

# AAS

## APPLICATION NOTES

The measurement of Al, Cr, Cu, Ni, Pb, Si, Sn, Ti and V in engine oil

AAS



## 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 1940s<sup>1</sup>. 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 would be due to piston or ring wear. Copper is indicative of coolant leaking into the lubrication system via cracks or leaking seals. Some elements present in the oil may indicate other problems, for example silicon present in the oil suggests dirt or sand intrusion and indicates that the air cleaner may need to be cleaned or changed. Periodical analysis of the lubricants enables such troubles to be located and corrected before they cause a major breakdown.

Wear metals are different from naturally occurring trace metals in that they are commonly found in the form of fine metallic particles or a colloidal suspension. As a result, they differ in response to the same metals present as soluble organic salts (e.g., oils with additives) or in working standards. However, experience has shown that the particle size is frequently so small that the metal is completely atomised in a furnace, allowing excellent results to be obtained from synthetic standards made up from organometallics.

This paper describes the parameters and conditions required for the determination of Al, Cr, Cu, Ni, Pb, Si, Sn, Ti and V in engine oil after dilution of the oil sample in di-isobutylketone (DIBK).

## Experimental

### Instrumentation

A GBC atomic absorption spectrometer, equipped with the unique Hyper-Pulse deuterium arc background correction system and GBC automated graphite furnace were used. The graphite furnace system consists of the graphite furnace power supply (GF) and programmable automatic sample loader (PAL). The GBC AAS software provides control of the entire system: spectrometer, furnace and autosampler. It allows the operator to develop furnace methods and to collect and store data. Real time colour graphics of simultaneous signal absorbance and background traces allow the operator to optimise furnace conditions. All graphics traces for standards and samples are stored on the computer, as are all methods applications, results files and graphics files, allowing recall for method assessment and refinement. The instrumental conditions for the determination of Al, Cr, Cu, Ni, Pb, Si, Sn, Ti and V are shown in Table 1.

GBC total pyrolytic graphite platforms were used for all analyses. For the determination of Al, Cr, Cu, Si, Ti and V, GBC hollow cathode lamps were used. For the determination of Ni, Pb and Sn GBC Super Lamps were used.

	<b>Al</b>	<b>Cr</b>	<b>Cu</b>	<b>Ni</b>	<b>Pb</b>	<b>Si</b>	<b>Sn</b>	<b>Ti</b>	<b>V</b>
<b>Wavelength (nm)</b>	309.3	357.9	324.7	232.0	217.0	251.6	235.5	364.3	318.5
<b>Lamp Current (mA)</b>	10	6	4	15	8	15	15	18	18
<b>Slit Width</b>	0.5	0.2	0.5	0.2	1	0.2	0.5	0.2	0.2
<b>Slit Height</b>	Reduced	Reduced	Reduced	Reduced	Reduced	Reduced	Reduced	Reduced	reduced

**Table 1: Instrument parameters used for this study**

## Standard and sample preparation

Conostan<sup>2</sup> organometallic standards were used. These are prepared from alkylarylsulphonates in a base oil and 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 500 ppm weight Conostan S-21 multi-element standard was used to prepare the following intermediate standards:

<b>Al</b>	100 ppb	<b>Cr</b>	100 ppb	<b>Cu</b>	50 ppb
<b>Ni</b>	100 ppb	<b>Pb</b>	100 ppb	<b>Si</b>	80 ppb
<b>Sn</b>	250 ppb	<b>Ti</b>	500 ppb	<b>V</b>	500 ppb

Some practical hints for the handling of thick oils and low viscosity volatile organic solvents together with furnace analysis are given below:

1. The standards should be made in accordance with the manufacturers instructions<sup>2</sup>.
2. 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. The method employed used a disposable glass pipette and accurate weighing with an analytical balance.
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. The low viscosity of the organic solvents requires the PAL dispensing tip to be positioned much closer to the furnace platform than would be the case for aqueous samples. This ensures that the solvent does not creep up outside the sampler tip.
10. Adjusting the PAL injection speed from 9  $\mu\text{L/s}$  to 4, 2 or 1  $\mu\text{L/s}$  will ensure that the sample does not spread, but dries in as small an area as possible, thus increasing sensitivity and precision.
11. The autosampler rinse solution used was high purity water containing 0.01% Triton-X nonionic detergent and 0.01% nitric acid.

