

## Rapid and Accurate Element Determination in Lubricating Oils Using Inductively Coupled Plasma Optical Emission Spectrometry\*

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The internal standard method has been applied to element determination in lubricating oils using inductively coupled plasma (ICP) optical emission spectrometry in order to achieve high accuracy. On-line dilution allows rapid determination without sample pre-treatment. Various lubricating oils can be handled with a single procedure because the effects of lubricant additive components are eliminated. A good analytical performance (relative standard deviation=5%) is achieved under routine operating conditions. Wear particle sizes up to 10  $\mu\text{m}$  are tolerated by the ICP.

**Keywords:** Inductively coupled plasma optical emission spectrometry; element determination; lubricating oil; on-line dilution; internal standard

The spectrometric analysis of lubricating oils includes the determination of wear metals, and contaminant and additive elements. Engine condition monitoring through used oil analysis is common practice for systems where large amounts of lubricating oils are involved or where engine wear is critical. For this purpose samples are submitted for analysis at regular time intervals. Engine wear patterns are monitored by the wear metal analysis results. Used oil contamination originating from dirt and leaks can be traced by contaminant element determination. Additive packages for lubricating oils consist of, among others, antiwear agents, antioxidants, dispersants, detergents and viscosity index improvers. Some of these additives consist of organometallic components. The additive element concentration, which might be as much as several % m/m, is determined for product characterization and for quality control.

X-ray fluorescence (XRF) spectrometry is commonly used for the determination of additive elements in fresh oil. As inductively coupled plasma optical emission spectrometry (ICP-OES) offers high sensitivity and multi-element analysis capability, this technique is applied to wear, contaminant and additive element determination in used oils as in the Kuwait Routine Analysis System.

The viscosity of lubricating oils is too high for nebulization with the commercially available nebulizers. Algeo *et al.*<sup>1</sup> approached the problem by modifying the nebulizer with a sample heater. A more common solution is to dilute the sample with a low viscosity solvent prior to nebulization.<sup>2-7</sup>

Comprehensive studies on the use of various organic solvents in the ICP have been published by Maessen *et al.*<sup>8</sup> and by Nygaard *et al.*<sup>9</sup> Botto<sup>7</sup> examined several solvents for applications in the petroleum industry. For lubricating oil application, kerosene proved to be the most practical because of its good solvent properties, low volatility and toxicity.

Large amounts of samples have to be analysed within short time periods, therefore, accurate results are required with a minimum of sample handling. Granchi *et al.*<sup>5</sup> have described a reduction in sample handling by the application of robotics. In our approach a more cost effective method to reduce sample pre-treatment was selected by using an on-line dilution system.<sup>6</sup> A 5-fold dilution was applied to maintain sufficient detection power for routine trace element analysis.

The internal standard method has to be applied to

compensate for lubricating oil matrix effects. With this method calculations are performed by using the analyte to Co intensity ratio. The internal standard element Co, which is not present in lubricating oils, is added to the diluent to obtain analysis without sample pre-treatment. The effect of the viscosity index improver additive was also investigated.

### Experimental

#### Instrumentation

The ICP-OES measurements were obtained using a Jobin-Yvon (Longjumeau Cedex, France) JY-70-plus system. The spectrometer consists of a monochromator and a dual polychromator. The latter was used for lubricating oil analyses to allow the rapid determination of 21 elements in the wavelength range of 179–800 nm. The dispersion is 0.5 nm mm<sup>-1</sup> in the first order. The spectrometer is equipped with a demountable torch which has an aluminium injector. The V-groove nebulizer was used for sample introduction and the generator operated at 40 MHz. Typical operating conditions for analysis of oil samples are presented in Table 1.

The on-line dilution system includes two Gilson peristaltic pumps and a double-needle system. The latter, mounted on the arm of the computer driven sample changer, consists of two concentric stainless-steel needles. The dilution solvent is pumped with the first peristaltic pump into the space between the two needles. The second peristaltic pump draws the sample and diluent through the inner tube to the nebulizer. For organic solutions, Gilson isoversinic pump tubing was used. Day-to-day variations in dilution rate are compensated for by using standardization samples with each sample batch.

