Challenge
Direct determination of trace elements in diesel exhibiting complex emission spectra

Solution
ICP-OES with high spectral resolution to resolve severe spectral interferences and robust plasma to handle undiluted volatile organic samples such as diesel

Intended audience
Petrochemical industry, refineries, specialized contract labs

Analysis of elemental impurities in diesel by HR ICP-OES according to ASTM D7111-16

Introduction

Diesel is a mixture of kerosene and different middle distillate fractions, which are produced by fractionation of crude oil. Further components of diesel products may be a certain portion of biodiesel (up to 7%) and additives (ppm concentration range) to adjust properties such as ignitability, cetane number, lubricity, acidity and stability.

Elemental impurities in diesel products contribute to properties like shelf life, wear of engine components and exhaust treatment devices as well as emission levels of environmental pollutants and particulate matter. Copper, for instance, plays a significant role as catalyst in the oxidation process resulting in high molecular weight compounds with limited solubility in the diesel mixture. Hence, low copper levels are essential to guarantee long shelf life. Alkaline and alkaline earth metals like sodium, potassium, magnesium and calcium may be present as metal soaps or abrasive solids, which increase the wear of engine components (injector, fuel pump, etc.) and may cause filter plugging and engine deposits.

The level of sulfur is one of the major specification parameters for diesel fuel. Regulations in Europe, North America and the Asia Pacific region continuously decreased the maximum allowable level of sulfur to 10 mg/kg over the past decades. Sulfur as well as phosphorus contents need to be kept at a minimum level since their combustion products are potentially harmful for exhaust treatment devices and increase the wear of small engine parts. This in turn results in shorter maintenance intervals or eventually in engine failure.

Furthermore, sulfates and sulfur dioxide emission as a product of diesel combustion can be reduced significantly by using ultra-low-sulfur diesel (ULSD) as fuel in on- and off-road vehicles.
Diesel is a challenging sample matrix to be analyzed by ICP techniques. The high load and carbon content of the organic matrix requires a robust sample introduction and plasma system, which reliably excites the samples within the ICP and does not suffer from carbon build-up within

the torch system. For this challenge, the vertical geometry of the V-Shuttle torch and the robust generator of the PlasmaQuant 9x00 series have proven themselves, which is confirmed by the direct analysis of undiluted diesel. Spectral interferences originating from the unspecific carbon background of the sample matrix are a major challenge to reliably measure trace concentrations of elements like lead, arsenic, sodium or zinc. To account for these interferences, classical ICP-OES needs to employ laborious calibration strategies such as standard addition calibration or to select alternative emission lines with less sensitivity, which compromises the achievable limits of detection (LOD). The high-resolution optical system of the PlasmaQuant 9200 Elite (2 pm @ 200 nm) in combination with the CSI software algorithm (correction of spectral interferences) avoid such compromises since the most sensitive emission lines remain interference-free and hence, available for measurement.

The here presented methodology analyzes diesel samples by using an external calibration in kerosene as described in ASTM D7111-16. The use of primary emission lines throughout all investigated elements as well as the possibility to run undiluted samples allow for LODs in the range of 1 µg/kg and below on a routine basis.

Materials and Methods

Samples and reagents

- 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)
- 100 mg/kg arsenic standard (Conostan, 20 cSt)
- 1,000 mg/kg sulfur organometallic standard (Conostan, 20 cSt)
- Kerosene (Honeywell, purum)

Sample preparation

Two diesel samples were submitted for the analysis of trace element impurities. The shown chemicals were used for the preparation of standards, blanks, QC samples and samples. All measurement solutions and stock solutions were prepared as described hereinafter.