The samples were prepared by adding 1 g of the oil and dissolving it in 100 mL DIBK. 5 µL of the sample was then atomised.

No attempt was made to matrix match the standards with the samples as the standard additions technique was used. The AUTOMIX facility of the PAL was used to automatically prepare the three additions in the furnace. The volumes used are shown in Table 2.

Sample Type	Blank Vol.	Std Vol.	Sample Vol.	Modifier Vol.	Aux-Mod Vol.
Sample	15	0	5	0	0
Blank	15	0	0	0	0
Std. 1	10	5	5	0	0
Std. 2	5	10	5	0	0
Std. 3	0	15	5	0	0

**Table 2: PAL autosampler conditions for the preparation of the working standards and subsequent analysis**

The concentration of the intermediate standard prepared and the concentration of the three additions is shown in Table 3.

Element	Intermediate Std. (ng/g)	Addn. 1	Addn. 2	Addn. 3
Al	100	100	200	300
Cr	100	100	200	300
Cu	50	50	100	150
Ni	100	100	200	300
Pb	100	100	200	300
Si	80	80	160	240
Sn	250	250	500	750
Ti	500	500	1000	1500
V	500	500	1000	1500

**Table 3: Standard concentrations using the intermediate standard concentrations and PAL autosampler conditions from Table 2**

The furnace parameters were optimised for maximum sensitivity and minimum background. Table 4 shows the furnace parameters used for the analysis of lead. An injection rate of 1 µL/s was used and injected prior to Step 2. Figure 1 shows a triplicate analysis of 5 µL of 100 ppb lead standard. Excellent sensitivity was obtained (0.126 abs) with negligible background. The precision obtained was excellent with absorbances of 0.126, 0.126 and 0.126 respectively. The %RSD obtained was 0.16%.

Step	Final Temp. (°C)	Ramp Time (s)	Hold Time (s)	Gas Type	Read	Signal Graphics
1	90	0.1	1.0	Inert	Off	Off
2	180	10.0	20.0	Inert	Off	Off
3	400	10.0	5.0	Inert	Off	Off
4	400	0.0	1.0	None	Off	Off
5	2000	0.8	1.5	None	On	On
6	2600	0.3	3.0	Inert	Off	Off

**Table 4: Furnace parameters for lead determination**

## Results and discussion

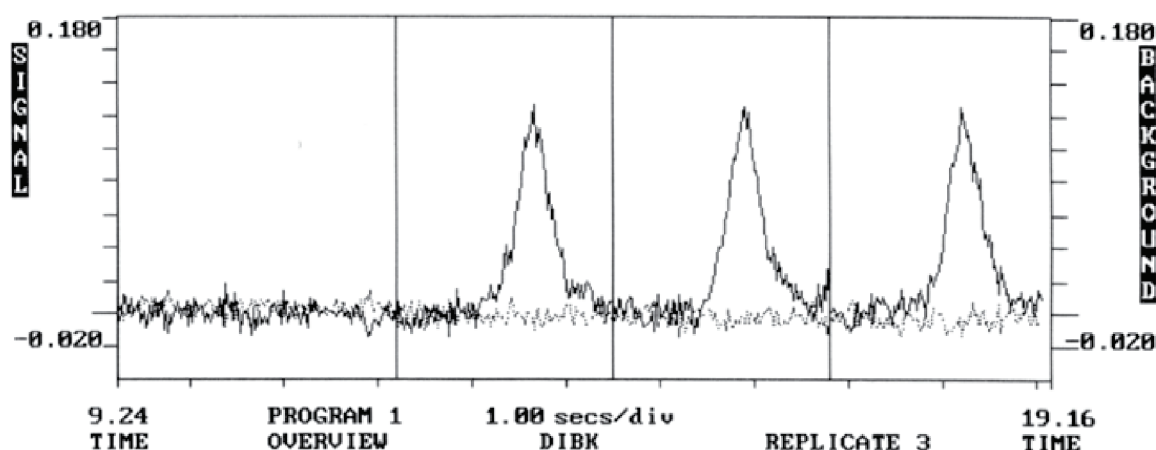
For lead, a calibration curve was constructed using standard additions mode (Figure 2). An excellent correlation was obtained showing the linearity of this calibration technique. The 'Convert' facility found in the Calibration Curve Graphics Display window was used to calculate the characteristic concentration (the concentration that will give 0.0044 abs). This was calculated by entering 0.0044 in the 'Absorbance' field; the corresponding concentration is then shown in the 'Concentration' field.

