

Advantages of Sophisticated Sample Introduction Accessories for the Trace Element Analysis of Wear Metals in Organic Sample Matrices by ICP-OES

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ABSTRACT

Organic samples require special attention during sample preparation and for introduction into the plasma. Especially the analysis of wear metals in engine coolants and lubricating oils can give inaccurate results if samples are not prepared correctly.

The analysis of wear metals, additives and contaminants in engine fluids such as lubricating oils, hydraulic or coolant liquids provides valuable information to determine the status of the machinery. Wear metal analysis helps to avoid costly damage and extensive down-time of high value engines, generators, gears and other important equipment. Monitoring of specific analytes indicates the health status of the system allowing for preventive maintenance to be appropriately scheduled. Once the engine liquid has been sampled, analysis by ICP-OES is very useful for aiding with maintenance scheduling, basing decisions on the results of analysis. ICP-OES is an ideal technique due to its high temperature source which dissociates any organometallic compounds such as zinc dialkyldithio-phosphates, an additive used as anti-wear in motor oil, and also has the ability to handle difficult organic solvent matrices. This allows the oil or coolant to be directly aspirated into the instrument after a simple dilution, negating the need for any time consuming sample preparation like acid digestion and consequently enabling faster turnaround times.

This poster demonstrates the best practices and advantages of elaborate sample introduction accessories during engine fluid analysis with ICP-OES. Since time is a key factor in preventive maintenance and reducing down-time, a robust and high throughput method is presented in this work.

INTRODUCTION

The analysis of engine fluids is a powerful tool in preventative maintenance of engines and machinery. Regular sampling and trend analysis will give precious information about the state of a motor, gear transmission or mechanical part, and signify the need for maintenance before critical failures. In particular, elemental analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is used to determine the concentration of wear metals, contaminants and additives present in used oils and coolants that can be sampled from car to train fleets, or even large construction or mining machines.

MATERIALS AND METHODS

Analysis of unused and used oil samples

Calibration standards for oil analysis were prepared by diluting multi-element oil based standards in a suitable solvent on weight basis. A base oil was added so that all solutions contained 10% oil. An internal standard was added to the solvent to make up for potential physical interferences. A check standard was prepared from a second source and prepared likewise. Three oil samples with different hours of usage were analyzed.

Instrumentation

The Thermo Scientific™ iCAP™ 7600 ICP-OES Radial was chosen for the analysis. The radial instrument configuration was selected for its high matrix tolerance and reduced matrix interferences. For sample introduction to the instrument, a Teledyne CETAC ASX-7400 Stirring autosampler which ensures good homogeneity of the solutions analyzed, was used. For ultimate throughput, the fast sample introduction valve on the iCAP 7600 ICP-OES was equipped with an organics resistant Sprint Valve.

