Application Note: 41636

Analysis of Oils

ARL ADVANT'X Series with IntelliPower™ Sequential X-Ray Fluorescence Spectrometer

Key Words

- ARL ADVANT'X
  - 1200W
  - 2500W
  - 3600W
- Oils
- X-Ray Fluorescence
- XRF

Introduction

X-ray fluorescence (XRF) permits the determination of various elements, already present in or added to oils, in the concentration range from part per million to percentage levels.

Instrumentation

Thermo Scientific ARL ADVANT'X Series spectrometers were used to derive the results presented in this note. The spectrometers are fitted with a Rh anode X-ray tube, type 4 GN. The geometry of the instruments is optimized to provide the highest sensitivity. Ease of operation is obtained through the state-of-the-art WinXRF software running under MS-Windows® environment.

For optimal analysis of liquids, a helium environment is used in the primary chamber (sample chamber). The ARL ADVANT'X Series are equipped with a shutter so that the spectrometer tank is kept under vacuum while the sample chamber is flushed with helium gas. This permits a rapid changeover from a vacuum to a helium environment and vice versa (solids to liquid analysis).

In addition, all the analytical components of the spectrometers are maintained under a stable vacuum environment. The goniometer is also protected from any liquid spillage and helium consumption is kept to a minimum.

Sample preparation

A series of samples were prepared from a Conostan standard containing 50 ppm of the elements listed in Table 1. Dilution with base oil produces samples containing concentrations of 5 ppm and 10 ppm respectively. The oil samples are poured directly into special liquid cells which are fitted with 6 micron thick polypropylene film.

Analytical procedure

Helium gas is used to fill the primary chamber while the spectrometer chamber is maintained under vacuum. X-ray tube excitation is modulated in order to get optimum excitation of the various elements. Measurements of the oil samples allow creation of calibration curves which are used to calculate sensitivities and limits of detection. The base oil is used as a blank sample. In practice, the counting time (analysis time) chosen for each element depends on the precision and throughput required. In Table 1, limits of detection have been calculated for 100 seconds counting time.

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Results

Elements measured, crystals and detectors used, Standard Error of Estimate and limits of detection achieved are shown in Table 1.

ELEMENT	CRYSTAL DETECTOR	SEE [ppm]	ARL ADVANT'X 3600 W LOD [ppm]	ARL ADVANT'X 2500 W LOD [ppm]	ARL ADVANT'X 1200 W LOD [ppm]
Mg	AX06/FPC	1.7	2.2	2.64	3.7
Al	PET/FPC	0.5	0.67	0.80	1.14
Si	PET/FPC	0.6	0.38	0.46	0.65
S	GE111/FPC	0.5	0.25	0.30	0.43
Ca	LIF200/FPC	0.1	0.17	0.20	0.29
Cr	LIF200/FPC	0.2	0.14	0.17	0.24
Mn	LIF200/FPC	0.2	0.14	0.17	0.24
Fe	LIF200/FPC	0.2	0.15	0.18	0.26
Cu	LIF200/SC	0.2	0.12	0.14	0.2
Zn	LIF200/SC	0.2	0.11	0.13	0.19
Sn	LIF200/FPC	0.4	0.57	0.68	0.97
Pb	LIF200/SC	0.1	0.14	0.17	0.24

Table 1: Analytical results

FPC = flow proportional counter
SC = scintillation counter
SEE = Standard error estimate = a measure of accuracy
LOD = Limit of detection = 3√ BEC/Qt
BEC = background equivalent concentration
Q = sensitivity
t = time

Table 2 shows the results of a precision (repeatability) test performed by analyzing an oil sample 10 times, the sample remaining in the spectrometer. A counting time of 40 seconds per element was used on the ARL ADVANT'X at 2500W. The results show excellent precision for Fe, Pb, Si and S.

RUN	Fe [ppm]	Pb [ppm]	Si [ppm]	S [ppm]
1	5.1	4.5	4.7	12.4
2	4.9	4.1	4.6	12.8
3	5.0	4.1	4.9	12.4
4	5.2	4.0	5.3	12.7
5	5.3	4.4	4.8	12.3
6	5.4	4.5	4.7	12.7
7	5.2	5.0	4.0	12.3
8	5.6	4.1	4.9	12.6
9	5.4	4.7	4.2	12.6
10	5.6	5.0	4.7	12.3
Avg [ppm]	5.3	4 4	4.7	12.5
Sd [ppm]	0.2	0.4	0.4	0.2
Rsd (%)	4.4	8.7	7.9	1.4

Table 2: Precision test

Concentration values in ppm
Avg = average
SD = standard deviation (1 sigma)
RSD = relative standard deviation

Conclusion

Limits of detection well below the 1 ppm level are achieved by XRF for most elements found in oil samples. X-ray fluorescence for the lighter elements is absorbed by the plastic foil that keeps the sample in the analysis cell, hence their limits of detection are higher. High reproducibility can be obtained even for elements present at concentration levels below 10 ppm.

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