

Unmixing ATR- μ FTIR spectroscopic images of historical paint cross-sections



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ATR- μ FTIR maps the chemistry of a paint cross-section

- **Microscopic sampling**

A small fragment is extracted from a selected location in the painting.

- **Cross-section preparation**

The fragment is embedded in resin and polished to expose its layer sequence.

- **ATR- μ FTIR mapping**

The polished surface contacts the ATR crystal and is scanned spatially.

- **Hyperspectral output**

Each pixel provides an absorbance spectrum, producing an $H \times W \times B$ cube.

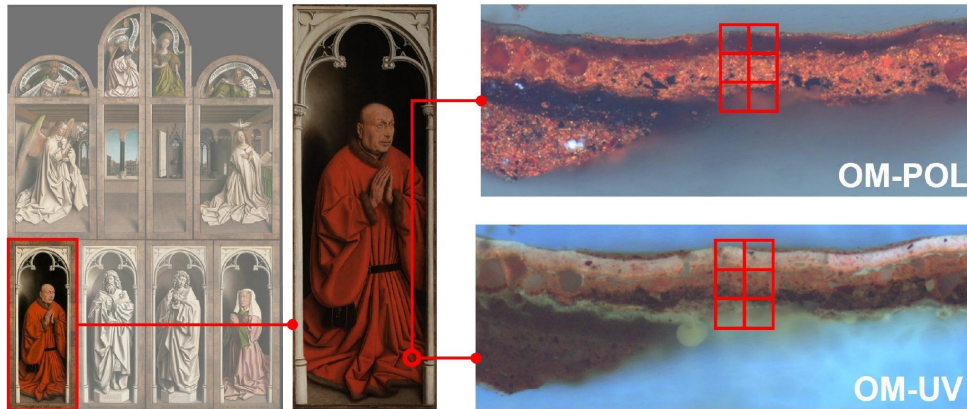


Fig. 1: Cross-section from a part of Ghent altarpiece dataset.

One ATR- μ FTIR pixel can contain several materials

- A measured spectrum may combine signals from several chemical compounds.
- **Endmember spectra:** estimate the contributing spectral signatures.
- **Abundance maps:** localise their relative spatial contributions.
- The number and identities of the components are unknown.
- Pure-material pixels are not guaranteed.
- The 1504 bands have unequal reliability and include CO₂, H₂O and acquisition artefacts.
- Ground-truth endmembers and abundance maps are unavailable.

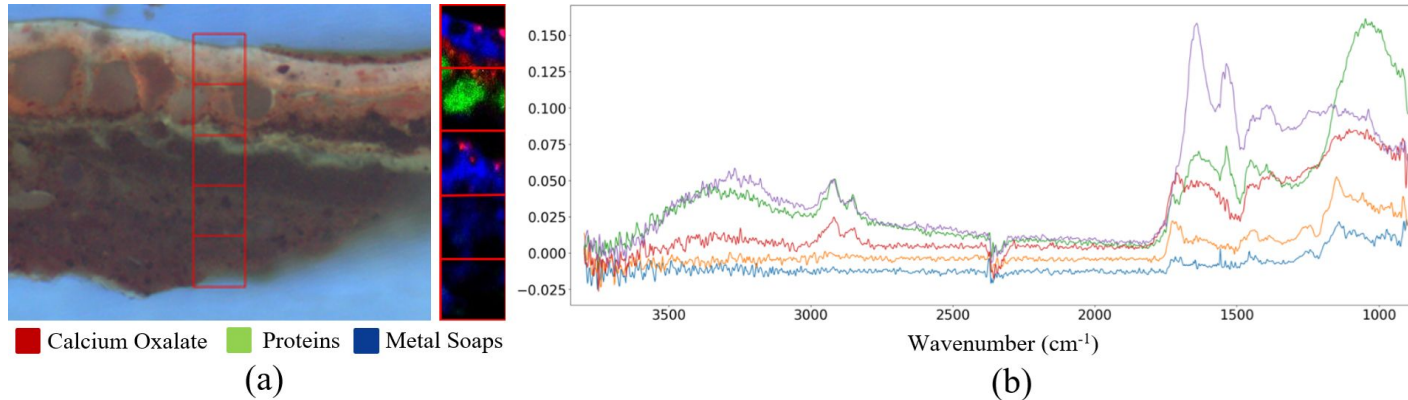


Fig. 2: (a) Cross-section from the Ghent altarpiece dataset with qualitative abundances. (b) Spectra of five randomly selected pixels