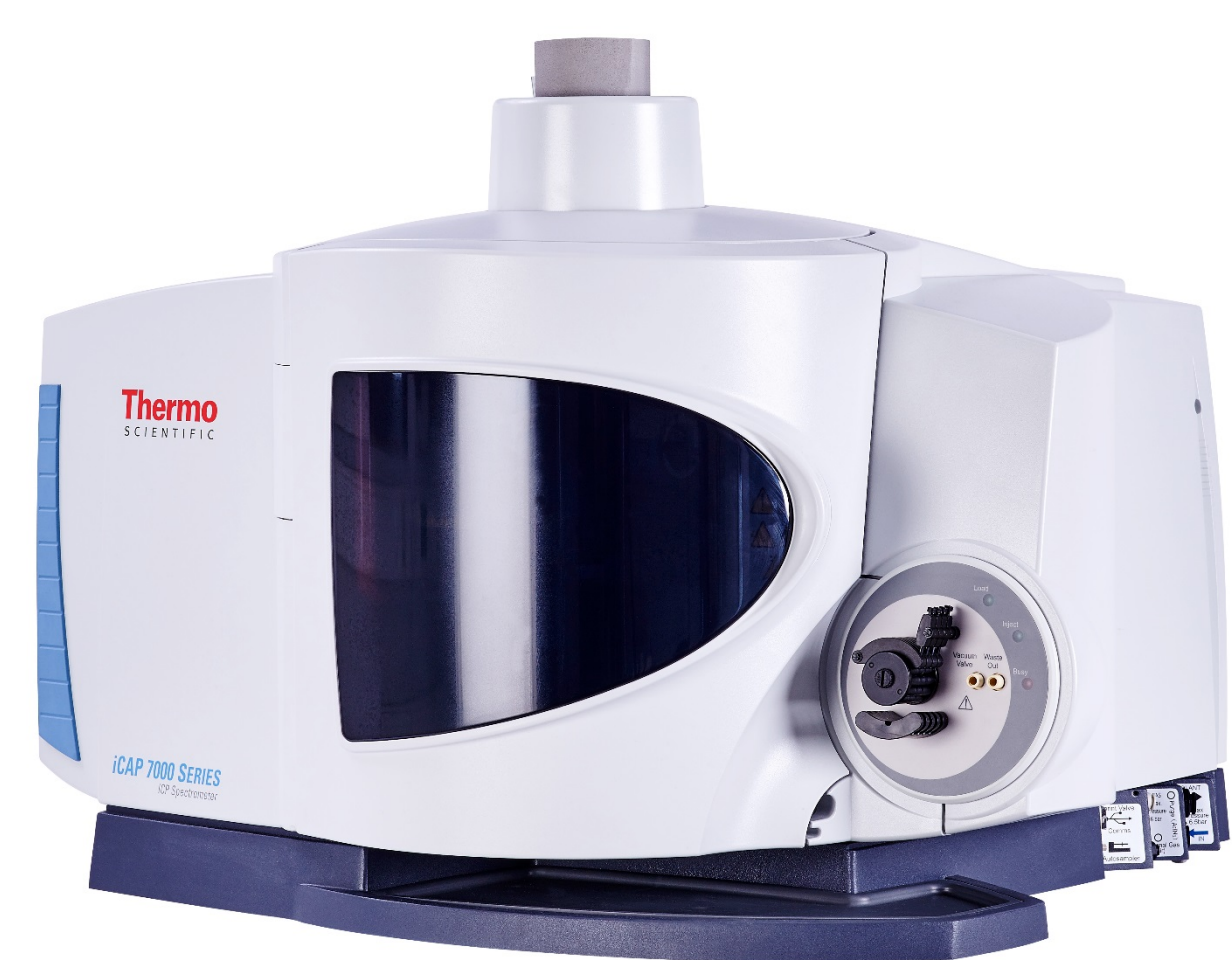


Figure 1. The Thermo Scientific iCAP 7600 ICP-OES.

Table 1. Typical operating parameters for organics analysis with the iCAP 7600 ICP-OES.

Parameter	Value
Pump Tubing	Drain Solvent Flex yellow/blue
	Sample Solvent Flex white/white
Spray Chamber	Baffled cyclonic
Nebulizer	V-groove
Center Tube	1.0 mm
Pump Speed	40 rpm
Nebulizer Gas Flow	0.4 L·min ⁻¹
Auxiliary Gas Flow	1.5 L·min ⁻¹
Coolant Gas Flow	14 L·min ⁻¹
RF Power	1350 W
Radial Viewing Height	12 mm



Figure 2. The Teledyne CETAC ASX-7400 Stirring autosampler.

Using the intuitive wavelength selection tool of the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, wavelengths were selected that were most likely to be free from interferences in this matrix. Methods like the ASTM D5185 also give non-exhaustive lists of suggested wavelengths that can be used as a guideline. Once each of the samples and standards were analyzed the sub-array plots were examined and changes were made to correct for interferences, as necessary. From the results obtained it was found that no mathematical correction factors such as Inter-Element Correction (IEC) were required.

RESULTS

Analysis according to ASTM D5185

The results of the sample analysis can be seen in Table 2. Although the iCAP 7600 ICP-OES Radial is capable of detecting low concentrations, as demonstrated by the results of elements such as aluminium, ASTM D5185 expects detectability in the low mg·kg⁻¹ range for most elements to be sufficient. Focus is on trend analysis and identification of high concentrations of wear metals and additives in the oil/engine under study. The recovery of the check standard was better than ±5% for the analyses performed. As described in the standard method, certified standards should be regularly analyzed to verify accuracy and precision of the instrument calibration.

