The Analysis of Lubricating Oil Additives

Application Note

Atomic Absorption

Author

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Introduction

Blends containing barium, calcium and zinc salts are frequently added to certain lubricating oils. Usually the concentration of these salts is relatively high so that atomic absorption spectrophotometry is ideally suited to the rapid and accurate analysis of these metals.

The choice of suitable solvents for lubricating oils has been investigated by J. B. Willis et al [1]. They found that both kerosene and iso-butylmethyl ketone (MIBK) were suitable solvents. p-Xylene has also been recommended as a suitable solvent [2].

A description is given of a method employed at Agilent Technologies for the analysis of barium, calcium and zinc in lubricating oil additive blends.

Agilent Technologies

Experimental

Instrument

Conditions for Techtron AA-5 atomic absorption spectrophotometer

	Barium	Calcium	Zinc
Wavelength	5535.5 Å	4226.7Å	2138.6 Å
Photomultiplier	R-213	R-213	R-213
Lamp current	10 mA	4 m	A 6 mA
Slit width	3.3 Å	3.3 Å	3.3 Å
Flame Lean	$N_2OC_2H_2$	Lean $N_2OC_2H_2$	Lean $N_2OC_2H_2$
Burner	AB-50	AB-50 rotated 10°	AB-51

Oil Sample Solutions

For a typical oil additive blend containing the following concentrations of metals:

5–7% Ba

2–4% Ca

0.5–1.5% Zn

Weigh out approximately 0.25 g of the oil accurately into a dry 100 mL volumetric flask and make up to 100 mL with kerosene.

This solution will contain approximately:

125–175 ppm Ba

50–100 ppm Ca

12.5–37.5 ppm Zn

Aliquots of this sample solution are further diluted with kerosene in order to bring the metals into the appropriate concentration range for measurement by atomic absorption spectrophotometry.

For barium the solution is diluted 4-fold to give a final metal concentration of approximately 40 ppm Ba. The diluted solution should also contain an excess of an ionization suppressant such as 1,000 ppm K or Na.

For calcium a 25-fold dilution is made, giving approximately a 2–4 ppm Ca solution. Again the diluted solution should contain at least 1,000 ppm K or Na.

A 25-fold dilution is similarly made for zinc, giving approximately a 0.5–1.5 ppm Zn solution. In this case no ionization suppressant is required.

Standard Solutions

Barium and Calcium

0. 1718 g of barium cyclohexanebutyrate (29.1% Ba) is dissolved in 3 mL of xylene and 5 mL of 2-ethylhexanoic acid and diluted to exactly 50 mL with kerosene, giving a 1,000 ppm Ba stock solution.

Similarly, a 250 ppm Ca stock solution is prepared from 0.1000 g of calcium 2-ethylhexanoate (12.5% Ca).

The following composite standard Ba and Ca kerosene solutions, each containing 1,000 ppm Na as an ionization suppressant, are made up:

20 ppm Ba + 1.25 ppm Ca + 1 000 ppm Na

40 ppm Ba + 2.5 ppm Ca + 1 000 ppm Na

60 ppm Ba + 5.0 ppm Ca + 1 000 ppm Na

A stock 5,000 ppm sodium solution is prepared by weighing out and dissolving 2.100 g of sodium cyclohexanebutyrate (11.9 % Na) in 15 mL of xylene and 25 mL of 2-ethylhexanoic acid and diluting to 50 mL with kerosene.

Zinc

0.1501 g of zinc cyclohexanebutyrate (16.66 % Zn) is dissolved in 3 mL of xylene and 5 mL of 2-ethylhexanoic acid and diluted to exactly 50 mL with kerosene, giving a 500 ppm Zn stock solution.

The following standard Zn kerosene solutions are made up:

0.5; 1.0; 1.5; 2.0 ppm Zn.*

A blank solution of kerosene is used in the Zn determinations, but in the Ba and Ca measurements a blank solution of kerosene containing 1,000 ppm Na is used.

Notes on Individual Determinations

Barium

The atomic absorption measurements are made at the 5535.5 Å resonance line, using a very fuel-lean N_2O-C_2H_2 flame.

*The above Ba, Ca, Zn and Na organic salts (atomic absorption spectrometry standards) are obtainable from:

- Alfa Inorganics, Inc., 8 Congress St., Beverly, Mass. 01915, USA
- Eastman Kodak Co., Rochester, New York 14650, USA, or Kodak Ltd., Kirkby, Liverpool, England.

Calcium

The atomic absorption measurements are made at the 4226.7 Å resonance line, using a very fuel-lean N_2O-C_2H_2 flame.

Zinc

The atomic absorption measurements are made at the 2138.6 Å resonance line, using a very fuel-lean air-C_2H_2 flame.

In order to extend the analytical concentration range burner rotation may be carried out in all cases.

Atomic absorption measurements may also be carried out on ashed oil samples which have been dissolved in suitable mineral acids.

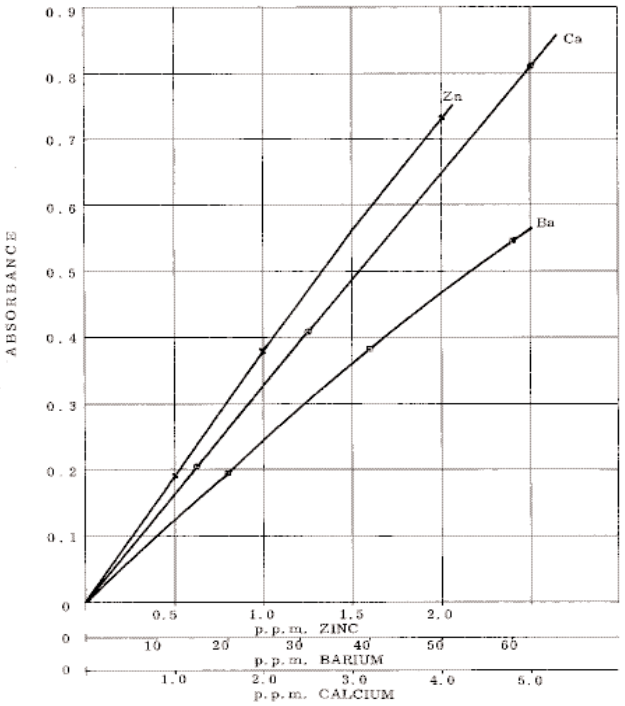
For example: weigh 10–20 g of oil into a crucible (Pt, silica, or porcelain); heat, ignite and burn the oil carefully. The residue is then heated in a muffle furnace at 550–600 °C until all the carbon has been oxidized. The residue is dissolved in a few drops of concentrated hydrochloric acid or aqua regia and finally diluted to a suitable volume.

Some Typical Results

Element	Approximate composition	A. A. results	Mean
Ba	5-7%	5.65_4 5.57_3 5.53_4	5.58_7%
Ca	2-4%	3.47_8 3.41_1 3.49_8	3.46_2%
Zn	0.5-1.5%	1.27_5 1.27_5 1.27_6	1.27_5%

Conclusion

It is estimated that a suitably equipped laboratory set up for the routine analysis of such samples could carry out the determination of these elements within 2 to 3 hours of receipt of the sample. The receipt of a larger number of samples would lead to significant increases in overall efficiency.



References

1. J. A. Burrows, J. C. Heerdt, J. B. Willis, Analytical Chemistry, **1965**, 37(4) 579-582.
2. S. Sprague and W. Slavin, Atomic Absorption Newsletter, **1963**, No. 12, April.

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