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Application of a tunable Fabry-Pérot filtometer to mid-infrared gas sensing

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ABSTRACT

The design and application of a versatile, tunable filtometer based on a Fabry-Pérot (FP) tunable filter – detector, covering the spectral range from 1250 to 1850 cm^{-1} at a spectral resolution of approximately 30 cm^{-1}, is presented. The tunable filter was characterized and calibrated using a FTIR spectrometer. Gas mixtures comprising iso-butane, 1-butene, 1,3- butadiene were prepared and measured. The obtained gas spectra were validated by FTIR measurements. Quantitative analysis based on the whole tuning range of the filtometer and employing partial least squares (PLS) calibration revealed fully satisfactory results with root mean square error of prediction (RMSEP) of 0.03, 0.04 and 0.26% for iso-butane, 1-butene and 1,3 butadiene respectively. As the tunable FP filtometer also allows measurements at pre-selected spectral windows a calibration based on multiple linear regression (MLR) was performed as well obtaining similar results. The results clearly show that tunable Fabry-Pérot filters can be used in a new generation of filtometers and provide a low-cost option for the quantitative and fast multicomponent gas sensing.

1. Introduction

With increasing requirements on monitoring of chemical as well as pharmaceutical processes, the demand for powerful, robust and low priced sensors increases. Trends in PAC (process analytical chemistry) or PAT (process analytical technologies) point towards portable analyzers, which can be used in different environments for at-line, but ideally for on- or in-line analysis. The sensor systems have to be fit for purpose, exhibiting adequate analytical performance for a moderate and reasonable price. In principle infrared and Raman spectroscopies are highly interesting techniques in this regard as they provide direct molecular specific information. Concerning mid-IR spectroscopy, Fourier transform spectrometers present the so far most widely used technique [1,2]. These instruments provide a broad spectral coverage and can be successfully applied to solve a broad variety of different analytical problems often by employing chemometric techniques for data analysis. As of today rugged FT-IR spectrometers for on-line or in-line applications are in generally available in every form factor, albeit at a rather high cost. An interesting alternative to established FTIR spectrometers concern spectrometer developments based on broadly tuning, but still prohibitively expensive laser sources, such as external cavity quantum cascade lasers (EC-QCLs). Such spectrometers have been used for gas [3,4], as well as liquid sensing [5–7]. This approach, in order to be fit for purpose, needs to target applications where gas traces need to be recorded at high speed or where increased ruggedness for liquid sensing is required to justify the high cost.

For providing an answer to some sensing tasks, however, the spectroscopic performance of an FT-IR spectrometer is not required as a restricted spectral range sometimes can provide the required selectivity to solve a given problem. Furthermore, in many applications the high sensitivities as offered by mid-IR laser spectroscopy are not needed, either. This is often the case when major and minor components of industrial gas mixtures need to be monitored. A cost effective solution for addressing such applications is possible by addressing selected spectral regions by the use of filters instead of using an interferometer or lasers. Thus, analyzers using a small, but constant portion of the IR spectrum, as obtainable with static IR filters, have emerged over the years. Such filter based spectrometers are also known as filtometers, a term coined from “filter” and “photometer”. The commercial success of such filtometers made it apparent, that the compromise between performance and price allows attractive solutions for certain measurement problems. Examples are the oil-in-water analyzers by Wilks Entreprise [8] (Spectro Scientific) or first iterations of filtometers for the determination of casein content in milk and milk products [9]. Also concerning absorption or photoacoustic gas measurements filter based instruments have found their application in the recent past.

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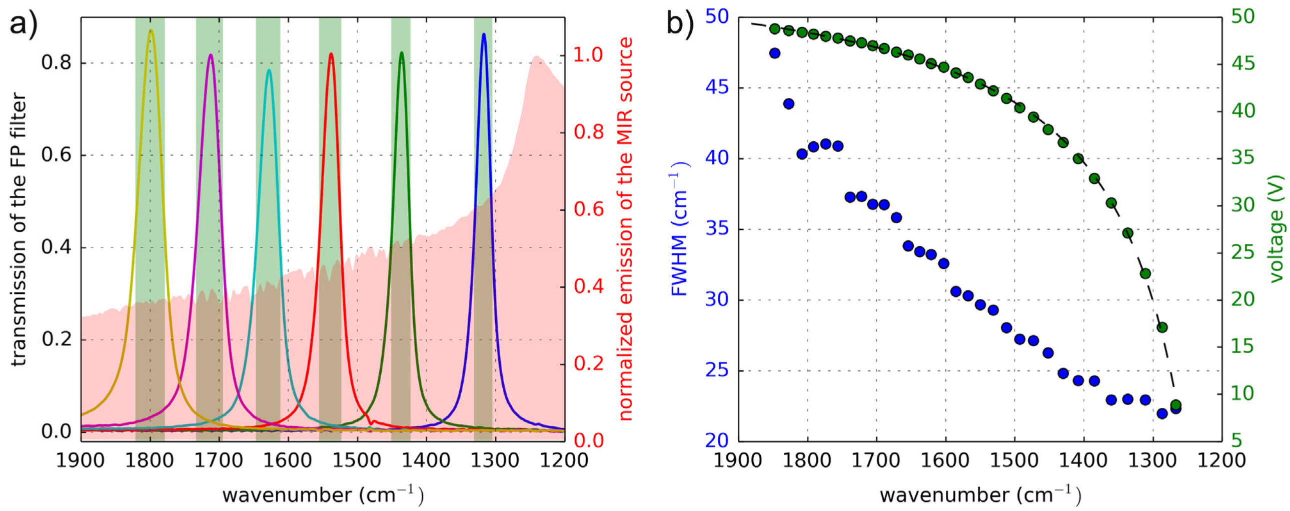

