



X-ray fluorescence analysis of additives and wear metals in used lubricating oils

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The determination of metal concentrations in lubricating oils is a very important diagnostic development. Such analysis dates back over 50 years, when one of its earliest uses was to assess engine oil from trains. Today, the analysis of both new and used lubricating oils, as well as the monitoring of trends in the metal concentrations and additives they contain, has become an essential control. Since its origins, many methods have been employed for wear metal analysis.

X-ray fluorescence spectrometry (XRF) quickly became established in the petrochemical industry for the analysis of sulphur, and the unique qualities of the technique - simple sample preparation, high accuracy and good to excellent detection limits across large parts of the periodic table - mean that XRF is also a powerful tool for the analysis of wear metals in lubricating oils.

In this article we report on data obtained using a new package, Oil-Trace (PANalytical), in the XRF analysis of four common additives and 13 wear metals in used lubricating oils.

Monitoring wear metals for predictive maintenance

Lubricating oil is the single most important factor affecting the life of moving parts in a machine. It prevents metal-to-metal contact between all sliding and rolling surfaces, thereby reducing friction. Lubricating oils also protect surfaces from corrosive substances, absorb and transfer heat, transport wear particles and contaminants to filters and transmit force and motion in hydraulics.

Industry is placing an increasing reliance on the performance of lubricating oils and on predictive machine maintenance through wear metals analysis. Metals in lubricating oils, Cu or Fe for example, may be an indication of a worn component. Some metals, such as Na and Si, often indicate contamination. Common oil additives, which include Zn and Ca, can be analyzed for depletion, which in turn can be a factor causing wear. As the metal content of oils change over time, so their useful properties decrease, making replacement vital.

Additionally, the different metals detected in used lubricating oils can provide a fingerprint of a worn component, enabling its rapid identification. This further increases safety and reduces repair and diagnosis costs.

Using Oil-Trace with XRF

PANalytical's new Oil-Trace package was designed specifically to address the problems of unknown matrices, the hydrocarbon and oxygen content of lubricating oils, and to deal with variations in sample density and volume:

Dark matrix characterization

XRF is a relative technique; therefore oil samples are best quantified against calibrations comprising standards of similar matrix composition. However, the wide variety of lubricating and hydraulic oils, together with their oxidation and degradation over time, mean that the matrix composition of used oils is invariably unknown.

The hydrocarbon and oxygen content of oils (referred to here as the Dark-Matrix) cannot be determined directly by XRF due to the foils used to support the sample during analysis. Variations in the oxygen concentration of a light matrix sample - such as oil - influences the accuracy of the measurements significantly.

Oil-Trace uses an innovative method of indirectly characterizing the Dark-Matrix composition so that accurate matrix corrections can be made for the analyte elements. With Oil-Trace, single calibrations can be used for quantifying additives and wear metals in unused and used lubricating oils, independent of the variations in Dark-Matrix composition. There is no need for additional oxygen and hydrocarbon determinations.

Solving problems of sample density and volume variation

The finite thickness characteristics of light matrix oil samples means that their analysis is sensitive to density variations between routine samples and standards, and to the volume of oil being analyzed. Traditionally, these issues were partially solved by analyzing a constant weight of material for both calibration standards and routine samples. Varying this amount in an uncontrolled way causes inaccuracies in both calibrations and routine results.

Oil-Trace corrects for these inaccuracies by taking into account the amount of sample that is being

Table 2: Measurement times on peak and background positions

Element	Na	Mg	Al	Si	P	S	Ca	V	Cr	Mn	Fe	Ni	Cu	Zn	Sn	Ba	Pb
Measurement time on peak (s)	50	30	30	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Measurement time on background (s)	60	40	10	10	10	10	10	10	10	10	10	10	10	10	20	10	20

analyzed. This is accomplished using an integrated wedge-effect correction, which can easily handle mass variations of thirty percent or more.

XRF analysis of additives and wear metals in used lubricating oils

A series of commercially available lubricating oil standards from Analytical Services (Texas, U.S.) was used to set up the calibrations for the determination of Na, Mg, Al, Si, P, S, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Sn, Ba and Pb in unused and used lubricating oils. The concentration ranges of the elements are listed in Table 1.