The experiments on wear particle sizes were carried out with a Tribometrics (Berkeley, CA, USA) Model 56 wear particle analyser, which collects wear particles as the samples are drawn through a magnetic filter. The increase

Table 1 Instrument operating conditions

Parameter	Setting
Power	1.2 kW
Plasma argon flow rate	14 l min <sup>-1</sup>
Auxiliary argon flow rate	1.2 l min <sup>-1</sup>
Sheathing argon flow rate	0.3 l min <sup>-1</sup>
Carrier argon flow rate	1 l min <sup>-1</sup>
Sample uptake rate	4 ml min <sup>-1</sup>

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in magnetic flux is converted into micrograms of metallic Fe. Filter sizes vary from 1 to 10  $\mu\text{m}$ .

### Reagents

Multi-element organometallic standard solutions were used for calibration and standardization. For wear metal and contaminant element determination, covering the concentration range between 1 and 200  $\text{mg kg}^{-1}$ , Conostan S-21 (Conoco, Ponca City, OK, USA) standards were used. The upper limit for Fe and Cu extended to 1000  $\text{mg kg}^{-1}$ . Additive elements were calibrated in the 0.01–2% m/m range using multi-element standards prepared from metal organic concentrates (Ångström, Belleville, MI, USA). Standards covering the appropriate concentration range were prepared from stock solutions by dilution with base oil (SAE 30 grade). Prior to analysis, the standard and sample solutions were diluted with kerosene using the on-line dilutor.

In the experiments where the internal standard method was applied, calibration graphs were plotted for all elements by using the analyte to Co intensity ratio. Cobalt was added to the diluent at a concentration of 10  $\text{mg l}^{-1}$ .

## Results and Discussion

### Viscosity Index Improver

Incomplete element recovery was found in the direct analysis of multi-grade engine oils. Severe loss of accuracy occurred with the 5-fold dilution, which was the dilution rate used when applying the on-line dilution system, as shown in Table 2 for a 15W-40 engine oil. Accuracy improved when the dilution rate was increased, however, not sufficiently and at the sacrifice of a loss in detection power.

Lubricating oils contain chemical additives, which give different characteristics to the oils. A typical additive for multi-grade engine oils is the viscosity index (VI) improver. Viscosity index improvers are high relative molecular mass polymers that are added to the lubricating oils to influence the change in viscosity with temperature.

Experiments showed that the VI improver had an effect on the nebulizer efficiency and therefore on the element recovery. This effect appeared to be independent of the nebulizer used. During engine operation, shear forces will cause the break down of the polymer chains. In used oils, therefore, the effect on the nebulizer efficiency will decrease with operating time. However, even small amounts of the VI improver diminish the accuracy of the analysis results (Fig. 1).

This effect can be overcome by applying the internal standard method. The degradation of nebulizer efficiency caused by the VI improver will have a similar impact on the analyte and Co, added to the sample by the diluent. The net effect on the analyte to Co intensity ratio is negligible (see Fig. 1).

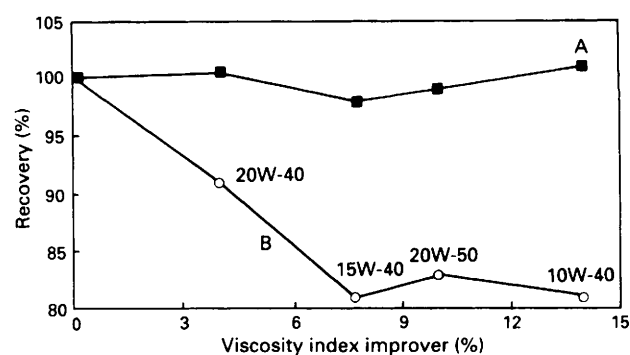


Fig. 1 Internal standard (A) versus direct (B) on-line dilution method for multi-grade engine oils

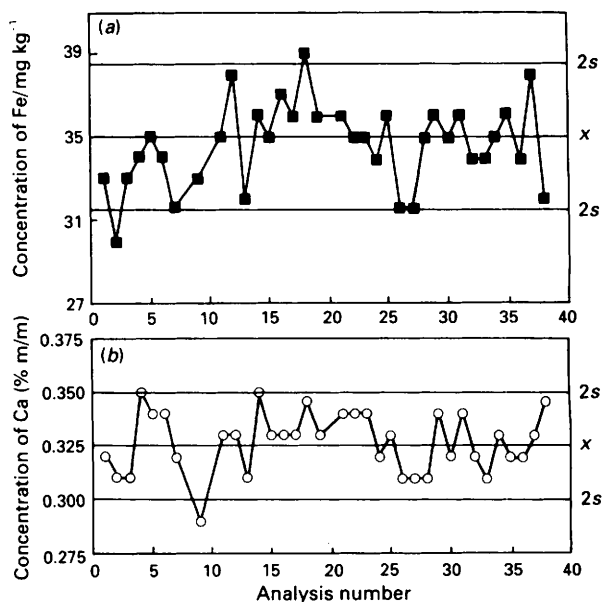


Fig. 2 Long term stability for wear metal and additive element determination: (a) control chart for Fe; and (b) control chart for Ca

