



### Challenge

Analysis of trace elements with low LOD in water-methanol-oil mixtures featuring complex emission spectra originating from the sample matrix.

### Solution

HR ICP-OES with high-resolution optical system, superior sensitivity and matrix tolerance to achieve lowest LOD for trace element analysis in complex water-alcohol-oil samples.

## Trace Metals Analysis in Water-Methanol-Oil Mixtures by HR ICP-OES

### Introduction

Water-methanol-oil mixtures in varying compositions are used as additive in internal combustion engines. Here, water injection, also known as anti-detonant injection systems (ADI), is used to spray water or a water/methanol mixture into the fuel/air mixture in order to cool the introduction system avoiding premature ignition of the fuel. This leads to improved behavior in terms of engine knocking and compression ratio in engines of aircrafts and racing cars. Results are increased power and fuel efficiency, improved power output for short duration such as increase of thrust of jets during takeoff, and reduction of NOX and CO emissions by decreased soot formation during the combustion process.

In ADI fluids, methanol serves as an anti-freezing agent and as combustible additive. The small fraction of water-soluble oil mainly acts as corrosion inhibitor but also serves as lubrication agent. Quality control of ADI fluids in terms of trace element analysis is required to ensure the absence of compounds that compromise efficiency or trigger corrosion and eventually cause technical breakdown of the engine. Therefore, the lowest possible specification limits (e.g., limits of detection) are of high interest for QC laboratories. The complexity of the matrix of ADI fluids, however, demonstrates a demanding challenge for atomic spectrometry methods such as ICP-OES. A highly robust plasma for reliable excitation of the sample is a pre-requisite to achieve high precision and accuracy of the results. Additionally, exceptional optical resolution is required to resolve spectral interferences originating from matrix-based (methanol/oil) unspecific emission.

In this study, an aqueous ADI solution containing 7% of methanol and trace levels of oil was submitted to a limit control analysis of Al, As, Bi, Ca, Cd, Co, Cr, Cu, Fe, In, Mg, Mn, Ni, Sb, Sn, W, and Zn by the PlasmaQuant 9100 Elite. Aided by its argon counter gas technology, the highly transparent optical path of the PlasmaQuant 9100 Elite provides the lowest limits of detection in ICP-OES. In particular for arsenic and tin with their most sensitive emission lines located in the UV-range, the absence of oxygen, air, or nitrogen benefits their increased detectability and quality RSD values. Additionally, spectral interferences originating from unspecific emission lines of the organic matrix (methanol, oil) are removed successfully by the high-resolution optics (FWHM < 3 pm at 200 nm) and/or the CSI software tool. Furthermore, the high plasma robustness of the high-frequency generator and the sample introduction system with its centerpiece, the V-Shuttle torch, allow for the analysis of high matrix samples with high accuracy and precision.

## Materials and Methods

### Samples and Reagent/ /Sample Preparation

An aqueous ADI solution containing 7% of methanol and trace levels of oil was submitted to a limit control analysis of Al, As, Bi, Ca, Cd, Co, Cr, Cu, Fe, In, Mg, Mn, Ni, Sb, Sn, W and Zn by the PlasmaQuant 9100 Elite.

### Calibration

In the absence of a suitable material for matrix-matching of calibration standards additions calibration was conducted instead. A multi-element standard (ICP IV, MERCK, 1000 ppm) and single-element standards for As, Sb, Sn and W (SIGMA-ALDRICH) were used to realize spiked concentrations of 100, 200 und 500 µg/L.

Table 1: Concentration of calibration standards

Element	Unit	Add. Cal.0	Add. Cal.1	Add. Cal.2	Add. Cal.3
Al, As, Bi, Ca, Cd, Co, Cr, Cu, Fe, In, Mg, Mn, Ni, Sb, Sn, W, Zn	µg/L	0	100	200	

### Instrument Settings/Method Parameters

For the analysis, a PlasmaQuant 9100 Elite equipped with standard sample introduction kit and ASPQ 3300 autosampler was used. The detailed system configuration is given in Table 2.

Table 2: Plasma configuration and set-up of the sample introduction system

Parameter	Specification
Power	1400 W
Plasma gas flow	13.5 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	0.25 L/min
Nebulizer	Borosilicate concentric nebulizer, 0.4 mL/min
Spray chamber	Borosilicate cyclonic spray chamber, 50 mL
Room temperature	20 °C
Injector	Quartz, inner diameter 1 mm
Outer tube / Inner tube	Quartz/Quartz
Pump tubing	PVC
Sample pump flow	0.75 mL/min
Rinse / Read delay	60 s
Autosampler	ASPQ 3300

