Challenge

Analyzing volatile organic solvents often associated with plasma destabilization, signal drift due to cone clogging and carbon-based polyatomic interferences.

Solution

PlasmaQuant MS with cooled spray chamber, Nitrox gas accessory and hydrogen reaction gas in interference management mode for accurate and precise analysis of organic solvents.

Analysis of Elemental Impurities in Naphtha by ICP-MS according to ASTM D8110-17

Introduction

Naphtha is a petroleum fraction containing C5-C12 hydrocarbon compounds, which 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 metal contents in naphtha is important for a number of reasons[1]. In fuel production, the presence of metals such as calcium, magnesium, sodium, and potassium can form hard deposits and create excessive wear on the engine components. On the other hand, the presence of nickel during the cracking process can poison the expensive catalyst, while vanadium causes corrosion problems. During the refining process, the release of toxic metals such as lead, mercury, and arsenic has to be monitored and minimized since they are of environmental concern.

For the analysis of small impurities in naphtha, lowest limits of detection need to be achieved which makes ICP-MS the technique of choice. However, due to the complex nature of naphtha, the analysis by ICP-MS requires special attention to minimize the formation of carbon deposits on the sampler and skimmer cones and avoid the instability or even the complete extinction of the plasma due to organic vapor overloading. Interferences due to polyatomic species, originating from the carbon matrix and plasma, must also be considered and eliminated.

This application note demonstrates the performance of the PlasmaQuant MS and its unmatched tolerance to organic solvents, which allow routine analysis of highly volatile organic solvent samples according to ASTM D8110-17 with results exceeding the requirements for accuracy and plasma stability over time[2].

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Materials and Methods

Samples and Reagents

Four naphtha samples were measured in this study. A weighed portion (approximately 1 g) of a thoroughly homogenized light or middle distillate petroleum sample was diluted 1:10 by mass with n-Hexan solvent (for organic trace analysis UniSolv®, Merck). Any suitable solvent such as o-xylene or others may also be used.

Multi-element stock standards were prepared from organometallic multi- and single element standards, As and Hg organometallic standards diluted with n-Hexan. Four multi-element calibration standards ranging from 0.5 ng/g to 10 ng/g were prepared for the target elements by weight. The diluent solution was used as a blank for the calibration. Yttrium was spiked with 25 ng/g to all solutions as internal standard to compensate for variations in test specimen introduction efficiency and element ionization efficiency in the plasma. The sample introduction system was rinsed using n-Hexan between each sample analysis.

Pb was determined using the sum of the intensities for its three major isotopes (^{206}Pb, ^{207}Pb and ^{208}Pb) to account for isotopic variation in the samples and standards.

Calibration

For quantification of trace elements in naphtha in accordance with ASTM D8110-17, a minimum of three calibration standards and a blank are required for external calibration. The performance criterion for the calibration is a minimum correlation of $r^2 \geq 0.995$. Figure 1 shows the calibration of some elements investigated in naphtha. All the elements measured fulfill the calibration precision criterion (>0.997 in all cases).

Instrumentation

All analytical work was performed on the PlasmaQuant MS ICP-MS with an optimized configuration of the sample introduction system to take account of the high organic content and sample volatility. Naphtha samples were introduced directly into the ICP-MS system by self-aspiration. A MicroMist™ nebulizer 0.4 mL/min was connected to a spray chamber which was drained by black/black Viton® pump tubing with a peristaltic pump speed of 30 rpm. In order to minimize solvent loading to the plasma, a plasma torch with 1.5 mm injector, a Scott type spray chamber chilled to -10 ºC and aerosol dilution option were used to stabilize the plasma during all measurements. Oxygen was introduced to the auxiliary gas flow via the Nitrox gas accessory to effectively prevent non-ionized carbon deposition mainly on the sampler cone orifice. The oxygen flow was optimized with respect to the carbon chain length of the matrix, as both correlate directly. However, excessive addition of oxygen can promote the formation of oxides, especially with easily ionizable elements. Due to the corrosive environment created by the addition of oxygen, platinum cones were used. Carbon-based polyatomic interference species were eliminated using hydrogen as reaction gas via the integrated Collision Reaction Cell (iCRC). The BOOST option was used to improve the signal/noise ratio and to achieve lower detection limits. Table 1 shows instrument settings and the method parameters used.

