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Taking into account light path-length modifications induced by water in near infrared spectroscopy

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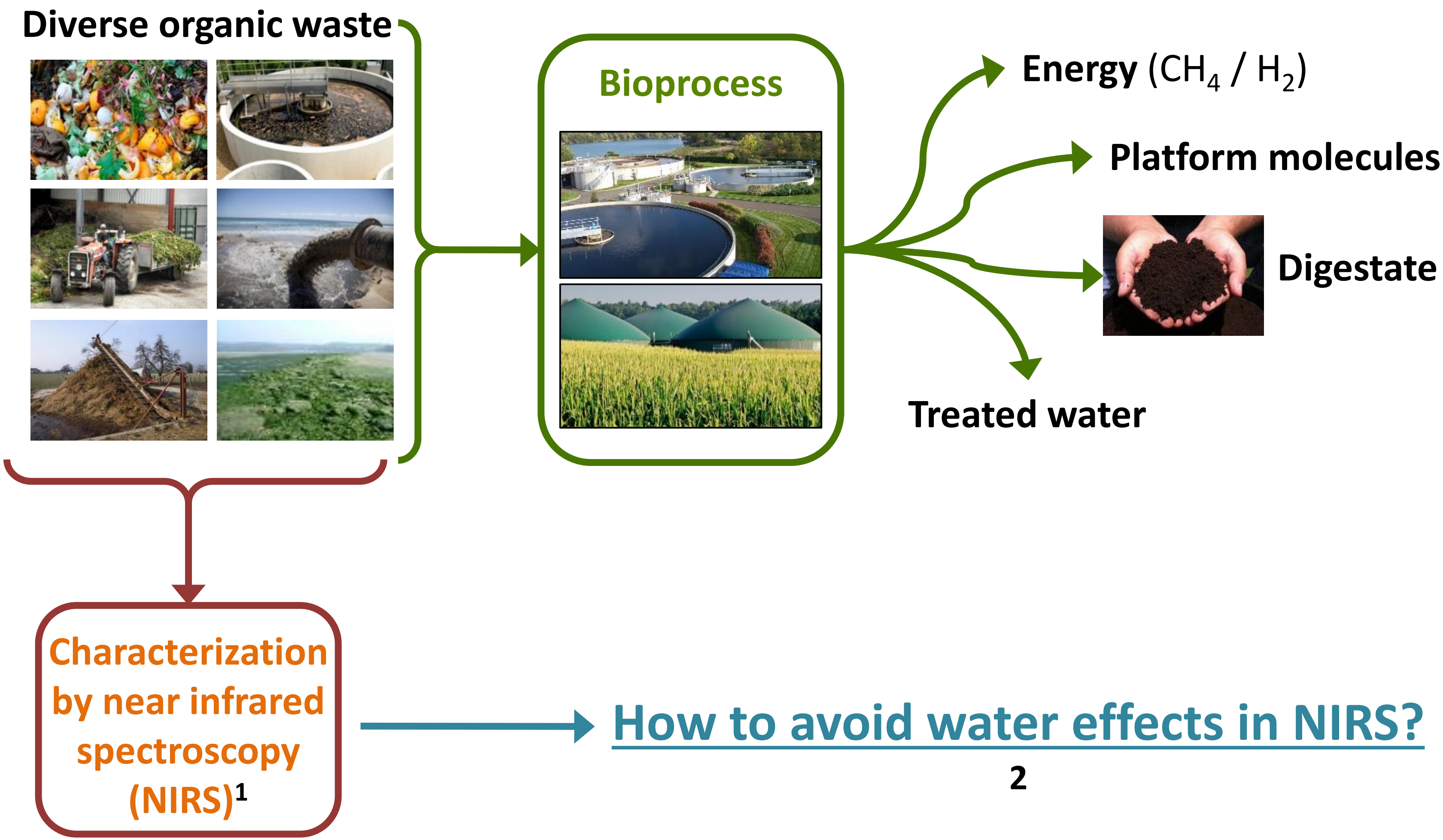
1.1 Introduction and context

