Optical characterization of the composition and scatterer size distributions of turbid liquids from Vis/NIR spectroscopy

W. Saeys, A. Postelmans, R. Watté, R. Van Beers, B. Aernouts
Wouter.saeys@kuleuven.be
Overview

• Introduction

• From optical measurements to bulk optical properties
  o Double integrating spheres
  o Spatially resolved spectroscopy

• From scattering spectra to particle size distribution
  o Shape dependent
  o Shape independent
  o Case study polystyrene particles

• Conclusions
Introduction
Light propagation in turbid media

Incident light → Absorption

Scattering
Bulk scattering and absorption coefficient

- **Bulk absorption coefficient** $\mu_a$
  - Probability of photon absorption per unit infinitesimal pathlength

- **Bulk scattering coefficient** $\mu_s$
  - Probability of photon scattering per unit infinitesimal pathlength
  - Non-linear effect on light extinction
Anisotropy factor $g$

Particle $<<$ wavelength
Anisotropy $= 0$
Isotrope scattering

Particle $\approx$ wavelength
Anisotropy $\approx 0.6$

Particle $> \text{wavelength}$
Anisotropy $\rightarrow 1$
Optical properties and product characteristics

• Why interest in bulk optical properties?
  → Related to emulsion/suspension characteristics

Bulk optical properties

- Chemical composition
- Particle size distribution
- Volume fraction

Chemical

Physical

\[ \mu_a \]  
\[ \mu_s \]
Research hypothesis

Chemometrics

Composition

Absorption $\mu_a$

Microstructure

Scattering $\mu_s$ & $g$

Inverse microscale light propagation models

Inverse light propagation models

$R(t,r)$

$T(t,r)$
Bulk optical properties

From optical measurements to BOP
BOP from optical measurements

- Calculate BOP from multiple (uncorrelated) measurements

**Reflectance & transmittance**
- Double integrating spheres (DIS)
- Unscattered transmission (UT)

**Multiple distances from light source**
- Spatially resolved spectroscopy (SRS)
Double integrating spheres set-up

550 – 2250 nm

Monochromator

Unscattered transmission

Total reflection

Total transmission

Inverse adding-doubling (IAD)

- Find optical properties that correspond to measured reflection and transmission

- 3 optical measurements
  - Diffuse reflection
  - Diffuse transmission
  - Unscattered transmission

- Iterative process
Inverse adding-doubling (IAD)

- Initial guess BOP
- Calculate reflection + transmission
- Update BOP
- Calculated vs. measured
  - Match?
  - BOP found

- Thin slab
  - Known BOP, reflection, transmission
  - Adding or Doubling
  - Correct thickness?
  - Reflection + transmission found
  - Summing reflections and transmission contributions
Example: optical phantoms

- Intralipid concentration
- Methylene blue concentration

$R^2 = 0.996$ (up to 70 µM)
Spatially resolved spectroscopy (SRS)

- Detectors at multiple distances from light source
- Interaction history is function of distance $d$
  - Further from light source
    - Lower signal
    - More interaction with tissue
- Intensity profile $R(d)$
- Possible for dense samples without dilution
Estimate BOP from SRS data

• Forward light propagation model
  o Adding-doubling → no 2D information
  o Diffusion approximation → assumptions not valid
  o Monte Carlo simulations → computationally expensive

→ Data-based metamodelling approach
  • Stochastic Kriging
  • Train on set of liquid phantoms covering wide range of BOP

Wavelength by wavelength

- Iterative optical properties estimation
  - Nelder-Mead optimizer for minimization
    - Cost function = sum of squared relative errors
  - No assumptions on scattering or absorption profiles used

Constrained optimization

- Include expert knowledge: \( \mu_s' \) as parametric function
  - Trade-off smoothness - flexibility
    \[
    \mu_s'(WL) = p_1 \cdot \exp(p_2 \cdot WL) + p_3 + p_4 \cdot WL + p_5 \cdot WL^2 + p_6 \cdot WL^3
    \]
- Minimising cost function over entire wavelength range
- Construction of ‘information grid’ to select best combination
Particle size distribution estimation

From scattering spectra to PSD
Forward problem

- Calculate optical properties for known PSD

**MICROSCEALE**

Physical information
- Particle size distribution
- Volume fraction scatterers
- Refractive indices

**MACROSCEALE**

Bulk optical properties
- Bulk absorption coefficient
- Bulk scattering coefficient
- Anisotropy factor