Table 1: PlasmaQuant MS settings and method parameters for naphtha analysis.

Parameter	Specification	Parameter	Specification
Plasma gas flow	10.5 L/min	Pump rate (drain spray chamber)	30 rpm – black/black Viton® pump tubing
Auxiliary gas flow	1.50 L/min	Stabilization delay	20 s
Sheath gas flow	0.50 L/min	iCRC	H_2 – 200 mL/min
Nebulizer gas flow	0.40 L/min	Nitrox	O_2 – 180 mL/min
Plasma RF power	1.30 kW	Skimmer Bias (BOOST)	10 V
Nebulizer type	MicroMist™ 0.4 mL/min (quartz concentric)	Dwell time	20 ms
Cones	Platinum	Scan mode	peak hopping, 1 pt/peak
Torch	Fassel torch with 1.5 mm injector	No. of scans per replicate	25
Spray chamber type and temperature	Glass Scott with Peltier chiller, -10 ºC	No. of replicates per sample	5
Sample introduction	Self aspiration	Acquisition time	140 s

Results and Discussion

Detection limits

ICP-MS detection limits for all elements of interest were determined as follows: a blank solution with internal standard was prepared, sealed and well mixed. Seven consecutive analyses of this solution were performed under the same conditions as the calibration standards. The method detection limit (MDL) is calculated as

$$MDL=(t)x(s)x(d)$$

with:

t = student's t value for 99% confidence level and with n-1 degrees of freedom (t = 3.14 for seven replicates),
s = standard deviation of the replicate analysis,
d = dilution factor applied to all samples (10).
Table 2 shows typical MDLs in ng/g.

Table 2: Method detection limits in blank solvent (ng/g).

Isotope	MDL	Isotope	MDL	Isotope	MDL	Isotope	MDL
^{10}B	3.3	^{52}Cr	0.03	^{66}Zn	0.30	^{118}Sn	0.02
^{24}Mg	1.1	^{55}Mn	0.09	^{75}As	0.06	^{137}Ba	0.04
^{49}Ti	1.3	^{56}Fe	0.25	^{98}Mo	0.02	^{200}Hg	0.04
^{51}V	0.11	^{60}Ni	0.65	^{114}Cd	0.01	$^{206+207+208}$Pb	0.01