Introduction to research activity

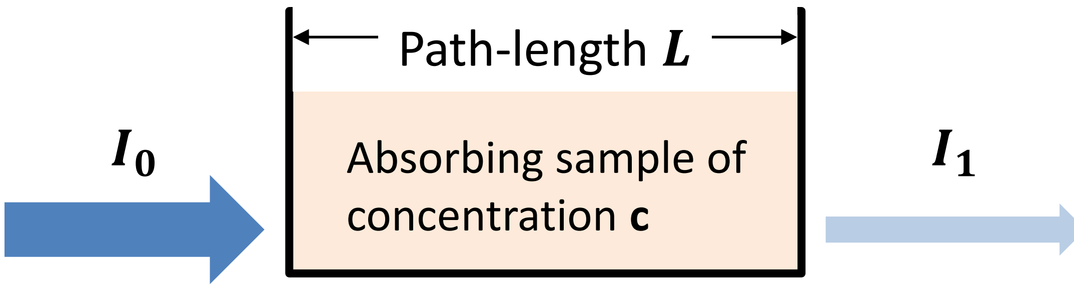


1. M. Lesteur, E. Latrille, V.B. Maurel, J.M. Roger, C. Gonzalez, G. Junqua, J.P. Steyer, 2011. https://doi.org/10.1016/j.biortech.2010.10.044.
2. A. Mallet, C. Charnier, É. Latrille, R. Bendoula, J.-P. Steyer, J.-M. Roger, 2021. https://doi.org/10.1016/j.wasman.2020.12.019.

1.1 Introduction and context

The Bouguer-Beer-Lambert (BBL) law

❖ **Transmission measurements:**



$$\boldsymbol{A = -log(T) = -log\left(\frac{I_1}{I_0}\right) = \varepsilon_\lambda . L . c}$$

With $\boldsymbol{A}$ the **absorbance**, $\boldsymbol{T}$ the **transmittance**, $\boldsymbol{\varepsilon_\lambda}$ the **extinction coefficient**

❖ **BBL law holds in very strict conditions[3-4]:**

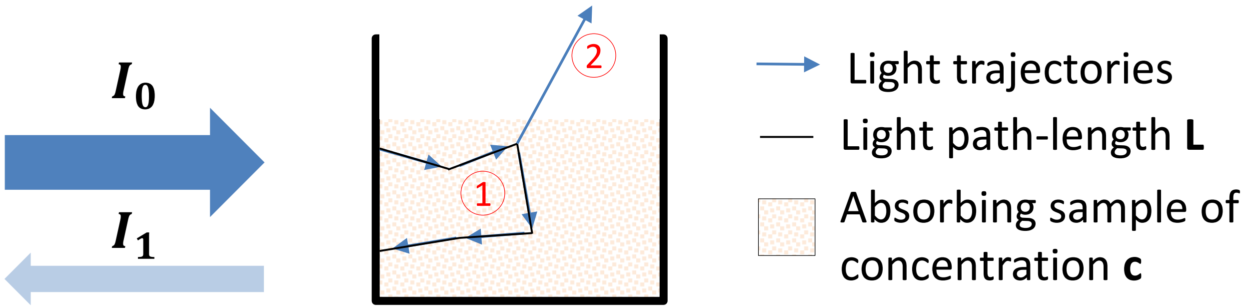
- Homogeneous and fully transmitting medium
- Low concentrations
- Independence of absorbers
- Use of monochromatic light

3. D.F. Swinehart, 1962. https://doi.org/10.1021/ed039p333.
4. Mayerhöfer, T.G., Pahlow, S., Popp, J., 2020. https://doi.org/10.1002/cphc.202000464

1.1 Introduction and context

Application to scattering media

❖ **Scattering media (powder, suspension):**



❖ **Light scattering** results in **two phenomena**[5]:

