AN APPLICATION BRIEF FROM
SPECTRO ANALYTICAL INSTRUMENTS

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When results matter

Cost-Effective Analysis of Wear Metals and Additives in Oil Using an ICP-OES

Introduction

The elemental analysis of used lubricating oil has become an essential part of *condition monitoring* — the use of physical and chemical techniques to assess the ongoing condition of machinery and equipment. Lubricating oil analysis can be applied to most mechanical systems, including engines, gear transmissions, and hydraulics. These are important components of critical, often high-value equipment in areas such as power generation, petrochemical and other industrial processes, construction machinery, and transportation (including aviation, fleet operations, and public transport).

Responsible personnel in all these areas as well as in contract service laboratories must analyze hundreds of oil samples per day for a wide range of elements. Aims: to find component wear by detecting the presence of foreign matter that may accelerate such wear, or detecting higher-than-normal concentrations of certain elements that may indicate it; and to analyze diminishing levels of any additives present for further help in determining the “health” of the oil. Such systematic analyses of lubricating oils in service can predict and enable correction of developing faults. This “early warning” allows for fewer costly repairs, more effective maintenance programs, reduced downtimes, and extended plant and equipment lifetimes — all of which can significantly lower operating expenses.

A number of spectrometric techniques have been employed to carry out these analyses. This paper will briefly consider flame AAS, sequential OES, and rotrode analyzers, before focusing on the benefits of simultaneous ICP-OES technology.

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FAAS and other alternatives

For most elements, the concentrations involved are well within the scope of spectroscopic elemental analysis techniques such as *flame atomic absorption spectrometry (FAAS;* also known simply as *AAS)*. However, although FAAS instruments have been a popular oil analysis method for many years, they suffer significant drawbacks.

Flame AAS, which incorporates a hollow cathode tube, for years has been the hot choice in wear element analysis. But the increasing affordability of advanced, high-productivity ICP-OES casts a brighter light on AAS disadvantages.

Flame AAS atomizes sample constituents using acetylene as fuel and either air or nitrous oxide as an oxidant to reach the high flame temperatures required for determination of elements such as silicon and aluminum. AAS cannot measure sulfur content at all, and in determining phosphorus, its limits of detection are three orders of magnitude higher than those of another popular oil analysis technology known as ICP-OES (see below). Additionally, AAS possesses a relatively narrow linear dynamic range, so it has difficultly coping with wide concentration ranges, and often requires multiple sample dilutions. Further, because they depend on flames and pressurized flammable gases, AAS instruments cannot safely run unattended.

Finally, AAS instruments must normally measure each element in turn, instead of *simultaneously* (as with many ICP-OES devices). When faced with samples containing more than a few elements, this sequential examination demands relatively long analysis times — one of the major disadvantages of AAS technology.

Other approaches sometimes applied in oil evaluation also suffer from prolonged analyses. For example, some ICP-OES devices use sequential, not simultaneous, technology. And *rotrode* instruments demand manual operation, contributing to their long analysis times and comparatively low throughput. In addition, they suffer from relatively low sensitivity and stability (compared to ICP-OES systems).

The ICP-OES solution

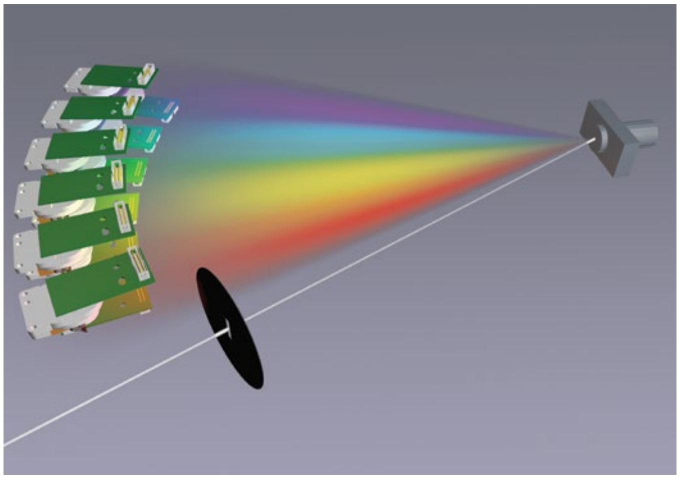
Where AAS techniques have proven unsatisfactory, several national and international standard methods describe or recommend the use of *inductively coupled plasma optical emission spectrometry (ICP-OES)* for the analysis of fuels and lubricating oils. (See ASTM methods D4951, D5708, D5185, D7111, D7260, D7691, D5184, D7040, and D7303, as well as EN 14538 and 16924.)

