

High-throughput/high-performance wear metal analysis using ICP

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Used oil-based materials, such as engine oils, transmission oils, and other lubrication oils, are regularly monitored for the presence of particles deposited from the components that they are designed to protect. These particles gradually build up in the oil because of the normal wear of the component. For this reason, the analysis of used oils is often referred to as wear metals or trend analysis. This technique can be used to accurately identify and predict compo-

not supply the necessary throughput.

However, complicating a laboratory's ability to obtain high levels of sample throughput is the need to determine some elements at low concentration. For example, both Sn and Pb are usually present in oils at the single ppm level. In addition, both of these elements exhibit low sensitivity in the ICP, requiring longer integration times to achieve the desired levels of precision and detectability. Thus, these elements become the limiting factor when de-

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nent failure, based on the composition of the metals and the speed at which they accumulate over time (Table 1). In addition, lubricating fluids should also be monitored for external contaminants (metals from sources such as dust and dirt) that should not be present for any reason.

Because of the importance of wear metal analysis and the number of pieces of equipment in operation, many high-productivity wear metal laboratories (including geological, agricultural, food, and environmental laboratories) are required to analyze hundreds of samples a day. If the element suite is large enough, then the only inductively coupled plasma (ICP) capable of handling the sample load for these laboratories is a fixed-channel simultaneous system, since sequential designs can-

termining the appropriate integration time, in turn adversely affecting the overall sample throughput. Consequently, most ICPs perform

Table 1
Potential problems discovered by wear metal analysis

Wear metal	Source	Potential effect
Cr, Fe, Mo	Broken or stuck piston rings	Ring, liner wear
Al, Cr, Fe, Si	Dirt ingestion, poor air filtration	Piston, ring, or liner wear
Al, Fe, Pb, Si	Dirt in lower engine	Crankshaft bearing wear
Al, Cu, Fe	Oil degradation or contamination	Piston, ring, and liner wear
Al, Cr, Fe	Abnormal operating temp., oil degradation	Crankshaft bearing wear
Al, Pb	Oil degradation or contamination	Bear damage, piston, ring liner wear

Table 2
Analytical wavelengths, background points, and detector gains

Element	Wavelength	Background	PMT gain
1 Ag	328.068	328.042	2
2 Al	308.215	308.190	2
3 B	249.678	249.658	1
4 Ba	455.403	455.367	1
5 Be	234.861	234.888	1
6 Bi	223.061	223.043	3
7 Ca	317.933	317.908	1
8 Cd	214.438	214.421	2
9 Cr	267.716	267.695	2
10 Cu	324.754	324.791	2
11 Fe	259.940	259.919	2
12 K	766.490	766.429	3
13 Mg	279.079	279.111	1
14 Mn	403.076	403.122	2
15 Mo	277.540	277.518	2
16 Na	589.592	589.545	3
17 P	213.618	213.643	3
18 Pb	220.353	220.335	3
19 Si	251.611	215.591	2
20 Sn	189.926	189.911	3
21 Ti	334.941	334.980	2
22 V	310.230	310.205	2
23 Y	371.030	—	2
24 Zn	206.200	206.224	1

an analysis on a wear metal sample in approx. 1 min, translating into about 480 analyses in an 8-hr shift. Contained in this number are also the calibration and periodic check standard measurements, further reducing the overall throughput.

This paper will demonstrate the effectiveness of a the multichannel Profile ICP system (Leeman Labs, Hudson, NH) in supplying high-throughput wear metal analysis at under 30 sec per analysis.

Instrument and method

The Profile high-throughput/

high-performance (HT/HP) ICP with multichannel option was used for all the analyses. The system was equipped with 23 analytical channels to cover all the ele-

ments of interest. In addition, the gain of each channel is set independently to allow the greatest versatility in concentration range. This, combined with the high dy-

namic range of the individual detectors, eliminates the need for a preburn measurement to determine which elements are present at high concentration. The analytical wavelengths, background correction points, and gain settings are listed in *Table 2*.