1) **Path-length modifications**
2) **Photons loss**

❖ One way of modeling[6]:

1) **multiplicative effect** **(kL)**
2) **additive effect** **(f) :**

$$\boxed{A = -log(R) = -log\left(\frac{I_1}{I_0}\right) = \varepsilon_\lambda . kL . c + f}$$

With k and f constants

5. Gobrecht, A., Roger, J.M., Bellon-Maurel, V., 2014. https://doi.org/10.1016/B978-0-12-420225-2.00004-2
6. Martens, H., Nielsen, J.P., Engelsen, S.B., 2003. https://doi.org/10.1021/ac020194w

1.1 Introduction and context

When extinction coefficients are of importance

- **Aquaphotomics[7] approach: peak positions and relative intensities specific to water structures, water functionalities**

- **What makes up the first overtone OH region?**
  - SG2: 6 water species (Sr, S0-S4)[8]
  - SG2/2D-COS: two-state model[9]
  - MCR-ALS: three components[10], with dependence of salt ionic strength
  - Gaussian non-linear fitting procedures: 6 water species[11]
  - Genetic algorithms: ten spectral components corresponding to nine water structures[12]
  - Aquaphotomics approach: 12 to 14 absorbance peaks[13]

- **How to consolidate such water structure and water state specific absorbance assignments in scattering media?**

7. R. Tsenkova, 2009. https://doi.org/10.1255/jnirs.869.
8. H. Maeda, Y. Ozaki, M. Tanaka, N. Hayashi, T. Kojima, 1995. https://doi.org/10.1255/jnirs.69.
9. V.H. Segtnan, Š. Šašić, T. Isaksson, Y. Ozaki, 2001. https://doi.org/10.1021/ac010102n.
10. A.A. Gowen, J.M. Amigo, R. Tsenkova, 2013. https://doi.org/10.1016/j.aca.2012.10.007.
11. X. Cui, W. Cai, X. Shao, 2016. https://doi.org/10.1039/c6ra18912a.
12. J. Tan, Y. Sun, L. Ma, H. Feng, Y. Guo, W. Cai, X. Shao, 2020. https://doi.org/10.1016/j.chemolab.2020.104150.
13. J. Muncan, R. Tsenkova, 2019. https://doi.org/10.3390/molecules24152742.

1.1 Introduction and context

New modeling of light path-length in BBL

❖ **Proposal of a new way of modeling light path-length in wet scattering media:**

Hypothesis: Light path-length is directly related to water content by a power law:

$$L_{\lambda,c} = L_0 . c^{a_\lambda}$$

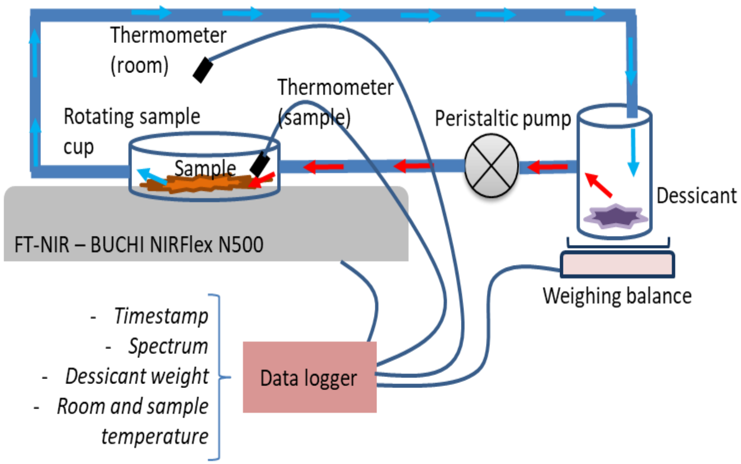
With c water content, L_0 and a_λ constants