Thus ICP-OES has become the technique of choice for many users. Example: the SPECTRO GENESIS simultaneous ICP-OES — an affordable, compact, but high-throughput instrument specifically developed for such routine analysis. Its advanced detector technology and remarkably low running costs provide a powerful and efficient tool. Also advantageous: its sample preparation usually requires only a single, simple dilution with a solvent such as kerosene. It uses proprietary software for continuous optical system monitoring plus optimum ease of use. And the instrument is available with a complete set of factory methods plus step-by-step standard operating procedures (SOPs) for used oil analysis, as well as an automated front-end sample introduction system. So users can move straight into "plug & analyze" performance without time-consuming method development.

The challenge: condition analysis

In lubricated mechanisms, various causes of wear (such as friction between moving surfaces; abrasion by contaminants such as grit; corrosion processes; or entry of foreign matter, as by failing seals) give rise to the presence of microscopic particles in the lubricant as components wear away.

Quantitative measurement of elements present in the oil can therefore be a useful indicator of wear. Furthermore, as different materials are used to manufacture different components, elemental analysis can often provide a clue as to which components are subject to wear. Condition monitoring can also detect the presence and possibly the origin of foreign matter in the oil, such as dust that may have entered an engine via a defective filter. Additionally, it may signal undesirable changes such as dilution by fuels or contamination by water or antifreeze. Processes such as oxidation can lead to changes in lubricant properties like viscosity, leading to accelerated wear rates. And levels of additives introduced to extend lubricant life must be monitored, lest additive depletion lead to increased wear.



Advanced ICP-OES optics: the ORCA system in a SPECTRO GENESIS analyzer separates light emitted in the plasma, and enables full simultaneous measurement of the relevant spectrum and elements.

Unless wear is severe, metallic particles entering the lubricant are usually very finely divided (5 microns or less) and remain largely suspended in the oil without settling out. Typical concentration levels for wear metals lie in the range from 1 to 500 parts per million (ppm); some additive elements can be found at several thousand ppm.

Key ICP-OES components

In the basic ICP-OES technique, elements and ions emit a characteristic number of specific spectral lines with different wavelengths when excited within a high-temperature argon plasma. Emitted light is resolved into these separate lines by optical components such as diffraction gratings; the light is finally directed onto a detector array that quantifies light intensities at these different wavelengths. Thus differing elemental components of a sample can be measured, analyzed, and quantified.

Powerful generator. Some ICP-OES systems suffer from plasma instability when attempting to analyze challenging organic matrix samples. In extreme cases, the plasma may even be extinguished. Fortunately, the SPECTRO GENESIS analyzer produces its plasma via an air-cooled, free-running RF generator that remains stable even under such heavy plasma loads.

Simple sample introduction system. For ICP-OES oil analysis, a single dilution of the sample with kerosene is normally sufficient to overcome viscosity effects and measure all elemental concentrations. (By contrast, AAS often requires several dilutions to bring different elements within the linear measurement range.) The design of the GENESIS sample introduction system provides a very short sample pathway to the plasma, so signals stabilize quickly and very short flush times are achieved between samples. GENESIS can be integrated with an autosampler/dilutor system under full computer control. When dealing with only a few elements per sample, some AAS instruments may exhibit slightly faster analysis. However, if an instrument must routinely analyze moe than 50 samples and 10 elements per day, a heavy-duty, simultaneous ICP-OES such as SPECTRO GENESIS can definitely deliver higher throughput rates, and will usually be the better choice.

Advanced optics and detectors. SPECTRO GENESIS utilizes a series of 15 charge coupled device (CCD) linear detector arrays with a concave grating arrangement. This fast, flexible, proprietary Optimized Rowland Circle Arrangement (ORCA) design covers the entire relevant spectrum from 175 to 770 nanometers (nm). The system's high-speed readout system can read all 15 CCD detectors and provide the complete emission spectrum in only 3 seconds. Finally, with a minimum number of optical components to attenuate light throughput, ORCA is highly luminescent; this contributes to analytical sensitivity plus low detection limits.