For the internal standard stock solution, 2.5 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 50 g to give a final concentration of 50 mg/kg.
For the blank, 9.8 g of kerosene were accurately weighed into a HDPE plastic container. Internal standard stock solution was added to bring the solution mass a nominal 10g.
For the arsenic calibration stock solution, 0.2 g of the arsenic organometallic standard was accurately weighed into a HDPE plastic container. Kerosene was added to bring the solution mass to a nominal 20 g to give a final concentration of 1.0 mg/kg.
For the sulfur calibration stock solution, 0.2 g of the sulfur organometallic standard was accurately weighed into a HDPE plastic container. Kerosene was added to bring the solution mass to a nominal 20 g to give a final concentration of 10 mg/kg.
For the multi -element calibration stock solution, 0.045 g of the multi-element (885 mg/kg, S21+K) organometallic standard was accurately weighed into a HDPE plastic container. Kerosene was added to bring the solution mass to a nominal 40 g to give final concentration of 1.0 mg/kg.
For the QC standard stock solution, 0.1 g of the arsenic, sulfur and multi-element (100 mg/kg, S21+K) organometallic standard were accurately weighed into a HDPE plastic container. Kerosene was added to bring the solution mass to a nominal 20 g to give final concentration of 0.5 mg/kg (multi-elements + arsenic) and 5 mg/kg (sulfur), respectively.
For the working standard solutions, 9.8 g of each calibration and QC standard stock solution were accurately weighed into a HDPE plastic container and spiked with 0.2 g of internal standard stock solution.
For the sample measurement solutions, 9.8 g of each sample was accurately weighed and combined with 0.2 g of internal standard stock solution into a HDPE plastic container.
For the spiked sample solutions, 9.8 g of a representative sample was accurately weighed and combined with 0.2 g of internal standard stock solution. This particular internal standard stock solution was additionally spiked with appropriate concentrations of the desired elements, e.g. 50 mg/kg to achieve a final spiked concentration of 1 mg/kg in the sample.

Calibration

As described in ASTM D7111-16, a two point calibration including the blank and the respective working standard solution was carried out. The exact concentration levels are shown in Table 1.

Table 1: Concentration levels of working standard and QC standard solutions

Element	Concentration [mg/kg]		
	Working Std.	QC Std.	Sample spike
As	1.06	0.53	1.14
S	10.7	5.33	3.13
Multi-element	1.13	0.57	1.00

Instrument settings

For the analysis, a PlasmaQuant 9100 Elite with an organic kit and a cyclonic spray chamber with dip tube was used. Representative test measurments on a PlasmaQuant 9200 Elite confirmed consistent performance under the adjusted plasma conditions. The detailed system configurations are provided in table 2.

Table 2: Plasma parameters and setup of the sample introduction system

Parameter	Specification 9100 Elite	Specification 9200 Elite
Plasma power	1450 W	1450 W
Plasma gas flow	15 L/min	10 L/min
Auxiliary gas flow	1.75 (0.25[B]) L/min	1.75[A] (0.25[B]) L/min
Nebulizer gas flow	0.4 (0.36[B]) L/min	0.45[A] (0.36[B]) L/min
Oxygen gas flow	(0.04[B]) L/min	0.0[A] (0.04[B]) L/min
Nebulizer	Concentric, 0.4 mL/min, Borosilicate	
Spray chamber	Cyclonic spray chamber with dip tube, 50 mL, Borosilicate	
Outer tube/Inner tube	Quartz/Quartz	
Injector	Quartz, ID 1mm	
Pump tubing	Viton (black, black)	
Sample pump rate	0.4 mL/min	
Delay time	90 s	
Torch position[C]	-3[A] (0[B]) mm	-2[A] (0[B]) 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

For all elements yttrium was used as an internal standard correction.

Table 3: Overview of method-specific evaluation parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixel	Baseline fit	Polyn. degree	Correction
Ag	328.068	axial	peak	3	3	ABC	auto	-
Al	396.152	axial	peak	3	3	static	auto	CSI
As	188.979	axial	peak	10	3	ABC	auto	CSI
B	249.773	axial	peak	3	3	ABC	auto	-
Ba	455.403	axial	peak	3	3	ABC	auto	CSI
Ca	315.887	axial	peak	3	3	ABC	auto	CSI
Cd	214.441	axial	peak	3	3	ABC	auto	-
Cr	267.716	axial	peak	3	3	ABC	auto	CSI
Cu	324.754	axial	peak	3	3	ABC	auto	-
Fe	259.940	axial	peak	3	3	ABC	auto	-
K[1]	766.491	axial	peak	3	3	ABC	auto	-
Mg	280.271	axial	peak	3	3	ABC	auto	CSI
Mn	257.610	axial	peak	3	3	ABC	auto	CSI
Mo	202.030	axial	peak	3	3	ABC	auto	-
Na[1]	589.592	axial	peak	3	3	ABC	auto	-
Ni	221.648	axial	peal	3	3	ABC	auto	CSI
P	213.618	axial	peak	10	3	ABC	auto	CSI
Pb	220.353	axial	peak	10	3	ABC	auto	CSI
S	180.672	axial	peak	10	3	ABC	auto	-
Si	251.611	axial	peak	3	3	ABC	auto	-
Sn	189.611	axial	peak	3	3	ABC	auto	CSI
Ti	334.941	axial	peak	3	3	ABC	auto	CSI
V	309.311	axial	peak	3	3	ABC	auto	CSI
Zn	213.856	axial	peak	3	3	ABC	auto	CSI