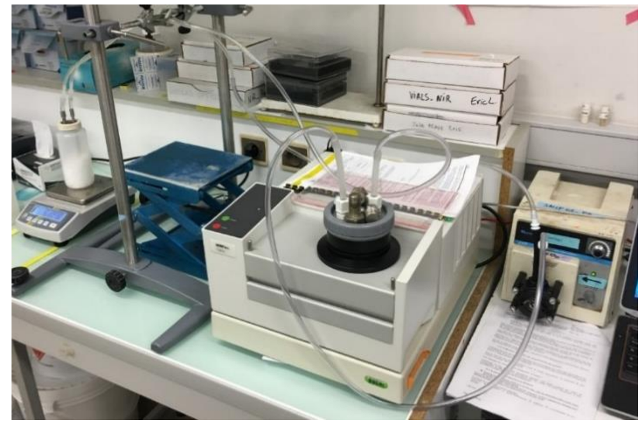
$$\Rightarrow A_{\lambda,c} = \varepsilon_\lambda . L_0 . c^{a_\lambda + 1} + f_{\lambda,c}$$

2.1 Materials & Methods

Dynamic NIRS during drying

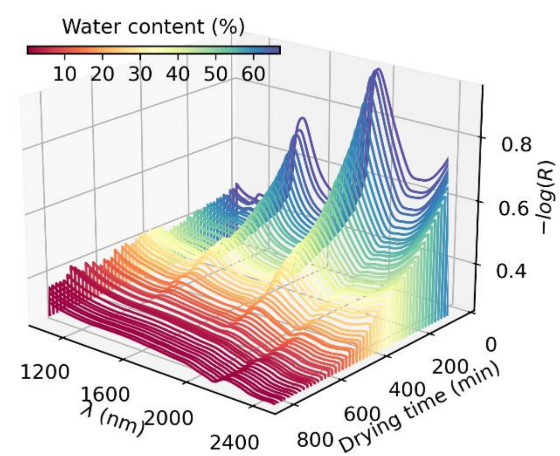
❖ Closed circuit air-drying system with NIRS and water content monitoring





❖ Aluminum paper pellets with water

❖ Evolution of NIR spectra with water content %



2.1 Materials & Methods
Validation of new modeling method

❖ **Proposal of a new way of modeling light path-length:**

Hypothesis: Light path-length is directly related to water content by a power law:

$$L_{\lambda,c} = L_0 . c^{a_\lambda}$$

With L_0 and a_λ constants

$$\Rightarrow A_{\lambda,c} = \varepsilon_\lambda . L_0 . c^{a_\lambda + 1} + f_{\lambda,c}$$

❖ **To show this, additive effects $f_{\lambda,c}$ were removed using extended multiplicative scatter correction (EMSC)[14] to obtain $A_{\lambda,c} - f_{\lambda,c}$**

❖ **Then, a log-log least squares regression was run between $log(A_{\lambda,c} - f_{\lambda,c})$ and $log(c)$:**

$$\boldsymbol{log(A_{\lambda,c} - f_{\lambda,c})} = log(\varepsilon_\lambda . L_0) + (a_\lambda + 1) . \boldsymbol{log(c)}$$

