



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 high-resolution optical system, superior sensitivity and matrix tolerance to achieve lowest detection limits for trace element analysis in volatile organic compounds.

Specification Analysis of Gasoline by HR 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. The value of petroleum is often defined by the specification of such elements. 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, UOP389, and DIN EN 228, requesting maximum levels in the ppb range for elements such as V, Fe, Al, K, Na, Ni, P, As, Si, and Pb.

VOC are among the most challenging samples to be analyzed by ICP techniques. For specification analysis in the low $\mu\text{g}/\text{kg}$ range, ICP-MS is often the method of choice as conventional OES instruments lack sensitivity due to sample dilution and 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.

Thanks 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® PQ 9000 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® PQ 9000 Elite represents a feasible alternative to ICP-MS instrumentation for the analysis of VOC.

Carbon-based spectral interferences are successfully removed thanks to the unmatched spectral resolution of the High-Resolution Optics. However, for sodium and potassium analysis, oxygen addition is recommended. 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® PQ 9000 Elite.

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® PQ 9000 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 | Specification |
|-----------------------|--|
| Power | 1600 W |
| Plasma gas flow | 15A (16B) L/min |
| Auxillary gas flow | 1.2A (0.3B) L/min |
| Oxygen gas flow | 0A (0.03B) L/min |
| Nebulizer gas flow | 0.35 L/min |
| Nebulizer | 0.4A (0.1B) 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; distance to coil set to - 2 mmC |
| Outer Tube/Inner Tube | Quartz / Quartz |
| Pump tubing | Viton (0.76 mm ID) black/black |
| Sample pump rate | 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 | No. of Pixel | No. of Pixel | 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 | ± | 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® PQ 9000 Elite for highly volatile samples. The detailed results are displayed in table 5. Figure 11 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 |

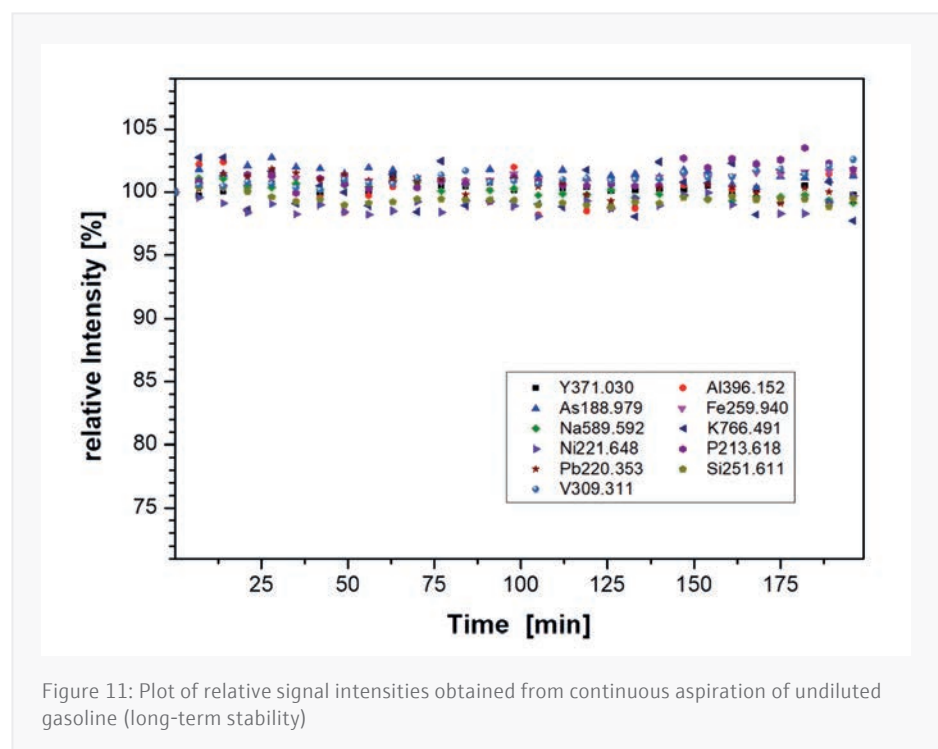
1 results were obtained after 30 minutes of continuous aspiration of undiluted gasoline (including warm-up and calibration)

2 RSD values from three replicate measurements

3 results were obtained after 2 hours of continuous aspiration of undiluted gasoline

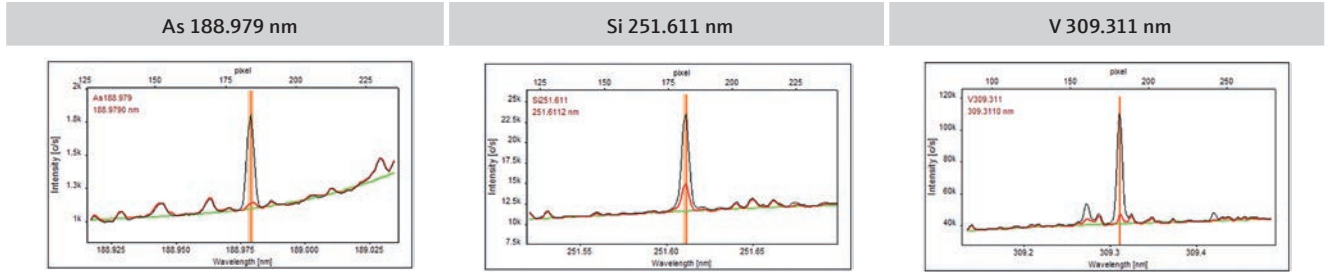
4 results were obtained after 3.5 hours of continuous aspiration of undiluted gasoline