## Evaluation Parameters

Table 3: Overview of method specific evaluation parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of Pixel	Baseline fit	Polynomial degree	Correction
Al	396.15	axial	spectrum	3	3	ABC <sup>1</sup>	auto	-
As	193.70	axial	spectrum	3	3	ABC	auto	-
Bi	223.06	axial	spectrum	3	3	ABC	auto	-
Ca	315.89	axial	spectrum	3	3	ABC	auto	-
Cd	214.44	axial	spectrum	3	3	ABC	auto	-
Cd	228.80	axial	spectrum	3	3	ABC	auto	-
Co	228.62	axial	spectrum	3	3	ABC	auto	-
Cr	267.72	axial	spectrum	3	3	ABC	auto	-
Cu	324.75	axial	spectrum	3	3	ABC	auto	-
Fe	259.94	axial	spectrum	3	3	ABC	auto	-
In	325.61	axial	spectrum	3	3	ABC	auto	-
Mg	285.22	axial	spectrum	3	3	ABC	auto	-
Mn	257.61	axial	spectrum	3	3	ABC	auto	-
Ni	231.60	axial	spectrum	3	3	ABC	auto	-
Sb	217.58	axial	spectrum	3	3	ABC	auto	-
Sn	189.93	axial	spectrum	3	3	ABC	auto	CSI <sup>2</sup>
W	207.91	axial	spectrum	3	3	ABC	auto	-
Zn	206.20	axial	spectrum	3	3	ABC	auto	-

1 ... automatic baseline correction (ABC)

2 ... internal standard, mathematical correction of spectral interferences (CSI) recommended

## Results and Discussion

The complex matrix of ADI fluids exhibits line-rich emission spectra resulting in a high potential of spectral interferences. Often spectrally interfered lines like Ca 315.887 or As 193.698, which are amongst their most sensitive lines, are interference-free on the PlasmaQuant 9100 Elite. The small number of elements that are still partially overlapped by the unspecific matrix-based emission, in this case Sn 189.927, benefit from the CSI tool, a software algorithm that allows for easy subtraction of matrix based emission lines to achieve an interference-free signal. A selection of typically recorded high-resolution spectra is shown in Table 4.

Table 4: Exemplary high-resolution spectral data and applicability of the CSI Software tool

Element / description	Spectrum
<b>As 193.698 nm</b> red ... ADI sample green ... ADI sample plus 100 ppb spike grey ... ADI sample plus 200 ppb spike blue ... ADI sample plus 500 ppb spike baseline fit (ABC, green) * ... unspecific emission lines originating from the organic matrix	
<b>Ca 315.887 nm</b> red ... ADI sample green ... ADI sample plus 100 ppb spike grey ... ADI sample plus 200 ppb spike blue ... ADI sample plus 500 ppb spike baseline fit (ABC, green)	
<b>Sn 189.927 nm</b> red ... ADI sample green ... ADI sample plus 100 ppb spike grey ... ADI sample plus 200 ppb spike blue ... ADI sample plus 500 ppb spike baseline fit (ABC, green) * ... unspecific emission lines originating from the organic matrix	

The here developed methodology for the analysis of ADI fluids allows for matrix specific limits of detection between 5-50  $\mu\text{g/L}$  for all investigated elements. The analysis of the submitted sample revealed elevated levels of arsenic and tin, which agrees with the expectations for this particular sample. All remaining elements were detected in the range of the limit of detection or below. A summary of all obtained results is given in Table 5.

Table 5: Overview of results for specification testing of an ADI fluid and matrix specific detection limits

Element	Line [nm]	Measured concentration	Matrix specific LOD
		[µg/L]	
Al	396.15	(15.55) <sup>1</sup>	13.2
As	193.70	145.7	15.9
Bi	223.06	< LOD	51.0
Ca	315.89	(22.27) <sup>1</sup>	19.1
Cd	214.44	< LOD	11.8
Cd	228.80	< LOD	30.6
Co	228.62	< LOD	36.1
Cr	267.72	< LOD	19.0
Cu	324.75	< LOD	6.11
Fe	259.94	< LOD	14.1
In	325.61	< LOD	44.4
Mg	285.22	< LOD	4.72
Mn	257.61	< LOD	6.98
Ni	231.60	< LOD	29.2
Sb	217.58	< LOD	38.3
Sn	189.93	254.2	41.9
W	207.91	< LOD	17.6
Zn	206.20	< LOD	36.7

1 ... measured concentration is slightly higher than detection limit

## Conclusion

Quality control of fuel additives for internal combustion engines, such as fluids used for anti-detonant injection systems (ADI), requires the determination of trace elements that are known for triggering internal corrosion processes that can lead to the technical breakdown of the engines.

High precision and accuracy of results for samples containing organic compounds requires a robust sample introduction and plasma system. The PlasmaQuant 9100 Elite perfectly addresses this issue with its vertical torch design (V-Shuttle Torch) and high-frequency generator, ensuring uniform excitation and therefore great short-term and long-term stability for the analysis of matrix-rich samples.

Unspecific emission lines from the methanol-oil matrix of ADI fluids that partially overlap the emission lines of trace elements represent a major challenge for the analysis of water-alcohol-oil samples. Thanks to the high spectral resolution of PlasmaQuant 9100 Elite and its CSI Software tool, the interference-free analysis of all investigated elements was possible. The high sensitivity offered by the PlasmaQuant 9100 Elite results in matrix-specific limits of detection of less than 50 µg/L for trace elements in ADI samples.

This exceptional analytical performance accompanied with ease of use enabled by the CSI and ABC software tools makes the PlasmaQuant 9100 Elite the ideal instrument for the quality control of additives for internal combustion engines.

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