Figure 2 shows the standard additions calibration for lead. The characteristic concentration was 2.755 ng/g. As 5 µL of the sample was injected, the sensitivity in mass is  $5 \times 2.755 = 13.78$  pg.

Similarly, the characteristic concentration was determined for the other elements investigated. These are summarised in Table 5, together with the ash and atomisation temperature used.

The furnace program shown in Table 3 was used with a maximum ramp rate. The sensitivity for a 5 mL injection for each element is also shown.

1 g of an aircraft engine oil sample was weighed into a 100 mL volumetric flask and made to volume with DIBK. This was then analysed and the results are shown in Table 6.



**Figure 1: Signal graphic for a blank and then three 0.5 ng lead injections using the 217.0 nm line (note the very low background and excellent reproducibility for the three replicates)**

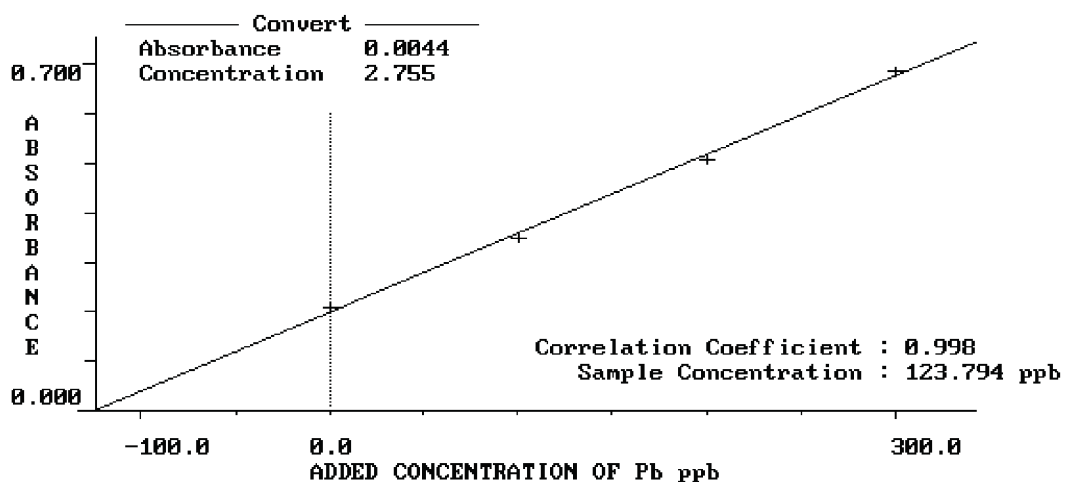


Figure 2: Standard additions plot for lead. The calculated characteristic concentration is also shown

Element	Ash (°C)	Atomise (°C)	Sensitivity (µg)
Al	1400	2500	11
Cr	1150	2500	3
Cu	800	2300	8
Ni	900	2400	20
Pb	400	2000	14
Si	1000	2700	6
Sn	800	2600	20
Ti	1400	2900	88
V	1400	2800	46

Table 5: Summary of the furnace conditions used for a 5 µL sample of 1 g engine oil dissolved in 100 mL DIBK

Element	Conc. In Solutions (ng/g)	Conc. In oil (µg/g)
Al	118	11.8
Cr	29	2.9
Cu	96.5	9.6
Ni	43	4.3
Pb	124	12.4
Si	133	13.3
Sn	233	23
Ti	396	39.6
V	316	31.6

Table 6: Results for the aircraft oil sample

## Conclusion

Analytical programs for the determination of Aluminium, Chromium, Copper, Nickel, Lead, Silicon, Tin, Titanium and Vanadium in engine oil have been developed. These are suitable for the routine monitoring of wear metals for oil lubricated engines or equipment. The use of the graphite furnace power supply allows the determination of very low levels of these elements, providing a convenient early warning of possible component failure. The loss of the element during the ash step is minimised by using the pyrolytic graphite platform.

## References

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2. CONOSTAN, Metallo-organic Standards, Conostan Division, Continental Oil Company Ponca City, Oklahoma.
3. Graphite Furnace Methods Manual, GBC Scientific Equipment Pty Ltd, Braeside, Australia.