Fifteen grams of each lubricating oil standard was weighed into a P2 "de Kat" liquid cell, assembled using 2.5µm polyester (Mylar) supporting foil. The foil ensures high transmission of the analyte wavelengths for light elements (such as Na and Mg) and provides excellent chemical resistance against lubricating oils and their additives.

Instrumentation

The PANalytical Axios-Petro, a fully integrated wavelength-dispersive XRF analyzer, was used in this study. The Axios-Petro system consists of a spectrometer, X-Y sample handler and SuperQ software. Axios-Petro was used in combination with the new Oil-Trace package, which includes software and liquid standards for C, H and O characterization.

Measurement conditions

Total measurement time of the analytical program was approximately 11 minutes per sample. Measurement times for the individual peak and background measuring positions are given in Table 2. Single unshared backgrounds were used for most channels and two background positions were used for Na, Mg and Sn. K_L lines were measured for all elements except Ba (L_L) and Pb (L_L).

Axios-Petro's SuperQ software contains a template for this application. Calibration is therefore a simple procedure, requiring measurement of suitable oil standards.

Table 1. Concentration ranges and calibration RMS values

Element	Concentration range (ppm)	Calibration RMS (ppm)
Na	0 - 500	7.1
Mg	0 - 500	5.6
Al	0 - 500	7.5
Si	0 - 500	3.1
P	0 - 0.150 wt%	14.5
S	0 - 2.500 wt%	96
Ca	0 - 0.500 wt%	8.6
V	0 - 300	6.0
Cr	0 - 300	2.6
Mn	0 - 500	4.6
Fe	0 - 500	3.7
Ni	0 - 300	1.7
Cu	0 - 300	2.7
Zn	0 - 0.200 wt%	8.0
Sn	0 - 500	1.7
Ba	0 - 500	2.3
Pb	0 - 500	3.6

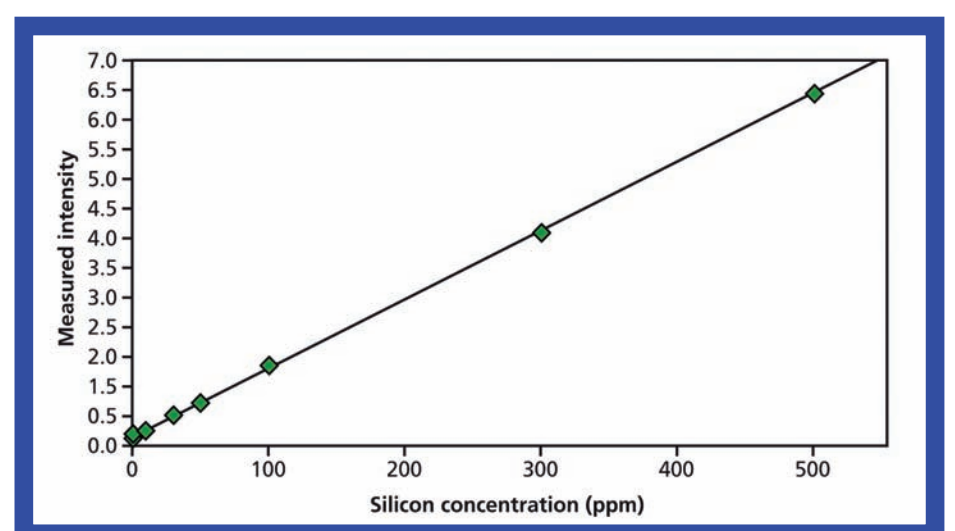


Figure 1: Calibration plot for silicon in unused lubricating oil

Analytical Instrumentation

The Axios-Petro used in this study was upgraded with curved analyzing crystals to further enhance sensitivity and resolution for Al (PE002 curved), Si (InSb111 curved), P and S (Ge111 curved).