14. Martens, H., Nielsen, J.P., Engelsen, S.B., 2003. https://doi.org/10.1021/ac020194w

2.1 Materials & Methods

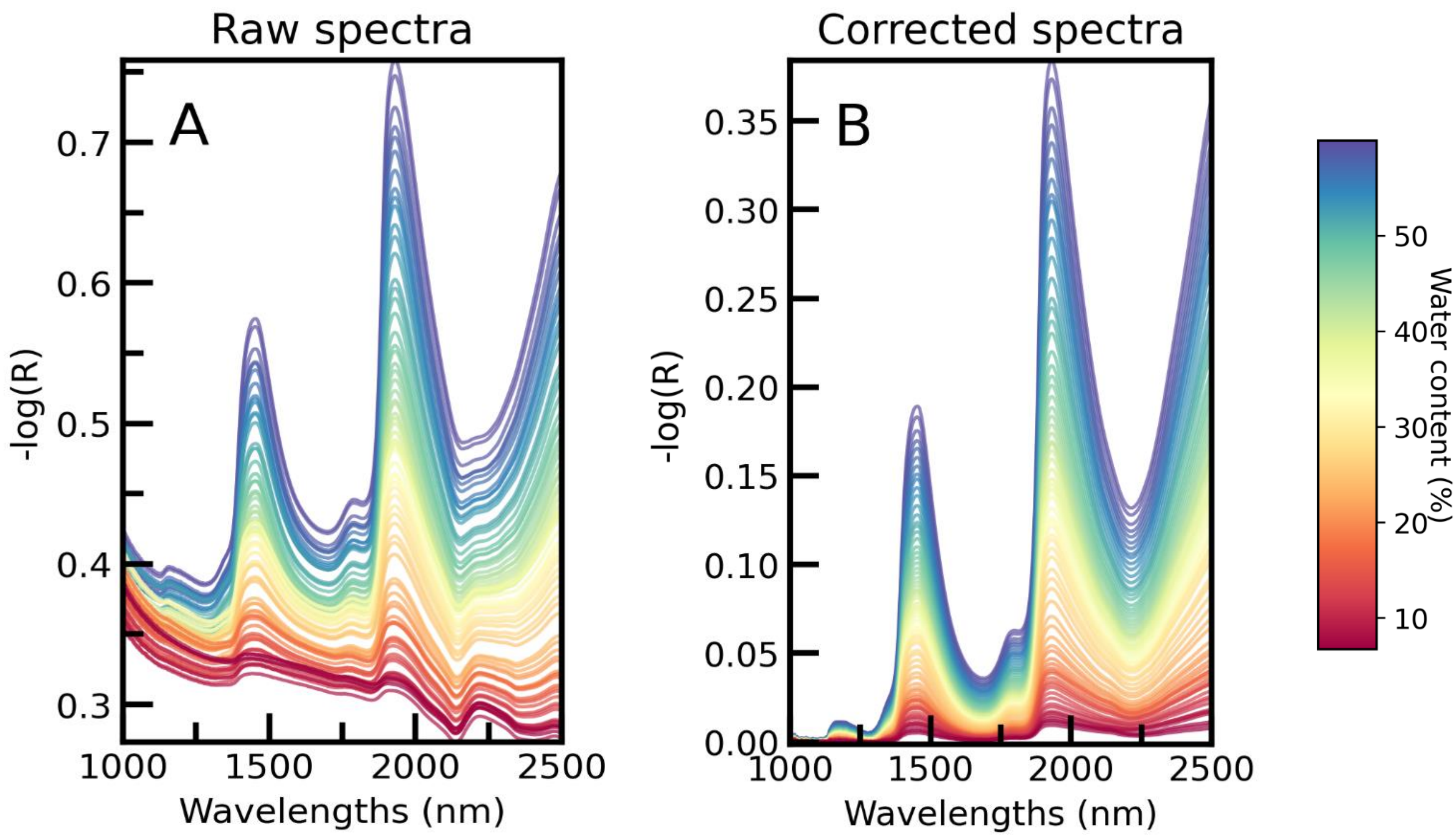
Removal of additive effects using EMSC

- **Extended Multiplicative Scatter Correction (EMSC)[14] model:**
  - $A_{obs,i}(\lambda) = a_i . A_{pure\ water}(\lambda) + b_i + c_i . \lambda + d_i . \lambda^2 + e_i . A_{pure\ aluminum}(\lambda)$ + r
  - Fit model to each spectrum using **weighted least squares (WLS) regression with weights** defined **as the inverse of the pure water transmission spectrum**
  - **Correction of only additive effects:**
    - $A_{cor,i}(\lambda) = A_{observed,i}(\lambda) - (b_i + c_i . \lambda + d_i . \lambda^2 + e_i . A_{pure\ aluminum}(\lambda))$

