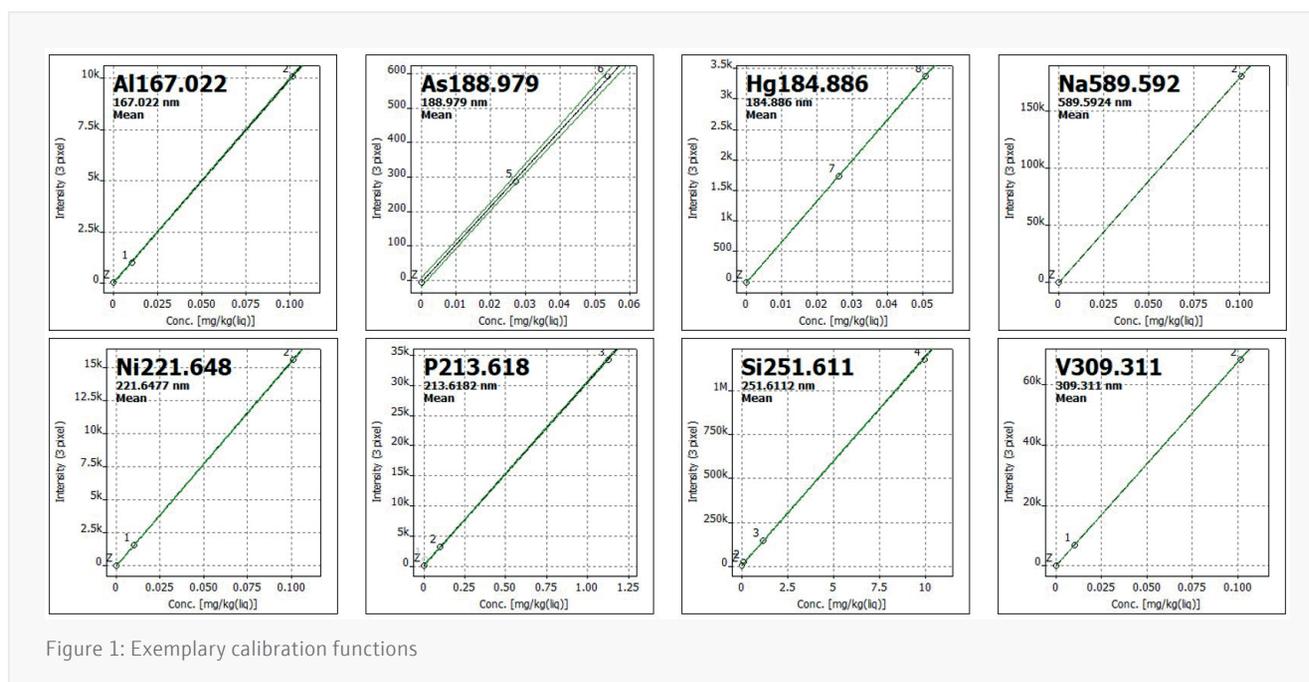
Figure 1: Exemplary calibration functions

Instrumentation

The analysis was performed on a PlasmaQuant 9100 Elite ICP-OES. The instrument was equipped with the organic kit, comprising of a cyclonic spray chamber with dip tube, a 1.0 mm i.d. injector tube, and a solvent resistant tubing. Additionally, a Peltier-cooled spray chamber (Isomist™) was used in conjunction with a 0.4 mL/min glass concentric nebulizer for this analysis.

Instrument settings

A summary of individual settings and components is given in table 2.

Table 2: Instrument settings

Parameter	Normal plasma mode[A]	Oxygen ashing mode[B]
Plasma power	1450 W	1450 W
Plasma gas flow	15 L/min	15 L/min
Auxiliary gas flow	1.75 L/min	0.25 L/min
Nebulizer gas flow	0.30 L/min	0.25 L/min
Oxygen gas flow	0 L/min	0.05 L/min
Nebulizer	Concentric, 0.4 mL/min, Borosilicate	Concentric, 0.4 mL/min, Borosilicate
Spray chamber	Isomist™, tempered (T = -5°C) cyclonic spray chamber with dip tube, 50 mL, Borosilicate	
Outer tube/inner tube	Quartz/Quartz	Quartz/Quartz
Injector	Quartz, ID: 1 mm	Quartz, ID: 1 mm
Pump tubing	Viton (black, black)	Viton (black, black)
Sample pump rate	0.4 mL/min	0.4 mL/min
Delay time	60 s	60 s
Torch position[C]	-3 mm	0 mm

