

ICP-OES

APPLICATION NOTES

The analysis of wear metals in lubricating oils by ICP-OES



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Introduction

The analysis of engine oil for the early detection of machine component failure has been an important area of investigation since first applied by railroad companies in the 1940s¹. An increase in the metal content of sump oil and circulated lubricating oils signifies a source of potential trouble in an engine.

The metal found may indicate the location of the problem. The presence of lead or tin for example, may be caused by wear in a bearing. The presence of chromium, aluminium or nickel could be due to piston or ring wear.

Copper is indicative of coolant leaking into the lubrication system via cracks or leaking seals. Silicon present in the oil suggests dirt or sand intrusion indicating that the air cleaner may need to be cleaned or changed. Phosphorus is another important element that requires monitoring. Phosphorus can occur in oil either naturally or be introduced by contamination. Phosphorus poisons platinum catalysts found in modern catalytic converters and is also used as a gasoline additive.

Sulphur is found in compounds in most crude oils in varying concentrations. It is associated with unpleasant odours, corrosion, and air pollution and inhibition of antiknock effectiveness in gasoline. Sulphur compounds are also added as oxidation inhibitors in lubricating oils and as corrosion inhibitors in gear lubricants. Periodical analysis of the lubricants enables such troubles to be located and corrected before they cause a major breakdown.

Some of the above mentioned elements have until recent times been analysed by flame Atomic Absorption Spectrometry (AAS) or graphite furnace AAS. However, the advent of low priced Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) systems has resulted in ICP-OES becoming the technique of choice for the determination of wear metals in oils²⁻³.

Offering the higher productivity of a multi-element technique, ICP-OES also offers better sensitivity for the refractory elements and non-metals such as phosphorus, sulphur and boron. Further, the wider dynamic range ensures greater laboratory productivity with the requirement for sample dilutions being much less frequent compared to flame AAS.

This paper describes the parameters and conditions required for the determination of various elements in engine oil.

Experimental

Instrument operating parameters

As GBC ICP-OES Spectrometer provides computer control of over 200 instrument parameters, operating parameters optimized for the individual elements can readily be determined and stored in method files to be recalled at any time for analysis. GBC ICP-OES Spectrometer's unique and sophisticated auto-optimization software can be used to optimize the operating parameters according to user specified optimization criteria driven by the application.

In this application, the instrument was optimized for maximum performance on the heavy metals. These parameters were:

Viewing Height Individually Optimized	3–20 mm
Power	1300 w
Nebulizer Flow Optimized for Pb	0.4 L/min (160 kPa)
Plasma Gas Flow	12 L/min
Auxiliary Gas Flow	1.0 L/min
Total Gas Flow	13.4 L/min
Sample Uptake Rate	8 rpm (1.0 mL/min)
PMT Voltage	Individually optimized from 340–600 V depending on concentration level

Measurement conditions for detection limit measurement:

Integration Time On Peak	10 s
Replicates	11
Background Correction	Fixed Point

Measurement conditions for sample analysis measurement:

Integration Time On Peak	2 s
Replicates	3
Background Correction	Dynamic
Scan Windows	0.08 nm 1st Order 0.04 nm 2nd Order 0.027 nm 3rd Order 0.02 nm 4th Order
Data Points	50
Integration Time per Data Point	0.1 s

Table 1: Instrument operating parameters used

Sample preparation

In order to ensure consistent viscosity, and therefore consistent nebulization, the total oil content in samples, standards and blank should be constant. Therefore, a neutral base oil was used for the blank which was then made up to volume with kerosene.

Samples were prepared by performing 1 in 10 dilutions with kerosene. This dilution ratio ensures that both standards and samples have similar viscosity, which may not be possible if the crude oil is not diluted. If this dilution ratio results in too high a dilution of elements presents in low concentrations, then perform a 1 in 5 dilution. Whilst dilution ratios as low as 1 to 1 are also possible, there can be a risk that samples and standards are not matrix matched. If the levels of the analytes in the used oil are sufficiently low to require a 1 in 1 dilution, then standard additions or spike recovery is the preferred calibration and analysis.

Standard preparation

Conostan⁴ organometallic standards prepared from alkylarylsulphonates in a base oil are available as individual concentrates or multi-element blends. Conostan standards are extremely stable and easy to handle and are soluble in ketones, paraffinic and aromatic hydrocarbons.

A 10 ppm multi-element standard can be prepared using the procedure:

Into a 50 mL volumetric flask accurately weigh:

1. 5 g of a 100 ppm by weight Conostan S-21 multi-element organometallic standard.
2. 0.05 g of a 10,000 ppm by weight Merck sulphur organometallic standard.
3. 5 g of a 100 ppm by weight Conostan As organometallic standard.
4. 5 g of a 100 ppm by weight Conostan Hg organometallic standard.
5. Make up to volume with kerosene.