Table 2. Analysis results of used and unused engine oils.

Element and Wavelength (nm)	New Oil	Intermediate Oil	Old Oil
Ag 338.389 nm	0.76	0.87	0.94
Al 308.215 nm	0.09	0.05	0.05
B 208.959 nm	2.14	1.63	2.46
Ba 223.527 nm	<QL	0.46	0.82
Ca 184.006 nm	1103	2293	3014
Cd 214.438 nm	0.15	0.17	0.27
Cr 267.716 nm	0.12	1.15	2.54
Cu 324.754 nm	0.58	2.03	3.49
Fe 238.204 nm	2.76	23.2	30.8
Mg 279.553 nm	870.8	631.2	323.4
Mn 293.930 nm	0.21	0.63	0.89
Mo 281.615 nm	<QL	0.16	0.38
Na 589.592 nm	5.71	5.2	3.71
Ni 231.604 nm	0.73	0.59	0.48
P 178.284 nm	972.4	1045	984.1
Pb 220.353 nm	16	12.1	8
S 180.731 nm	5731	5776	5134
Si 212.412 nm	7.15	10.3	10.8
Sn 283.999 nm	7.7	4.58	2.53
Ti 334.941 nm	0.4	0.48	0.51
V 309.311 nm	2.2	1.46	0.7
Zn 213.856 nm	1038	1143	1106

*<QL: below quantification limit

Figure 3 shows that as the oil is used in an engine, the elemental composition changes. In this case, the concentration of iron has increased which indicates possible wear of a number of components such as piston rings, ball/roller bearings or gears. The concentration of magnesium decreased with increased usage, possibly indicating that the additive components were consumed or lost from the solution, and the concentration of silicon remained constant which would indicate that the air filter is still intact and preventing dust entering the engine.