14. Martens, H., Nielsen, J.P., Engelsen, S.B., 2003. https://doi.org/10.1021/ac020194w

3.1 Results & Discussion

Correction of additive effects in spectra

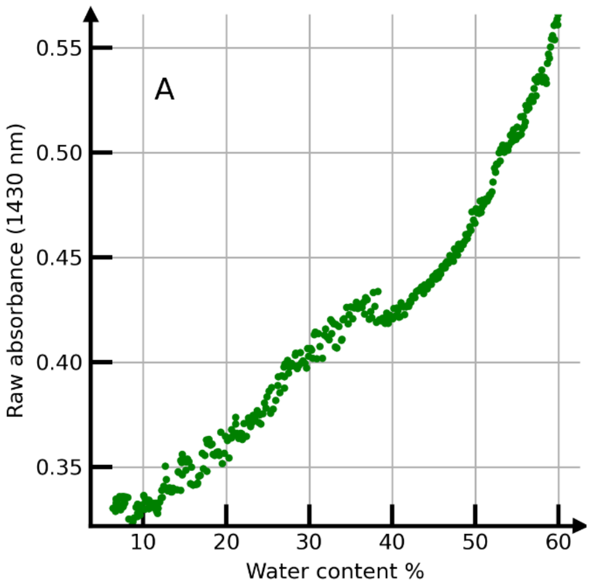


3.1 Results & Discussion

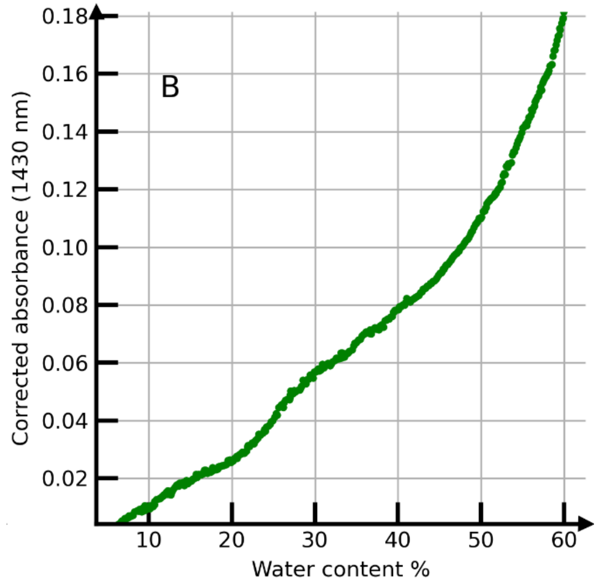
Results for one wavelength

