Photothermal Gas Analysis

Parts-per-billion sensitivity in microliter volumes

Technology Information Summary | © Fraunhofer IPM

Introduction

Photothermal gas analysis

describes the **detection** and **quantification** of **gaseous substances** by photothermal spectroscopic methods. Originating from greek for »**light**« and »**heat**«, photothermal spectroscopy measures absorptions at characteristic wavelengths by the deposited heat in the sample in order to detect trace concentrations of target substances.

While closely related to photoacoustic methods, in photothermal sensing, the deposited heat sigal is read out by optical means, e.g. the distortion of a probe laser beam.

Photothermal sensing features distinct strengths compared to conventional laser absorption spectroscopy – their **high sensitivity** in **small measurement volumes** especially when applications require the detection of very low concentrations and provide only limited amounts of sample gas.

Key applications

Breath analysis

Life sciences

Leak detection

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Background

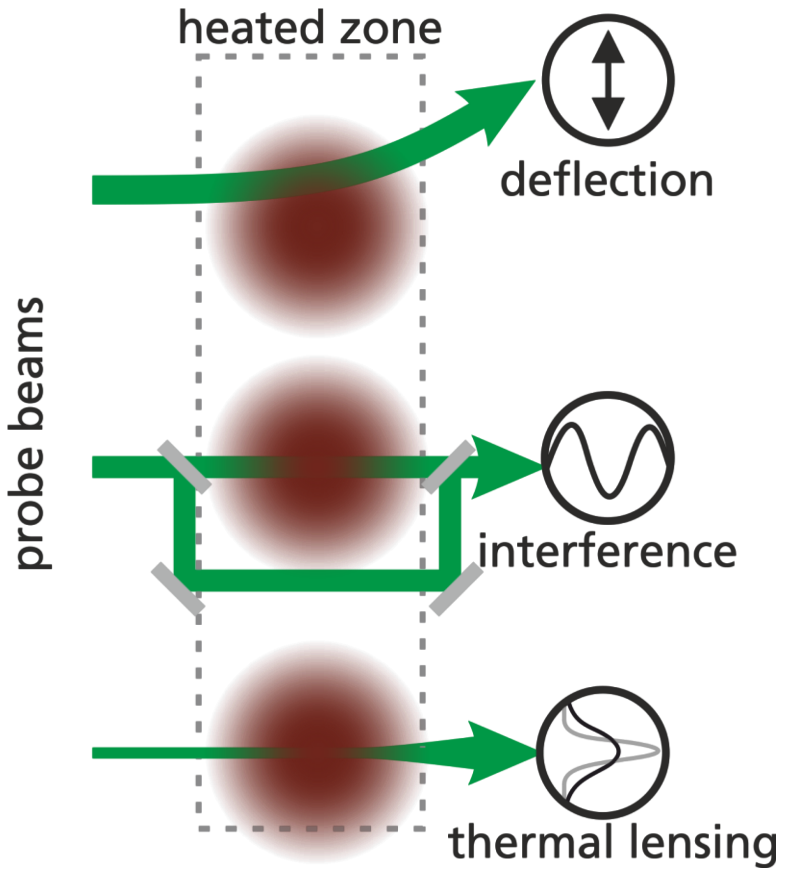
Photothermal spectroscopy

Spectroscopy examines the interaction of substances with electromagnetic radiation. Target molecules are **detected** and **recognized** due to their **specific absorption** spectra. Especially infrared spectroscopy is a key method for substance detection, characterization and monitoring in **scientific**, **environmental**, **medical** and **industrial** scenarios.

When light is absorbed by a species of interest, conventionally the **attenuation** of radiation is measured. The sensitivity is then limited by light source stability and detector noise, which pose a challenge especially in the mid-infrared. **Long path cells** can boost the sensitivity in transmission spectroscopy but come at the cost of additional optics and **larger** required sample **volumes**.

Alternatively, the absorbed energy converted to heat in the sample can be measured. Photothermal methods utilize the **change in refractive index** induced by heating in a sample, that can be probed optically, typically with a **secondary laser**, by beam deflection, interference or thermal lensing.