* A ... Setting used for elements that are unaffected by unspecific spectral interferences from organic matrix
 B ... Setting for oxygen addition to the plasma that reduces unspecific spectral interferences from organic matrix and carbon deposits (injector tip)
 C ... Spacing between injector and coil further suppresses carbon deposits (injector tip)

Method and Evaluation Parameters

Table 3: Method and evaluation parameters

Element	Line [nm]	Plasma view	Integration mode	Read Time [s]	Evaluation			
					No. of pixel	Baseline fit, Pixel No.	Polyn. degree	Correction
Al	167.022	axial	Peak	3	3	ABC[1]	auto	CSI[2], Y[3]
As	188.979	axial	Peak	10	3	ABC	auto	CSI, Y
B	249.773	axial	Peak	3	3	ABC	auto	CSI, Y
Ba	455.403	axial	Peak	1	3	static	auto	CSI, Y
Ca	396.847	axial	Peak	1	3	ABC	auto	CSI, Y
Cd	214.441	axial	Peak	3	3	ABC	auto	Y
Cr	267.716	axial	Peak	3	3	ABC	auto	CSI, Y
Cu	324.754	axial	Peak	3	3	ABC	auto	CSI, Y

Table 3 (continued): Method and evaluation parameters

Element	Line [nm]	Plasma view	Integration mode	Read Time [s]	Evaluation			
					No. of pixel	Baseline fit, Pixel No.	Polyn. degree	Correction
Hg	184.886	axial	Peak	10	3	ABC	auto	CSI, Y
Fe	259.940	axial	Peak	2	3	ABC	auto	CSI, Y
K[4]	766.491	axial	Peak	3	3	ABC	auto	CSI, Y
Mg	280.271	axial	Peak	3	3	ABC	auto	CSI, Y
Mn	257.610	axial	Peak	2	3	ABC	auto	CSI, Y
Mo	202.030	axial	Peak	3	3	ABC	auto	Y
Na[4]	589.592	axial	Peak	3	3	ABC	auto	CSI, Y
Ni	221.648	axial	Peak	3	3	ABC	auto	CSI, Y
P	213.618	axial	Peak	5	3	ABC	auto	CSI, Y
Pb	220.353	axial	Peak	10	3	ABC	auto	CSI, Y
S	180.672	axial	Peak	3	3	ABC	auto	Y
Sb	217.581	axial	Peak	3	3	ABC	auto	CSI, Y
Se	196.028	axial	Peak	10	3	ABC	auto	CSI, Y
Si	251.611	axial	Peak	3	3	ABC	auto	Y
Sn	189.611	axial	Peak	10	3	static	auto	CSI, Y
Ti	334.941	axial	Peak	3	3	ABC	auto	CSI, Y
V	309.311	axial	Peak	3	3	ABC	auto	CSI, Y
Zn	202.548	axial	Peak	3	3	ABC	auto	Y
Zr	343.823	axial	Peak	3	3	ABC	auto	CSI, Y

* 1 … **A**utomated **B**aseline **C**orrection
  2 … mathematical **C**orrection of **S**pectral **I**nterferences originating from organics
  3 … Internal Standard, Correction (using Yttrium)
  4 … measured with oxygen addition to the plasma

Results and Discussion

The measurement of trace elements in naphtha was carried out using external calibration and applying lowest dilution factors (DFs) to achieve best limits of detection. Therefore, hexane was used to mimic the highly volatile naphtha fraction in the calibration standards and the blank value. The analysis of volatile organic compounds (VOC) regarding the determination of trace element contents represents one of the most demanding tasks for ICP-OES. The high volatility of the samples often leads to unstable plasma conditions, resulting in severe signal drifts as well as poor accuracy and precision of the obtained results. In this context, dilution (with high DFs) in less volatile solvents or alterations to the plasma gas composition are required for conventional ICP-OES instrumentation. Due to the high-frequency generator in combination with the vertical orientation of the V Shuttle Torch, the PlasmaQuant 9100 Elite can measure VOC (with lowest DFs) with great precision, accuracy, and long-term stability. Furthermore, an optimized torch position guarantees minimal soot formation and hence, excellent long-term stability of the measurements.

