Challenge
Determination of trace elements in volatile organic compounds such as gasoline with high robustness and low limits of detection.

Solution
HR ICP-OES with superior sensitivity and matrix tolerance to achieve lowest detection limits for trace element analysis in volatile organic compounds.

Intended audience
Refinery & fuel testing labs, petroleum & petrochemical producers, analytical chemists responsible for trace metal analysis, ICP-OES users working with volatile organic samples.

Specification analysis of gasoline by high-resolution ICP-OES

Introduction

Volatile Organic Compounds (VOC) such as gasoline and naphtha are subject to specification analysis in terms of trace elemental analysis of environmental pollutants (e.g. lead) and compounds that are potentially harmful to engines and turbines. Elements such as vanadium, iron, nickel, or silicon contribute to corrosion processes and therefore bear the risk of engine or sensor failure in automobiles or aircrafts. Due to the potential environmental hazard and risk of technical breakdown caused by trace elemental impurities, their analysis is subject of many regulations, such as ASTM D5708, ASTM D7111, UOP 389, and DIN EN 228, requesting maximum levels in the ppb range for elements such as Al, As, Fe, K, Na, Ni, P, Pb, Si and V. The value of petroleum is often defined by the specification of such elements.

VOC are among the most challenging samples to be analyzed by 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 occurence of spectral interferences. Typical analytical challenges are the poor short-term and long-term stability due to the high volatility of the samples and to the high risk of soot formation caused by the high carbon content of the samples. Furthermore, the carbon-based emission complicates the spectra as-recorded and bears the risk of severe spectral interferences. Conventional ICP-OES instrumentation is forced to use less sensitive lines for many analytes, since interferences on primary lines cannot be resolved properly.

Due to the vertical plasma geometry of the V Shuttle Torch and the unique plasma performance of its High-Frequency Generator, direct analysis of undiluted gasoline proved feasible for the analytical routine on the PlasmaQuant 9200 Elite. By avoiding soot formation and memory effects, frequent torch replacement becomes a relic of the past and detection limits below 1 µg/kg for iron, nickel, and vanadium push the boundaries of ICP-OES detectability. Hence, the PlasmaQuant 9200 Elite represents

a suitable alternative to ICP-MS instrumentation for the analysis of VOC. Carbon-based spectral interferences are successfully removed by the high spectral resolution of the High-Resolution Optics. Excellent method robustness was confirmed by a continuous aspiration test, which showed minor intensity drifting of all emission lines during 3.5 hours of uninterrupted submission of undiluted gasoline.

Materials and Methods

Samples and reagents

Low-boiling point gasoline (straight-run) was submitted to direct analysis of Al, As, Fe, Ni, Na, K, P, Pb, Si and V on PlasmaQuant 9200 Elite.

The analysis was performed on an PlasmaQuant 9100 Elite ICP-OES. Representative test measurements on a PlasmaQuant 9200 Elite confirmed consistent performance under adjusted plasma conditions.

Sample preparation / Calibration

In the absence of a high-purity gasoline reference, a standard addition calibration routine was employed and organometallic S-21+K (100 ppm) and As (100 ppm) from CONOSTAN were used to prepare calibration standards as shown in Table 1.

Table 1: Concentration of calibration standards for standard addition

Element	Unit	Add.Cal.1	Add.Cal.2	Add.Cal.3	Add.Cal.4	Add.Cal.5
Al, Fe, K, Na, Ni, P, Pb, Si, V	mg/kg	0.051	0.102	0.220	0.305	0.540
As	mg/kg	0.050	0.100	0.216	0.300	0.530

Instrument settings / method parameters

For the analysis, a PlasmaQuant 9200 Elite equipped with Organic-Kit and cooled spray chamber was used.
The detailed system configuration is given in Table 2.

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

Parameter	Setting 9100 Elite normal plasma mode [A]	Setting 9200 Elite normal plasma mode [A]	Setting 9100 Elite oxygen ashing mode [B]	Setting 9200 Elite oxygen ashing mode [B]
Power	1600 W			
Plasma gas flow	15 L/min	11 L/min	16 L/min	12 L/min
Auxillary gas flow	1.2 L/min	1.5 L/min	0.3 L/min	0.2 L/min
Oxygen gas flow	0 L/min		0.03 L/min	0.05 L/min
Nebulizer gas flow	0.35 L/min			
Nebulizer	0.4 mL/min concentric nebulizer, borosilicate		0.1 mL/min concentric nebulizer, borosilicate	
Spray chamber	IsoMist cyclonic spray chamber with dip tube, 50 mL, Peltier cooled to -14°C			
Injector	Quartz, 1 mm;			
Torch position [C]	Distance to coil set to -2 mm		Distance to coil set to +1 mm	Distance to coil set to +2 mm
Outer tube/Inner tube	Quartz / quartz			
Pump tubing	Viton (0.76 mm ID) black/black			
Sample pump rate	0.4 mL/min		0.1 mL/min	
Rinse/ Read delay	180 s			

A standard settings for undiluted gasoline
B settings for oxygen addition to the plasma that reduces unspecific spectral interferences from gasoline matrix (see Table 7)
C spacing between injector and coil further suppresses the carbon built-up at the injector tip (prolonging torch life time); not applicable with oxygen addition;
Please note, that change of plasma conditions does not require for the plasma to be turned off.