**Discretise PSD**

+ Mie theory
Inverse estimation PSD

Scattering spectra $\mu_s, \mu_s', \text{or } g$

Particle Size Distribution (PSD)

Inverse estimation polydisperse PSD

Mathematical solutions

Non-negative solutions

Conform literature/measurements

Shape dependent → Assume shape

Shape independent → Smoothness condition

Regularization
Shape dependent PSD estimation

- Assume probability density function
  - Monomodal: \( \text{PSD} = \logn(\mu_1, \sigma_1) \)
  - Bimodal: \( \text{PSD} = \text{scale} \cdot \logn(\mu_1, \sigma_1) + (1-\text{scale}) \cdot \logn(\mu_2, \sigma_2) \)

- Robust against noise
- Limited flexibility

Estimate parameter values and volume fraction

Minimize sum of relative least squared errors

\[
\min\sum_{i=1}^{N_s} \left( \frac{\mu_{s,i} - \mu_{s,i}}{\mu_{s,i}} \right)^2
\]
Shape independent PSD estimation

• Approximate PSD by weighted sum of splines

- Find B-spline weights

\[ \mu_s(\lambda) = \int_{r_{\text{min}}}^{r_{\text{max}}} \text{PSD}(r) \cdot \sigma_s(r, \lambda) dr = \int_{r_{\text{min}}}^{r_{\text{max}}} \sum_{j=1}^{NB} w_j \cdot B_j(r) \cdot \sigma_s(r, \lambda) dr = \sum_{j=1}^{NB} w_j \cdot \mu_{s,j}(\lambda) \]

- Calculate volume fraction from weights
Shape independent PSD estimation

- Tikhonov regularization
  - Non-negative least squares
    \[ \min \|Aw - \mu_s\|^2 + \gamma \|Lw\|^2, \quad w \geq 0 \]
    \[ \mu_s = \sum w_i \cdot \mu_s, \text{spline i} \]
    - Non-smoothness penalty
    - \( \gamma \): regularization parameter, strength
    - \( L \): regularization matrix, discrete 2nd derivative
  - More flexible
  - Less robust, regularization needed

- Chahine algorithm
  - Iterative update spline weights
    \[ w_{j+1} = w_j \cdot \frac{\mu_{s, \text{calc}}(\lambda_j)}{\mu_{s, \text{meas}}(\lambda_j)} \]
Case study polystyrene particles

Reference PSD

+ Measured BOP

DIS + UT 500-1850 nm

IAD → BOP

Laser diffraction DLS

Input PSD

BOP

Forward simulation

Add noise

Input scattering spectrum

Measured data

Simulated data

Inverse estimation

Estimated PSD

Estimated BOP

Check

Measured data

Check
Results polystyrene
Monomodal shape dependent

- 3µm reference: \( \mu = 1.5015 \), \( \sigma = 0.043472 \)
- 6µm reference: \( \mu = 3.1259 \), \( \sigma = 0.066031 \)
- 10µm reference: \( \mu = 4.9887 \), \( \sigma = 0.20495 \)

\[ \mu_s \text{ [µm}^{-1} \] vs. wavelength [µm]

\[ \mu_s \text{ [µm}^{-1} \] vs. radius [µm]
Results polystyrene
Monomodal shape dependent

![Graph of g vs wavelength and radius](image)

- $1\mu m$ input, VF = 0.75%
- $1\mu m$ estimated

- 1µm reference
  - $\mu = 0.50673$ $\sigma = 0.083152$
Results simulated fat in water
Bimodal shape dependent bimodal
Results simulated fat in water
Shape independent
Applications

• Link to product properties and quality attributes
  o Viscosity, creaming, mouth feeling/creaminess perception, nutrient uptake...

• Quality monitoring during production and storage
Conclusions

• Accurate determination of bulk optical properties from
  o Reflectance & transmittance data
    • DIS + UT
  o Multiple reflectance measurements
    • SRS

• Use of BOP for characterizing emulsions/suspensions
  o Absorption: chemical composition
  o Scattering: PSD, volume fraction scatterers
Conclusions

• PSD estimation from Vis/NIR bulk scattering spectra

• Shape dependent method
  o Good estimation if correct choice of probability density function

• Shape independent method
  o Flexible, but more prone to artefacts
  o Good estimation if good regularization and choice B-spline basis

• Opportunities for (on-line) optical determination of microphysical emulsion/suspension quality
Questions?

Contact:
www.biophotonics.be
Wouter.saeys@kuleuven.be