1 ... measured with oxygen addition to the plasma

ABC = **A**utomatic **B**aseline **C**orrection

CSI = mathematical **C**orrection of **S**pectral **I**nterferences originating from kerosene

Results and Discussion

The spectral resolution of the PlasmaQuant 9200 Elite in combination with the CSI software tool allows for an interference-free analysis of all investigated elements. The CSI tool precisely removes background signals from the recorded sample spectrum resulting in a clean and simple to analyzed peak. Figure 1 shows the effectiveness of the CSI correction tool on the examples of magnesium and zinc. On the left hand side, as-recorded spectra with significant contribution of background signals are displayed. Evaluating such a peak will result in a false quantification of the respective analyte. The corrected spectra, as displayed on the right hand side of figure 1, show an easily and reliably to evaluate analyte peak resulting in excellent accuracy and precision of the obtained results.

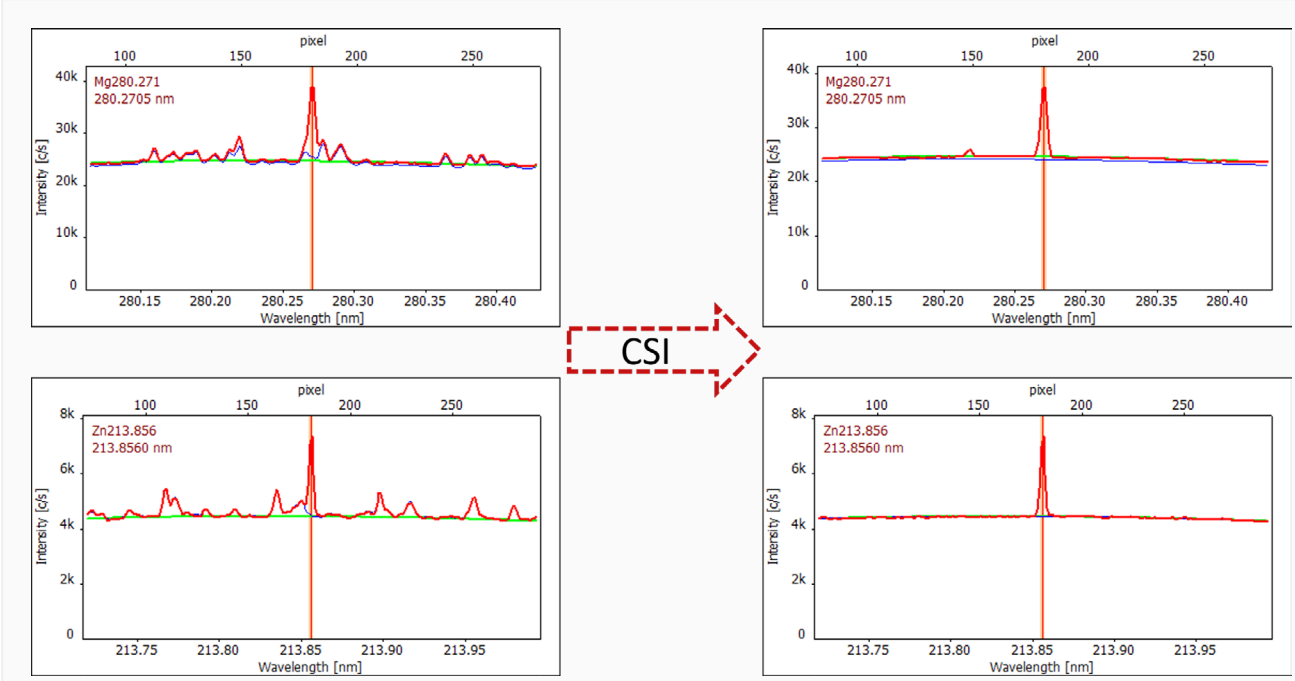

Figure 1: Spectra of Mg 280.271 and Zn 213.856 before (left) and after (right) spectral correction via CSI software tool