Linear mixing model for FTIR Unmixing

Applicable for unmixing of FTIR spectra (following Beer Lambert's law [1])

Assumes multiple recorded pixels are linear combination of the individual constituents/ endmembers

$$x = Ea + v$$

E : Endmembers/material ($E > 0$)

a : Abundances/fractions ($a > 0$) and ($\sum a = 1$)

v : Noise

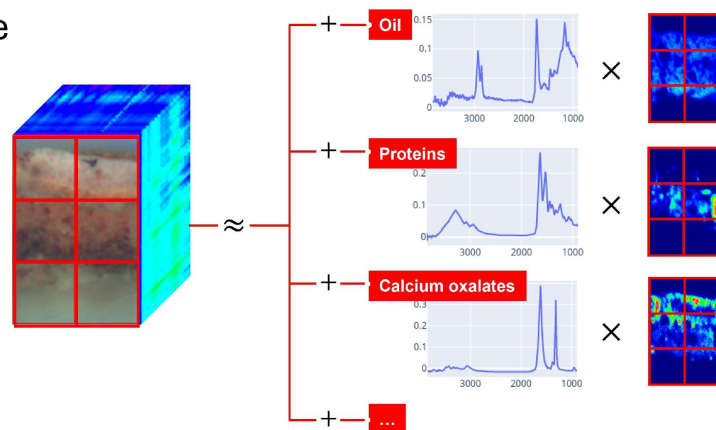


Fig. 3: Representative pigment mixing in the painting cross-section

Autoencoder based unmixing

- Asymmetrical Encoder-Decoder architecture
- Input: Raw spectra (x)
- Encoded representation: Abundances $\hat{a} = F_E(x)$
- Linear decoder weights: Endmembers $\hat{E}$
- Estimated abundances and endmembers are used to reconstruct the raw spectra ($\hat{x} = \hat{E}\hat{a}$)
- Trained on reconstruction based loss like spectral angle distance (SAD)

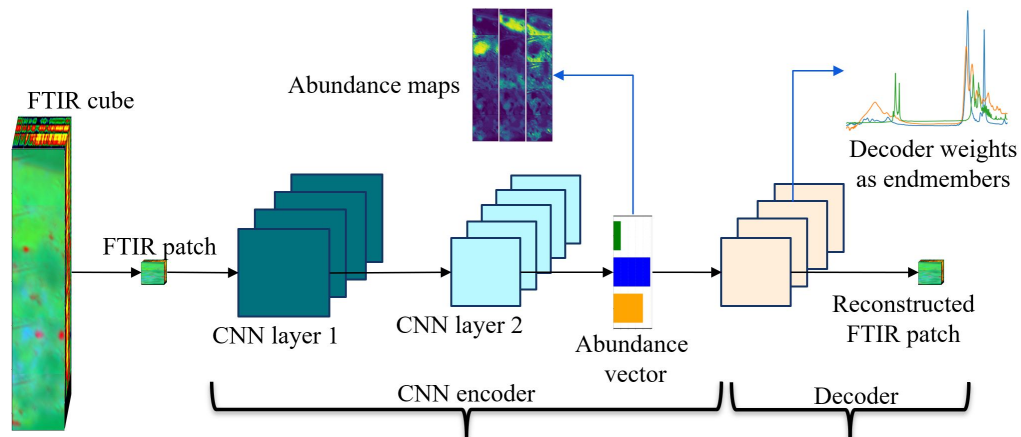


Fig. 4: Schematic of autoencoder based unmixing

$$\text{SAD Loss} = \cos^{-1} \left(\frac{\mathbf{x}^T \cdot \hat{\mathbf{x}}}{\|\mathbf{x}^T\|_2 \|\mathbf{x}\|_2 + \varepsilon} \right) + \text{Regularisation}$$

Autoencoder based unmixing: FTIR Unmixer

Challenges with SAD:

- Gives equal contribution to all the bands.
- Noisy and less reliable bands also considered for unmixing

Solution: Reliability aware/Weighted SAD loss with band dependent weighting parameter $\mathbf{w}$.