To obtain the highest possible sensitivity, the instrument was configured for the axial viewing mode. In addition, a high-sensitivity sample introduction system consisting of a cyclonic spray chamber and V-groove nebulizer was used. This combination allows the use of short integration time: The on-

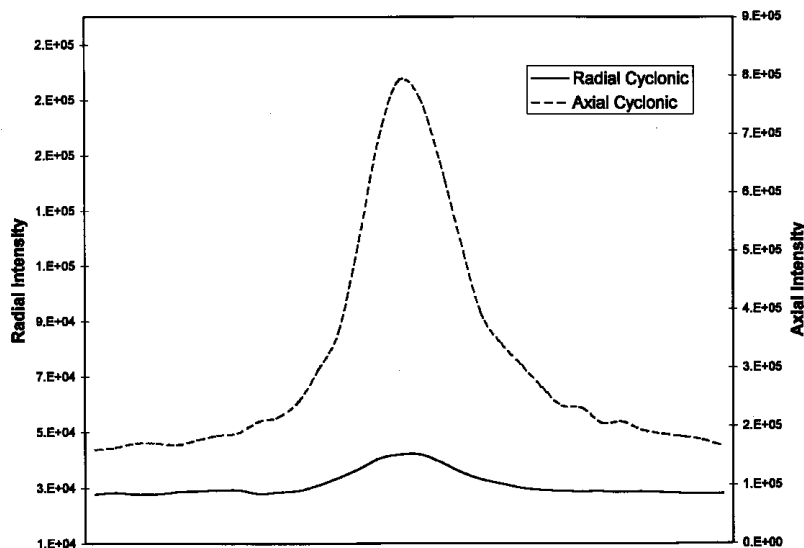


Figure 1 Radial and axial sensitivity comparison with 2 ppm Sn.

Table 3

Analysis conditions	
RF power	1.2 kW
Coolant flow	20 lpm
Auxiliary flow	1.2 lpm
Nebulizer pressure	50 psi
Pump rate	0.50 mL/min

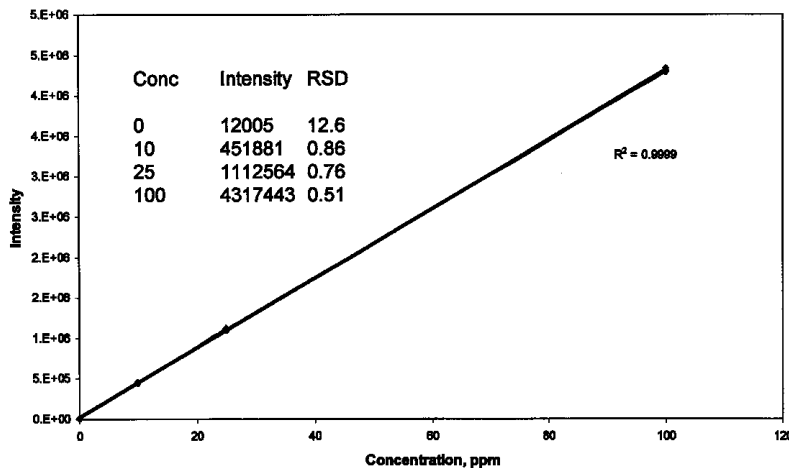


Figure 2 *Pb* calibration plot.

peak measurement times for all elements were 1 sec with 0.5 sec background correction times. The plasma was operated under the conditions listed in *Table 3*.

Calibration standards were pre-

pared from multielement stock solutions and base oil (Conostan S-21 and Conostan 75 base oil, **Conostan**, Ponca City, OK). The oil samples in this study were diluted 5× with kerosene. All con-

centration data refer to the undiluted sample. Oil samples and verification check standards were obtained from an independent wear metals laboratory.

Results and discussion

Axial viewing

The first step in achieving an HT/HP wear metal analysis system is to switch the traditional viewing orientation from radial to axial. By doing this, the sensitivity will be improved by a factor of 5–20, depending on the element. *Figure 1* illustrates the sensitivity enhancement of 2 ppm obtained by switching to the axial mode.