The measurement per refractive index distortion is **highly sensitive**, only generates a signal in case of absorption and **suffers less from gas matrix** effects than e.g., resonant photoacoustics.



Mechanisms of photothermal signal generation

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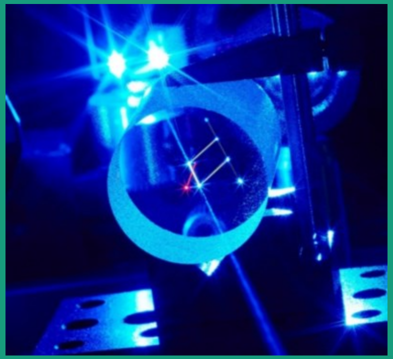
Photothermal common-path interferometry

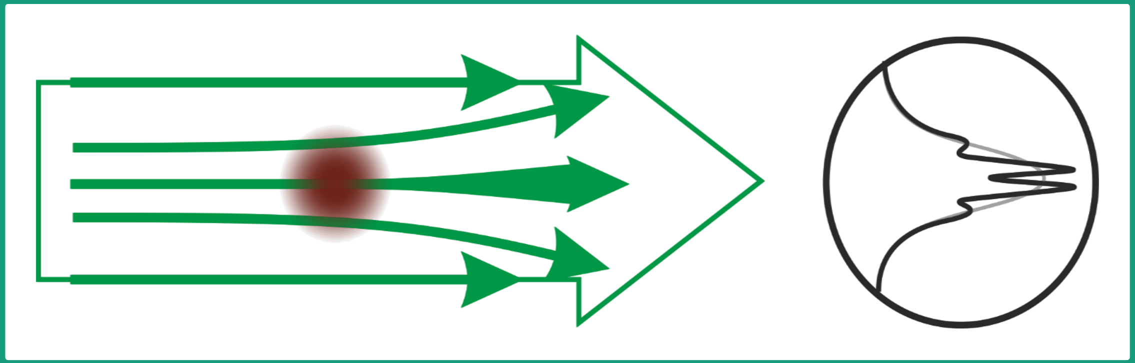
Minimized measurement volume

Fraunhofer IPM develops gas sensing methods that are based on »photothermal common-path onterferometry« (PCI), a technique originating from solid state absorption spectroscopy[1]. A **heating beam** at characteristic absorption wavelengths is **crossed** and **enveloped** by a **probe beam** of larger diameter. The thermal distortion imprints a pattern onto the probe beam profile. The strength of this pattern is proportional to the absorbed pump beam.

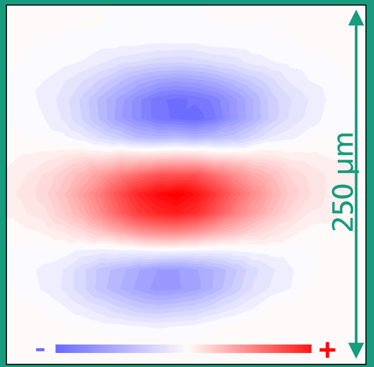
The actual volume of measurement is given by the overlap of the two laser beams. In solid state spectroscopy, this allows for high-resolution spatial absorption scanning of samples. For gas sensing, it means that the sample volume required for a high-sensitivity measurement can be reduced to the order of **microliters**.