❖ **Analysis at a given wavelength (1430 nm) shows very good fit:**

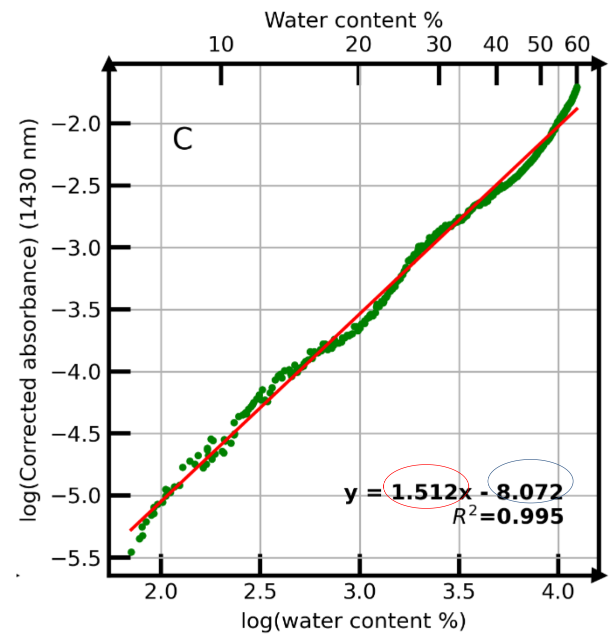
Raw absorbance



Corrected absorbance



Log-log plot

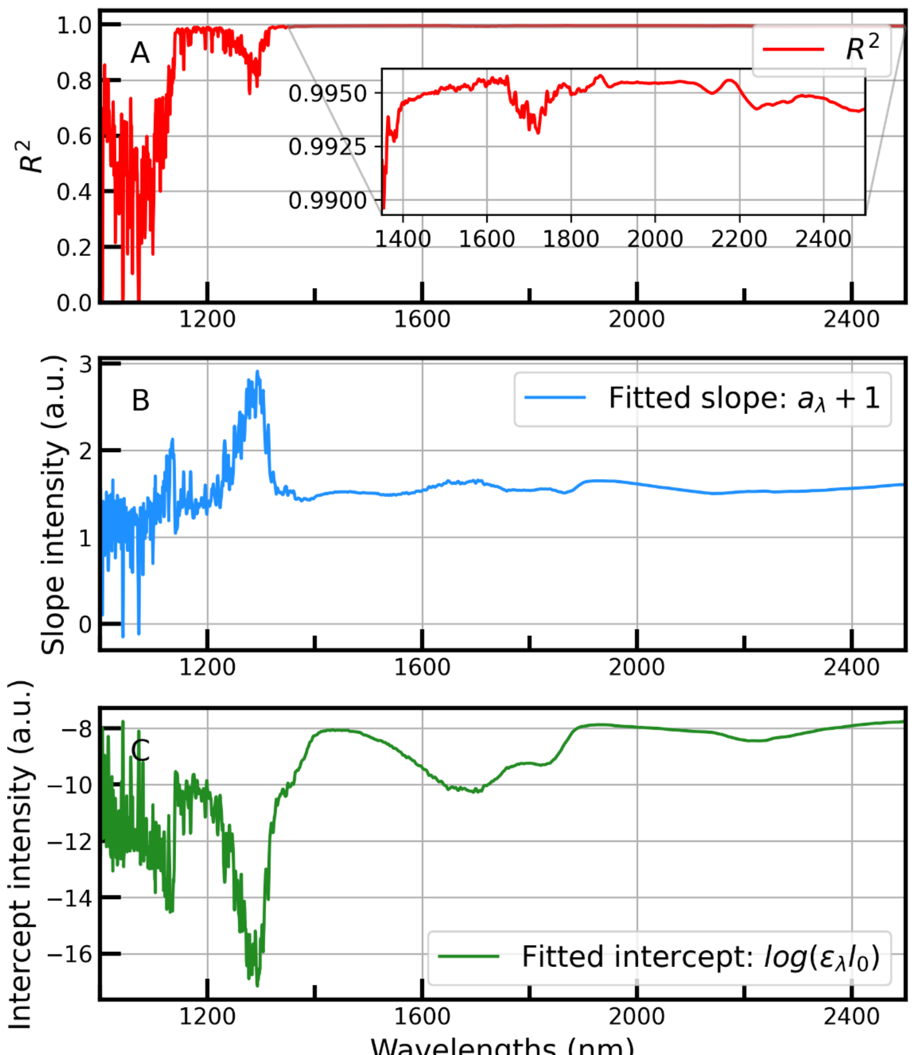


$$\boldsymbol{log(A_{\lambda,c} - f_{\lambda,c}) = log(\varepsilon_\lambda . l_0) + (a_\lambda + 1). log(c)}$$

