Innovative Multipurpose vis-NIR Spectroscopy for Real-time Physical and Chemical Characteristics of Dense Media & Counterfeit Detection

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Process Spectroscopy

- Light-induced fluorescence
- Raman
- UV-vis
- NIR
- MIR/FTIR

But in many processes the fluids are often turbid, containing light-scattering components (particulate, emulsion etc.) that varies the optical path length.
Motivation

- **Real time assurance**
  - Continuous product quality monitoring
  - Efficient control of process
  - End point prediction

- **Real-time estimation of physical and chemical characteristics of particulate systems**

- **Model reliability and robustness to changes in light scattering effect**

- **Ultimately, free from building calibration model**
Absorption Spectroscopy

- **Beer-Lambert Law**

\[ A(\lambda) = -\ln(T_c) = -\ln \left( \frac{I(\lambda)}{I_0(\lambda)} \right) \]

\[ = l \sum_{i=1}^{n} \sigma_{a,i}(\lambda) c_i \]

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- \( \sigma_a \): absorption cross-section
- \( c \): concentration
- \( \mu_a \): bulk absorption coefficient (mm\(^{-1}\))

**Beer-Lambert law hold when:**

i) pure absorption (no scattering);

ii) single scattering

(extinction spectra = absorption + single scattering spectra)
Light Scattering Spectroscopy

• When light is scattered multiple times

  i) Scattering is wavelength dependent
     ➔ Complex scattering steps

  ii) Optical path length no longer a constant
     ➔ Beer’s law for absorption is no longer valid

  iii) Collimated transmittance could be contaminated by forward scattered light
     ➔ Diffuse reflectance & transmittance spectra is more difficult to analyse
Light Scattering Effect

- Characteristics of light scattering effect

**Occurs at interface – mismatched refractive index**

Non-linear

\[ \mu_s(\lambda) = \sigma_s(\lambda) \cdot c \]

- \( \sigma_s \): scattering cross-section
- \( c \): concentration of scatters
- \( \mu_s \): bulk scattering coefficient (mm\(^{-1}\))

Anisotropic

\[ \sigma_s(\lambda) = 2\pi \int_0^\infty \int_0^{\pi} f(D)F(\theta, D, m, \lambda) \sin \theta d\theta dD \]

- \( F \): Differential cross-section
- \( D \): Characteristic dimension of the particle
- \( f(D) \): Population density function (particle size distribution)
- \( m(\lambda) \): Complex refractive index = \( n(\lambda) + ik(\lambda) \)

Anisotropic factor \( g(\lambda) \):

- Describe angular distribution of scattered light.
- Related to:
  - Refractive indices of particulate & dispersant
  - Particle size
  - Particle shape
Bulk Optical Properties (Polystyrene Nanoparticles)

\( \mu_a \) : 1-40% polystyrene

\( \mu_s \) : 100-500nm diameter @ 10% particle conc.

\( g \) : 100-500nm diameter

\( \mu_a \) : Linearly dependent on conc.

\( \mu_s \) : Featureless profile, non-linear change to size

\( g \) : Non-linear change of the wavy shape
Radiative Transfer Theory

- Radiative transfer equation (RTE):
  \[
  \frac{dI(r,s)}{ds} = - \left( \mu_a + \mu_s \right) I(r,s) + \frac{\mu_s}{4\pi} \int p(s,\hat{s}) I(r,\hat{s}) d\omega
  \]
  \[
  \mu_a : \text{bulk absorption coefficient}
  \]
  \[
  \mu_s : \text{bulk scattering coefficient}
  \]

- Exact Solution: Adding-Doubling (ADD) Approach
  \[
  \text{Reflectance} = \int_0^1 R(\mu_0,\mu) I(\mu_0) 2\mu_0 d\mu_0
  \]
  \[
  \text{Transmittance} = \int_0^1 T(\mu_0,\mu) I(\mu_0) 2\mu_0 d\mu_0
  \]

- Approximation: Kubelka-Munk (K-M) Theory
  \[
  I - I' = dI = (K+S) I dx - S J dx
  \]
  \[
  J - J' = dJ = -(K+S) J dx + S I dx
  \]
  \[
  K : \text{K-M absorption parameter}
  \]
  \[
  S : \text{K-M scattering parameter}
  \]
Solving RTE

Biological fluid model system

<table>
<thead>
<tr>
<th>Variables</th>
<th>Intralipid</th>
<th>Glucose</th>
<th>Urea</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition / g/dL</td>
<td>5 – 10</td>
<td>0.52 – 3.74</td>
<td>1.61 – 2.98</td>
<td>85 – 93</td>
</tr>
<tr>
<td>Intralipid</td>
<td>1.00</td>
<td>-0.13</td>
<td>0.21</td>
<td>-0.39</td>
</tr>
<tr>
<td>Glucose</td>
<td>-0.13</td>
<td>1.00</td>
<td>-0.05</td>
<td>-0.27</td>
</tr>
<tr>
<td>Urea</td>
<td>0.21</td>
<td>-0.05</td>
<td>1.00</td>
<td>-0.15</td>
</tr>
<tr>
<td>Water</td>
<td>-0.39</td>
<td>-0.27</td>
<td>-0.15</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Total 50 samples: 40 in calibration data set + 10 in test data set

- Intralipid® : emulsified soya milk, light scatterer
- Glucose : primary analyte
- Urea : secondary analyte
- Water : sample matrix
Diffuse Approximation (DA)

- ADD & K-M approaches need reflectance & transmittance measurements
  ➔ Not feasible for inline measurement
- DA requires multiple reflectance measurement
  ➔ A probe-base system??

