Analysis of Organic Solvents with ICP-OES – A Universal Challenge

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ABSTRACT

One of the major advantages of ICP-OES is the high flexibility in terms of sample matrix, as it can more easily handle also organic solvents in comparison to ICP-MS. Therefore, ICP-OES is a well-established technique for petrochemical analysis, but also other applications benefit from this characteristic. For example, USP chapter <233> explicitly mentions the option to directly dissolve a raw material or a finished drug product in an organic solvent in case it may be easier.
However, for high throughput and consistent results, the analysis of organic solvents requires special configuration of the instrument and the sample introduction system. For example, a vertical torch orientation combined with radial observation of the plasma offers higher robustness and less interference contribution from the matrix components. A modular approach to configure the sample introduction system components helps to rapidly switch to other sample matrices if needed.
Also, to avoid unnecessary downtime, the system should be easy to maintain on a routine basis to allow for quick inspection of the exposed components, such as the torch, injector tube or entrance to the spectrometer.
This poster will show examples for the analysis of organic solvents using ICP-OES and demonstrate how intelligent instrument design allows the user to analyze more samples at a time, and therefore effectively reduce instrument cost.

INTRODUCTION

The analysis of trace metals in used coolant samples by ICP-OES is a good example for the importance of analyzing organic solvents using ICP-OES. Based upon the results of a measurement, the performance of cooling systems is assessed preventive maintenance is scheduled. It is applicable to any closed loop cooling system, but is primarily applied to diesel and gasoline engines since these are more vulnerable to damage from a poorly operating cooling system. The longevity of liquid cooled transmission and hydraulic system components used in industrial production lines are also dependent on a properly operating cooling system. Overheating, due to a failure in the cooling system, reduces oil based lubrication potentially damaging any oil wetted components. Overheating can also contribute to corrosion of components, leading to eventual system failure.

Evaluation of new coolant and antifreeze materials indicates that corrosion protection and solution integrity are strongly dependent on the concentrations of various components. For example, inorganic salts (e.g. silicates, borates, phosphates and molybdates) used as corrosion inhibitors require accurate quantitation as part of the development process of coolant formulations.

MATERIALS AND METHODS

Instrumentation

For the sample analysis, and since the coolant components are water soluble, the Thermo Scientific™ iCAP™ 7400 ICP-OES Radial (Figure 1.) was used together with an aqueous sample introduction kit. A Teledyne CETAC Technologies ASX-560 Autosampler was used to transfer the samples to the introduction system of the ICP-OES.
The iCAP 7400 ICP-OES Radial is well suited for this type of application due to its high matrix tolerance and its ability to optimize the radial viewing height. This optimization is critical as interferences from carbon based emissions can be reduced, especially in the visible region of the spectrum. The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used for data acquisition and provides easy options for post-analysis data manipulation.
The parameters used for the method can be found in Table 1. The plasma was ignited and the instrument allowed to warm up for a period of 20 minutes. A spectrometer optimization was performed directly before each analysis.

Figure 1. The Thermo Scientific iCAP 7400 ICP-OES.

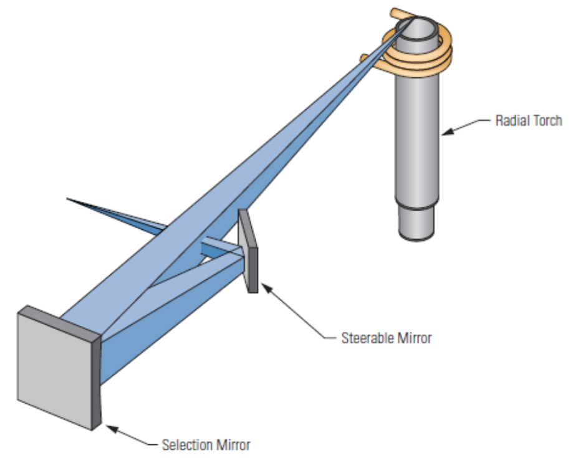

Figure 2. Fore-optics of the iCAP 7400 ICP-OES Radial system.