Table 3: Plasma configurations and setup of the sample introduction system

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixel	Background correction	Polynomial degree	Correction
Al	396.152	axial	peak	10	3	ABC[2]	auto	-
As	188.979	axial	peak	10	3	ABC	auto	-
Fe	259.940	axial	peak	10	3	ABC	auto	-
K	766.491 [1]	axial	peak	10	3	ABC	auto	-
Na	589.592 [1]	axial	peak	10	3	ABC	auto	-
Ni	221.648	axial	peak	10	3	ABC	auto	-
P	213.618	axial	peak	10	3	ABC	auto	-
Pb	220.353	axial	peak	10	3	ABC	auto	-
Si	251.611	axial	peak	10	3	ABC	auto	-
V	309.311	axial	peak	10	3	ABC	auto	-

1 measured with oxygen addition to the plasma
2 automatic baseline correction

Results and Discussion

Using a high-resolution ICP-OES enables the interference-free analysis of trace elements as displayed in Table 4. Neither matrix based nor inter-element interferences were observed for the majority of the analyzed trace elements in volatile organic compounds. The investigation resulted in exceptional matrix-specific limits of detection in the sub-ppb range (< 5 µg/kg) for all investigated elements.

Table 4: Overview of results for gasoline sample

Element	Line [nm]	Content [µg/kg]	Confidence interval	Matrix specific LOD [µg/kg]
Al	396.152	284.4	± 7.8	1.83
As	188.979	21.6	± 5.8	2.72
Fe	259.940	7.1	± 5.7	0.45
K	766.491 [1]	<DL	<DL	0.76
Na	589.592 [1]	99.2	± 10.4	4.28
Ni	221.648	8.2	± 5.6	0.43
P	213.618	97	± 17.9	2.89
Pb	220.353	33.1	± 6.5	1.83
Si	251.611	77.5	± 5.7	0.56
V	309.311	24.6	± 5.6	0.38

1 measured with oxygen addition to the plasma

Method validation as well as a long-term stability investigation was performed by measuring QC recovery of Add.Cal.3 (undiluted gasoline) constantly for up to 3.5 hours. Recovery values between 97% and 107% at RSD values of significantly less than 1.5% were achieved. Except for sodium and potassium, these results were achieved without the addition of oxygen to the plasma, which demonstrates the exceptional plasma performance of the PlasmaQuant 9200 Elite for highly volatile samples. The detailed results are displayed in Table 5. Figure 1 displays the results of the constant signal reading of the QC standard Add.Cal.3, with minimum drift (97 to 103%) on the long-term measurement for 3.5 hours.

Table 5: Overview of results for continuous aspiration test of gasoline matrix (Add.Cal.3)

Element	After 30 min [1]		After 2 hours [3]		After 3.5 hours [4]	
	RSD [%] [2]	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]	Recovery [%]
Al	0.56	97.3	0.46	105	1.26	102
As	0.53	102	0.43	101	0.9	101
Fe	0.02	101	0.38	102	0.17	102
K	0.71	104 [5]	0.72	104 [5]	1.33	102 [5]
Na	0.46	102 [5]	1.32	101 [5]	0.2	99.9 [5]
Ni	0.34	98.4	0.44	98.9	0.17	98.9
P	2.25	103	1.46	103	0.21	107
Pb	0.37	101	0.65	101	0.73	99.7
Si	0.52	99.3	0.38	98.2	0.52	98.4
V	0.2	101	0.46	101	0.3	102

1 results were obtained after 30 minutes of continuous aspiration of undiluted gasoline (including warm-up and calibration)
2 RSD values from three replicate measurements
3 results were obtained after 2 hours of continuous aspiration of undiluted gasoline
4 results were obtained after 3.5 hours of continuous aspiration of undiluted gasoline
5 measured with oxygen addition to the plasma

