FT-IR-iPAS – A tool for industrial multicomponent gas measurement

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1 Introduction

Modern adsorption IR spectrometer and their optical detectors are developed close to the theoretical performance limits. [Kauppinen et. al., 2004; Koskinen et. al., 2007] Thus, increasing the optical path length is the sole option to enhance the sensitivity of the IR absorption technique. [Kauppinen et. al., 2004; Koskinen et. al., 2007; Koskinen et. al., 2006] By enlarging the optical path length, the absorption cell becomes bulky, the sample volume increases and the light absorption is nonlinear. [Koskinen et. al., 2008] The nonlinear behaviour is especially pronounced by measuring wet gases, which is quite often the case in industry, since both the analyte and water respond nonlinear. [Kuusela et. al., 2007; Koskinen et. al., 2008] In sum, a significant improvement in sensitivity of the absorption technique is not anymore possible. To gain a higher sensitivity, other techniques have to be found, such as the photoacoustic method, which offers a zero background signal. [Kauppinen et. al., 2004; Koskinen et. al., 2007; Kuusela et. al., 2007]

However, the common photoacoustic method using a capacitive membrane microphone also suffers from restrictions, like the nonlinear pressure response, which is due to the three dimensional membrane stretch and the poor sensitivity, due to the 'damping effect' caused by the air flow between the rigid electrode and the flexible membrane. [Kauppinen et. al., 2004; Kuusela et. al., 2007; Fonsen et. al., 2009] In the recent past, Kauppinen from the University of Turku invented the optical readout cantilever microphone. The optical readout cantilever microphone is not subjected to the limitations of the condenser microphone, allowing improvements to the sensitivity and the dynamic range. [Kauppinen et. al., 2004; Kuusela et. al., 2007; Sievila et. al., 2007] The sensitivity of photoacoustics can be 100 times better when using the optical cantilever detection (abbr. iPAS: improved photoacoustic spectroscopy) instead of the conventional capacitive microphone. [Koskinen et. al., 2007; Lindley et. al., 2007; Olafsson et. al., 1999]

So far, photoacoustic gas spectroscopy using optical cantilever detection has only been set up with lasers, diode lasers and blackbody radiators with filters. However, lasers and blackbody radiator-filter combinations are not optimal for measuring multicomponent samples. This is the driving force to combine iPAS with a highly selective, but broadband detecting technique, like a FT-IR with a black body radiator. This novel combination: an FT-IR-iPAS prototype was realized by GASERA, Finland in 2008. In 2009 the performance of the prototype was extensively tested at University of Oulu and VTT Oulu [Hirschmann et. al., 2010]. Some of those performance tests will be presented here.

2 Objectives of the research

The objective of this research is to develop and establish FT-IR-iPAS as a new technique for accurate, multicomponent gas measurements in industry. FT-IR-iPAS brings several benefits, compared to the present absorption technique, which makes it superior for industrial gas measurements. So far the performance of the first built prototype was tested and compared with the absorption technique. After the positive

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verification, now the focus is to develop measurement systems for various applications, like the industrial measurement of VOC. This development will be done in the EU-SME-Project 'ZERO-VOC'. The target of this project is to develop and built a measurement system for the industrial measurement of VOCs.

3 Results

The main investigated performance criteria are the sensitivity, selectivity, multicomponent ability and the linearity. These performance tests are reported and discussed in the following.

3.1 Selectivity & Multicomponent ability

The selectivity was studies on several gases. The spectra of the individual gases were measured consecutively. In the software, the spectra were put on top of each other to one resulting spectrum. Figure 1 shows the spectrum of each gas and the resulting spectrum. The raw spectra are background corrected and the water bands are subtracted.

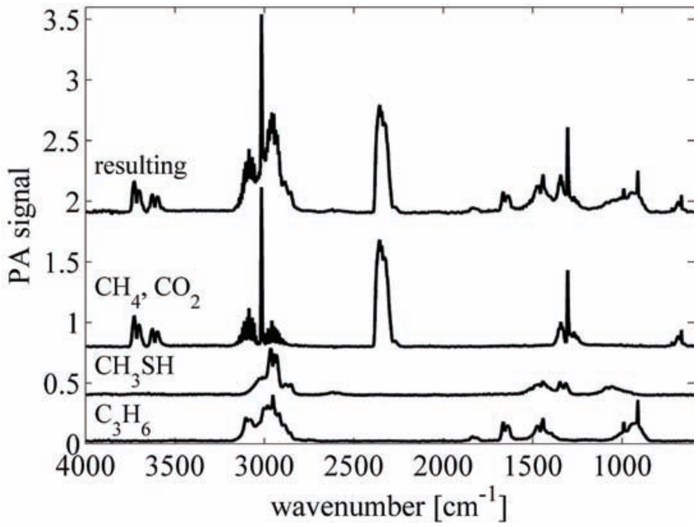

Figure 1 *Single spectra and the resulting combined methane (1000 ppm), carbon dioxide (5000 ppm), propene (1000 ppm), and methylmercaptane (2000 ppm) spectrum.*

In some spectral regions, like from 2900 until 3150 cm^{-1} the spectra are overlapping, which makes a quantitative determination highly difficult. However also spectral regions can be found, where the single spectra are not overlapping each other. Using multivariate calibration methods, like Partial Least Square Regression (PLS) or Science Based Calibration (SBC), it won't be a problem to quantitatively calibrate the four components. Even, with the classical 'one wavelength calibration method' it would be possible to set up a quantitative calibration in the spectral non-overlapping areas.

3.2 Sensitivity

The sensitivity is a meaningful attribute characterising the performance of spectrometers. One parameter to express the sensitivity is the signal to noise ratio (SNR). The SNR relates the gained signal to the unwanted noise in the spectrum. Table 1 shows the analysis of the sensitivity.