When analyzing organic sample materials, carbon causes two major issues. It deposits on the torch material, preferably the outer tube and the injector, which causes poor precision of the obtained results and loss of sensitivity over time. In severe cases, the soot deposition will terminate the analysis by clogging the injector or local overheating and subsequent damage of the torch outer tube. Vertical torch designs prolong these effects. A further measure to reduce carbon deposition is the addition of small amounts of oxygen to the plasma. Carbon is oxidized to carbon dioxide, which is then removed from the plasma compartment by the exhaust system. Hence, carbon does not deposit and the required maintenance cycles are reduced to a minimum.

A further beneficial effect of oxygen addition is the reduction of the carbon based spectral background. A very prominent example is the quantification of sodium in diesel samples as depicted in figure 2. The peak of Na 589.592 without oxygen addition is embedded within a prominent carbon based spectral surrounding, which makes the peak evaluation rather difficult. Additionally, the high background only allows for LODs in the 50 µg/kg range. The background is significantly lowered by the addition of oxygen to the plasma, which results in roughly a ten times improved LOD. Further improvement can be obtained by the use of the CSI tool.

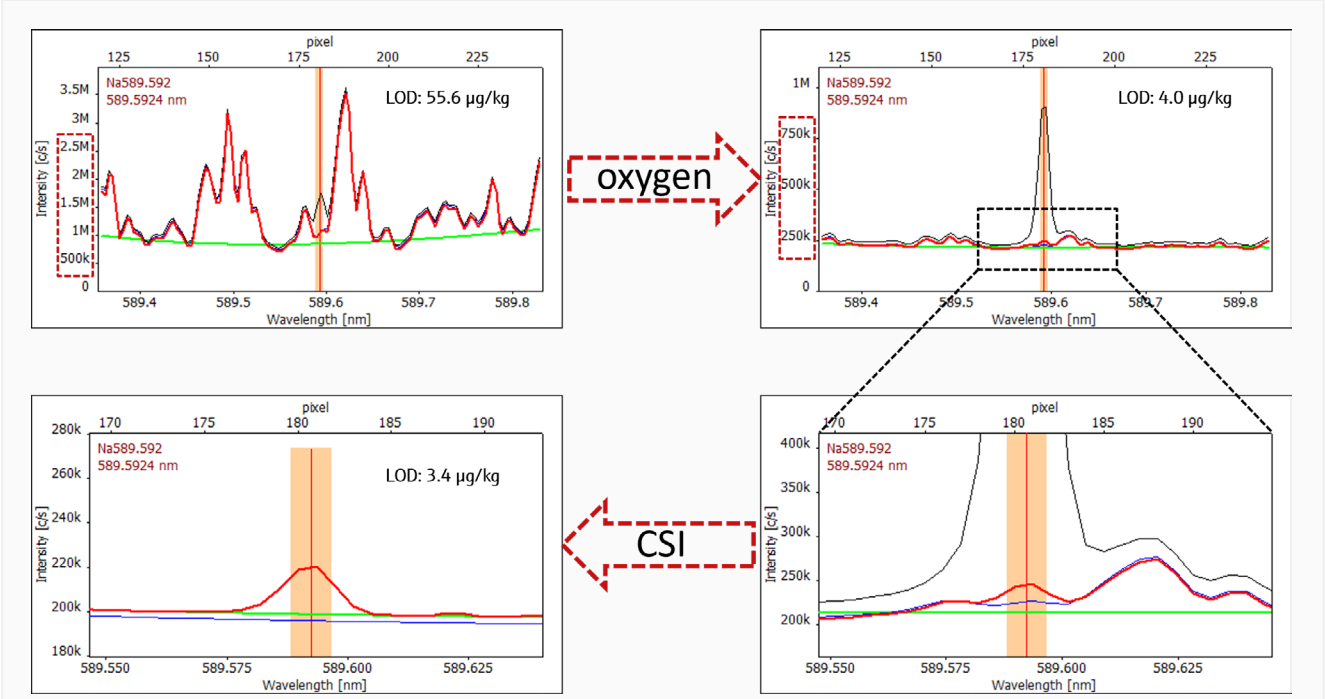

Figure 2: Spectra (red – sample, black – calibration standard, blue – blank, green – automated baseline correction) of Na 589.592 without oxygen addition (top left), with oxygen addition (right) and with CSI correction (bottom left)

In all cases described above, as-recorded as well as corrected spectra, an automatic baseline correction was applied to reliably obtain the results listed in Table 4. Here, the results of two commercially available diesel samples are reported. It was found that both samples can be classified as ULSD as their sulfur content is significantly below the requested 10 mg/kg. The achievable LOD for sulfur is well below the requested limits (low µg/kg) in diesel fuel which ensures a reliable quantification in a routinely employed methodology. Limits of detection in the range of 1 µg/kg and below were achieved for all investigated elements.