3.1 Results & Discussion

Results for all wavelengths

❖ **Analysis for all wavelengths:**

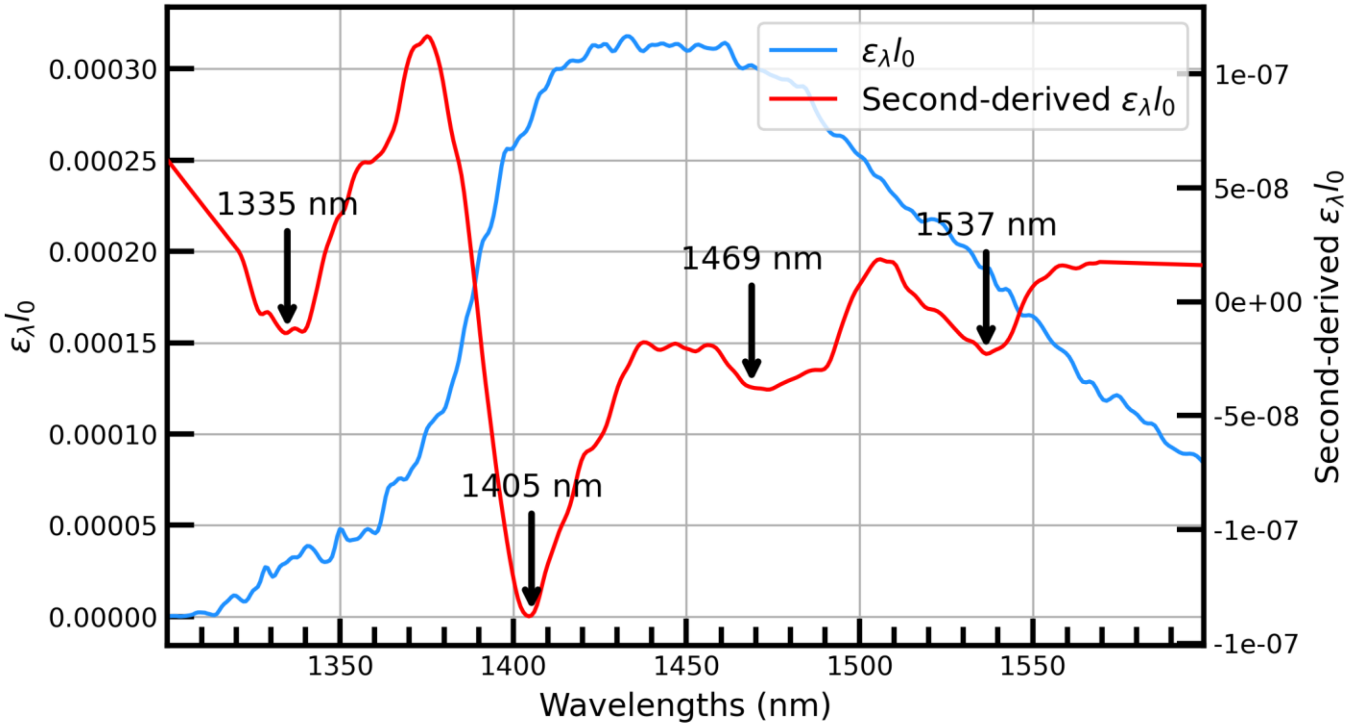


- **Good fit for all wavelengths** (>1250nm)
- **Stable slope values** (~1.5)
- **Fitted intercepts correspond to the log of extinction coefficients**

3.1 Results & Discussion

Analysis of extinction coefficients

- OH first overtone region, use of second derivative for deconvolution to analyze extinction coefficients :



- Two main subpeaks found (1405 nm and 1469 nm), similar to subpeaks found in pure water transmission measurements

4.1 Conclusions & Perspectives

Conclusions & Perspectives

- **Main take-aways:**
  - In scattering media with water, **path-length modifications can be related directly to water content by a power law**
  - Taking into account this law could allow a **better identification and analysis of pure extinction coefficients position and relative intensity**

- **Further investigations:**
  - **Investigate this law on other systems**, including a mixture of water with an absorbing constituent
  - Investigate the **implications on quantitative calibrations made on wet samples**

Thank you!

Alexandre Mallet, Roumiana Tsenkova, Jelena Muncan, Cyrille Charnier, Éric Latrille, Ryad Bendoula, Jean-Philippe Steyer, and Jean-Michel Roger

Check out our paper here:
https://doi.org/10.1021/acs.analchem.1c00811.