Informative bands: $\mathbf{w} \approx 1$

Unreliable bands: $\mathbf{w} \approx \mathbf{w}_{\min}$

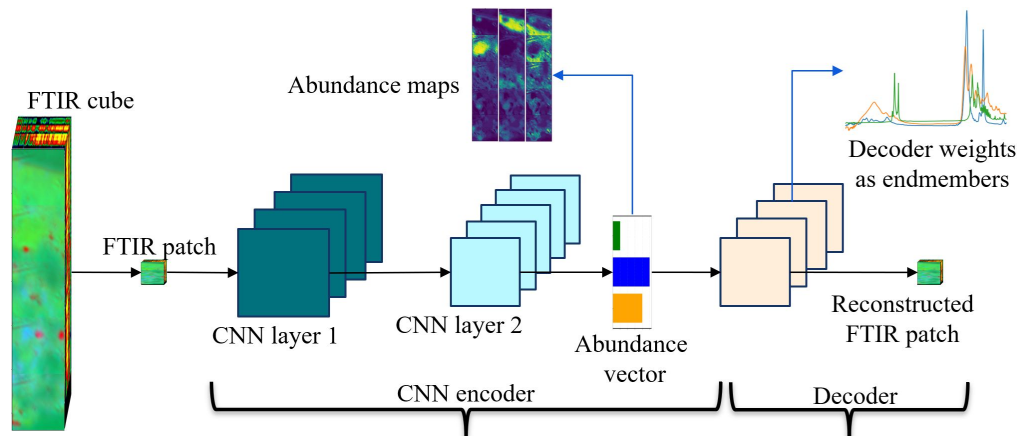


Fig. 4: Schematic of autoencoder based unmixing

$$\text{WSAD Loss} = \cos^{-1} \left(\frac{(\mathbf{w} \odot \mathbf{x}^T) \cdot (\mathbf{w} \odot \hat{\mathbf{x}})}{\|\mathbf{w} \odot \mathbf{x}^T\|_2 \|\mathbf{w} \odot \hat{\mathbf{x}}\|_2 + \varepsilon} \right) + \text{Regularisation}$$

Autoencoder based unmixing: FTIR Unmixer

01 Neighbour agreement

Low adjacent-band correlation flags channels that disagree with their local spectral context.

02 Spectral roughness

Abnormally high curvature in the median spectrum captures spikes and detector glitches.

03 Spatial flatness

Unusually low variance across pixels identifies homogeneous nuisance or uninformative bands.

04 Robust score -> weight

MAD-normalised outlier scores are combined and mapped through a sigmoid to $[w_{min}, 1]$.

No labels, reference spectra or hand-selected bad-band list are required.

