Detection and analysis of waste engine oil (WEO) residues in asphalt cements using X-Ray Fluorescence (XRF) spectroscopy

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There is a strong correlation between the presence of waste engine oil (WEO) residue in asphalt cement and premature deterioration of pavements in Northern Ontario.

X-Ray Fluorescence (XRF) provides an excellent method for the detection and analysis of WEO residues in asphalt cement.
The Bruker Tracer III Hand-Held XRF Analyser

Can be operated by an iPAC (pocket computer) or connected to a laptop.
X-Ray Fluorescence (XRF)

40 keV incident X-ray beam

Ionization of atom (electron ejected from inner shell)

Electrons in shells (K, L, M, etc.)

Atomic Nucleus

fluorescent X-ray beam (element-specific energies)

Electron transition
L to K shell (Kα)
M to K shell (Kβ)

X-Ray Analyzer

X-Ray Analyzer
Engine Lubricating Oils

Zinc dialkyldithiophosphate (ZDTP) is a universal anti-wear additive used in commercial engine oils.

![Zinc dialkyldithiophosphate (ZDTP) molecular structure](image)

(R = alkyl)

Molybdenum disulphide MoS$_2$ is also used.

These compounds end up in the residue from the re-refining of waste engine oil. This material is often used as an asphalt extender.

Zn and Mo can be detected by XRF analysis.
XRF spectra of two motor oils and a sample of WEO residue

Note: The spectra of the oils have been multiplied by 10.
XRF spectra of pure Cold Lake asphalt and mixtures containing 4, 8, 12, 16 and 20% waste engine oil (WEO) residue.

Comments: Boldface symbols are Kα lines. Small face symbols for Ca and Fe are Kβ lines. It can be seen that small amounts of S, V, Cr and Ni are present in the pure asphalt. Ca, Mn, Fe and Cu increase with increasing % WEO.
XRF spectra of various amounts of WEO residue mixed with pure Cold Lake Alberta asphalt
The intensities (counts) of the zinc (Kα) peaks in the XRF spectra give a calibration curve for WEO residue in Cold Lake Alberta asphalt.

\[ r^2 = 0.98 \]
XRF Spectra for Seven Binders for Timmins Ontario Trial Pavements in 2003

Approximate Levels of WEO residue:

- ~ 8-10%
- ~ 15%
- None
- ~ 2-4%
- ~ 8-10%
Section 4

- High zinc content (High WEO residue in asphalt cement).
- Severe cracking in both lanes.
- Transverse cracks sprouting out from wheel path and joint.
- Cracking is beyond repair.
Section 5

- No zinc found. (No WEO residue)
- Largely free of distress.
- Centerline joint and shoulders in almost perfect condition.
- Made with linear SBS-modified asphalt cement (4% polymer)
Summary

- X-ray fluorescence spectroscopy provides a simple and rapid method to detect zinc and molybdenum in asphalt cement.

- Zinc and molybdenum are not found in straight asphalt.

- Zinc and molybdenum are present in the residues from re-refining of waste engine oil (WEO).
Conclusions

- The presence of zinc and molybdenum in asphalt cement indicates that WEO residue is present in the asphalt cement.

- The amount of WEO residue present in an asphalt cement can be estimated from the intensity (counts) of the zinc Kα line in the XRF spectrum.

- WEO residue is very likely a contributing factor in widespread premature and excessive pavement cracking.
P.S. Zinc (from ZnO) is also found in asphalts prepared using crumb rubber. In such cases the XRF spectrum shows a peak at 11.9 keV due to bromine from the rubber. (The Mo peak shows that WEO residue also is present)

NOTE: Zinc oxide is occasionally used to scavenge H₂S in polymer-modified asphalt. Again, a Mo peak will show the presence of WEO residue.