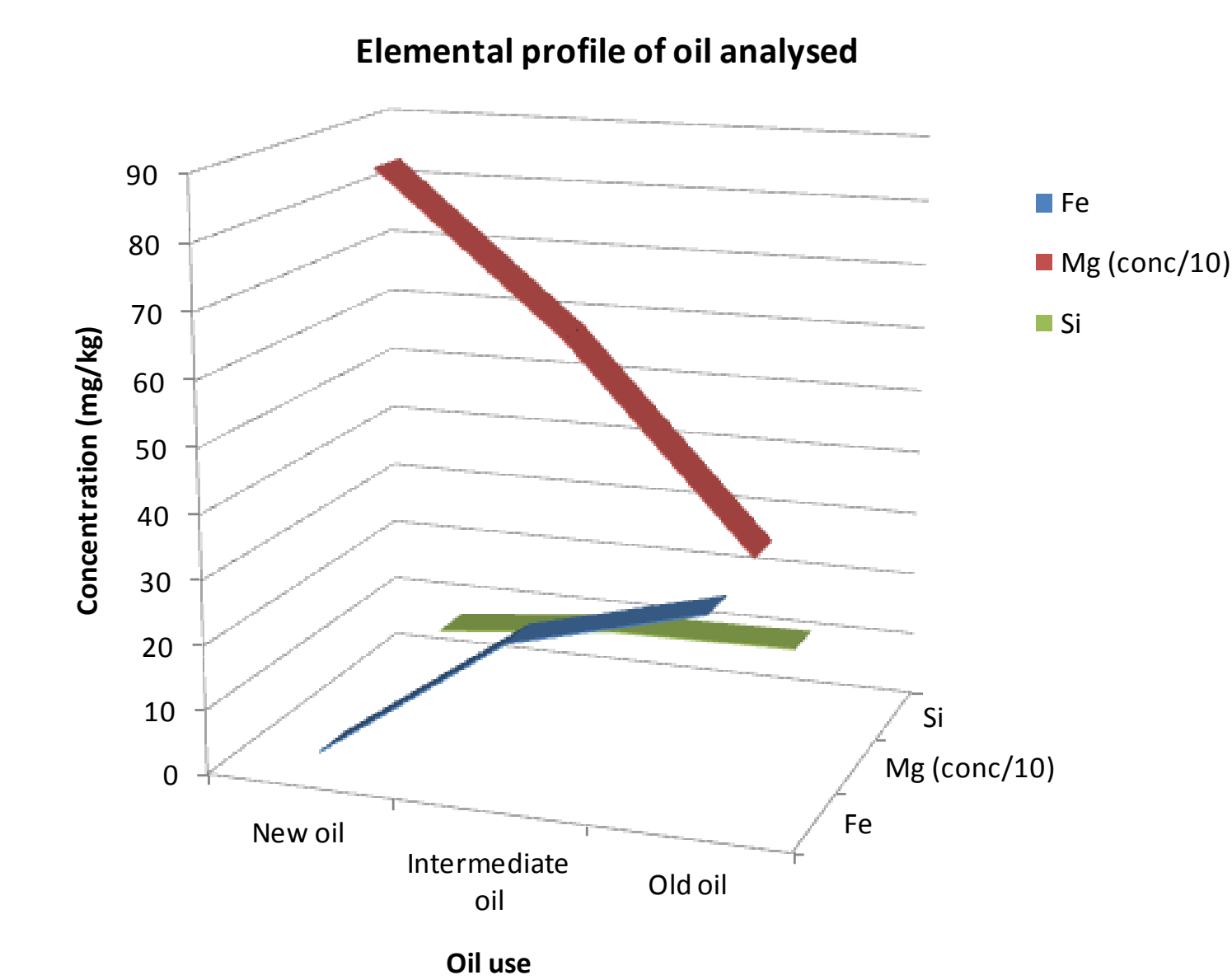


Figure 3. Certain elemental profiles in unused and used engine oils.

Furthermore, to demonstrate the capability of the stirring functionality of an autosampler, the results of the analysis of the stirred samples were compared to the result of a duplicate of that sample that was not stirred. Figure 4 clearly indicates the advantage of stirring oil samples.



Figure 4. Used and unused oil results with and without stirring.

Since stirring of a sample is taking place while the beforehand sample is being analyzed there is no time penalty when using the stirring functionality. However, it is typical for organics analysis to use lower pump speeds to reduce the amount of sample reaching the plasma. Due to the long time for the sample transport the overall analysis time is increased.

Speed lubricating oil analysis

With the standard autosampler setup, lubricating oil analysis by ICP-OES has a typical analysis time of around 3 minutes per sample. When sample numbers increase, even faster turnaround times are required. In this case, a Sprint Valve can help to increase sample throughput by allowing for much faster sample transport.

This section describes how coupling an innovative sample introduction system to powerful instrumentation enables analysis time to be reduced significantly while retaining the analytical requirement of the industry. In turn, this allows rapid decisions to be taken and imminent mechanical failure to be identified.