5 measured with oxygen addition to the plasma



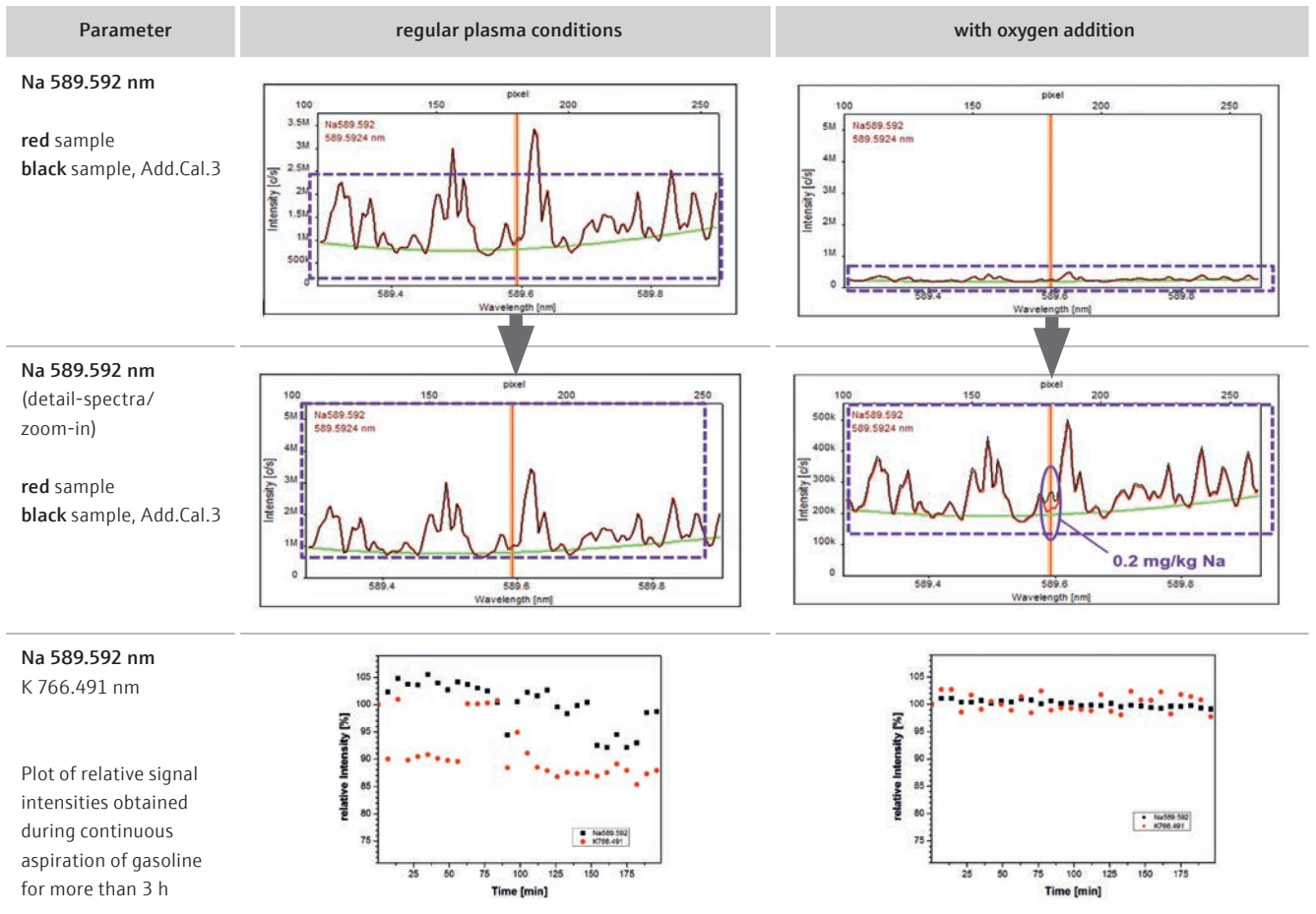
Interference-free detection of elements on their most sensitive emission lines, e.g. As 188.979, Si, 251.611, V 309.311 or Pb 220.353 is feasible resulting in exceptionally low matrix specific limits of detection in the ppt to ppb range (0.38 µg/kg for Vanadium). A selection of high-resolution emission 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)



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 (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 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 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 4.28 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



Conclusion

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. Thanks to the HF generator in combination with the vertical torch orientation of the V-Shuttle Torch, the PlasmaQuant® PQ 9000 Elite can measure undiluted VOC with great precision, accuracy, and long-term stability.

The high resolution of the PlasmaQuant® PQ 9000 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® PQ 9000 Elite superior to conventional ICP-OES and a feasible alternative to ICP-MS instrumentation.

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