Dataset: Ghent Altarpiece Cross-section

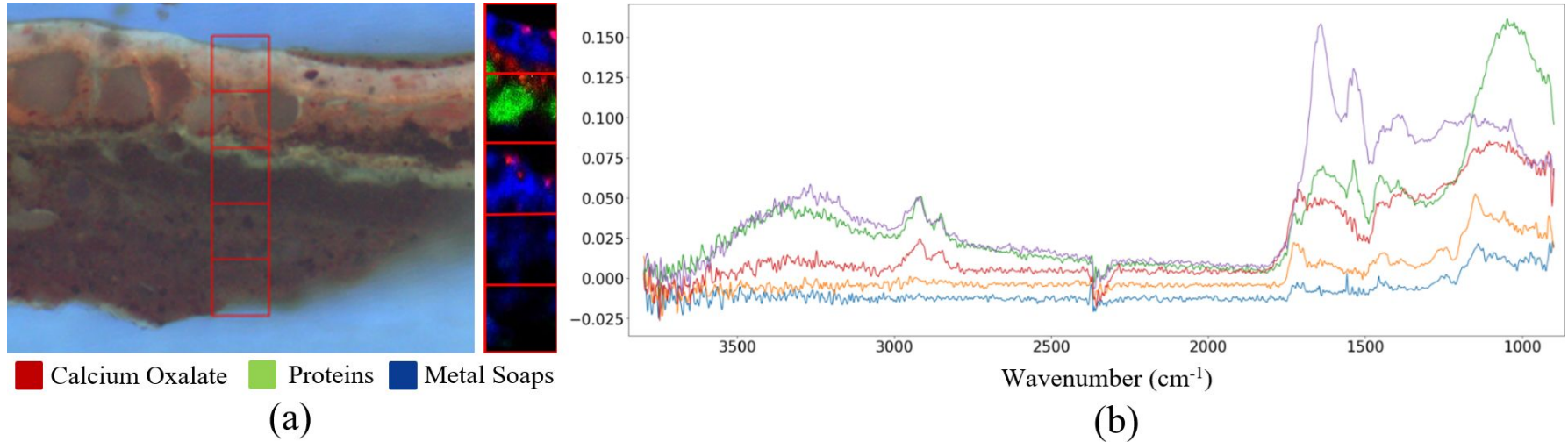


Fig. 5: (a) Cross-section from the Ghent altarpiece dataset with qualitative abundances. (b) Spectra of five randomly selected pixels

5 consecutive tiles

64 × 64 pixels each

1504 spectral bands

CO₂ / H₂O near 2350 cm^{-1}

Selecting number of Endmembers

We identify plausible number of components by iteratively unmixing the spectra by varying k from 6 to 20.

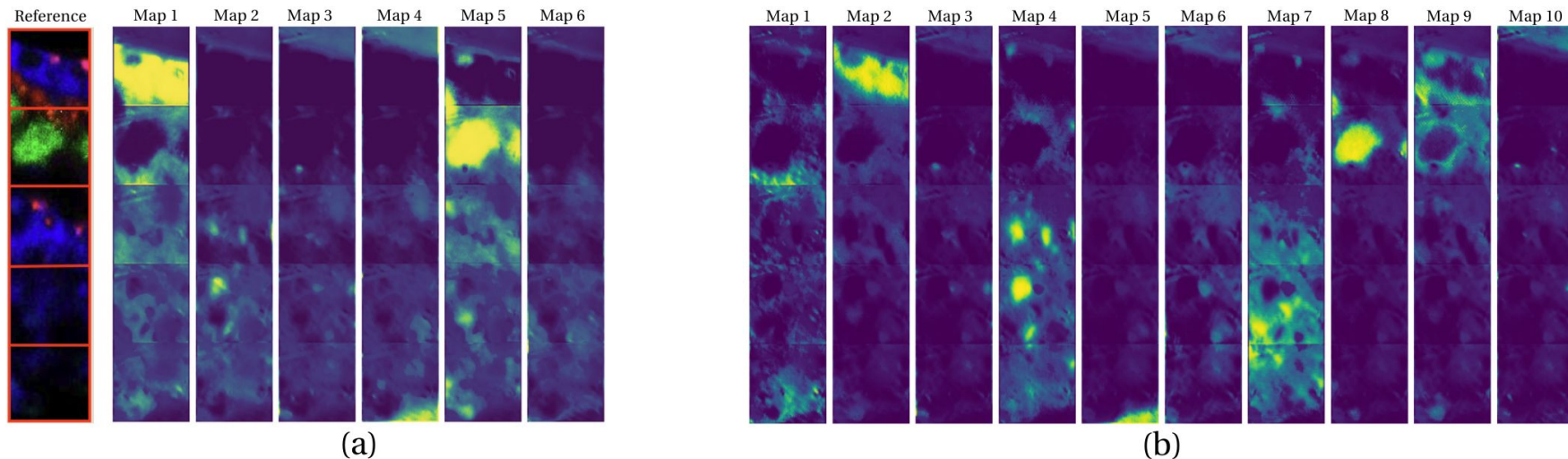


Fig. 6: (a) Abundance maps with $K = 6$. (b) Abundance maps with $K = 10$

Merged components

Components separate

Candidates: $K = 6 \dots 20$

5×5 patches · 20,000 patches · 500 epochs · Adam optimizer, learning rate = 0.005