Calibration accuracy

The accuracy of Axios-Petro with Oil-Trace for the analysis of additives and wear metals in lubricating oils is excellent. This is illustrated by calibration curves for silicon and iron (Figures 1 and 2) and by the calibration RMS values for all the elements (Table 1). The calibration RMS (1 standard deviation) is a statistical comparison of the certified chemical concentrations of the standards, with the concentrations calculated by regression in the calibration procedure.

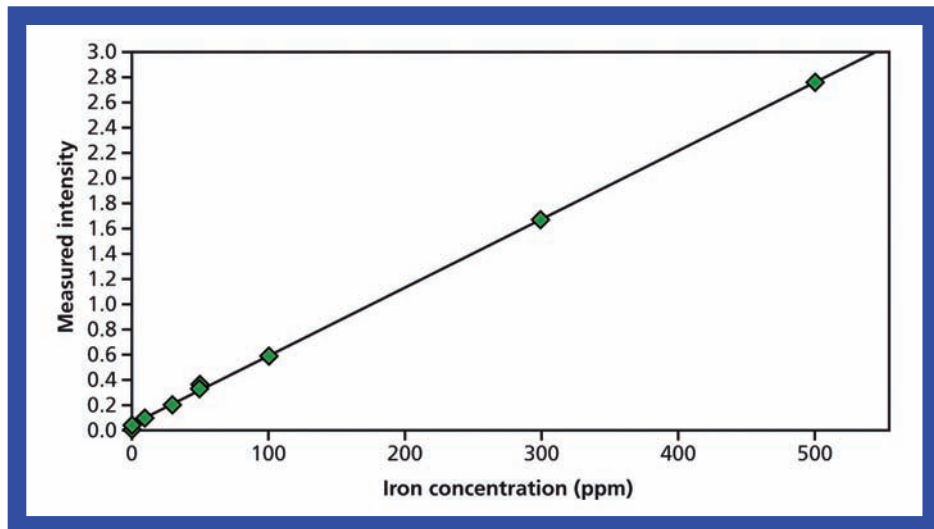


Figure 2: Calibration plot for iron in unused lubricating oil

Increased accuracy with Oil-Trace

The need for careful characterization of the Dark-Matrix is demonstrated in Table 3. In this example a used lubricating oil was analyzed against calibrations defined by unused lubricating oil standards. The Dark-Matrix composition differs between the routine sample and calibration standards - the major difference being an increased oxygen concentration in the used lubricating oil.

If oxygen content of the matrix is ignored (i.e. no Dark-Matrix correction), the calculated concentrations are lower than the certified concentrations (see first row of Table 3). This is especially true for the light elements (Na, Mg and Al). In contrast, the second row of Table 3 shows a much closer correspondence between the calculated and certified concentrations using the Dark-Matrix correction of Oil-Trace.

The accuracy of analyzing used lubricating oils by Oil-Trace is further emphasized by the data shown in Table 4. For most elements the calculated concentrations are within the RMS error of the calibration.

Table 3: Comparison of certified vs calculated concentrations (with and without Oil-Trace Dark-Matrix correction) for wear metals and additives in a used lubricating oil.

Concentrations (ppm)	Na	Mg	Al	Si	P	S	Ca	V	Cr	Mn	Fe	Ni	Cu	Zn	Sn	Ba	Pb
No Dark-Matrix correction	255	270	271	3	10	0	25	47	143	6	143	4	0	54	189	0	30
With Dark-Matrix correction	320	323	342	0	7	0	33	72	184	7	187	6	0	62	195	0	31
Certified concentration	314	315	322	0	0	0	31	63	188	6	188	6	0	63	188	0	31

Table 4: Comparison of certified vs calculated concentrations (with Oil-Trace Dark-Matrix correction) for wear metals and additives in two samples of used lubricating oil

Concentrations (ppm)	Na	Mg	Al	Si	P	S	Ca	V	Cr	Mn	Fe	Ni	Cu	Zn	Sn	Ba	Pb
Routine sample 1	4	198	66	31	188	0	195	62	7	6	2	190	0	32	62	6	62
Certified concentration	1	188	63	31	188	0	188	63	0	6	6	188	0	31	63	6	63
Routine sample 2	212	8	200	19	334	0	5	5	8	198	31	67	67	0	67	67	188
Certified concentration	226	7	201	20	337	0	0	7	7	201	33	67	67	0	67	67	188