Crossed beams in solid state PCI measurement



Schematic beam cross sections and distortion pattern in the probe beam



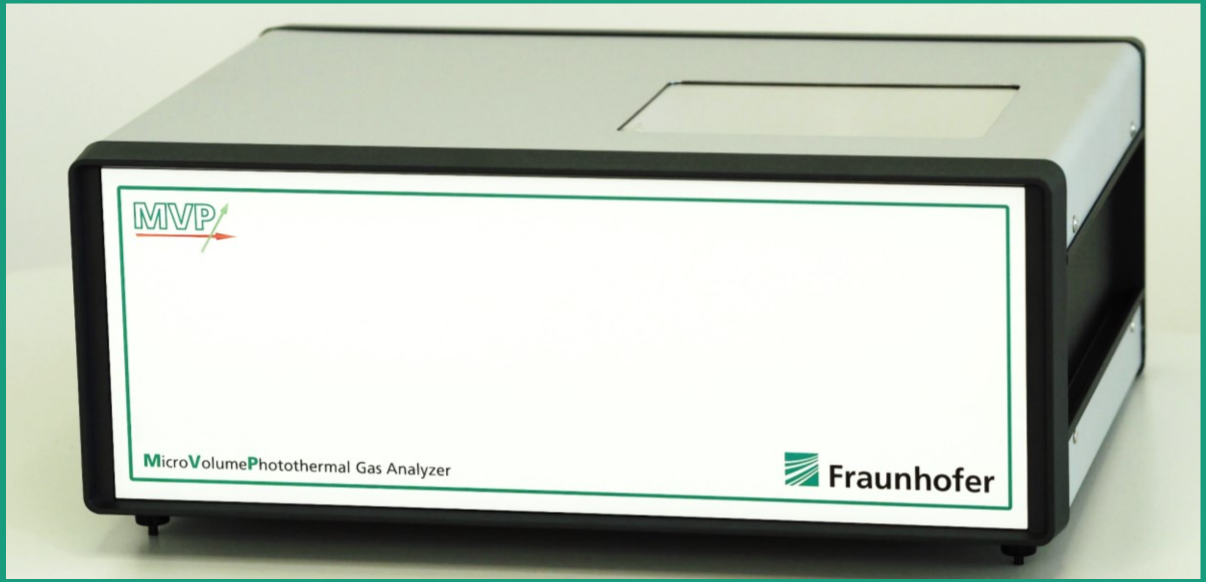
Scan of imprinted probe beam modulation by gas absorption

[1] *Alexandrovski et al., DOI:10.1117/12.814813*

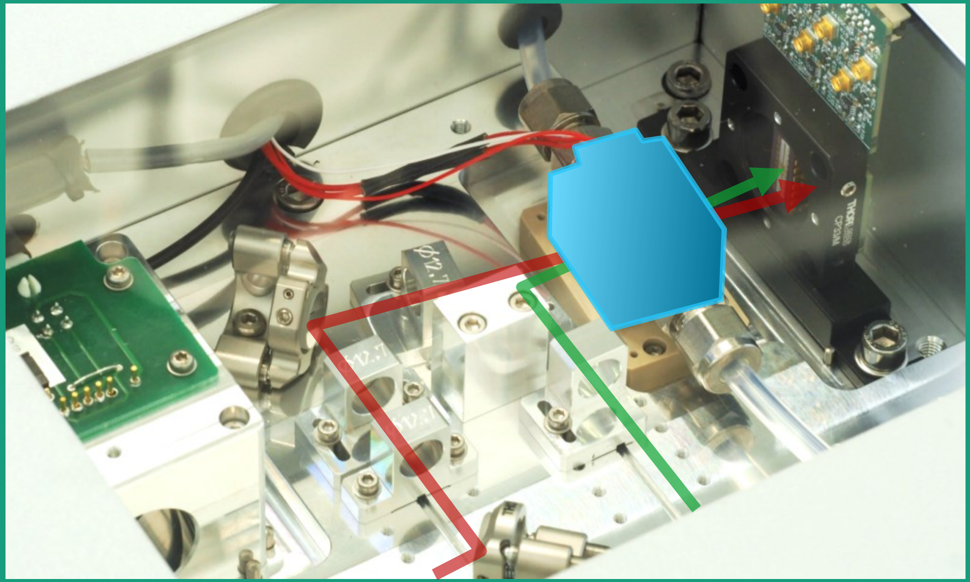
MicroVolume Photothermal Gas Analyzer

Technology demonstrator system

Fraunhofer IPM, in cooperation with Fraunhofer IAF in a Fraunhofer internally funded programme, have developed a technology demonstrator system – the MicroVolume Photothermal Gas Analyzer. The analyzer – a standalone tabletop sytem – is configured for sensing of ammonia (NH_3), sampled e.g. from human breath. Target species can be selected by swap of the excitation laser.