Resisting interference

Sample nebulization and transport effects. A simple sample introduction system such as the one mentioned above uses a pumped nebulizer/spray chamber design. The nebulizer converts the liquid sample into an aerosol spray, which is then transported (via a carrier gas, usually argon) into the plasma. Where variations in sample viscosity might impair accurate measurement, instruments such as SPECTRO GENESIS employ the *internal standard* technique — adding a known concentration of an element not found in the sample. Any variations due to sample introduction efficiency are reflected in the values obtained for the internal standard, and are used to automatically correct the measurements.

Matrix effects. Organic matrix samples can significantly impact plasma excitation efficiency. The ability of an ICP-OES system to cope with variations in sample type and plasma loading is described as *robustness*. SPECTRO GENESIS exhibits a high degree of this quality, with relative resilience to changes in the solvent or the matrix composition. Should matrix effects still remain, they are efficiently handled by the internal standard technique.

Plasma viewing. The choice of plasma viewing position — end-on, or *axial*, versus side-on, or *radial* — can significantly impact a spectrometer design's suitability for a given application. Axial viewing delivers higher sensitivity, but at the cost of increased complexity and more matrix effects. Instead, instruments such as SPECTRO GENESIS are equipped with a radial interface, seeing only a “slice” across the plasma from side to side. Providing sufficient sensitivity with less background radiation and noise, better stability and precision, no significant matrix interferences, and greater linear dynamic range, this is the clear choice for wear metal applications.

Table 1

Limits of Detection		
	λ [nm]	LOD (3σ) [µg/kg]
Ag	328.068	3.3
Al	308.215	25
B	249.773	3.0
Ba	455.404	0.5
Ca	315.887	7
Ca	317.933	5
Ca	393.366	0.3
Cd	214.438	2.1
Cd	226.502	2.2
Cr	283.563	2.9
Cu	324.778	2.4
Fe	259.940	4.2
Mg	279.079	28
Mg	280.270	0.3
Mn	257.610	0.4
Mo	202.095	6.3
Na	588.995	22
Ni	221.648	7
P	177.495	29
Pb	220.351	28
S	180.731	39
Si	251.612	9
Sn	189.991	17
Ti	323.452	1.9
V	311.071	3.6
Zn	213.856	3.1

Measurable results

The GENESIS achievable limits of detection (LODs) given below were obtained using organometallic standards relevant to real-world wear metal analysis. They were made up to constant volume with base oil, then diluted with kerosene (Table 1).

While these LODs show that SPECTRO GENESIS has more than enough sensitivity to detect and measure the required elements in used oil, measurement precision and accuracy are equally, if not more, important. Table 2 shows the certified and measured values obtained on a certified reference material, NIST Standard Reference Material 1084a “Wear Metals in Lubricating Oil”:

Table 2

Analysis of NIST SRM 1084a			
	Certified Conc. [mg/kg]	Measured Conc. [mg/kg]	Recovery [%]
Al	(104)	102	98.1
Ag	101.4 ± 1.5	100.5	99.1
Cr	98.3 ± 0.8	101.1	102.8
Cu	100 ± 1.9	103.8	103.8
Fe	98.9 ± 1.4	106.5	107.7
Mg	99.5 ± 1.7	97.7	98.1
Mo	100.3 ± 1.4	103.3	103
Ni	99.7 ± 1.6	105.7	106
Pb	101.1 ± 1.3	103	101.9
Sn	97.2 ± 2.6	100.7	103.6
Ti	100.4 ± 3.8	104.3	103.9
V	95.9 ± 9.4	102.4	106.8
S	(1700)	1570	92.4
Si	(103)	106.9	103.8

Excellent agreement is found between certified and measured values. Results for some elements not in this certified standard, but encountered in oil additives, were obtained on a commercially available standard material — Fluxana (Table 3).

Table 3

Analysis of FLX ASTMP-0116-01			
	Certified Conc. [mg/kg]	Measured Conc. [mg/kg]	Recovery [%]
Ca	5020	5390	107.3
P	10420	10530	101.1
S	5030	4830	96.0
Zn	5010	5300	105.8

Conclusion

Simultaneous ICP-OES has many advantages for the analysis of used oils and other petroleum products. In particular, the SPECTRO GENESIS spectrometer is optimized to eliminate most of the difficulties associated with using a new technique or instrument. It is simple to commission and operate, delivers good precision and throughput, and is a cost-effective tool for elemental analysis in wear metal condition monitoring.

Fig 1: SPECTRO GENESIS analyzer. Providing accurate, high-productivity assessment of component wear trends — along with low operating and consumables costs plus an optional automated sample introduction system.

For more information, see the SPECTRO white paper "Why Flame AAS Users Are Moving Up to ICP-OES."

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