Quantitative Issues In Asphalt Infrared Spectra Interpretation

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Acknowledgements:

SHRP PROGRAM

The Transportation Technology Staff at WRI

Federal Highway Administration
Quantitative Issues In Asphalt Infrared Spectra Interpretation

- Asphalt: The analyst’s nightmare
- Thousands of high boiling compounds
- Infrared provides information concerning functional groups, but analysis for compounds is very difficult
- The spectrum is not a pure compound. It is the sum of a complex mixture of compounds
Problem:

Sophisticated studies, (ie, mechanistic kinetics, phase field studies) require the best precision and accuracy obtainable.

How can we get more and better information from the IR spectra?
• The relationship between the absorbance and the actual concentration of the functional group is given by Beer’s law:

\[ A = \varepsilon bc \]

- The molar absorptivity value ONLY applies to a given compound in a given solvent.
Unfortunately, the absorbtivity of a functional group varies with the molecule it is attached to.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Location</th>
<th>Molar Absorbtivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl sulfoxide</td>
<td>1056</td>
<td>2446</td>
</tr>
<tr>
<td>Butyl sulfoxide</td>
<td>1037</td>
<td>4498</td>
</tr>
<tr>
<td>Didecyl sulfoxide</td>
<td>1055</td>
<td>7439</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>1070</td>
<td>4633</td>
</tr>
<tr>
<td>Pentyl sulfoxide</td>
<td>1043</td>
<td>2939</td>
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</tbody>
</table>
Possible improvements

- Reference Subtraction (works well with oxidation studies)
- Solvent defined separations
- Derivatization (Chemical reactions with functional groups, functional group analysis)
- Peak Series Expansion
- Multivariable Linear Regression
Full Spectra of eight aged asphalts (20 atm) in carbon disulfide
Reference Subtraction

Full Spectra of eight aged asphalts (20 atm) in carbon disulfide after subtracting rtfo spectrum
New Jersey asphalt SARA fractions ATR Spectra (courtesy Troy Pauli WRI)

- Naphthalene Aromatics
- Polar Aromatics
- Saturates

Graph showing the absorbance versus wave number for different fractions.

Absorbance - dimensionless
Wave Number 1/cm

-600  800  1000  1200  1400  1600
This is an example of a differential Spectrum for determining Carboxylic acid after silylation.
Functional Group Analysis

• Functional group analysis is the best available method for detailed separations of overlapping functional groups.
• Requires a skilled analyst, and considerable time and effort.
• Limited to the groups addressed in derivatization scheme (phenols, pyrroles, ketones, carboxylic acids, 2-quinolones, anhydrides, sulfoxides).
• Other methods to address additional functional groups could be designed.
Quantitative Issues In Asphalt Infrared Spectra Interpretation

Peak Series Analysis

AAB 80C 480 hr PAV

Wave Number 1/cm

Adsorbance - dimensionless

Abs and frequency columns in a Peak Shape Function Location Parameter

Width Parameter

Amplitude or Height

\[
\begin{align*}
\text{Abs} & = \sum_{i} SP_{i} \omega_{i} \\
\text{Width} & = 2 \sum_{i} P_{i} \omega_{i} \\
\text{Amplitude} & = \text{Height}
\end{align*}
\]
Many investigators have attempted this approach

- Typically, a sum of squares error function employed or matrix methods
- Typically, a single spectrum is examined
- Plagued by lack uniqueness issues
Mitigation of Uniqueness Issues

- A regression problem over a series of spectra (aging series)
- The error function includes derivatives to indicate hidden peaks
Set of $\sigma$ and $\omega_0$ the same for all asphalts?

\[
P(\omega) = A_i e^{-\frac{(\omega-\omega_i)^2}{2\sigma_i^2}}
\]

\[
S(\omega_j) = \sum_{i=1}^{n} A_i \chi_i
\]

\[
\chi_i = e^{-\frac{(\omega_j-\omega_i)^2}{2\sigma_i^2}}
\]
20 atm 80 C aged SHRP asphalts 480 hours
-2nd Derivative Peak Width Study

- differential Adsorbance -1/cm\(^2\)

Wave Number 1/cm

Graph showing the 2nd derivative peak width study for 20 atm 80 C aged SHRP asphalts over 480 hours.
AAB 20 atm aged spectra (11)
-2nd Derivative

- differential Adsorbance -1/cm^2

Wave Number 1/cm
Quantitative Issues In Asphalt Infrared Spectra Interpretation

Peak Series Analysis – Preliminary results

AAB 80C 480 hr PAV

Wave Number 1/cm

Adsorbance - dimensionless
Peak Series Analysis - Regression results

<p>| | | | | |</p>
<table>
<thead>
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<th></th>
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Quantitative Issues In Asphalt

Infrared Spectra Interpretation

Peak Series Analysis - First Derivative Fit

AAB 80C 480 hr PAV

![Graph](image-url)
Quantitative Issues In Asphalt Infrared Spectra Interpretation

Peak Series Analysis - 2nd Derivative Fit

AAB 80C 480 hr PAV

Wave Number 1/cm

Adsorbance - dimensionless
Peak Series Analysis

- This method shows promise as a research tool, both for asphalt and other complex systems.
- Use at the spec test level unlikely, except possibly over narrow regions.
- The uniqueness concerns still remain and critical areas of the spectra would need to be verified with model compounds and/or chemical derivatization methods, if possible.
Multivariable Linear Regression

- Very easy to use, and fast
- Produces much the same information as Peak Series
- WRI is producing a software product specifically designed for spectral applications
Multivariable Linear Regression

Eight Asphalt 1037 and 1700 Change Fit to Change $\ln(G^*)$

$r^2 = 0.91$ (74 Spectra)

$\ln(G^*) = 0.01 + 1.38 \times 1037 + 3.20 \times 1700$
Multivariable Linear Regression-Simple

AJDRSQR 0.9110

<table>
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<tr>
<th>x</th>
<th>Coefficient</th>
<th>group no.</th>
<th>F</th>
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Quantitative Issues In Asphalt Infrared Spectra Interpretation
Multivariable Linear Regression

• Adding peak overlap correctors results in significant improvement of fit

Eight Asphalt 1037 and 1700 Change Fit to Change ln(G*)
r^2=0.97
With overlap correctors

![Graph showing correlation between Predicted Ln(G*) and Measured Ln(G*) with r^2=0.97]
**Multivariable Linear Regression**

Regression data

<table>
<thead>
<tr>
<th>Code by Ron</th>
<th>Variable x</th>
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- **Adding peak overlap correctors – How do we do that?**
Deconvolution not helpful

\[(f(t) * g(t)) = \int_{-\infty}^{\infty} f(\tau)g(t - \tau)\,d\tau\]

- Convolution and De-convolution
SUMMARY

• Quantitative molar values in asphalt spectra will have fairly high uncertainty.

• A number of methods exist to increase the likelihood that the absorbance measurement describes the target functional group.

• Quite good relationships can be obtained using absorbance without computing molarity.

• WRI will employing many of the described methods in our current aging studies.