Table 4: Results of diesel sample A and B

Element	Line [nm]	LOD [µg/kg]	Sample A		Sample B	
			Mass fraction [µg/kg]	RSD [%]	Mass fraction [µg/kg]	RSD [%]
Ag	328.068	0.43	39.6	1.8	16.5	1.3
Al	396.152	2.29	<LOD	-	<LOD	-
As	188.979	1.26	<LOD	-	<LOD	-
B	249.773	0.39	10.1	3.0	16.1	2.2
Ba	455.403	0.37	12.7	6.9	2.6	0.3
Ca	315.887	0.60	3.6	6.0	11.9	3.0
Cd	214.441	0.13	2.1	1.6	1.6	2.0
Cr	267.716	0.11	<LOD	-	<LOD	-
Cu	324.754	0.21	22.7	0.8	4.3	1.5
Fe	259.940	0.29	9.3	3.9	35.8	1.9
K	766.491	1.19	7.2	9.2	55.0	2.3

LOD = Method-specific limits of detection obtained from calibration method
RSD = Relative standard deviation from 3 replicate measurements

Table 4: Results of diesel sample A and B

Element	Line [nm]	LOD [µg/kg]	Sample A		Sample B	
			Mass fraction [µg/kg]	RSD [%]	Mass fraction [µg/kg]	RSD [%]
Mg	280.271	0.06	0.6	7.9	2.7	2.3
Mn	257.610	0.04	0.4	3.1	0.6	4.4
Mo	202.030	0.91	<LOD	-	<LOD	-
Na	589.592	3.35	<LOD	-	42.1	1.8
Ni	221.648	0.57	<LOD	-	<LOD	-
P	213.618	2.72	<LOD	-	<LOD	-
Pb	220.353	3.50	<LOD	-	<LOD	-
S	180.672	4.11	841	0.7	8309	0.4
Si	251.611	0.79	932	0.9	1033	0.6
Sn	189.611	2.86	<LOD	-	<LOD	-
Ti	334.941	0.14	<LOD	-	<LOD	-
V	309.311	0.50	<LOD	-	1.8	3.7
Zn	213.856	0.19	55.7	0.4	16.3	0.5

LOD = Method-specific limits of detection obtained from calibration method
RSD = Relative standard deviation from 3 replicate measurements

Method validation was performed by investigating the recoveries of independently prepared QC standards in kerosene and spiked diesel samples. The according spike levels are enclosed in Table 2. The obtained recoveries are within a range of ±5% for QC standards and ±8% for spiked samples for all investigated elements as displayed in Figure 3. Hence, the here applied method complies with the requirements of ASTM D7111-16.