Check Standard – QC

At the beginning of the analysis of each batch of samples a calibration was performed and a check standard (QC – 2.54 ng/g) was used to verify if the obtained results were within a tolerated error of 10% of the expected concentration for all elements to be analyzed. This procedure was repeated every 10 samples. The blank solvent was aspirated between the standards to rinse the system prior to the next run. After running the highest calibration standard, element signal intensities were checked in three consecutive blank solvent measurements before analyzing the next samples in order to avoid cross-contamination. Figure 2 shows the stability over time of the QC – 2.54 ng/g check standard.
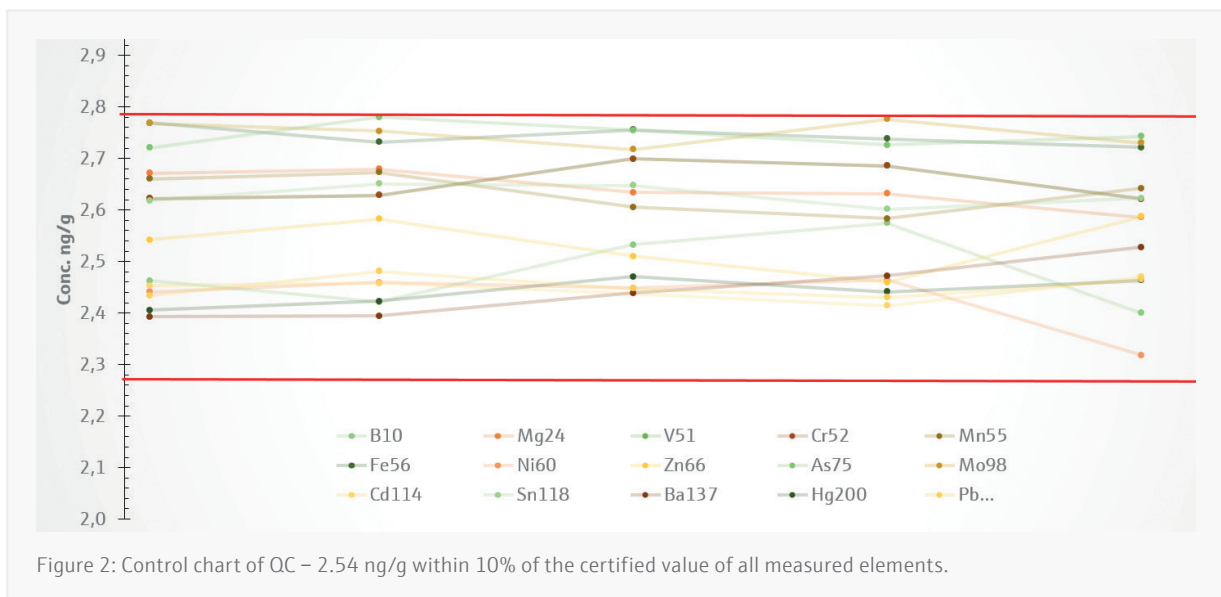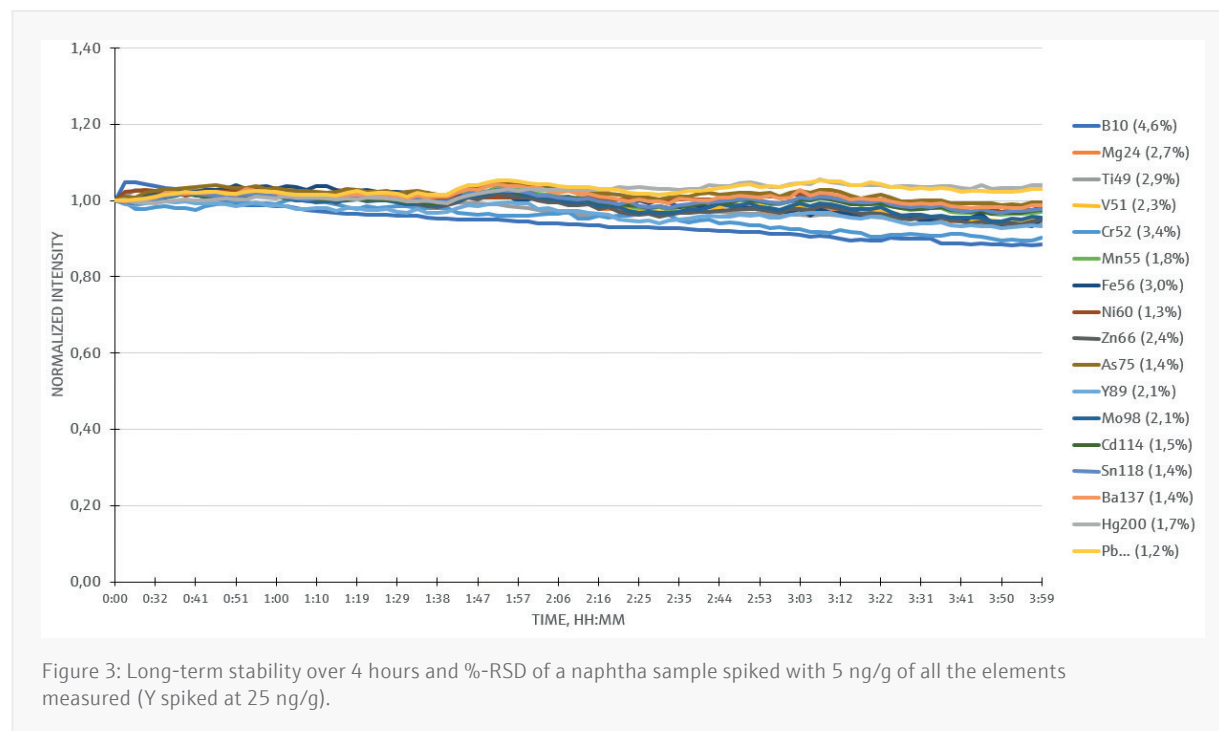