The MVP demonstrator system contains all optics, electronics and gas infrastructure for standalone operation



Detail view of the optics core. The mid-infrared, NH_3-specific laser (red) is crossed with the near-infrared probe beam (green) in the sample cell (blue). Only the probe beam is detected.

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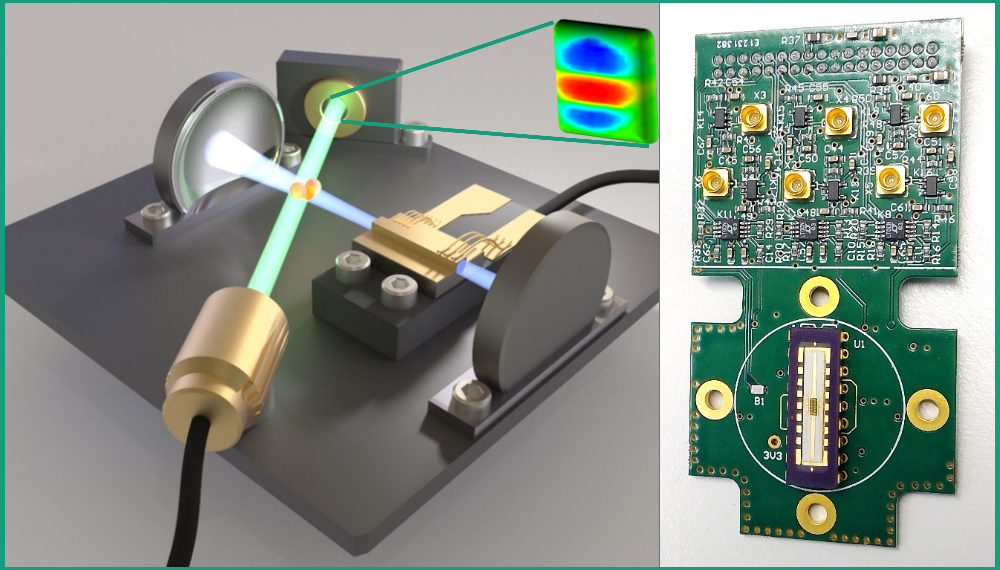
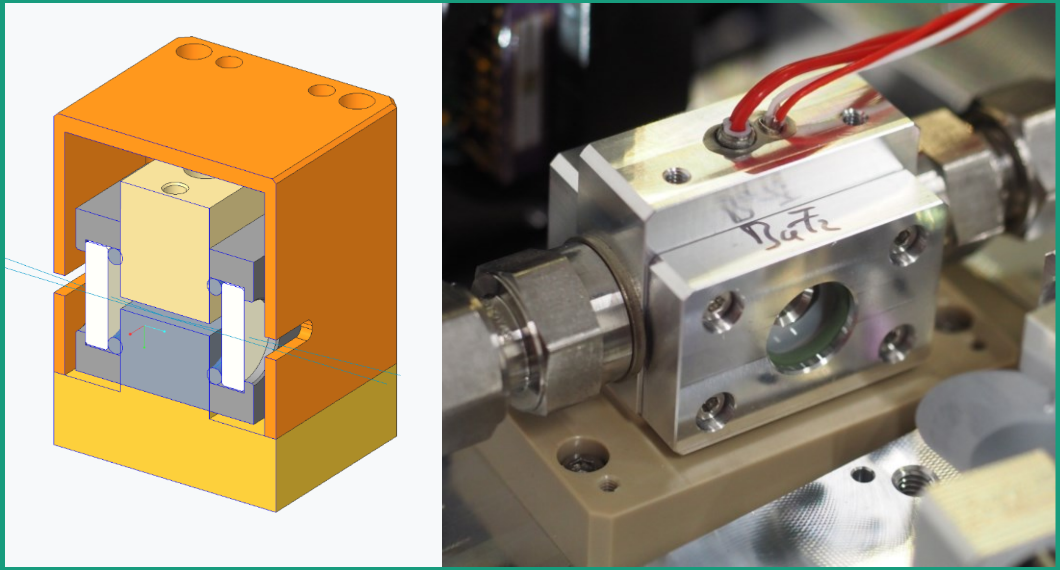
Tailor-Made Components