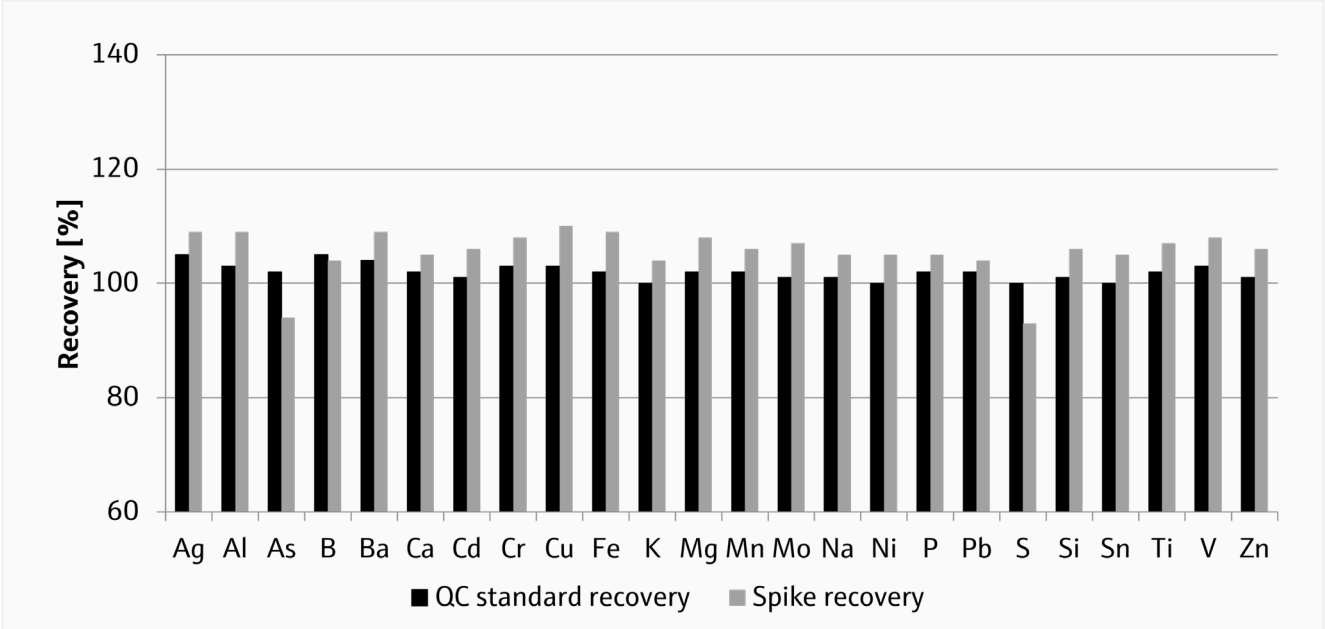

Figure 3: Recoveries of QC standards and spiked samples

The investigation of the long-term stability via an uninterrupted measurement of a spiked diesel sample revealed an excellent stability with an observed drift of less than 4% over an eight hour run (Figure 4).