Starting from simplest form of DA:

\[
R = \frac{\text{albedo}}{4 \pi} \left[ \frac{(\Delta z + 2zb)(1 + \mu_{\text{eff}} d_1) \exp(-\mu_{\text{eff}} d_1)}{d_1^3} + \frac{(\Delta z)(1 + \mu_{\text{eff}} d_2) \exp(-\mu_{\text{eff}} d_2)}{d_2^3} \right]
\]

\[
\mu_{\text{eff}} = \mu_a + \mu_s' \quad \text{where } \mu_s' = \mu_s(1 - g)
\]

\[
\text{albedo} = \frac{\mu_s'}{\mu_a + \mu_s'}
\]

Key assumptions:
- Point source & point collection
- first scattering @ the same place
- Strongly scattered : ( \( \mu_s' \gg \mu_a \) )
Inverting Optical Properties

Depend on the method used:
- require at least 2 spectra (from diff. configurations) to solve the 2 unknowns in DA

Iterative optimisation process

1. Guess **albedo** and **$\mu_{\text{eff}}$**
2. Run forward diffuse approximation.
3. Calculate error - the difference between calculated reflectance and real reflectance.
4. For error within tolerance, inversion was successful.
5. Obtain optical properties ($\mu_a$, $\mu'_s$)
6. For error outside tolerance ➔ Generate new guess parameter.
Conventional Probe-base Measurement

• Reflectance Probe

• Transmittance Probe

- Suspending Media Particulates (droplets, particles etc.)

• Single model probe for entire process
  - No flexibility for optimise config. to follow process
• Signal differentiation removed
  - Signal from different fibre distances are combined.
Spatially & angularly-resolved diffuse reflectance (SARDR)

For the fluid containing high particle contents, more light returns back from the sample than the light travels through it.

➔ Reflectance measurement is preferred.

- Spatially-resolved
- Spatially + Angularly-resolved

Adding another dimension of measurement!
Does the multi-mode probe work better?

- **Data Analysis Strategy**
  - Single mode probe look at combined signal from all collecting fibres.
  - Multi-mode probe capture difference in reflectance information from individual fibres
Configurations 1 – 4

- Using each source-detector fibre distance 1 – 4.
  - Sum up all fibres at each distance together and compare against using just 1 fibre.
  - To test if S/N gained by adding more fibres will give better model performance.
  - No pre-processing

**Open symbol : ‘Summed-up’; Close symbol : ‘Individual’**

Similar RMSECV curves profiles & RMSEP levels

⇒ S/N Improvement by adding more fibre is limited
Combining Configurations

- Configuration 5: Use all 4 distances, normally incident light.
- Configuration 6: Config 5 + one angular incident source.
- Configuration 7: Config 6 + 2nd angle
- No pre-processing.

Open symbol: ‘Summed-up’;
Close symbol: ‘Individual’

Better model performance from ‘Individual’ approach

Can we obtain better results using radiative transfer theory for separating absorption and scattering?
Indigestion and Heartburn remedy suspensions

- **Generic – 100% ($\lambda$@700nm)**

- **Generic – 10% ($\lambda$@700nm)**

- **Diff. conc. (from closest fibre)**

- **Diff. between Generic & Branded**:
  Spectral diff. attributes to diff. properties (physical/optical) of the particulate + diff. in the supplementary ingredients
Interpret the Spectral Difference (Simplest DA)

Baseline slope on \( \mu_a \): weaker scattering @ longer wavelength
(also evident on \( \mu_s' \))
Re-visit DA

• Simplest form for DA

\[
R = \frac{\text{albedo}}{4 \times \pi} \left[ \frac{(\Delta z + 2zb)(1 + \mu_{\text{eff}}d_1)\exp(-\mu_{\text{eff}}d_1)}{d_1^3} + \frac{(\Delta z)(1 + \mu_{\text{eff}}d_2)\exp(-\mu_{\text{eff}}d_2)}{d_2^3} \right]
\]

Key assumptions:

- 1\textsuperscript{st} scattering @ the same place  → Extended beam profile
- Point source & point collection → Fibre dia. need to be counted
- Strongly scattered: ( \( \mu_s' \gg \mu_a \) ) → Examine the validity

• Groenhuis’s eqn. for DA (Ext. beam profile)

\[
R(\rho) = \frac{1}{2\pi} \left( \frac{1 - r_S}{\pi} \right)^2 8\mu_s' \sum_{i=1}^{\infty} \frac{\Gamma_i z_i}{\left( k_i^2 + \mu_{\text{tr}}^2 \right)\lambda_i} I_1(\lambda_i r_f) K_0(\lambda_i \rho)
\]

• Raynold’s eqn. for DA (account for fibre dia.)

\[
R(\rho) = (1 - r_S)^2 \frac{8\mu_s'}{4\pi} \sum_{i=1}^{\infty} \frac{\Gamma_i z_i}{\left( k_i^2 + \mu_{\text{tr}}^2 \right)\lambda_i^2} \left[ \left( \frac{r_f^2}{2} - r_b \ast r_f K_1(\lambda_n r_b) I_1(\lambda_n r_f) - \frac{r_f^2}{2} - r_a \ast r_f K_1(\lambda_n r_a) I_1(\lambda_n r_f) \right) \right]
\]
Conclusions

• Potential to use physical-based method (RTE) to provide reliable source of information on physical & chemical characteristics
  - Multiple approach available to solve RTE
  - SARDR can be combined with DA for real-time monitoring

• Angularly-resolved diffuse reflectance spectroscopy add an extra dimension to capture sample information
  - Multi-mode SARDR probe better capture info. related to physical & chemical characteristics

• Multi-mode SARDR probe + physical-based algorithm (DA) can decouple physical & chemical characteristic in the spectra

• Performance on quantitative analysis using more realistic DA eqn. will need be established.
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