Best fit to the task

In a comprehensive development of the demonstrator system, laser, sample and detection components are all designed to maximize the strengths of the photothermal sensing approach. A specialized multi-pixel detector makes ideal use of the characteristic signal shape, while fitted sample cells provide just as much space as needed for the interacting beams – enabling the most rapid gas exchanges in sample volumes as low as 60 µl.



A dedicated multi-field detector (right) is optimally matched to the characteristic signal pattern, shown in the artist's view of the detection (left), providing low-noise, differential signals from a single beam[2].



CAD cross senction and close-up view of a sample cell Cell volumes can be easily adapted for best match to the sample flow rate, enabling second-resolved measurements even at flows of few ml/min.

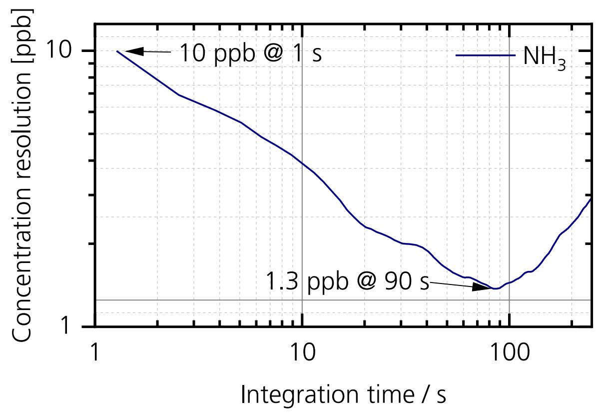
[2] *Patent pending.*

Technology demonstrator system

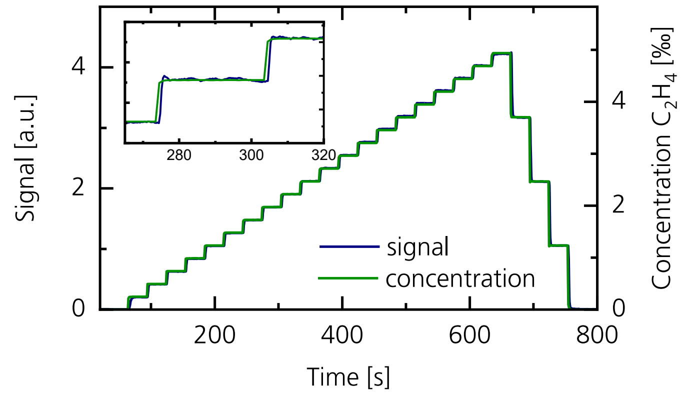
Demonstrator system features

Target species	Ammonia (NH_3)
Detection limit	< 50 ppb $Hz^{-1/2}$
Concentration resolution	< 15 ppb $Hz^{-1/2}$
Response $t_{90\%}$	< 1 s
Data rate	10 Hz
Sampling type	active (pump) and passive (pressure driven)
Sample flow	5 – 1000 ml/min
Sampling interface	Leak probe, respiratory mask, pressure line
System dimensions	19"-4HU standalone unit

Allan-deviation plot of NH_3 concentration resolution. At 1 s, 10 ppb of NH_3 are resolved.



Linearity and time response shown in a concentration series for C_2H_4.



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Parts-per-billion in microliters

Photothermal spectroscopy enables highly sensitive detection of trace substances in very limited amounts of gas phase samples.

Breath analysis for physiological studies and medical diagnostics benefit equally from these features as **life science** experiments and highly sensitive **leak detection**.

Best use is made of the sensitive photothermal signal generation with detailed **understanding** of the signal generation mechanism and **components optimized** accordingly.

Fraunhofer IPM has developed a **technology demonstrator** platform to showcase the strengths of the method in a number of **case studies**.

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