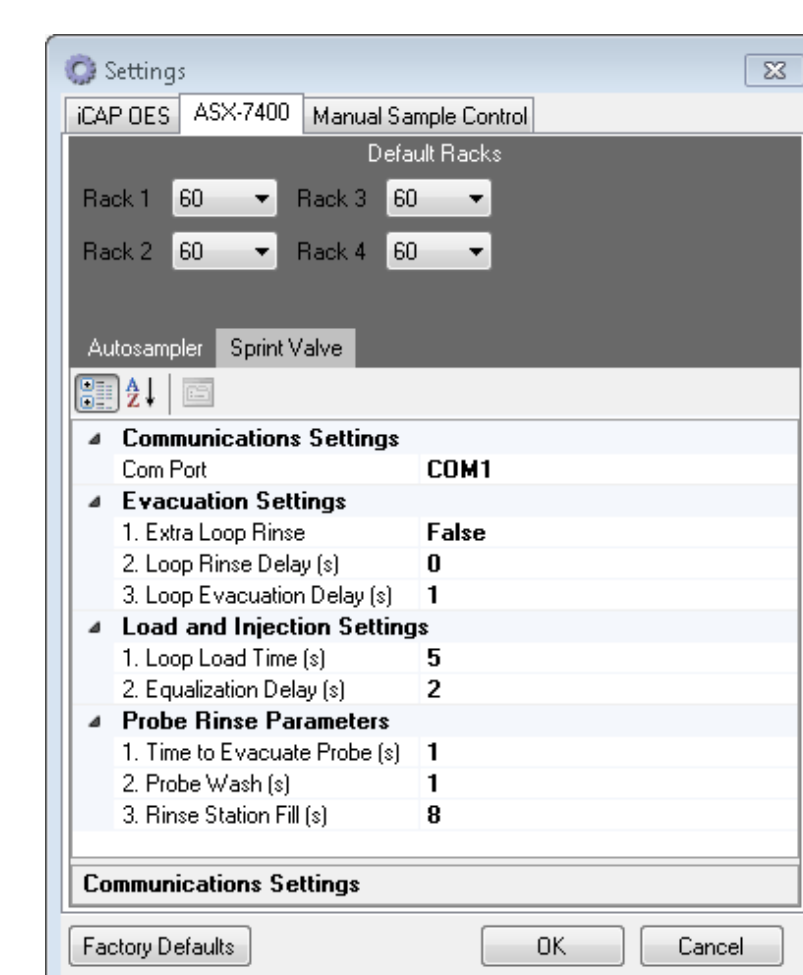


Figure 5. Sprint Valve settings used for speed lubricating oil analysis.

Furthermore, only two repeats were analyzed with an exposure time of only one second. The results are presented in Table 3.

Two typical oil samples (Oil A and Oil B) were analyzed following the Sprint method described previously. The results are shown in Table 3.

They were compared to the concentrations obtained for the same oils analyzed with a traditional Speed method using the instrument peristaltic pump in a conventional way (no Sprint Valve). Speed analysis mode was selected with five seconds integration time and two replicates. Analytical wavelengths were optimized for the method and may be different than defined in the Sprint analysis method.

Table 3. Results (mg·kg⁻¹) obtained for Oil A and Oil B with Sprint and Speed methods.

Element	Oil A		Oil B	
	Sprint	Speed	Sprint	Speed
Ag	< 0.5	< 0.1	< 0.5	< 0.1
Al	2.1	1.9	8.9	9.6
B	< 2	0.8	< 2	1.3
Ba	< 1	0.2	3	3.2
Ca	2740	2830	17330	17750
Cd	< 0.2	< 0.05	< 0.2	< 0.05
Cr	0.9	0.8	0.8	0.7
Cu	1.3	1.6	1.7	1.6
Fe	20.6	20.6	30.6	29.3
Mg	248	246	41	41
Mn	0.6	0.6	5	5.3
Mo	4.3	4.4	1.1	0.8
Na	7	7	87	84
Ni	< 0.5	0.3	67	70
P	1040	1060	360	369
Pb	< 2	1	< 2	< 0.5
S	8180	7670	15010	14030
Si	4.2	4.3	20	18.9
Sn	< 5	< 1	< 5	< 1
Ti	< 1	< 0.2	1.5	0.6
V	< 1	< 0.2	62	66
Zn	1220	1240	419	419

Comparison within the two methods was found to be good with relative standard deviation (RSD) below 5% for elements present at significant concentrations in Oil A and Oil B. Although detection limits for the Speed method are estimated to be five times lower than for the Sprint method, this is below the industry requirement which is typically around the single ppm level. The Sprint analysis was noticeably faster with 27 seconds analysis time per sample compared to approximately three times longer for samples analyzed with the Speed method.

COOLANT ANALYSIS

The same autosampler that is used for stirring oil samples can easily be configured to allow for stirring of aqueous samples. The double rinse station has two positions that can be changed by a screw in the front, therefore easy switching from organic analysis (oils, green light) to aqueous analysis (coolant, blue light) is possible.