Table 4: Results of the samples and method-specific limits of detection (MLD, considering dilution factor)

Element	MLD [µg/kg]	Sample A [mg/kg]	Sample B [mg/kg]	Sample C [mg/kg]	Sample D [mg/kg]	Sample E [mg/kg]	Sample F [mg/kg]
Al	0.55	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
As	4.20	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
B	0.80	0.006	<MLD	<MLD	<MLD	<MLD	<MLD
Ba	0.67	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Ca	0.42	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Cd	0.18	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Cr	1.01	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Cu	1.18	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Hg	0.54	<MLD	<MLD	<MLD	<MLD	<MLD	0.012
Fe	0.70	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
K	7.59	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Mg	0.10	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Mn	0.09	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Mo	1.87	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Na	3.90	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Ni	1.55	<MLD	<MLD	<MLD	0.021	<MLD	<MLD
P	5.29	0.183	<MLD	<MLD	<MLD	<MLD	0.113
Pb	4.14	<MLD	0.006	2.86	0.287	<MLD	<MLD
S	19.5	490	442	488	60.7	222	0.587
Sb	6.30	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Se	4.41	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Si	3.83	3.62	0.990	2.49	0.172	0.900	17.9
Sn	2.08	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Ti	0.22	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
V	0.74	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD
Zn	0.44	<MLD	<MLD	<MLD	0.005	<MLD	<MLD
Zr	1.22	<MLD	<MLD	<MLD	<MLD	<MLD	<MLD

Table 4 summarizes the results for all samples based on external calibration. The high spectral resolution of the PlasmaQuant 9100 Elite of 2 pm @ 200 nm in combination with the CSI software tool ensure a sufficient separation of analyte and background signals. Thus, the unspecific background resulting from the high carbon content in naphtha is efficiently separated from analyte emission lines and spectral interferences are eliminated (see figure 2). It allows for the use of most sensitive emission lines and therefore guarantees highest sensitivity for all investigated elements. Additionally, data evaluation is easily performed by automatically executed baseline and spectral corrections with the help of software tools like ABC and CSI. As a result, method-specific limits of detection in the range of 1 µg/kg are achieved for most analytes (see table 4), thus, ensuring precise and accurate determination of the analytes at required limits.
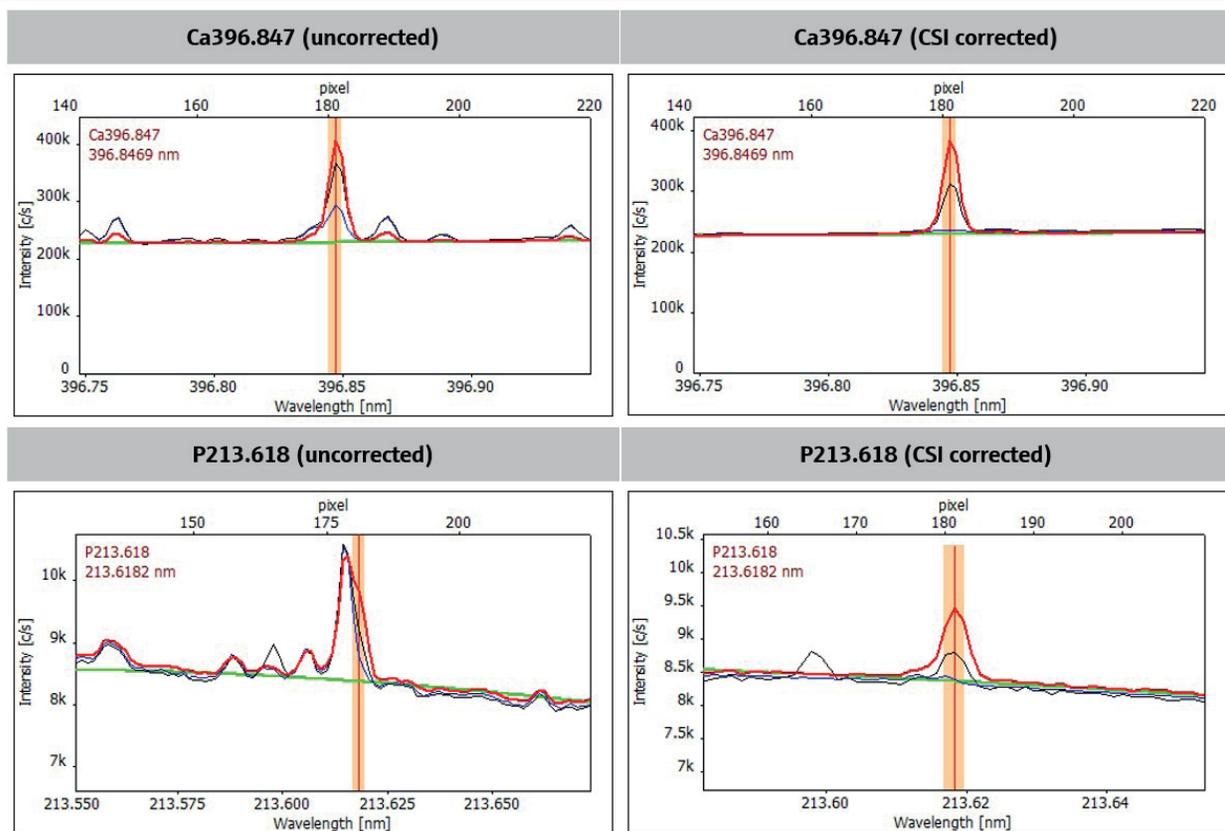
Figure 2: Application advantage of high resolution spectra and Correction of Spectral Interferences software tool (**red**: sample, **black**: 10 µg/kg Std., **blue**: Cal. 0, **green**: baseline correction).