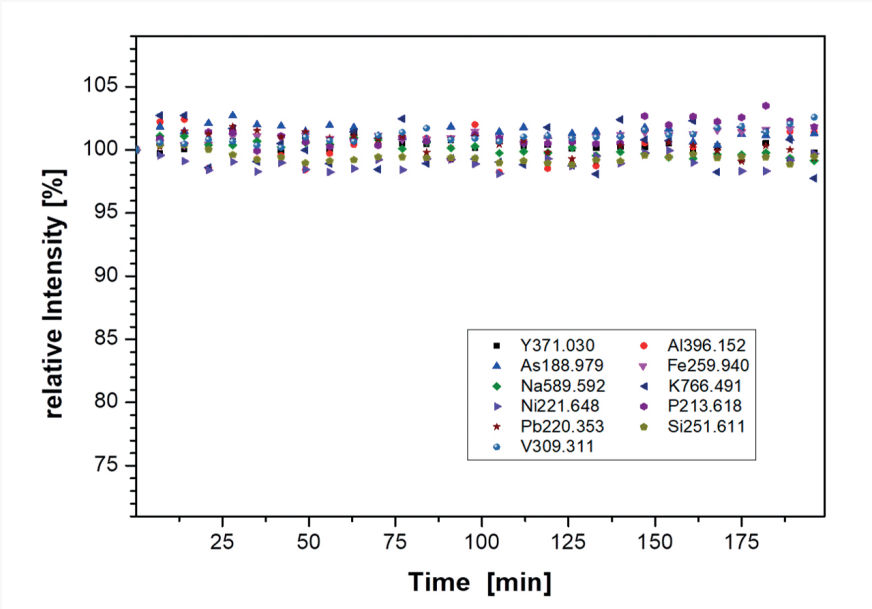
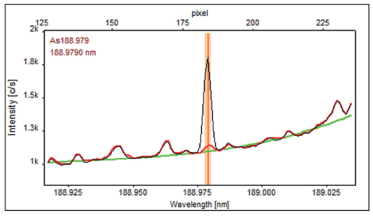
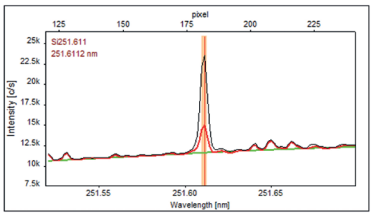
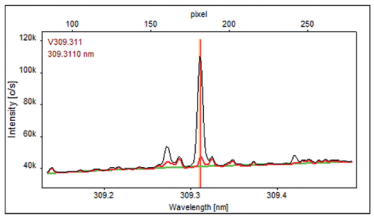


Figure 1: Plot of relative signal intensities obtained from continuous aspiration of undiluted gasoline (long-term stability)

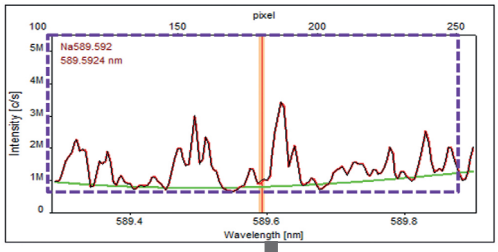
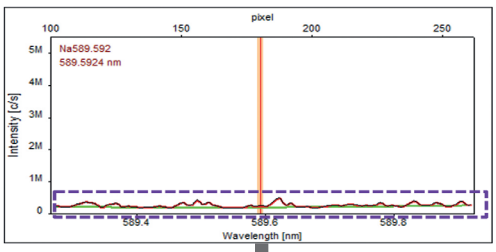
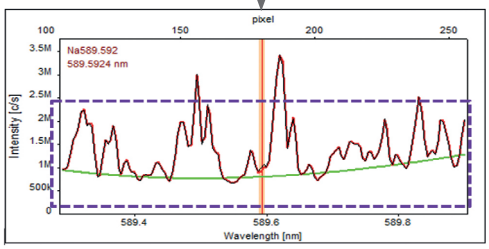
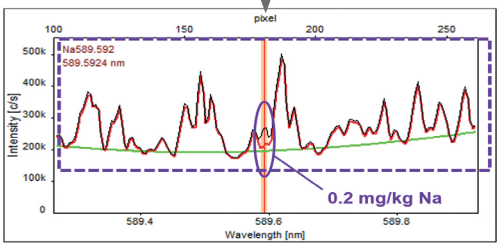
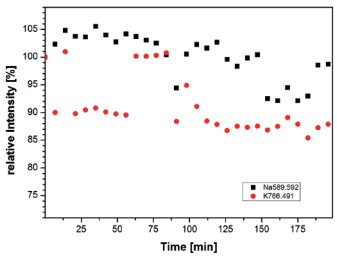
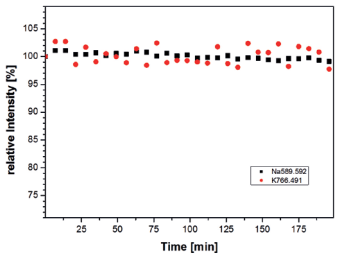
Interference-free detection of elements on their most sensitive emission lines, e.g. As 188.979, Si 251.611, V 309.311 or Pb 220.353 is feasible resulting in exceptionally low matrix specific limits of detection in the ppt to ppb range, e.g. 0.38 µg/kg for vanadium. A selection of high-resolution emission spectra including the applied automatic background correction (ABC) can be found in Table 6.

