Methoden der Validierung der FTIR-Spektrometrie in der Gasanalytik
Offen-Pfad- und passive Messungen

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VDI Guideline 4211, part 1
Burner and calibration gases
Calibration flame
Hot calibration gas cell
Instrumental Line Shape determination

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Relevant information from advisory standards

VDI Guideline "Atmospheric measurements near ground with FTIR spectroscopy. Measurements of gaseous emissions and immissions. Fundamentals" (VDI 4211, part 1)

CEN working group TC 264/WG 18 "Open path optical methods for the measurement of ambient air quality"

Use of reference spectra
IR gas cell with calibration gas in the radiation path of the spectrometer

Five concentration levels minimum, run through in 10 cycles according to VDI Guideline 2449 Part 1 or ISO standard 9169

Test gases are produced and metered into the gas cell statically or dynamically according to VDI Guideline 3490

Determination of calibration function with its confidence ranges in accordance with VDI Guideline 2449 Part 1 or ISO standard 9169
CEN
Control calibration

Determination of $\text{N}_2\text{O}$ (340 ppb) and $\text{CH}_4$ (1.7 ppm) concentration in ambient air

Determination of $\text{H}_2\text{O}$ concentration

Comparison with independent water vapour concentration measurements
CEN

Calibration by using spectral lines from data bases and determination ILS

Synthetic determination of calibration spectra with molecular spectroscopic database and quantitative ILS

Determination of actual ILS with measurement of laser or CO of known concentration (spectral resolution narrower than line width)
Evaluation of FTIR spectrometry applied for hot gas analyses

Evaluation of FTIR measurement results is necessary for routine application of the measurement method.

Different methodologies and techniques for this task were considered:

- calibration burner (high temperature gas producer),
- calibration flame,
- hot cell.
Calibration burner (high temperature gas producer)

Burner

356 kW

Fan

40000 l/min

Gas injection

50 cm

120 cm
Burner experiments
McKenna burner
Hot gas cell
Burner experiments
McKenna burner
Hot gas cell
Burner experiments
McKenna burner
Hot gas cell

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OPAG
CO injection

Wavenumber (cm⁻¹)

Arbitrary units

Spectra

- 00
- 01
- 02
- 03
- 04
- 05
- 06
- 07
- 08
- 09
- 10
- 11

2166 2168 2170 2172
Burner experiments

McKenna burner

Hot gas cell
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Burner experiments
McKenna burner
Hot gas cell
Burner experiments
McKenna burner
Hot gas cell

CO₂ (1/cm²)
Burner experiments

McKenna burner

Hot gas cell

CO (1/cm²)
Burner experiments

McKenna burner

Hot gas cell
Experiments with burner

CO and NO (pure calibration gases) were injected in the exhausts with different amounts as calibration gases to vary the concentration of these gases.

Relevant chemical transformation of the injected CO and NO in the exhaust plume.

Problems with homogeneous mixing.

Results show that this method is not accurate enough for operational use.
Distance and altitude of the flame were fixed.
Time of measurements was about 5 minutes.
Thermo image from McKenna burner powered with 30 % of C$_2$H$_4$ and 30 % of air
Thermo image from McKenna burner powered with 30 % of C₂H₄ and 30 % of air
Burner experiments
McKenna burner
Hot gas cell

Thermo image from McKenna burner powered with 30 % of C₂H₄ and 30 % of air
Thermo image from McKenna burner powered with 30 % of C₂H₄ and 30 % of air
Experiments with calibration flame

Measurements with a McKenna burner to determine CO and NO concentrations as well as temperature

Influences by any air streaming

Repeatability of the experiment is not reliable

Calibration flames are much easier to handle than a burner but the same difficulties exist with added calibration gases
Absorption path length: 50 cm
Diameter: 5.5 cm
Window material: Calcium fluoride
Calibrated gas mixture: 
$\text{CO}_2$ 3.5%, $\text{CO}$ 500ppmV and air
Temperature range: 300 - 750 K.
Burner experiments

McKenna burner

Hot gas cell

Graph 1

<table>
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<th>Wavenumbers (cm⁻¹)</th>
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CO T561 P0.92
CO T502 P0.92
CO T450 P0.92
CO T397 P0.92
CO T350 P0.91
CO T299 P0.91
CO T247 P0.91
CO T196 P0.91
Burner experiments

McKenna burner

Hot gas cell
Experiments with heatable gas cell

Experiments with the hot cell includes a heatable cell, thermo-couples for temperature control, manometer and a regulation device.

Cell was operated with a constant gas mixture (CO₂ and CO in synthetic air) in the cell during the measurement (no gas flow).

Materials for temperatures higher than 500°C are necessary.

In-homogeneities of temperature and mixed gases inside the cell and influences by windows and walls of the cell
Calibration with determination of real ILS

Example:
Radiative transfer model
Real ILS
Calculated and measured radiance

Non-linear Modelling Example: Spectrum of Ammonia

\[ \tau = e^{-\beta(\sigma) c l} \]

\[ A(\sigma) \]

\[ \Delta L \text{ (W/cm sr)} \]

\[ Meas. \Delta L_{Meas} = f(\cdots) \]

\[ Model \Delta L_{Model} \]
For an ideal interferometer operating with perfectly collimated radiation, the ideal instrumental line shape $A_0$ will be given by the Fourier transform of the function that will describe the finite movement of the mirror.
The path difference $x_\alpha$ between the two rays in question is:

$$x_\alpha = (AB + BC) - AC = x \cos \alpha$$
Determination of the real ILS

• Absorption experiment
  
  Gas with well separated lines and narrower than the resolution of the spectrometer: NH$_3$, CO

• Sub-models:
  
  Radiative transfer model
  
  Model of the ILS
Transmittance of a gas

Material: Stainless-steel
Optical depth: 1 cm
Field of view: 5 cm
Window material: BaF$_2$

NH$_3$, CO
Real ILS calculation

Calculation of the Instrument Line Shape (ILS):
Model for Real Instrument

Ideal ILS:

\[ A_0(\sigma, \Delta \sigma) \]

Model for the inherent ILS:

\[ A_{\text{inh}}(\sigma, P_1P_2) \]

Real ILS:

\[ A(\sigma) = A_0(\sigma, \Delta \sigma) \ast A_{\text{inh}}(\sigma, P_1P_2) \]
ILS determination

User Interface

Calibration

ILS Visualization

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Implementation

BH ILS

OPAG ILS
Acknowledgements

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