Some practical hints for the handling of thick oils and low viscosity volatile organic solvents for ICP-OES analysis are given below.

1. The standards should be made in accordance with the manufacturers instructions⁴.
2. Wear metals are typically present in oil as metallic particles rather than dissolved. The particle size and concentration of individual wear metals in oil differ from one element to another and depend on the engine type, the age of the oil and the efficiency of the oil filter. Normally most wear metal particles are less than 1 nm. Oil samples and standards will settle with time. Agitating the sample oil in an ultrasonic bath for five minutes prior to or during sampling is a convenient way of overcoming this problem.
3. The standards can be prepared on a weight per weight, weight per volume or volume per volume basis in the chosen organic solvent. It is therefore necessary to quote the method and solvent used as the concentration units are not equivalent. Conversion to other concentration units can be easily determined if the density of the diluting organic solvent is known.
4. Sample volume measurements require long pipette fill and then very long pipette drain times. If the oil is viscous this time can be significantly increased. The operator must also be able to reproducibly drain the pipette for the same time for each sample so that the same volume has been pipetted. Weighing the sample is therefore recommended as it offers increased convenience in terms of speed and reproducibility.
5. Samples and standards should be stored at low temperatures to guard against the evaporation of volatile solvents. Dilutions of the concentrated standards should be made fresh daily, prior to the analysis. Low concentration standards (less than 1 mg/L) may deteriorate over a period of days.
6. Contamination and toxicity are always problems in oil analyses. Volatile solvents should be handled in a fume cupboard and gloves should be worn.
7. The physical nature of the standards and the samples must be matched. This is achieved by adding the required amount of blank oil to the standards.
8. The blank made up from the unused oil should be used as the calibration blank.
9. For organic analysis, the yellow solvent flex peristaltic tubing is used. The black-black tubing is used for pumping the sample to the nebulizer, the red-red tubing is used for the sample drain.
10. Whilst GBC ICP-OES Spectrometer's standard sample introduction is capable of directly aspirating both aqueous and organic (oil) samples, it is highly recommended that two sets of sample introduction components, one set dedicated to each sample matrix, is used to ensure no cross-contamination.

Results and discussion

Table 1 displays the wavelengths selected and their corresponding measured detection limit. The detection limit reported is based on 3 standard deviations of the blank using 11 replicates of 10 s integrations.

Element I–Atomic Line II–Ionic Line	Wavelength (nm)	Detection Limit (ppb)
Ag I	328.068	2.0
Al I	167.081	2.0
As I	188.979	10.0
B I	249.773	2.0
Ba II	455.403	0.1
Ca II	317.933	2.0
Cd II	214.438	0.8
Cr II	283.563	2.0
Cu I	324.754	2.0
Fe I	259.940	1.5
Hg I	184.950	8.0
Mg I	279.553	0.1
Mn II	257.610	0.3
Mo II	202.030	5.0
Na I	588.995	10.0
Ni II	231.064	3.0
P I	177.495	8.0
Pb II	220.353	10.0
S I	180.731	15.0
Si I	251.612	2.0
Sn II	189.926	10.0
Ti II	334.941	1.5
V II	309.311	3.0
Zn I	213.856	1.0

Table 2: Analytical wavelength and detection limits

Spectral interferences from molecular band emission rarely occur with aqueous solutions.

With organic solvents, however, molecular bands are observed in the wavelength region above 330 nm⁵. These are CN (violet)³ C2 (Swan) ≥ CS ≥ OH ≥ NO ≥ CH ≥ NH ≥ CCl arranged in order of decreasing sensitivity.

These can cause structured background which can be eliminated through breaking of the molecular bonds at higher powers.

Conclusion

The GBC ICP-OES Spectrometer offers unique capabilities in the analysis of engine oils over conventional AA techniques. The advantages of using the GBC ICP-OES Spectrometer over flame or furnace AA include:

High sensitivity for all elements including the capability of measuring the rare earths, refractory elements, the non-metals (P & S) and other transition metals down to low $\mu\text{g/g}$ levels.

Wide dynamic range which allows the determination of both low ($\mu\text{g/g}$) and high (%wt) concentrations in the same solution, avoiding the need for time-consuming dilutions.

Computer Control of All Operating Parameters which allows fully automated instrument optimization and setup so that even first time ICP users can maximize the performance and productivity of their ICP-OES.

Mass flow control of the most critical parameter, gas flow through the nebulizer, which allows the highest possible analytical precision as well as immediate diagnosis of nebulizer blockages caused by metal particulates in the oil.

Speed of Analysis offered by the multi-element nature of the ICP, with the determination of 12 elements in a sample taking typically less than three minutes.

Low cost operation with the economies of a low argon flow torch (typically less than 13 L/min) and low power plasma (typically 1300 w).

This method is ideal for the routine monitoring of wear metals for oil lubricated engines or equipment down to trace levels, providing rapid early warning of possible component failure.

References

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