The PlasmaQuant 9100 Elite enables the suppression of carbon-based signals in the spectrum by removing carbon in the sample feed area including the plasma. To do so, a small flow of oxygen can be added to the plasma to convert carbon into carbon dioxide, which can easily be extracted by the ventilation of the system. The effects on the spectral complexity can be observed in the spectrum displayed in figure 3 (right) where the background level has dropped roughly by a factor of ten, whilst the signal to background ratio is kept the same. This allows for an approx. 15-fold increase in sodium detectability to a detection limit below 5 µg/kg. On top of this, the baseline is much smoother and a more reliable baseline fitting can be applied with the effects of a significantly improved precision in the trace detection range.
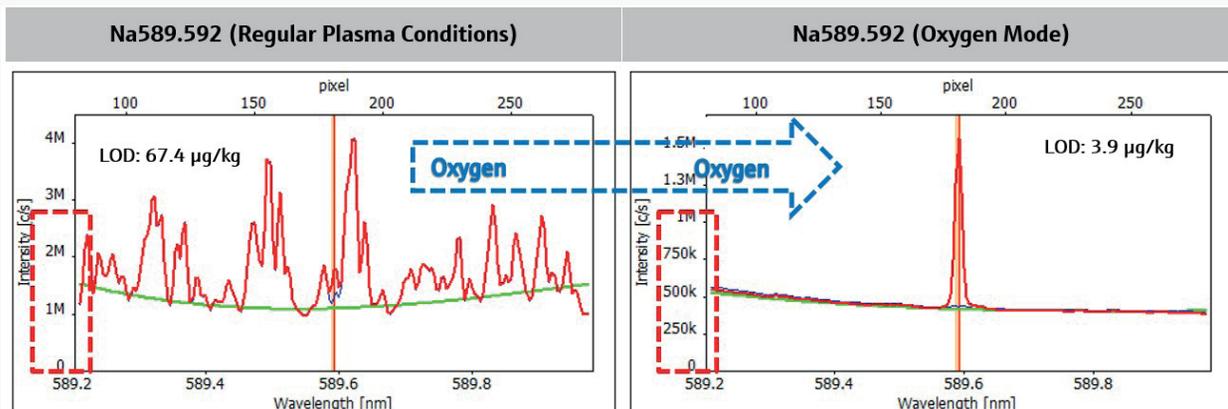
Figure 3: Impact of oxygen addition on signal intensity and spectral interferences illustrated on an analytical line of sodium (Na589.592; **red**: 1 mg/kg Std., **blue**: Cal. 0, **green**: baseline correction).

It is known that naphtha samples (depending on the origin of the crude oil) strongly vary in their composition of aromatic and aliphatic hydrocarbons as well as in their sulfur concentrations. These chemical differences might lead to various matrix effects affecting the overall recovery of analytes depending on the specific sample composition.

In order to judge about applicability of the analytical approach using external calibration and hexane as surrogate for the naphtha fraction in the calibration standards, spike recovery tests were carried out. Therefore, two samples (high and low sulfur content) were spiked with 0.5 mg/kg of a multi-element standard (table 5).