Table 6: Collection of High-Resolution spectral data for undiluted gasoline (red), Add.Cal.3 (black) and ABC (green)

As 188.979 nm	Si 251.611 nm	V 309.311 nm
		

Only the analysis of sodium and potassium required oxygen addition to the plasma in order to avoid interferences due to carbon-based unspecific emission. For regular plasma conditions, unspecific spectral interferences from the gasoline matrix gave rise to about 3.5 million counts in close spectral vicinity of Na 589.592 (Table 7, top, left). The sodium signal cannot be resolved from that of the gasoline matrix (Table 7, middle, left), which leads to significant line drifting of Na 589.592 during continuous aspiration (Table 7, bottom, left) and hence false quantification. Oxygen addition in turn reduces unspecific spectral interferences by about 90% (Table 7, top, right), hence allowing for sodium detection with good reproducibility (Table 7, middle, right). Besides, hardly any line drifting of Na 589.592 upon continuous aspiration of undiluted gasoline occurs (Table 7, bottom, right), which safeguards high precision of the trace analysis. Oxygen addition further improves matrix-specific detection limits from 8.0 to 4.3 µg/kg (for sodium) and from 4.0 to 0.76 µg/kg (for potassium).

Table 7: Impact of oxygen addition on signal intensity, spectral interferences and long term signal stability for sodium and potassium in undiluted gasoline

Parameter	regular plasma conditions	with oxygen addition
Na 589.592 nm **red** sample **black** sample, Add.Cal.3		
Na 589.592 nm (detail-spectra/ zoom-in) **red** sample **black** sample, Add.Cal.3		
Na 589.592 nm K 766.491 nm Plot of relative signal intensities obtained during continuous aspiration of gasoline for more than 3 h		

Summary

The analysis of volatile organic compounds such as naphtha or gasoline regarding the trace elemental contents represents one of the most demanding tasks for ICP techniques. The high volatility of the samples often leads to unsTable plasma conditions, resulting in severe signal drifts and poor accuracy and precision of the obtained results. Dilution in less volatile solvents or alterations to the plasma gas composition is required for conventional ICP-OES instrumentation. Due to the High-Frequency Generator in combination with the vertical torch orientation of the V-Shuttle Torch, the PlasmaQuant 9200 Elite can measure undiluted VOC with great precision, accuracy, and long-term stability.

The high resolution of the PlasmaQuant 9200 Elite is able to resolve spectral interferences originating from carbon-based emission and makes it possible to use the most sensitive lines for the majority of the investigated analytes. The use of the most sensitive lines and the possibility to run VOC undiluted result in detection limits in the ppt to ppb range and great long-term stability and make the PlasmaQuant 9200 Elite superior to conventional ICP-OES and a feasible alternative to ICP-MS instrumentation.

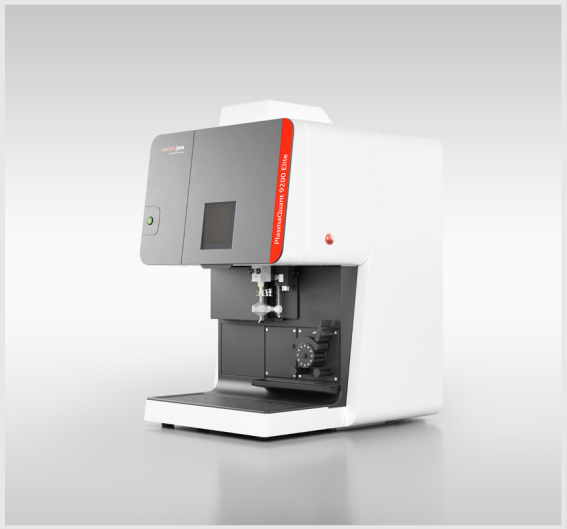


Figure 2: PlasmaQuant 9200 Elite

Recommended device configuration

Table 8: 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
Nebulizer 0.4 mL/min	418-13-410-480	Concentric borosilicate nebulizer
Nebulizer 0.1 mL/min	418-13-410-482	Concentric borosilicate nebulizer
ASPQ 3300	810-88002-0	Autosampler with integrated rinse function
Septum piercing kit for ASPQ 3300	418-10-405-013	Septum piercing kit as upgrade to ASPQ 3300 autosampler to automatically sample volatile organic samples from capped vials

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