Table 1. Instrument Parameters Used for Measurement.

Parameter	Value
Pump Tubing	Sample Tygon® orange/white Drain Tygon® white/white
Spray Chamber	Glass Cyclonic
Nebulizer	Glass Concentric
Center Tube	1.5 mm
Pump Speed	50 rpm
Nebulizer Gas Flow	0.45 L·min^{-1}
Auxiliary Gas Flow	1.5 L·min^{-1}
Coolant Gas Flow	12 L L·min^{-1}
RF Power	1350 W
Radial Viewing Height	10 mm
Exposure Time	UV 15 s, Vis 5 s

Standard and Sample preparation

Multi-element stock standards were prepared from aqueous single element solutions (1,000 mg·L^{-1} and 10,000 mg·L^{-1}, SPEX CertiPrep Group, Metuchen, US) to a concentration of 10 mg·L^{-1} and 100 mg·L^{-1}. Calibration standards and spike solutions were then prepared from the these stock standards. The individual solutions were made with 18 MΩ ultra-pure water and glycol (99.8%, Sigma-Aldrich, Germany), to a final concentration of 5% w/w glycol for each solution (for final calibration solution concentrations, see Table 1).
A coolant sample was taken from a 60 liter cooling system tank used for air conditioning (100% monoethylene-glycol). The sample was then diluted with 18 MΩ ultrapure water to a concentration of 5% w/w. To assess recovery and accuracy, the coolant samples were also spiked with 1 mg·L^{-1} of all the elements used for the calibration. To account for matrix effects in the samples and standards, an internal standard solution of cobalt (10 mg·L^{-1}) was added to all solutions.

Method development

Multiple wavelengths were used for the analysis. These were selected as they were mostly free from interferences and provided the sensitivity to quantify the elements of interest in the expected concentration range. The wavelength of the cobalt internal standard applied to each element was chosen according to the wavelength range (UV or Vis) used for the element measurement. For all further calculations, the average results of the different wavelengths for one element were used.

Table 2. List of Quality Control Samples.

QC Code	Purpose	Frequency	Limits
ICB	Checks the instrument carry over	After initial calibration	The concentration shall be within ±5% of the expected value.
ICV	Checks the calibration against a second source to verify accuracy	After initial calibration	The concentration shall be within ±5% of the expected value.
CCB	A continuing periodic check on instrument carry-over	After every 10 analyses and at the end of analysis sequence	The concentration shall be within ±5% of the expected value.
CCV	A continuing periodic check on instrument accuracy and drift	After every 10 analyses and at the end of analysis sequence	The concentration shall be within ±5% of the expected value.

For Quality Control (QC) checks, an Initial Calibration Blank (ICB) and Initial Calibration Verification (ICV) were run. Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) QC samples were also measured every 10 samples, and finally at the end of the sample sequence. QC limits are shown in Table 2.
A method was created in Qtegra ISDS Software based on ASTM Method D6130-11(2018)[1], which details direct analysis of silicon and other elements in engine coolant.

RESULTS

The results of the analysis summarized in Table 3 show that spike recoveries in the prepared sample for all elements determined were well within acceptable limits of ±5%.The method detection limits are also acceptable with most of the method detection limits in the low µg·L^{-1} range. The results of the stability study are presented graphically in Figure 3 and are also within acceptable limits. The first sample of this study is within ±5% of the prepared value
of 1,000 µg·L^{-1} and for the duration of the study, deviation from within these limits is not seen.

Table 3. Analysis Results (Dilution Factor of 20 Applied), Spike Recoveries and MDLs. All Values are Reported in µg·L^{-1}.