Fig. 1. Transmission windows (a) of the LFP5580 when different voltages are applied and FWHM (b, blue markers) of the transmission curves as a function of wavenumber as well as spectral center (green markers) in dependence of the applied voltage. The fitted curve is indicated as the black dashed line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Here, applications of filtometers primarily include gas-phase analysis of simple molecules, such as water and CO_2 [10,11].

Whereas early technological solutions employed a filter wheel for addressing different narrow spectral ranges for measurement, new technological developments are emerging and may change the way modern filtometers operate. New designs respond to the fact that it would often be advisable to monitor more than a single or a set of predefined narrow wavelength ranges. This added capability would increase the flexibility of filtometers and turn them into a more generally applicable analytical tool at remaining low cost and small footprint.

A key enabling technology for this development is Fabry-Pérot (FP) interferometry [12], where the transmitted wavelength is defined among other by the distance between two reflective surfaces. A range of discrete distances can be realized in a small device by circular (CVF) or linear variable filters (LVF). A combination of these with a linear IR detector array [13,14] allows to create compact mid-IR spectrometers, with a spectral resolution of at best 10–20 cm^{-1}, thus approaching the capabilities of a low resolution FT-IR spectrometer but showing sensor-like performance. In these instruments, like those of Pyreos [15], the reflective surfaces of the Fabry-Pérot cavity are kept in place by a wedged spacer in such a way, that the transmission window shifts through the length of the array [14]. Another approach toward compact sensor-like spectrometers consists in changing the distances between the reflective surfaces of the Fabry-Pérot cavity on demand by MEMS (micromechanical systems) fabricated springs or piezo-actuators. These tunable filters also include pyroelectric detector elements and are available in TO8 housings. Compact arrangements of such designs are realized in Infratec's multi-color FP detectors [16] or VTT's integrated solutions [17]. Fabry-Pérot pyro-detectors can therefore be manufactured in large quantities, covering different ranges of the MIR spectrum [18] and are therefore prime candidates for the construction of dedicated spectroscopic sensors. For operation pyro-detectors require modulation of the light intensity. In FT-IR spectrometers this is achieved by using a thermal light source [19], which provides a constant emission of infrared radiation modulated by the interferometer itself. In case of using adjustable Fabry-Pérot cavities for selection of narrow spectral windows practically no intensity modulation is achieved. Therefore, in these miniature, sensor-like spectrometers the intensity of the light source itself has to be modulated. The operation principle of FP-based filtometers permits arbitrary access to selected spectral regions, in addition to recording the whole spectra by a complete scan.

This work reports on the results obtained with a home-made prototype for gas sensing using a Fabry-Pérot pyro-detector and thermal light source, whose emitting element consists of a thin layer of diamond like carbon (DLC), that can be modulated with up to 100 Hz. A typical gas mixture found at butadiene plants of petrochemical refineries has been selected as target analyte composition (iso-butane, 1-buten, 1,3-butadiene). The obtained spectra are evaluated with multivariate data analysis techniques and the results compared.

2. Materials and methods

2.1. Tunable Fabry-Pérot (FP) filter

For characterization and wavelength calibration, the FP filter (LFP5580, InfraTec GmbH) with a tuning range from 5.5 to 8 μm (1830–1250 cm^{-1}) was coupled to a Bruker Vertex 80v FTIR spectrometer as an external detector using a parabolic off axis mirror (f = 156 mm). Spectra at different driving voltages (5–50 V) were collected by averaging 5 scans and setting the scanner velocity to 1.2 kHz (HeNe frequency). With the resulting transmission windows the filter was calibrated (Fig. 1a). The following relation between driving current and central transmission wavelength was found:

$$V_{driving} = V_{max} - \frac{c}{\tilde{\nu} - \tilde{\nu}_{min}} \quad (1)$$

where $V_{driving}$ is the driving voltage of the tunable FP, V_{max} is the maximum voltage, c is a constant factor and ν is the central wavenumber. Eq. (1) was fitted (shown in Fig. 1b as the dashed line) to the measured FTIR transmission spectra in order to calibrate the wavenumber axis and enable scanning with equidistant step size.

Furthermore, as shown in Fig. 1b, the full width at half maximum (FWHM, blue markers) of the transmission curves increases with increasing wavenumber.

2.2. FP-based MIR filtometer for gas sensing

The FP-based MIR filtometer (inset in Fig. 2) consisted of a custom built 30 cm gas cuvette employing two circular (diame-