Online NIR-Spectroscopy for the Live Monitoring of Hydrocarbon Index (HI) in Contaminated Soil Material
The Hydrocarbon Index (HI)

Definition

- It is a cumulative parameter
  - no absolute method
- Includes all hydrocarbons between $\text{C}_{10}\text{H}_{22}$ and $\text{C}_{40}\text{H}_{82}$ that...
  - boil between 175 and 525 °C
  - do are not absorbed by magnesium silicate (non-polar)
The Task
Description and Requirements

- contaminated waste is burned in cement factory to reduce amount of toxic hydrocarbons
  - only hydrocarbons between $C_{10}H_{22}$ and $C_{40}H_{82}$, with boiling points of 175 - 525 °C
  - only apolar substances

  ➢ Selectivity

- Online/Process Analysis before the oven
  - method should be fast and exact
  - no sample preparation should be needed
  - no sample destruction

- the instrument of choice should be robust and preferably cheap
The Task
Some Background Information

- Cement factory is used, because their ovens have $T \sim 1500 \, ^\circ C$
# The Old Methods

**FID/GC**

## F-9 Kohlenwasserstoff-Index C\textsubscript{10}–C\textsubscript{40} in Feststoffproben (GC FID)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Kohlenwasserstoff-Index C\textsubscript{10}–C\textsubscript{40}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Konserverung und Aufbewahrung</td>
<td>Keine besonderen Vorkehrungen; Proben in möglichst dicht verschlossenen Behältern (Glasgefäße, für größere Probenmengen Plastikflaschen) gekühlt transportieren und lagern.</td>
</tr>
<tr>
<td>Probenvorbereitung</td>
<td>Trocknen, Brechen, Mahlen gemäss Kapitel 4.2</td>
</tr>
<tr>
<td>Probenaufbereitung</td>
<td>Extraktion der feuchten oder getrockneten Probe mit Lösungsmittelgemisch gemäss Norm, Ab trennung von Aceton durch Extraktion mit Wasser und anschliessend Reinigen des Extraktes über Florisil.</td>
</tr>
<tr>
<td>Messmethode</td>
<td>Gaschromatographie mit FID-Detektion; Alle Bedingungen der SN EN 14 039 insbesondere in Bezug auf die QS-Massenahmen, Injektionsbedingungen und Kalibrierung müssen zwingend eingehalten werden (Konventionsmethode).</td>
</tr>
<tr>
<td>Auswertung</td>
<td>Integration aller Signale zwischen C\textsubscript{10} (n-Decan) und C\textsubscript{40} (n-Tetracontan). Kalibrierung mit Öl-Standard-Gemisch gemäss Norm.</td>
</tr>
<tr>
<td>Gehaltsangabe</td>
<td>in mg/kg bezogen auf das Trockengewicht (105 °C) der Probe.</td>
</tr>
<tr>
<td>Qualitätssicherung</td>
<td>Die Qualitätssicherungsmassnahmen der Normen (s. Literatur) in Bezug auf Aktivität des Florisils, der Wiederfindung des Ölstandards einhalten und dokumentieren.</td>
</tr>
<tr>
<td>Bestimmungsgrenze</td>
<td>20 mg/kg TS (aliphatische Kohlenwasserstoffe)</td>
</tr>
<tr>
<td></td>
<td>Diese Bestimmungsgrenze (BG) liegt unter derjenigen der zitierten Methode (100 mg/kg); sie kann jedoch bei Anwendung von leichten Modifikationen bei der Aufkonzentrierung und/oder Messung unter Verwendung von reinen Lösungsmitteln erreicht werden.</td>
</tr>
<tr>
<td>Literatur</td>
<td>[25]: SN EN 14039</td>
</tr>
<tr>
<td></td>
<td>[26]: ISO 16703</td>
</tr>
<tr>
<td>andere Verfahren</td>
<td>Da die erfasste Fraktion der Kohlenwasserstoffe über die Messmethode definiert ist, können keine alternativen Methoden eingesetzt werden.</td>
</tr>
</tbody>
</table>
The Old Methods

FID/GC

- extraction of grinded/powdered sample
  - with hexane/acetone and water
- filtration over Florisil (magnesium silicate)
- LOQ = 20 mg/kg (20 ppm)
- Area between $n$-Decan and $n$-Tetracontan used for HI-calculation
  - Calibration beforehand with standards/spikes
# The Old Methods

**FID/GC**

<table>
<thead>
<tr>
<th>Requirement</th>
<th>GC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selectivity for C&lt;sub&gt;10&lt;/sub&gt;-C&lt;sub&gt;40&lt;/sub&gt;</td>
<td>✔</td>
</tr>
<tr>
<td>exclude polar substances</td>
<td>✔</td>
</tr>
<tr>
<td>online/process Analysis</td>
<td>❌</td>
</tr>
<tr>
<td>robust</td>
<td>❌</td>
</tr>
<tr>
<td>fast measurement</td>
<td>❌</td>
</tr>
</tbody>
</table>
Near Infrared Spectroscopy
An Overview

NIR in the Electromagnetic Spectrum

- range: 12800 – 4000 cm\(^{-1}\) (780 – 2500 nm)
- shows Overtone & Combination Bands -> lower intensities
  - CH, OH, NH functionalities