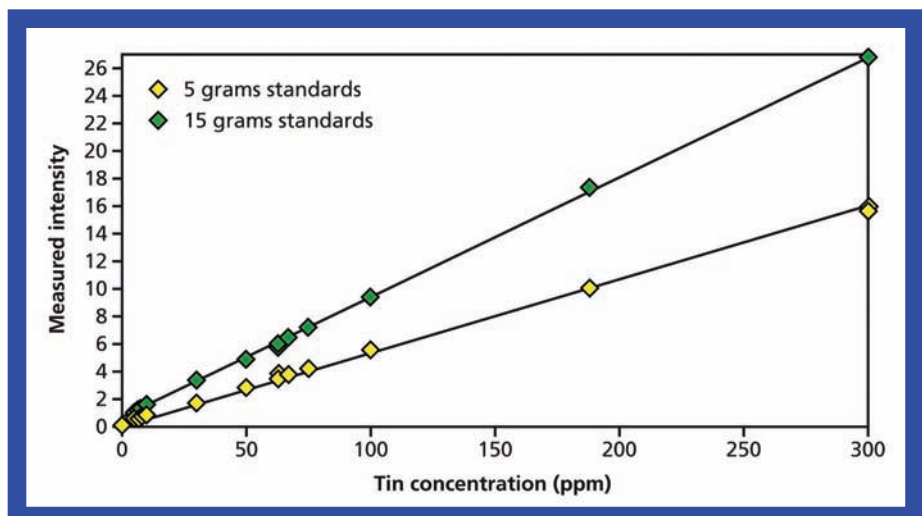


Figure 3: No wedge-effect correction: two distinct calibration plots for tin in lubricating oil can be seen for both five and fifteen grams of oil standards

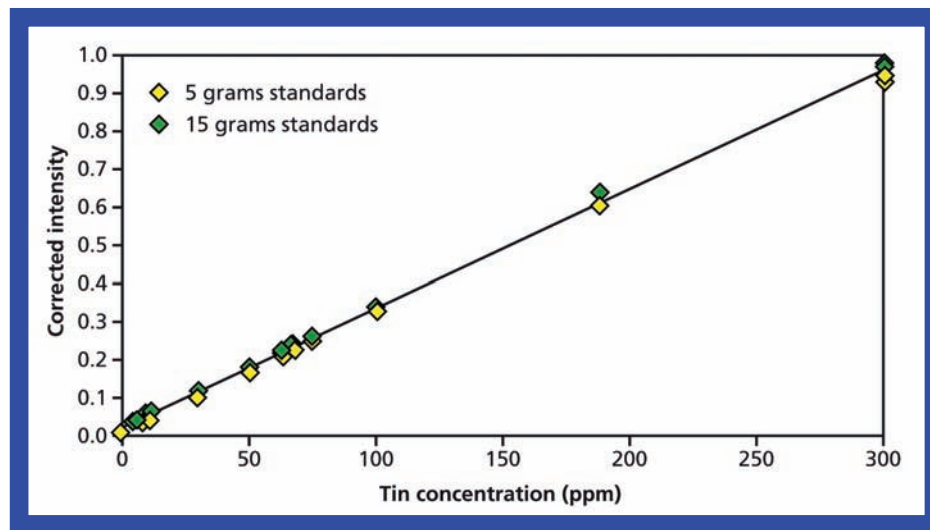


Figure 4: With wedge-effect correction: single calibration plot for tin in lubricating oil using both five and fifteen grams of oil standards to create the calibration

Robust calibrations by wedge-effect correction in Oil-Trace

The mass independency provided by Oil-Trace is illustrated in Figures 3 and 4. Without Oil-Trace's wedge-effect correction, 5g and 15g of standard material define two distinct calibration curves for tin in lubricating oil (Figure 3). However, an application of the wedge-effect correction in Oil-Trace results in a single calibration curve, which is effectively independent of the amount of sample analyzed (Figure 4).