Table 1 *Sensitivity analysis.*

	methane	carbon dioxide
gas concentration [ppm]	1000	5000
molecular bond	stretch C-H	asymmetrical stretch C=O
measurement time [seconds]	100	100
resolution [cm^{-1}]	4	4
spectral position of the signal [cm^{-1}]	3017	2356
spectral position of the noise [cm^{-1}]	3200-3250	3200-3250
PA signal	1.3	0.87
noise	$6.42 \cdot 10^{-4}$	$6.42 \cdot 10^{-4}$
SNR	2027	1362
LoD [ppm]	0.5	4

First theoretical evaluations were assuming that that the sensitivity of the FT-IR-iPAS is not as good as with blackbody radiator-filter and laser devices, because of the limited light throughput. This assumption is confirmed here, because in the literature LoDs for measuring methane are 0.5ppm (measurement time: 5 sec) [Fonsen et. al., 2009], 0.8ppb (measurement time: 100 sec) [Kauppinen et. al., 2004] and 13ppb (measurement time: 0.37 sec) [Uotila et. al., 2005].

However, the FT-IR-PAS still has the advantage of the multicompont ability. This means that one measurement is not only to measure one species, like the case with filter devices. Several species can be quantitative determined by only one measurement, as it is done here: one measurement was needed for both species methane and carbon dioxide. If this feature is also taken into account, and the devices are not only compared by the measurement time, instead by the amount of measured components per time, then FT-IR-iPAS will be the favourite. The appropriate area for application will the multicomponent measurements, when more than one gas should be measured, or only one gas which is mixed with gases interfering filter or laser based measurements. These applications can be found either in laboratory or in industry.

3.3 Results 3: Linearity

To discover the behaviour of the response, several concentrations of methane and carbon dioxide are measured. The absorption is averaged in the ranges between 3010 and 3020 cm^{-1} for methane (stretch C-H) and 2300 until 2380 cm^{-1} for carbon dioxide (asymmetric stretch C=O). The averaged absorption is plotted versus the concentration and displayed in Figure 2 for methane and Figure 3 for carbon dioxide.

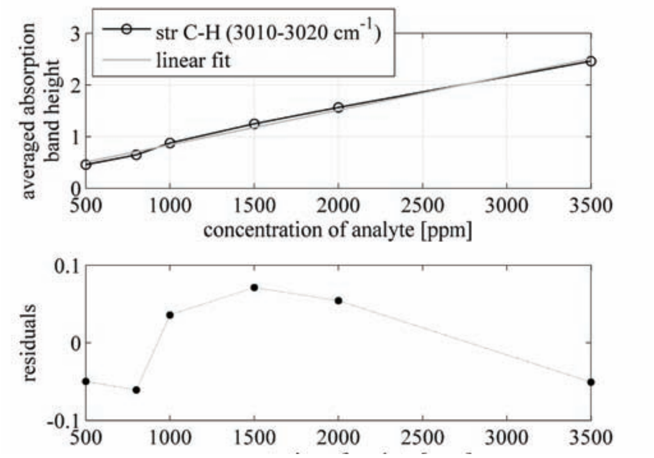

Figure 2 *Linearity analysis of the stretch C-H band of methane in the blend with carbon dioxide; top: Averaged band height on the concentration with the fitted lines; bottom: Residuals of the fit.*

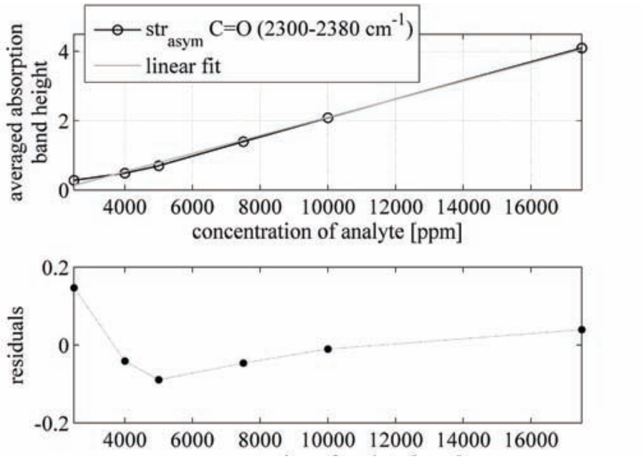

Figure 3 *Linearity analysis of the asymmetric stretch C=O band of carbon dioxide in the blend with methane; top: Averaged band height on the concentration with the fitted lines; bottom: Residuals of the fit.*

According to the graphics, the response can be said to be linear in the examined range. There are some deviations, but those can be explained by the practical gas mixing set-up. The linear signal response is a valuable gain for industrial applications. Only few, in the best case one gas spectrum is needed to set up a complete quantitative calibration. This allows quick calibration and easy adoption to different measurement problems.

4 Relevance of the research

The presented research is of high importance. FT-IR-iPAS opens the door to
1. Improve the sensitivity, selectivity and multicomponent ability;
2. Allow a linear response which is valuable for easy and fast calibration;
3. Perform an easy water subtraction, with no need for comprehensive libraries;
4. Be deployed in different areas, like laboratory, industry and environment;

5. Decrease the overall set up work and time for a new measurement application, due to the linear response, quick calibration and easy adoption to different measurement problems and places;
6. Make measurements at all possible in some areas, such as the industrial measurement of VOCs, where all current available techniques have clearly failed.

One indicator of the high importance of the research is the promotion of the research by the EU in the EU-SME-project 'ZERO-VOC' in which FT-IR-iPAS will be developed for industrial measurement of VOCs.

5 References

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