### Analytical Parameters

Important analytical parameters for element determination in lubricating oil include accuracy, precision, stability, viscosity and matrix effects. The proposed method showed precision data based on ten repetitive measurements of better than 1% relative standard deviation (RSD). Repeatability data published in standard test methods<sup>10,11</sup> show a 5% RSD for additive element determination in fresh oil and a 10% RSD for wear metals in used oil.

Long term stability determined by consecutive measurements on a used oil sample over a period of 40 d showed an RSD of 5%, both on wear metals and additive elements (Fig. 2).

Viscosity effects were virtually absent when the on-line internal standard method was applied. The variation in analysis results between multi-element standard solutions made up in base oil with different viscosities was within the over-all standard deviation (SD) (Fig. 3). The viscosity for regular used oil samples varied from 5 to 15  $\text{mm}^2 \text{s}^{-1}$  at 100 °C. By contamination with foreign materials or as a result of oxidation processes by the oil itself, used oils can have higher viscosities, however, even in higher viscosity ranges no significant effect on the results could be observed.

Table 2 Element recovery in the direct analysis of a multi-grade engine oil at various dilution rates

Dilution factor	Method	Recovery (%)
100	Manual	92
10	Manual	87
5	On-line	81
5*	On-line	77

\* Cross-flow nebulizer.

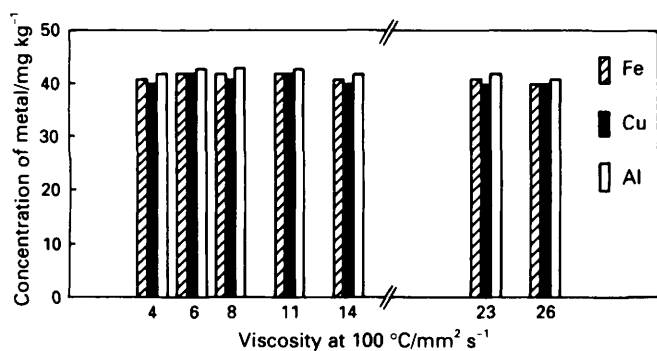


Fig. 3 Effect of viscosity on the recovery of various wear metals

Most lubricating oils consist of a mineral base oil originating from crude oils. As well as mineral oils, synthetic lube oils, made by the chemical combination of low relative molecular mass components, are also used. The main types of synthetic base fluid are hydrocarbons such as poly( $\alpha$ -olefins) or esters. By using the on-line internal standard method no significant effect could be observed by either type of synthetic fluid compared with the mineral oil (Table 3). This implies that various lubricating oils can be analysed using calibration graphs based on mineral oils. For the on-line direct method a slight effect was observed; however, the deviation was still within reasonable accuracy limits. X-ray fluorescence spectrometry is the recognized technique for the determination of an additive element in fresh lubricating oils. As shown in Table 3 the direct XRF method shows large deviations especially with ester-type synthetic base fluids.

Other possible interferences occurring in lubricating oil element determination are background shift and spectral overlap. Background shifts, which will affect the low determination limits, are dealt with by dynamic background correction. The analytical element lines are chosen such that spectral interferences are minimal. Most samples contain Ca in very high concentrations, up to 3.5% m/m. Therefore, some minor interference by Ca on the analytes cannot be avoided. Calcium spectral interference can be expected on the Si 251.6 nm and on Fe 238.2 nm lines. Accurate interference correction is relatively simple to obtain, as interfering elements are included in the analytical programme for lubricating oil element determination. Spectral interference correction, both linear and polynomial and also dynamic background correction, are provided in standard instrument software.