Near Infrared Spectroscopy
An Overview

<table>
<thead>
<tr>
<th>Band</th>
<th>Range</th>
<th>Wavelength (C-H) [nm]</th>
<th>Relative Intensity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fundamental</td>
<td>Mid-IR</td>
<td>3380-3510</td>
<td>100</td>
</tr>
<tr>
<td>1st overtone</td>
<td>Mid-IR or NIR</td>
<td>1690-1755</td>
<td>1</td>
</tr>
<tr>
<td>2nd overtone</td>
<td>NIR</td>
<td>1127-1170</td>
<td>0.1</td>
</tr>
<tr>
<td>3rd overtone</td>
<td>NIR</td>
<td>845-878</td>
<td>0.01</td>
</tr>
<tr>
<td>4th overtone</td>
<td>NIR</td>
<td>690-770</td>
<td>0.005</td>
</tr>
</tbody>
</table>

- Intensities much lower
  - Changes in concentration harder to detect
  - LOD = 0.1–0.5%

Near Infrared Spectroscopy

Important Features

- „fingerprint“
  - signature of the physical state of order observable
- no sample preparation needed
- penetration depth up to a few cm
- less scattering than in UV-Vis

Near Infrared Spectroscopy
The Spectrum

Monograph – NIR Spectroscopy; Metrohm
Near Infrared Spectroscopy
The Spectrum

Wavelength (nm)
Near Infrared Spectroscopy
The Spectrum

Near Infrared Spectroscopy
The Spectrum

- The spectrum is influenced by
  - particle size
  - porosity and surface
  - refractive index
  - packing density
  - temperature
  - water content
Near Infrared Spectroscopy

Measurement Techniques

Factors that Influence NIR Spectra

Water

- Wavelength shift due to water (also H-bonds)
- Peak shape varies with water content
  - Broadness increases with water content
- Baseline shift due to water content
- Absorption increases with water content

Factors that Influence NIR Spectra

Particle Size

- baseline shifts with particle size
- larger particles absorb more radiation

cellulose samples
a: 24 µm
b: 45.8 µm
c: 93.4 µm
d: 261 µm
e: 406 µm

Monograph – NIR Spectroscopy; Metrohm
Interesting Example

Norris, K.H.; J. Near Infrared Spectrosc., 1996, 4, p. 31-37
The calibration is the most important part for quantitative analysis. Take several hundred samples (inhomogeneous) to cover large concentration regions. Grind and dry samples. Spike samples with oil of known concentration. Measure and assign bands of importance. Use data to get a calibration curve and cross-check HI with GC method.

Data evaluation and calibration works by pattern recognition instead of single peak observation.
Statistical Techniques
Principle Component Analysis

- Linear data transformation
- Goals:
  - Information about relevance (variance)
  - Independent from each other (orthogonal)

1. Centering & Scaling
2. Matrix transformation $X = t_1 p_1^T + t_2 p_2^T + \cdots$
   So that all $t_x$ are orthogonal and each $t$ describes the maximum variance
3. The Eigenvalue of $p_x$ describes the fraction of the total variance
4. Selection of relevant Eigenvalues & plotting in the corresponding dimensions ($t_x$)

NIR of glucose/fructose/sucrose mixture

Statistical Techniques
Univariate Linear Regression

\[ A_3 = \epsilon c_3 \]
\[ A_2 = \epsilon c_2 \]
\[ A_1 = \epsilon c_1 \]

\[ c_A = \frac{1}{\epsilon l} A_A = b A_A \]
Statistical Techniques
Multiple Linear Regression (MLR)

\[ A_1 = \epsilon_{11} l c_1 + \epsilon_{12} l c_2 \]
\[ A_2 = \epsilon_{21} l c_1 + \epsilon_{22} l c_2 \]

\[ c_1 = b_{11} A_1 + b_{12} A_2 \]
\[ c_2 = b_{21} A_1 + b_{22} A_2 \]

Statistical Techniques
Partial Least Squares (PLS)

## Statistical Techniques

### Comparison MLR - PLS

<table>
<thead>
<tr>
<th>MLR</th>
<th>PLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proper choice of absorbances at different wavelengths is required. Not too many should be considered. In particular no collinear absorbances.</td>
<td>Visual results (loadings) might help for the interpretation. However physical meaning of the new coordinates are hard (if not impossible) to interpret, since they are linear combinations of the initial coordinates.</td>
</tr>
<tr>
<td>Struggles with multicollinearity i.e. strong correlations between absorbances at different wavelengths.</td>
<td>Can deal with multicollinearity.</td>
</tr>
<tr>
<td>Model requires more observations than predictor variables (absorbances).</td>
<td></td>
</tr>
</tbody>
</table>


## Alternative Methods

<table>
<thead>
<tr>
<th>Requirement</th>
<th>NIR</th>
<th>IR</th>
<th>Raman</th>
<th>GC</th>
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<tbody>
<tr>
<td>Selectivity for C_{10}-C_{40}</td>
<td>✔</td>
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<td>✔</td>
<td>(X)</td>
<td>✔</td>
<td>(X)</td>
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<td>robust</td>
<td>✔</td>
<td>✔</td>
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<td>(X)</td>
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<td>fast measurement</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>(X)</td>
</tr>
<tr>
<td>no sample preparation</td>
<td>✔</td>
<td>(X)</td>
<td>✔</td>
<td>(X)</td>
</tr>
<tr>
<td>limitations/problems</td>
<td>no structure elucidation</td>
<td>water interference</td>
<td>broad fluorescent baseline</td>
<td>time-consuming</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>saturation of detector</td>
<td></td>
</tr>
</tbody>
</table>

**Note:**

- "✔" indicates the method is suitable for the given requirement.
- "(X)" indicates the method is not suitable for the given requirement.
Thank you for your attention