Results: Abundance Maps and Endmembers

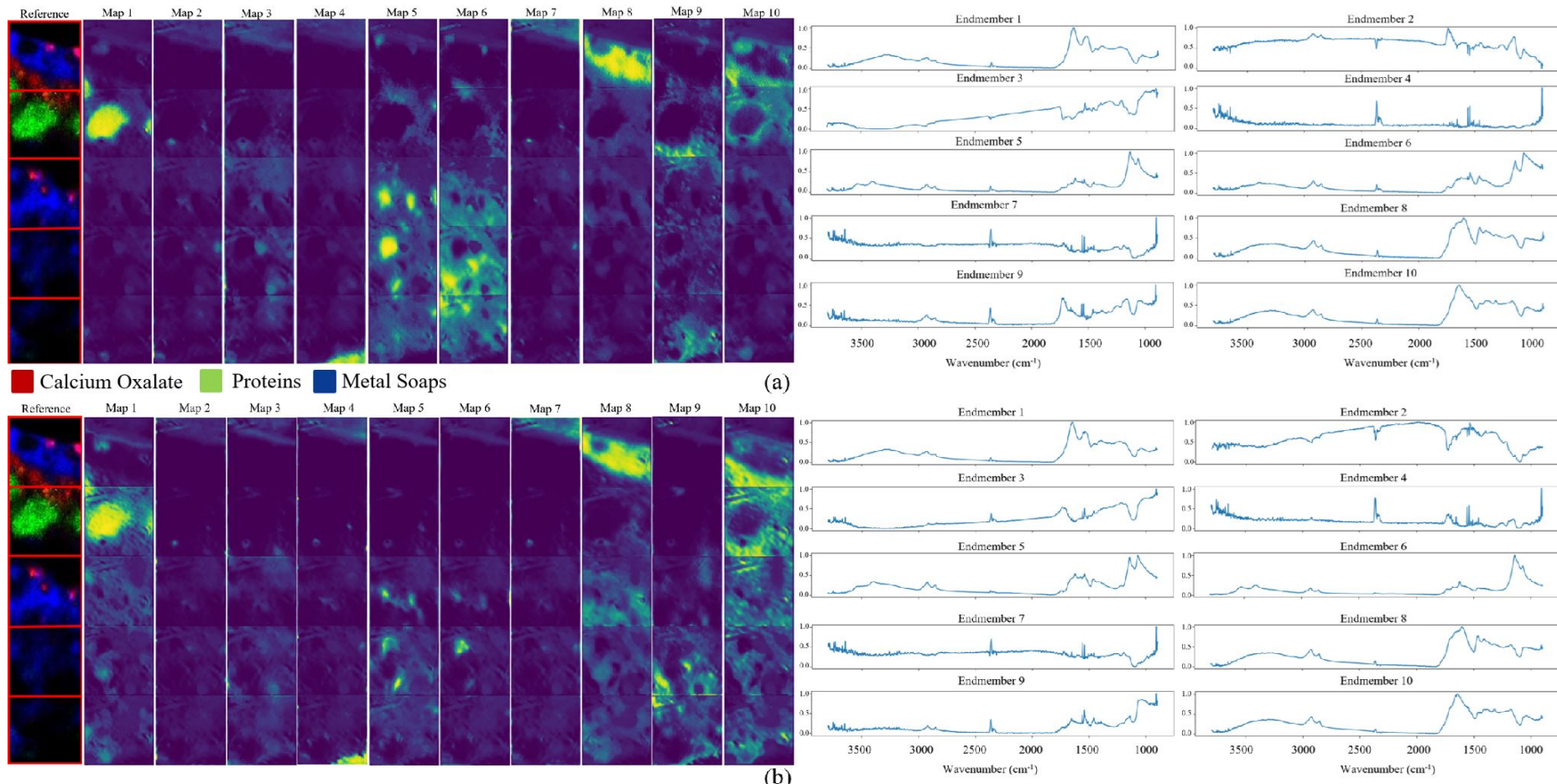


Fig. 7: (a) Abundance maps and endmembers with SAD. (b) Abundance maps and Endmembers with WSAD