Axially viewed plasmas have been most commonly used with aqueous samples because of the difficulty many ICP designs have sustaining the plasma with organic samples. The multichannel HT/HP ICP uses a water-cooled free-

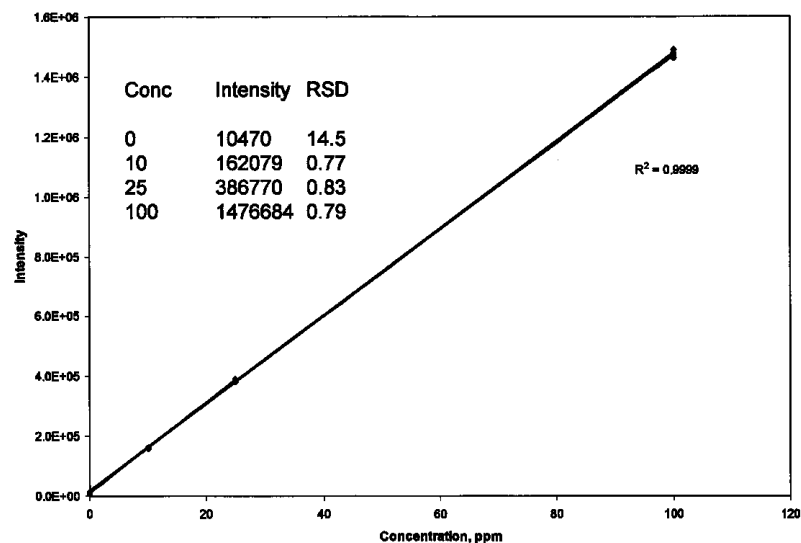


Figure 3 Sn calibration plot.

Table 4

Verification sample 1	Verification sample analysis result*								
	Cu	Fe	Cr	Al	Pb	Si	Na	Mo	Sn
Oil lab	295	16	6	16	27	185	120	11	—
Certified value	310	17	6	17	27	198	133	12	—
HT/HP	307	17	6	17	28	199	119	12	5
RSD	0.8	0.05	0.5	0.5	0.04	0.5	0.4	0.8	1.0
Verification sample 2									
Oil lab	7	219	3	9	1	100	20	13	—
Certified value	7	219	3	9	1	88	19	13	—
HT/HP	8	223	3	9	1	92	19	13	3
RSD	0.9	1.0	0.5	1.4	4.8	0.7	0.6	0.4	2.6
Verification sample 3									
Oil lab	—	—	—	—	—	—	—	—	—
Certified value	35	52	9	2	33	59	115	23	—
HT/HP	35	52	9	2	33	57	98	22	9
RSD	0.7	0.7	0.6	1	0.2	0.4	0	0.4	2.2

*All values are in ppm.

Table 5

Descriptive statistics for check standard data in Figure 4 (n = 81).

	Cu	Fe	Cr	Al	Pb	Si	Na	Mo	Sn
Mean	25.3	25.0	24.9	25.1	25.0	24.9	24.4	24.7	24.8
SD	0.7	0.8	0.6	0.41	1.2	0.7	0.4	1.0	1.3
RSD	2.7	3.2	2.4	1.6	4.8	2.8	1.6	4.0	5.0

running oscillator that exhibits very high tolerance to organic solvents. In addition, the system uses a shear gas to remove the recombination zone of the plasma. This configuration is better suited

for use with organic solvents than designs using counterflow streams or a high-flow extraction system combined with extended-length torches that may result in torch damage by overheating.

Sample introduction

The second step is to replace the Scott double-pass spray chamber with a cyclonic design. This is beneficial for two reasons. First, the cyclonic spray chamber is more efficient, increasing the signal 3× over the Scott. Second, the cyclonic has a much smaller internal volume and washes out much more quickly.

The nebulizer of choice for this application is the V-groove (Lee-man Labs). This nebulizer is made of inert polymer for resistance to the solvents used for wear metals analysis. In addition, it is designed to handle the large particles that may be present in these samples without clogging.

Sample uptake and rinse

The final step in developing an HT/HP wear metals system is to reduce the time required for the sample uptake/rinse cycle. Because of the short integration times used with the ICP system, this cycle becomes the limiting factor in determining the throughput.

The HT/HP system minimizes this cycle in three ways. First, as mentioned above, the small internal volume of the cyclonic spray chamber reduces the time required to rinse. Second, during the sample uptake, the peristaltic pump is set to maximum speed to accelerate the sample's arrival at the nebulizer. Third, a streamlined sample uptake option is used in the software. This option permits the user to specify the amount of time, before the sample analysis is complete, that the autosampler probe be sent back to the rinse station to begin the next cycle. Consequently, the system is performing two actions at once: analyzing a sample and rinsing for the next. With these factors in place, the time required to analyze a single sample is under 30 sec.