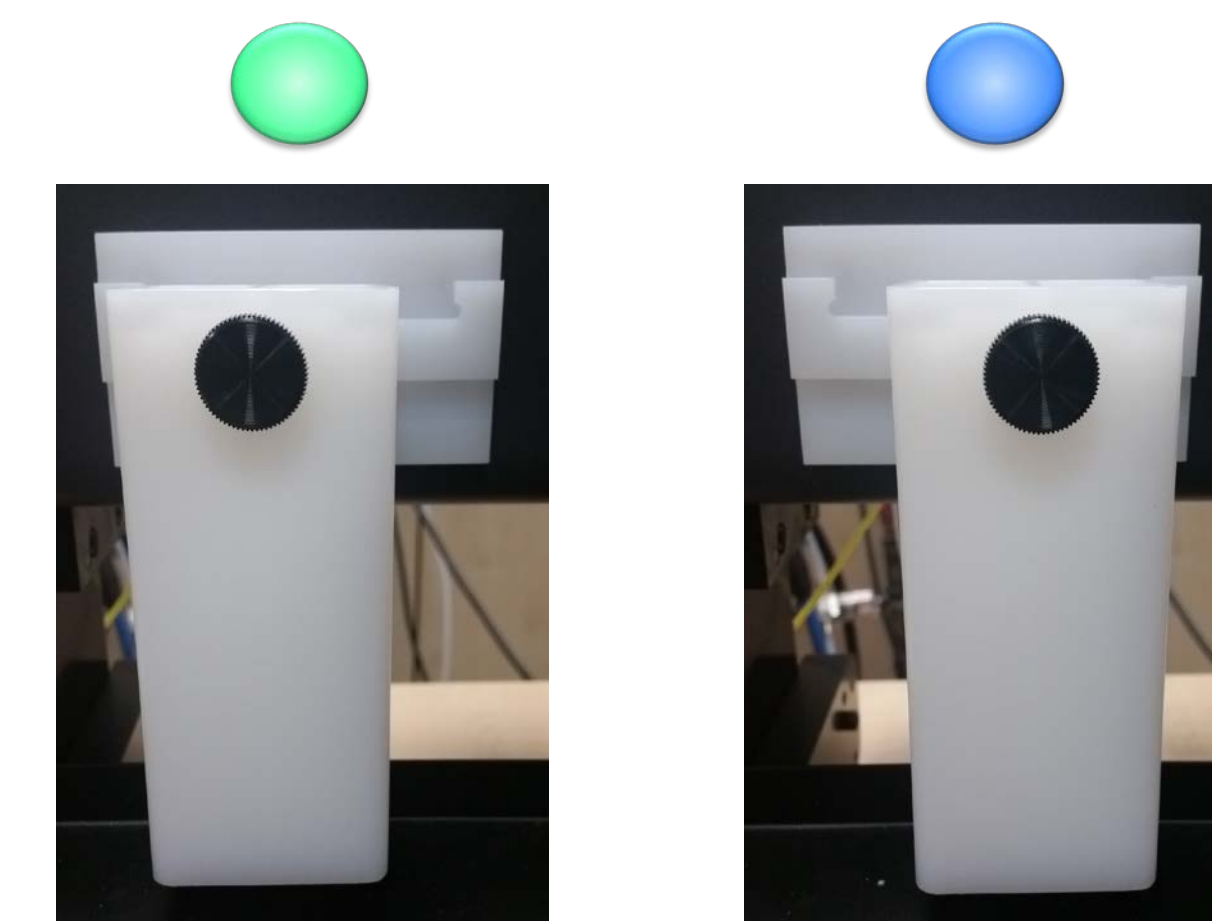


Figure 6. The two positions for the double rinse station: organics (left) and coolants (right).

CONCLUSION

Using the Thermo Scientific iCAP 7600 ICP-OES Radial in conjunction with an ASX-7400 Stirring autosampler delivers accurate and high throughput analysis of engine fluids. This allows for preventive maintenance to be scheduled on time and helps avoiding massive down-time of machinery. Easy swapping of a rinse station of the autosampler allows for quick switching between sample types, improving productivity in high volume laboratory environments.

TRADEMARKS

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