Element	Sample concentration	Sample + spike concentration	Spike recovery (%)	MDL
Al	18	21106	105	6.7
B	104	20823	104	2.7
Ca	5635	26650	105	0.11
Cu	719	21224	103	4.5
Fe	844	21161	102	1.7
Mg	139	20653	103	0.22
Mo	35710	56952	105	1.7
Na	24112	44676	103	13
P	<MDL	19615	97	7.5
Pb	<MDL	19889	98	4.3
Si	1455	20947	97	8.5
Sn	<MDL	19241	96	3.3
Zn	114	19654	98	0.79

*MDL= Method Detection Limit

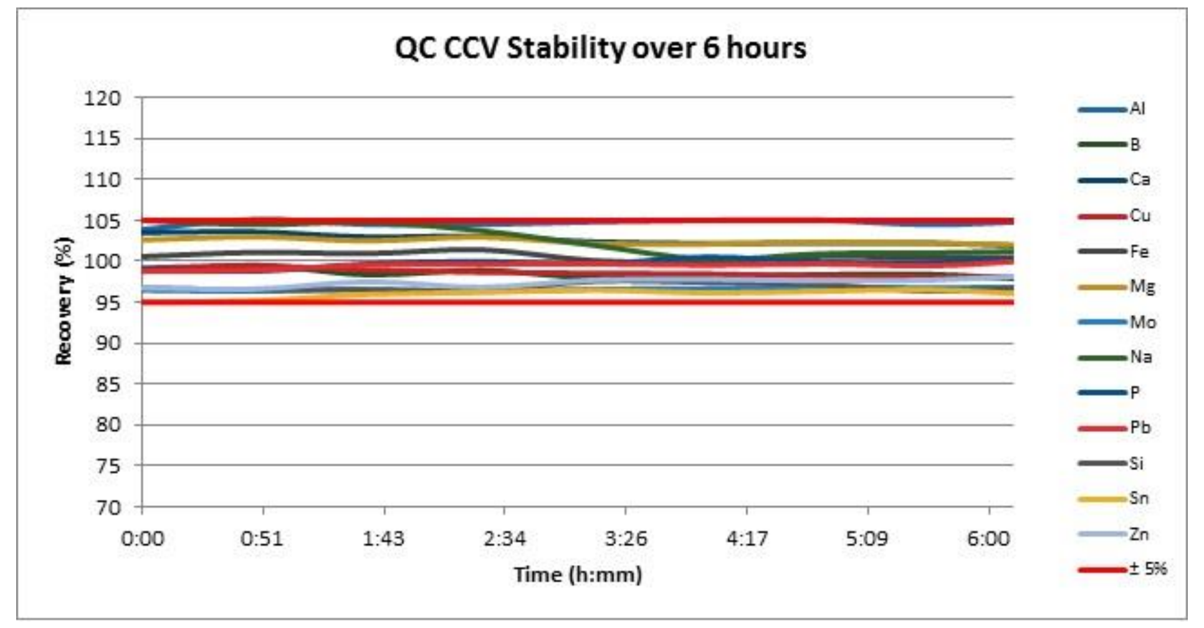

Figure 3. QC CCV Stability Data Over 6 Hours.

CONCLUSIONS

The iCAP 7400 ICP-OES Radial is capable of meeting the requirements of the standard method ASTM D6130-11(2018). The high matrix tolerance of the iCAP 7400 ICP-OES Radial is ideal for such challenging analysis whilst the speed of the instrument means it is capable of high throughput analysis, which is of high importance in industries where time is undeniably a key factor in reducing instrument downtime and costs by effective scheduling of preventative maintenance.

REFERENCES

1. ASTM D6130-11(2018), Standard Test Method for Determination of Silicon and Other Elements in Engine Coolant by Inductively Coupled Plasma-Atomic Emission Spectroscopy, ASTM International, West Conshohocken, PA, 2018, www.astm.org
2. Multi-element analysis of coolant and antifreeze products using the Thermo Scientific iCAP 7000 Plus Series ICP-OES; Application Note 44391; Thermo Fisher Scientific

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