Figure 2: Control chart of QC – 2.54 ng/g within 10% of the certified value of all measured elements.

Internal Standard stability

Figure 3 shows the stability of the method monitoring recoveries of all the elements in a naphtha sample diluted 1:10 and spiked with 5 ng/g over four hours. All elements showed remarkable stability (5%), even those that may be affected by polyatomic interferences in organic solvents, e.g., magnesium and chromium. The ASTM D8110-17 defines the internal standard performance in each sample to be within 50% to 150% to meet the requirements. In this study the internal standard yttrium showed a drift of 7%.

Figure 3: Long-term stability over 4 hours and %-RSD of a naphtha sample spiked with 5 ng/g of all the elements measured (Y spiked at 25 ng/g).

Precision

The precision at 2.5 ng/g level was checked against the repeatability as described in ASTM D8110-17 and determined by statistical analysis of laboratory results (Table 3). In addition, two naphtha samples diluted 1:10 were duplicated and measured (Table 4). The precision of the method clearly ensures data quality.

Table 3: Precision of the method compared to ASTM D8110-17 repeatability reported.

Isotope	ASTM Repeatability at 5 ng/g level	Precision of this study at 2.5 ng/g level	Isotope	ASTM Repeatability at 5 ng/g level	Precision of this study at 2.5 ng/g level
^{10}B	Not reported	2.98	^{66}Zn	Not reported	2.10
^{24}Mg	2.5	1.42	^{75}As	Not reported	0.87
^{49}Ti	Not reported	5.85	^{98}Mo	Not reported	0.90
^{51}V	Not reported	1.43	^{114}Cd	Not reported	0.87
^{52}Cr	Not reported	0.43	^{118}Sn	Not reported	0.78
^{55}Mn	Not reported	1.43	^{137}Ba	Not reported	2.33
^{56}Fe	1.81	0.70	^{200}Hg	Not reported	1.11
^{60}Ni	Not reported	2.52	$^{206+207+208}$Pb	3.93	0.86

Table 4: Precision achieved in two naphtha samples duplicated. Concentration in ng/g of 1:10 dilution.

Isotope	1968496	1968496 Duplicate	% RSD	1970837	1970837 Duplicate	% RSD
^{10}B	1.49	1.59	4.6	1.35	1.45	5.1
^{24}Mg	35.5	35.3	0.4	31.7	31.1	1.5
^{49}Ti	11.6	12.1	2.9	9.63	10.4	5.6
^{51}V	0.22	0.24	6.1	0.26	0.23	8.7
^{52}Cr	30.9	30.7	0.3	27.2	29.5	5.7
^{55}Mn	0.16	0.16	0.0	0.14	0.15	4.9
^{56}Fe	4.28	4.17	1.8	2.42	2.49	2.0
^{60}Ni	5.5	5.02	6.5	0.83	0.89	4.9
^{66}Zn	0.5	0.55	6.7	0.45	0.43	3.2
^{75}As	0.24	0.24	0.0	0.15	0.15	0.0
^{98}Mo	<MDL	<MDL	–	<MDL	<MDL	–
^{114}Cd	<MDL	<MDL	–	<MDL	<MDL	–
^{118}Sn	<MDL	<MDL	–	<MDL	<MDL	–
^{137}Ba	<MDL	<MDL	–	<MDL	<MDL	–
^{200}Hg	0.31	0.28	7.2	0.14	0.15	4.9
$^{206+207+208}$Pb	0.02	0.02	0.0	0.04	0.04	0.0