Table 3 Lubricating oil matrix effects

Matrix	Recovery (%)		
	Internal standard method (ICP)	Direct method (ICP)	Direct method (XRF)
All mineral	100	100	100
Poly( $\alpha$ -olefin)	101	105	109
Ester type	103	102	83

Table 4 Fe particles  $>2 \mu\text{m}$  versus total Fe concentration

Fe concentration/mg kg <sup>-1</sup>	
Total	$>2 \mu\text{m}$
240	22
150	8
100	10
50	3

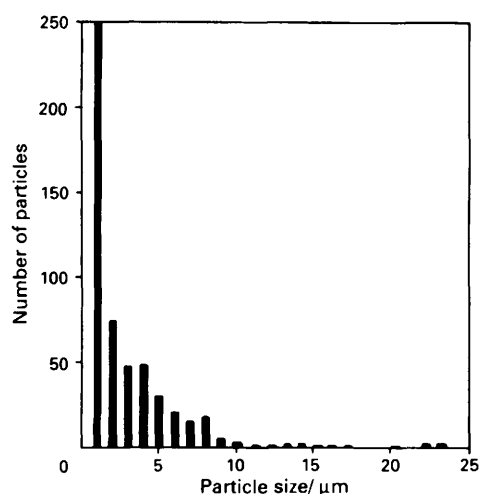


Fig. 4 Wear particle size distribution

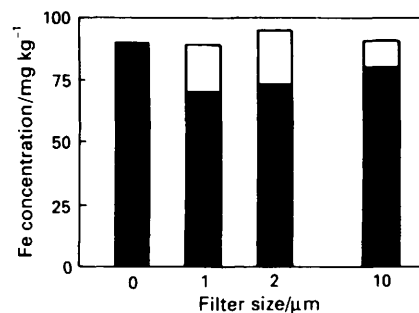


Fig. 5 ICP-OES measurements on Fe wear metals before and after filtration with the wear particle analyser: unshaded area, Fe on filter after filtration using the wear particle analyser; and shaded area, Fe in sample after filtration

### Wear Particle Size

Engine wear occurs, to some extent, during normal system operation. For many day-to-day samples the amount and size of Fe wear particles were recorded; some typical measurements are presented in Table 4. In general it can be stated that the average wear particle size is less than  $2 \mu\text{m}$ . This is supported by measurements using an image analysis system (Vidas, Kontron) (Fig. 4). It is, however, important to know the behaviour of the ICP with particles larger than  $2 \mu\text{m}$ , which can occur with serious engine failure. The ICP-OES measurements on samples before and after filtration using the wear particle analyser showed that particles up to  $10 \mu\text{m}$  can be tolerated (Fig. 5).

### Conclusion

When applying the internal standard method with on-line dilution, element determination in various lubricating oils can be carried out in a single procedure. The effects of lubricant components on the nebulizer efficiency are eliminated giving high accuracy and precision data. Interferences are virtually absent or can easily be corrected with standard instrument software.

The method was developed for used oil analysis. Additive element determination by XRF is currently the preferred method for fresh oil product characterization because of the high accuracy and the possibilities for direct analysis without sample handling. However, these qualities of direct

XRF analysis are not valid in certain instances when synthetic base oils are used. The ICP-OES analysis, which is the only sensitive and rapid method for wear metal and contaminant element determination in used oil, can also be applied to additive element determination. When used with the on-line internal standard method, ICP-OES might fulfil the requirements for fresh oil additive element determination.

### References

- 1 Algeo, J. D., Heine, D. R., Phillips, H. A., Hoek, F. B. G., Schneider, M. R., Freelin, J. M., and Denton, M. B., *Spectrochim. Acta, Part B*, 1985, **40**, 1447.
- 2 Brown, R. J., *Spectrochim. Acta, Part B*, 1983, **38**, 283.
- 3 Mason, P. R., *Anal. Proc.*, 1983, **20**, 471.
- 4 King, A. D., Hilligoss, D. R., and Wallace, G. F., *At. Spectrosc.*, 1984, **5**, 5.
- 5 Granchi, M. P., Biggerstaff, J. A., Hilliard, L. J., and Grey, P., *Spectrochim. Acta, Part B*, 1987, **42**, 169.
- 6 Evans, S. J., and Klueppel, R. J., *Spectrochim. Acta, Part B*, 1985, **40**, 49.
- 7 Botto, R. I., *Spectrochim. Acta, Part B*, 1987, **42**, 181.
- 8 Maessen, F. J. M. J., Seeverens, P. J. H., and Kreuning G., *Spectrochim. Acta, Part B*, 1984, **39**, 9.
- 9 Nygaard D. D., Schleicher, R. G., and Sotera, J. J., *Appl. Spectrosc.*, 1986, **40**, 1074.
- 10 Deutsche Industrie Norm, DIN 51391/3, 1991 and DIN 51396/1, 1990.
- 11 American Society for Testing and Materials, 1989, ASTM D 4951-89, Philadelphia, PA.

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