Take away

Spatial interpretation

- Components 1, 8 and 10 are retained
- Map 8 becomes more spatially coherent

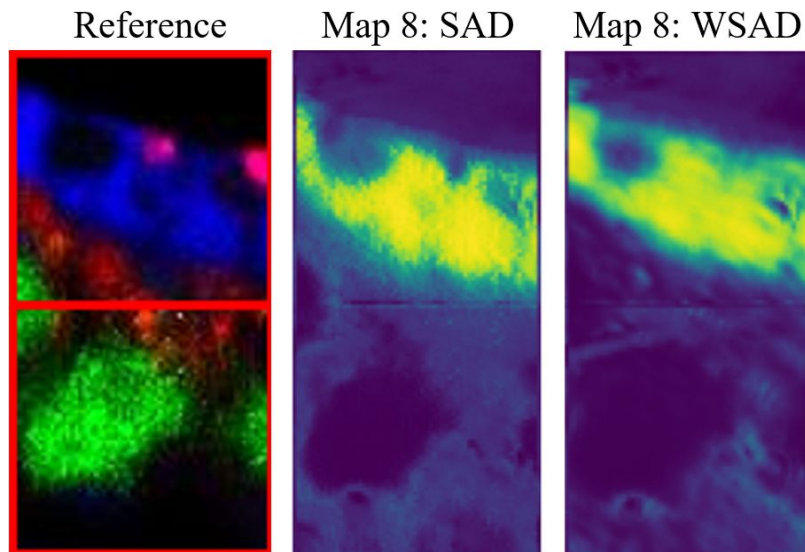


Fig. 9: Reference and abundance maps for Metal soaps with SAD and WSAD

Spectral interpretation

- SAD-derived endmembers retain stronger residual features around the CO_2 -affected region near 2350 cm^{-1} .
- WSAD downweights this unreliable region during training, reducing the CO_2 -related residuals.
- Chemically informative spectral structure is retained rather than manually removing the affected bands.

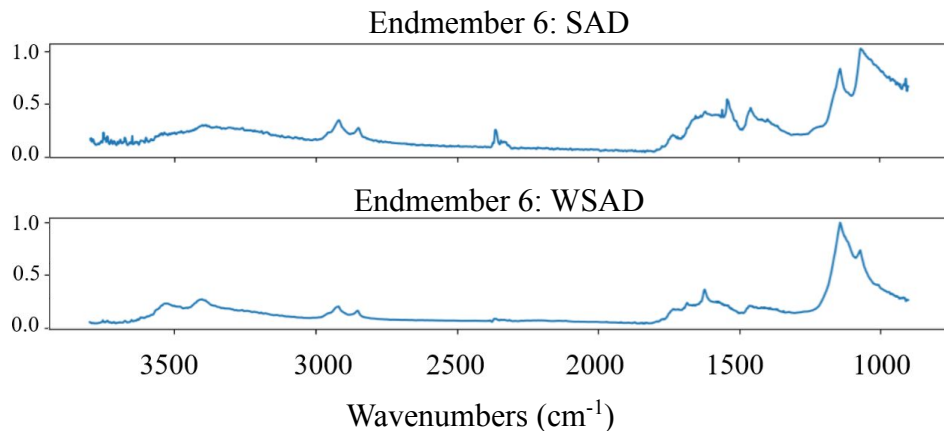


Fig. 10: 6th endmembers with SAD and WSAD showcasing suppression of CO_2 bands.

Conclusion

- A constrained CNN autoencoder can jointly estimate abundance maps and prospective endmembers.
- Automatic band weights reduce sensitivity to contamination-prone spectral regions.
- Spatial and spectral evidence supports proteins, metal soaps and calcium oxalates in the case study.

For future

- Test the method on labelled FTIR unmixing data, for accurate quantitative analysis
- Automatic estimation of the endmember count

References

[1] L. Baij, J. J. Hermans, K. Keune, and P. D. Iedema, “Time-dependent ATR-FTIR spectroscopic studies on solvent diffusion and film swelling in oil paint model systems,” *Macromolecules*, vol. 51, no. 18, pp. 7134– 7144, 2018.

Thank you