Analytical performance

In addition to the increased

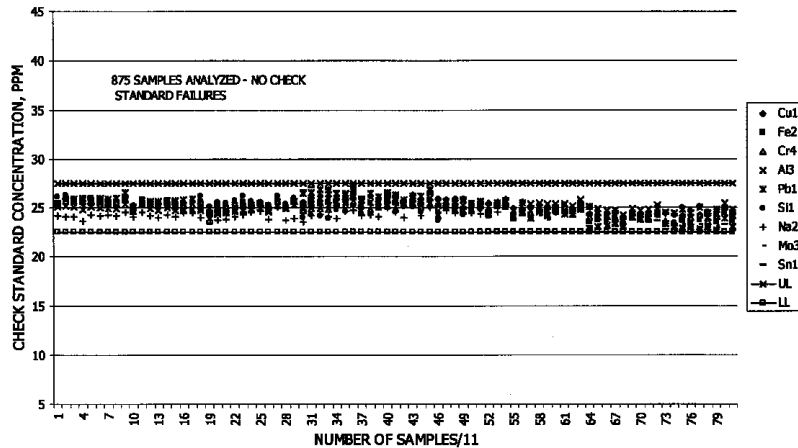


Figure 4 Check standard stability using Leeman Labs ICP running under HT/HP conditions.

sample throughput, the design criteria for the HT/HP system requires that there be no degradation of analytical performance relative to the conventional radial wear metal system. The data contained in this section demonstrate that the performance was actually enhanced.

Calibration

Figures 2 and 3 are typical calibration plots with precision data. Each point on the plots was generated by averaging two replicates consisting of two integrations each. The two elements selected, Sn and Pb, can be the most problematic in wear metal determinations due to their inherent low sensitivity and low concentration in real-world samples. With the increase in sensitivity observed with the HT/HP system, these elements now exhibit precision similar to the rest of the elements. For all elements, the precision for nonzero calibration standards was always <1%. As with samples, the time required for the analysis of a single calibration standard is <30 sec for each replicate measurement.

Accuracy

The results of the analysis of the three verification samples are

presented in Table 4. For comparison purposes, the results generated by an independent wear metal laboratory using a radially viewed torch are also included. The row labeled RSD refers to the precision of the measurement for the HT/HP system.

These data show excellent agreement between the certified values, the independent oil laboratories, and those generated by the HT/HP system. Levels of detection were found to be more than adequate for all the analyses, as demonstrated by the accuracy and precision, even at very low levels of analyte (such as Pb and Sn).

Stability

The ultimate test of a wear metal analysis system is its stability. High sample throughput is meaningless if samples have to be frequently rerun because of check standard failure caused by drift. Every aspect of a system's design affects stability—optics, RF power supply, and sample introduction are all crucial. Also critical is the system's ability to compensate for changes in its environment—wear metal laboratories are not always ideal locations for an ICP spectrometer.

The stability of the HT/HP system was tested by setting up a complete analytical sequence with used engine oils obtained from a

wear metals laboratory. These samples were prepared using the normal dilution with kerosene. The 25 ppm (5 ppm true) standard was used as a check standard and was analyzed after every 10 samples. The check standard result must be within $\pm 10\%$. (This interval is a bit tighter than necessary; many oil laboratories use a range of $\pm 12\text{--}15\%$.) If any element falls outside this interval, the system would be recalibrated and all the samples run since the last successful check standard would be reanalyzed. After a 15-min warmup period, the system was calibrated and the sample analysis begun.

A plot of all the check standard results obtained over an 8-hr run is shown in Figure 4, while the descriptive statistics are given in Table 5. This plot illustrates the stability of the HT/HP system: Over the entire run 875 samples were analyzed without a single check standard failure. No analytical updates or recalibrations were performed. The total number of analyses during this run was 956, including all samples and check standards. This level of throughput and performance demonstrates that the HT/HP system is able to perform well in demanding wear metals analysis laboratories.

Conclusion

The analysis of wear metals in lubricating fluids is a challenging but common application in ICP spectrometry. Generally, laboratories analyzing samples of this type require accurate, high-throughput analysis to provide quick turnaround time for their customers. The Profile HT/HP provides a high rate of sample throughput with optimum accuracy and precision under standard operating conditions.

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