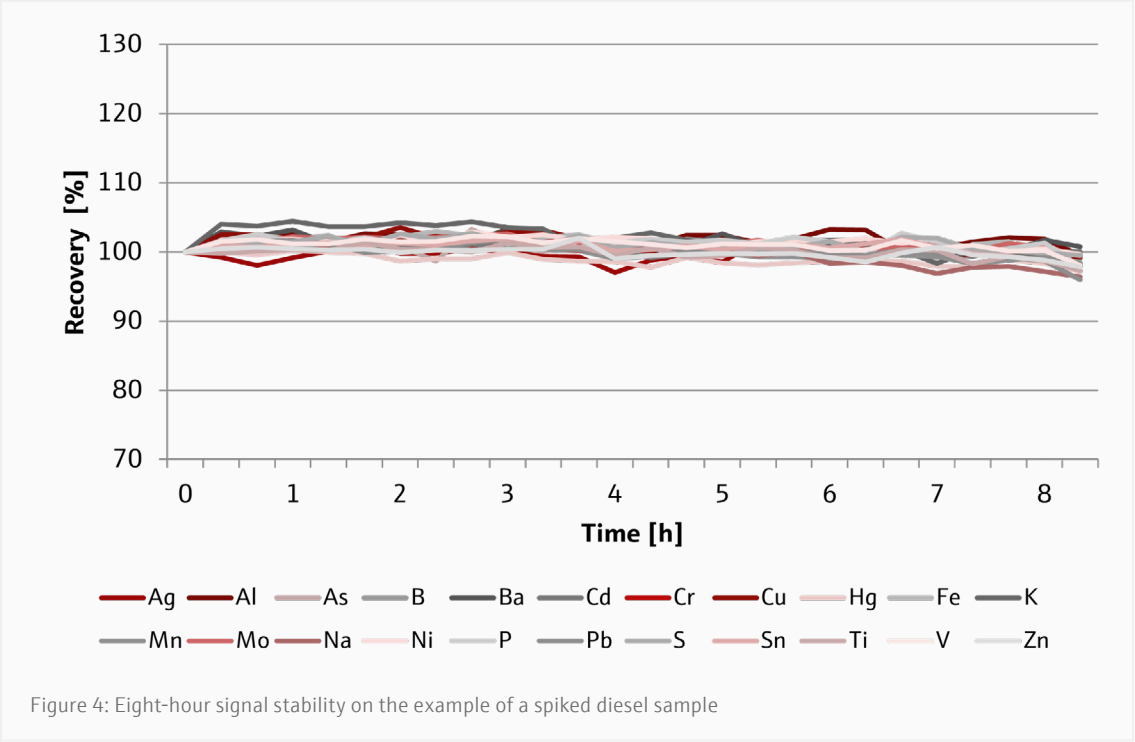

Figure 4: Eight-hour signal stability on the example of a spiked diesel sample

Summary

The here presented methodology allows for a simple routine analysis of trace impurities in diesel by means of ICP-OES according to ASTM D7771-16.

Typical challenges when analyzing organic samples such as diesel are plasma instability, signal fluctuation due to carbon deposition and matrix-based spectral interferences.

High accuracy and precision results are achieved by a uniform excitation of undiluted diesel samples using the PlasmaQuant 9200 Elite. Carbon deposits on the glassware can be suppressed by using a vertical torch design, such as the unique V Shuttle Torch. Furthermore, an optimized torch position as well as the addition of oxygen to the plasma guarantee minimal soot formation and hence, excellent long-term stability of the measurements with a signal drift of less than 4% over a eight hour analysis cycle.

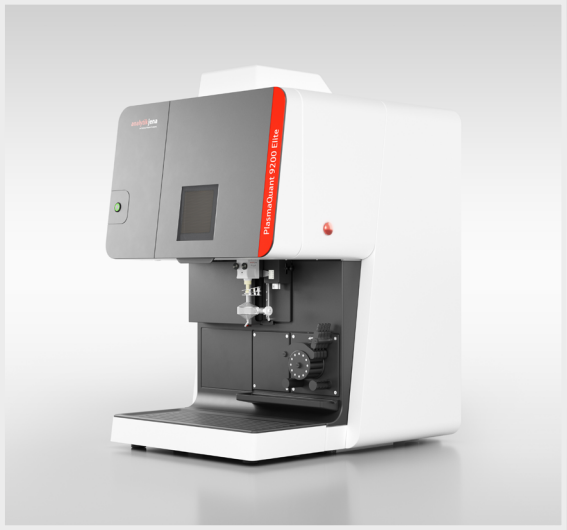

Figure 5: PlasmaQuant 9200 Elite

The high carbon content of diesel samples generates significant background levels and unspecific peaks resulting in a high risk of spectral interferences on the analyte emission lines. Sufficient separation of analyte and background signals is achieved by the high spectral resolution of the PlasmaQuant 9200 Elite of 2 pm @ 200 nm in combination with the CSI software tool. 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, limits of detection in the range of 1 µg/kg can be achieved, which ensures the precise and accurate determination of the required limits. It also allows refineries to push their specification limits to a new level, proving the superiority of their diesel products.

Recommended device configuration

Table 6: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9200 Elite	818-09201-2	High resolution ICP-OES
ORGANIC KIT for PlasmaQuant 9200	810-88562-0	Sample introduction kit for organic samples
Teledyne Cetac ASX-560	810-88015-0	Autosampler with integrated rinse function
ASX-560 Oil Upgrade Kit	418-88224-0	Organic resistant autosampler parts

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