Towards broadband mid-infrared trace gas sensing using a supercontinuum source

Qing Pan

Delft, 10-09-2019
Need for trace gas sensing

Environmental

Breath analysis

Combustion

Fresh fruit storage

Purity gases

Transport products

Green houses
Need for trace gas sensing

Environmental

Combustion

Fresh fruit storage

Transport products

Purity gases

Green houses
The objective

Reducing storage losses of agro-products

Production North-West Europe:

• Apples: 3.4 million tons
• Pears: 0.9 million tons
• Blueberries: 18000 tons
• Potatoes: 28.6 million tons

Estimated losses during storage: 3 – 5%
~60k Euro/year/farmer
The QCAP concept

Quality Control of Agro-Products

Challenges:

- Multi-species detection
- Sensitivity
- Stability
- Cost
Requirement: broad mid-IR spectral coverage
The supercontinuum light source

- Wavenumber (cm\(^{-1}\))
  - 4000 - 3333 - 2857 - 2500 - 2222
- Absorbance (1 ppm-meter at 25 °C)
  - 4.0 \times 10^{-4} - 3.0 \times 10^{-4} - 2.0 \times 10^{-4} - 1.0 \times 10^{-4}
- Wavelength (nm)
  - 1500 - 3000 - 4500
- Total power: > 450 mW
- Divergence: < 2 mrad
- ~200 μW/nm

SuperK MIR, NKT Photonics
Supercontinuum + multipass cell

Photodetector (VIGO) specific detectivity: $10^{11}$ cm·Hz$^{1/2}$/W
Supercontinuum + multipass cell

Methane

Ethane

Measurement

Simulation
Balanced detection
Balanced detection
Balanced detection
Broadband multi-species detection

Establish a reference database

\[
\begin{bmatrix}
\lambda_1^A & \lambda_1^B & \cdots & \lambda_1^K \\
\lambda_2^A & \lambda_2^B & \cdots & \lambda_2^K \\
\lambda_3^A & \lambda_3^B & \cdots & \lambda_3^K \\
\vdots & \vdots & \ddots & \vdots \\
\lambda_n^A & \lambda_n^B & \cdots & \lambda_n^K \\
\end{bmatrix}_{n \times K} = \mathbf{R}
\]
Least-square global curve fitting

\[ D_{n \times 1} = R_{n \times K} C_{K \times 1} + E_{n \times 1} \]

\[
\begin{bmatrix}
\lambda_1^A & \ldots & \lambda_1^K \\
\lambda_2^A & \ldots & \lambda_2^K \\
\vdots & \ddots & \vdots \\
\lambda_n^A & \ldots & \lambda_n^K
\end{bmatrix}_{n \times K} = R
\]

\[
\begin{bmatrix}
\lambda_1 \\
\lambda_2 \\
\vdots \\
\lambda_n
\end{bmatrix}_{n \times 1} = D
\]
Real-time data analysis

- Calibrated 5.0 ± 0.1 ppmv ethanol source
- 4.87 ± 0.32 ppmv obtained
System integration and validation

QCAP-1

Pear storage containers

Radboud University

Katholieke Universiteit Leuven

21-Jan-2019

210 km
Optical sensor vs. GC-MS
Optical sensor vs. GC-MS

Ethanol emission detected!
Optical sensor vs. GC-MS

Ethanol emission detected!
Optical sensor vs. GC-MS

Ethanol emission detected!
More recent field tests

QCAP-2

Installed for blueberries & apples

10-July-2019

Radboud University

420 km

ESTEBURG

OBSTBAUZENTRUM JORK
First measurement of apples (Elstar)

Methanol detected → signature of rotting apples (stored for 1 year)
Summary

❖ Supercontinuum light source
   → broadband spectroscopy

❖ Multipass cell + balanced detection
   → sub-ppm sensitivity

❖ Global curve fitting
   → multi-species detection

❖ Automatic operation
   → continuous monitoring

- More information: http://www.nweurope.eu/qcap
Upconversion: going beyond the horizon
Measuring the mid-IR features in the near-IR

Advantages:

- Enhanced robustness: no mechanical movement
- Enhanced photodetector sensitivity: 60% – 80% QE
- Enhanced detection speed: single-point detector → Si CCD array

~15 ppbv detection limit in 1 second
Upconversion: going beyond the horizon

Measuring the mid-IR features in the near-IR

Advantages:

❖ Enhanced robustness: no mechanical movement
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❖ Enhanced detection speed: single-point detector → Si CCD array

More information @ poster:

"Broadband Multi-species Trace Gas Detection by Upconverting Mid-Infrared Supercontinuum Light into the Near-Infrared"

Recently published paper:

Khalil Eslami Jahromi, et al., Optics Express, 2019, 27, 24469-24480.
Acknowledgements

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Paul Assman
Michiel Balster

Project partners:
Thank you
Multi-species detection

→ Non-negative least square curve fitting

\[
\begin{bmatrix}
\lambda_1 \\
\lambda_2 \\
\vdots \\
\lambda_n
\end{bmatrix}_{n \times 1} =
\begin{bmatrix}
\lambda_1^A & \lambda_1^B & \cdots & \lambda_1^K \\
\lambda_2^A & \lambda_2^B & \cdots & \lambda_2^K \\
\vdots & \vdots & \ddots & \vdots \\
\lambda_n^A & \lambda_n^B & \cdots & \lambda_n^K \\
\end{bmatrix}_{n \times K} \times
\begin{bmatrix}
C_1 \\
C_2 \\
\vdots \\
C_K
\end{bmatrix}_{K \times 1}
\]

\[
D_{n \times 1} = R_{n \times K} C_{K \times 1} + E_{n \times 1}
\]

\[
\text{Standard deviation of the concentration error}
\]

\[
\text{Signal-to-noise ratio}
\]
In practice, two-stage curve fitting

Stage 1

Stage 2

Fitting algorithm

Absorbance (1 ppmv)

Wavenumber (cm⁻¹)

2900 – 3160 cm⁻¹

Concentration (other species)

Global fit ↔ Reference shift (±2 cm⁻¹)

Minimum RMS error

Concentration (water and ethylene)

2725 – 3000 cm⁻¹
Evaluation with a calibrated gas mixture

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Calibrated concentration (ppmv)</th>
<th>Diluted concentration (expected, ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>5000 ± 25</td>
<td>~19.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>100 ± 0.5</td>
<td>~0.39</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>100 ± 5</td>
<td>~0.39</td>
</tr>
<tr>
<td>Methanol</td>
<td>100 ± 1</td>
<td>~0.39</td>
</tr>
<tr>
<td>Ethyl-acetate</td>
<td>100 ± 1</td>
<td>~0.39</td>
</tr>
<tr>
<td>Acetone</td>
<td>100 ± 0.5</td>
<td>~0.39</td>
</tr>
<tr>
<td>1-propanol</td>
<td>100 ± 1</td>
<td>~0.39</td>
</tr>
<tr>
<td>2-butanone</td>
<td>100 ± 5</td>
<td>~0.39</td>
</tr>
<tr>
<td>Propylene</td>
<td>100 ± 1</td>
<td>~0.39</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>100 ± 5</td>
<td>~0.39</td>
</tr>
</tbody>
</table>

Not included in the reference database
Evaluation with a calibrated gas mixture