Precision and instrument stability

The precision, repeatability and reproducibility of Axios-Petro are excellent, not only over a short-term period (20 consecutive measurements), but also for longer periods (measurements carried out over ten days, Table 5). The short-term repeatability shows RMS values better than 1-2% relative at the 40-70ppm level for most elements, for example, Si, Cr, Fe, Ni, Cu and Pb. More importantly, this level of precision was maintained over longer periods, illustrating the long-term stability of the system.

Comparison of the RMS value (1 standard deviation) with the Counting Statistical Error (CSE) shows the excellent precision of the method and the outstanding stability of the instrument (Table 5). Theoretically, the CSE is the minimum possible error. The similar magnitude of the RMS and CSE values shows that errors originating from the instrument are negligible.

Table 5: Analytical precision of Axios-Petro

Element	Al	Si	Ba	Cr	Fe	Ni	Cu	Pb	S
REPEATABILITY (20 consecutive measurements)									
Mean (ppm)	99.2	72.9	68.0	56.1	43.5	64.3	45.4	67.7	42.2
RMS (ppm)	1.5	1.4	0.6	0.3	0.3	0.3	0.3	0.4	2.2
RMS (rel%)	1.5	1.9	0.9	0.5	0.7	0.4	0.6	0.6	5.3
REPRODUCIBILITY (Measurements carried out over 10 days)									
Mean (ppm)	100.1	73.4	60.1	55.5	43.1	65.1	44.0	61.9	36.6
RMS (ppm)	1.2	1.2	2.4	0.2	0.4	0.3	0.3	0.9	2.4
RMS (rel%)	1.2	1.6	4.1	0.4	0.9	0.5	0.6	1.4	6.5
COUNTING STATISTICAL ERROR									
CSE (ppm)	1.1	0.5	0.7	0.3	0.3	0.2	0.2	0.4	1.7
CSE (rel%)	1.1	0.6	1.0	0.6	0.7	0.3	0.5	0.5	3.9

Detection limits

Detection limits for wear metals and additives in typical unused lubricating oil matrices are given in Table 6. The lower limit of detection (LLD) is calculated from:

$$LLD = \frac{3}{s} \sqrt{\frac{r_b}{t_b}}$$

Where s=sensitivity (cps/ppm); r_b=background count rate (cps); and t_b=counting time background (s).

The LLD values quoted in Table 6 are typical for the prepared unused lubricating oil samples. LLD values for individual samples vary according to sample matrix and the transmission characteristics of the supporting foil.

Table 6: Detection limits in typical lubricating oil samples

Detection limits	Na	Mg	Al	Si	P	S	Ca	V	Cr	Mn	Fe	Ni	Cu	Zn	Sn	Ba	Pb
LLD (ppm, 100 s)	5	1.5	0.4	0.3	1.1	0.4	0.5	0.15	0.2	0.2	0.2	0.1	0.15	0.1	1.0	0.7	0.1

Conclusion

Accurate trace element and trend analysis of wear metals in oils is important for many reasons: preventative and predictive maintenance programs to minimize potentially expensive repair costs; to reduce the likelihood of engine failure far from the home base; and to greatly increase safety margins by reducing the chances of catastrophic engine failure.

Axios-Petro, in combination with Oil-Trace, brings XRF analysis of oils and oil derivatives to the next level. Oil-Trace performs innovative corrections for variations in the Dark-Matrix composition and the wedge-effect. With Oil-Trace, a single calibration can be used for quantifying additives and wear metals in both unused and used lubricating oils, independent of the hydrocarbon and oxygen characteristics of the matrix and of the sample size (mass and density).

Oil-Trace offers universal calibrations for a range of elements in a wide variety of sample types, from fuel?bio-fuel mixtures to unused and used lubricating oils. The package enables simplification of application maintenance and analytical procedures, and cost savings through the use of relatively inexpensive oil standards.

The XRF method benefits from a simple sample preparation and the stability of data is such that individual calibrations can be used for months. Time-consuming and costly restandardizations are unnecessary and the resultant data are consistent over long periods, saving time and money.