Accuracy

According to ASTM D8110-17, reproducibility is not defined at present. A second interlaboratory study will be conducted within a five-year limit to produce enough data. However, since no commercial standard reference materials are available for naphtha, the accuracy of the method was checked in two naphtha samples spiked with 10 ng/g after 10-fold dilution with n-Hexane. Table 5 shows excellent recoveries ranging within 90% to 110% for all elements measured. This performance clearly shows the efficiency of the iCRC technology to remove the polyatomic interferences even in high carbon organic solvents.

Table 5: Spike recoveries in two naphtha samples. Concentration in ng/g of 1:10 dilution.

Isotope	1968779	Spiked	% Recovery	1968702	Spiked	% Recovery
^{10}B	1.16	11.8	106	0.45	11.2	108
^{24}Mg	5.18	14.6	94	2.79	12.2	94
^{49}Ti	0.65	10.3	97	0.03	9.23	92
^{51}V	0.40	10.3	99	<LOQ	8.99	90
^{52}Cr	0.01	9.06	91	<LOQ	9.61	96
^{55}Mn	0.21	10.5	103	0.23	10.1	99
^{56}Fe	2.47	12.0	95	2.92	13.6	107
^{60}Ni	1.09	10.7	96	1.24	10.2	90
^{66}Zn	0.64	10.5	99	<LOQ	9.39	94

Isotope	1968779	Spiked	% Recovery	1968702	Spiked	% Recovery
^{75}As	0.10	10.2	101	<LOQ	9.65	97
^{98}Mo	0.02	10.3	103	<LOQ	9.84	98
^{114}Cd	0.04	10.1	101	0.08	9.91	98
^{118}Sn	0.03	10.3	103	<LOQ	9.95	100
^{137}Ba	0.19	11.0	108	0.02	9.95	99
^{200}Hg	0.52	10.4	99	0.41	9.81	94
$^{206+207+208}$Pb	0.19	11.2	110	0.02	10.3	103

Conclusion

This work demonstrates the superior capability of the PlasmaQuant MS to analyze naphtha samples in accordance with the ASTM D8110-17 requirements. The combination of unique features, such as the Nitrox gas accessory for the addition of oxygen or nitrogen into the auxiliary gas flow, the iCRC for effective removal of polyatomic interferences and the BOOST option for maintaining sensitivity in hydrogen mode, ensures an outstanding and stable performance for the analysis of a challenging matrices.

The developed method allows to achieve excellent detection limits − all analyte elements surpass the calibration correlation criterion of r^2>0.995. The quality control actions that were routinely included in the sample analysis meet the performance requirements by <10% variation for the repetead analysis of the QC standard. Less than 7% drift of the monitored internal standard within four hours of routine analysis run underline the stability of the method. The precision for unknown samples was verified according to the ASTM D8110-17 with recovery measurements of a spike and duplicated sample analyses. Both tests proof the suitability of the method developed for the PlasmaQuant MS for the routine analysis of elemental impurities in naphtha.

References

[1] Kumar, S. J. and Gangadharan, S., Determination of trace elements in naphtha by Inductively Coupled Plasma Mass Spectrometry using water-in-oil emulsions, J. Anal. At. Spectrom., 1999, 14, pages 967-971

[2] ASTM D8110-17, Standard Test Method for Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), ASTM International; https://www.astm.org/Standards/D8110.htm