Table 5: Spike recovery of different analytes (0.5 mg/kg in naphtha samples with high (Sample C) and low (Sample F) sulfur content (external calibration with hexane and kerosene). For comparison, further spike recovery testing was carried out in a naphtha sample with high sulfur content (Sample C) using method of standard additions

Element	Sample C (high S)	Sample F (low S)	Sample C Std. Add.
	Recovery [%]		
Al	100	106	100
B	90	91	106
Ba	98	95	107
Ca	99	100	100
Cd	90	104	100
Cr	98	103	99
Cu	28	78	104
Fe	99	104	104
K	90	57	105
Mg	97	100	98
Mn	97	100	100
Mo	97	99	99
Na	100	77	95
Ni	98	105	100
P	98	111	96
Pb	98	105	105
Si	101	96	104
Sn	95	101	94
V	98	100	99
Zn	96	92	97

The spike recovery experiments clearly demonstrate the applicability of the external calibration approach for most of the analytes. Only the analytical lines of copper, potassium, and sodium are affected by specific matrix effects of the certain samples (underlined in table 5). Compensation for these effects can be therefore achieved by using method of standard additions.
The determination of long-term stability was performed by hourly analysis of a spiked test solution (see „Samples and Reagents" section). Between these measurements, a representative naphtha sample (diluted 1:1 with kerosene) was constantly injected. Recovery values between 92% and 105% at RSD values of less than 2.8% were achieved, which demonstrates the exceptional plasma robustness and superior performance of the PlasmaQuant 9100 Elite for organic matrices. Figure 4 displays the results of the 8-hour signal reading of the test solution for all analytes.

Figure 4: Percentage recoveries in the test solution throughout an 8-hour sequence. RSD values were below 2.8% for all elements.
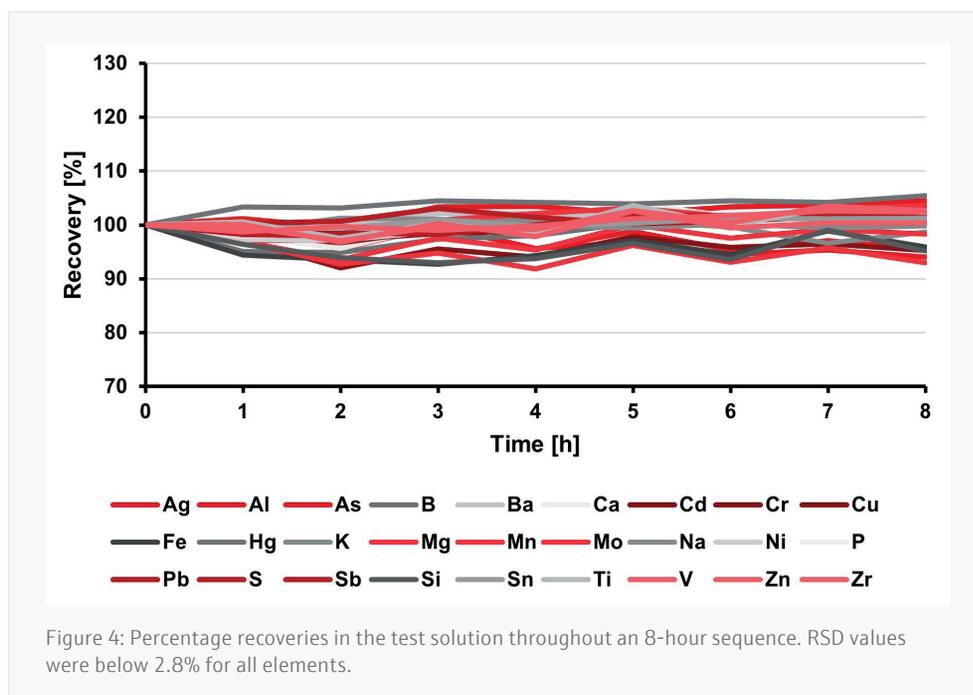
Conclusion

In summary, the PlasmaQuant 9100 Elite is well suited for the quality control of naphtha samples. Thanks to its high resolution, its plasma robustness, and long-term stability, the determination of trace elements can be easily achieved. Additional features include the intelligent torch design, the option of oxygen introduction, and the provided software tools. Limits of detection in the range of 1 µg/kg are achieved, which ensures the precise and accurate determination of critical elements, such as As, Hg, and Si. This improves the cost-effectiveness of the overall process and allows refineries to push their specification limits to a new level, proving the superiority of their naphtha products. Spike recovery testing indicated that an external calibration strategy (hexane/kerosene) combined with internal standardization can be applied for most of the elements in all samples. To exclude any matrix effects for a few analytes the more time-consuming method of standard additions seems to be inevitable.

Figure 5: PlasmaQuant 9100 Elite