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# Hollow fibers for compact infrared gas sensors

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## ABSTRACT

Hollow fibers can be used for compact infrared gas sensors. The guided light is absorbed by the gas introduced into the hollow core. High sensitivity and a very small sampling volume can be achieved depending on fiber parameters i.e. attenuation, flexibility, and gas exchange rates. Different types of infrared hollow fibers including photonic bandgap fibers were characterized using quantum cascade lasers and thermal radiation sources. Obtained data are compared with available product specifications. Measurements with a compact fiber based ethanol sensor are compared with a system simulation. First results on the detection of trace amounts of the explosive material TATP using hollow fibers and QCL will be shown.

**Keywords:** Hollow fibers, photonic bandgap fibers, gas sensors, infrared, explosive detection

## 1. INTRODUCTION

Gas sensors are indispensable in many fields such as technical, environmental, automotive, and medical applications. Cost effective solutions are required for concentration measurement of gases such as $NO_x$, $CO_2$, CO, or $CH_4$. Ethanol breath testing of car drivers is a common example, too. Several types of gas sensors are available on the market. Infrared optical gas sensors are frequently used because of their good selectivity and stability. Here, characteristic absorption lines arising from rotational-vibrational excitations of the molecules in the mid-infrared (MIR) spectral range are monitored. A typical sensor consists of an infrared source, absorption path (i.e. within a sample cell), and radiation detector. The non-dispersive infrared (NDIR) technique employed for many compact sensors frequently uses fixed optical filters mounted in front of the detector elements for spectral discrimination. Cost optimization is very important; thus thermal emitters, simple optics, and thermopiles or pyroelectric detectors are used.
The sensitivity of an infrared gas sensor depends on the interaction length between radiation and gas, i.e. a reduction in cell size generally results in a reduced sensitivity, too. Thus miniaturization is physically limited. Folding the optical path within the sample cell is the usual way to achieve a sufficient detection limit at a given system size. A low sample volume is crucial for many applications, i.e. for gas leak detection, where fast response times are required. Established solutions for multireflection cells (White or Herriott cells) often require special radiation sources (i.e. lasers), high quality coupling optics, and careful alignment. A completely new approach for miniaturization is to use photonic crystal sample cells. However, in this case fundamental technological work is still necessary.[1]
Hollow optical fibres are a promising alternative where the sample gas is flowing through the hollow fiber core, and the probing light is simultaneously guided in the same region. The following results show that on this basis compact gas sensors can be realized even with thermal radiation sources.
In contrast to classical optical fibers, hollow fibers have an air core and light is guided by reflection along that core. This can be either achieved by metallic or dielectric reflecting layers between air core and fiber mantle ( i.e. " leaky waveguide") or by several layers of alternating dielectric constants ("photonic bandgap hollow waveguides PBHWG"). Hollow fibers do not show absorption by the core material and no reflection losses at the incoupling and outcoupling fiber ends compared to conventional fibers, which makes them especially suitable for high laser power laser delivery.
By winding up hollow fibers a long optical pathlength and a small size and volume of an absorption cell is feasible. However, this strongly depends on the minimum bending radius, the bending losses and basic attenuation properties of a hollow fiber. Typical hollow fibers with core diameters of 500 to 1000µm have only a small core volume, which enables fast gas exchange even with small gas flow rates. Additionally, a flexible coupling of optical components i.e. radiation source and detector is feasible.
In the following an overview over different types of hollow fibers for the mid infrared (MIR) specral range is given. For two especially promising fibers manufactured by Polymicro (Polymicro Technologies, LLC, Phoenix, AZ, USA) and

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Omniguide (Omniguide Communications, Inc, Cambridge, MA, USA) fiber attenuation and bending losses were investigated. Based on the experimental data a system concept for a compact filter photometer with a coiled Polymicro fiber for measurement of ethanol gas is shown, and the detection limit is estimated. Measurement results obtained with a corresponding laboratory setup yield very good agreement.

## 2. HOLLOW FIBERS

**Fiber types**

An overview of the state of the art until 2000 can be found at Harrington et. al.[2] In "leaky waveguides" light guiding is achieved via a reflecting layer on the inner surface of the mantle substrate. Typical substrates are metal, glass or polymers. In the simple case, the reflection layer consists of a dielectric and a metallic layer. Metal hollow fibers made from nickel or silver tubes were developed by Miyagi et al.[3] and Bhardwaj et al.[4] Smallest bending radii are approximately 25 cm.

Very flexible hollow fibers can be prepared from polymer substrates. Croitoru et al.[5] have coated Teflon and Polyethylene tubes with silver (Ag) and silver iodide (AgI). However, the fibers show large scattering losses due to the bad surface quality of the polymers. Polymer hollow fibers of George und Harrington [6] consist of polycarbonate. Ag and AgI is also used as reflecting layer. Due to the better surface quality of polycarbonate compared to Teflon and polyethylene lower scattering losses are reported. The minimum bending radius of the polycarbonate fibers is approximately 5 cm.

Hollow glass fibers are also relatively flexible and have a better surface quality resulting in lower scattering losses compared to metal -or polymer fibers. Quartz glass fibers with Ag/AgI -coatings with bending radii down to 5 cm were studied by Matsuura et.al.[7] Such fibers are commercially available from Polymicro, Inc. For the minimum bending radius for 1mm inner diameter fibers a value of 15 cm is specified.

In recent publications further reflective coatings of quartz fibers with several layers and different metallic or dielectric materials were investigated. For example Ag/AgI double layers show a higher transmission and lower sensitivity on variation of the coupling angle compared to a single Ag/AgI layer.[8] However, these transmission measurements were only performed for a 10 cm long fiber with bending radii > 50 cm.

By optimization of complex reflective multilayer structures Temelkuran, Fink et al.[9] have developed new photonics hollow fibers based on the concept of omnidirectional reflectors. The reflection layer consists of several layers of alternating refractive indices, using $As_2Se_3$ (n=2.8) as high index and polyethersulfone PES(n=1.55) as low index materials. This structure forms a spectral bandgap in analogy to electronic band structures in semiconductors, thus the fibers are called "photonic bandgap hollow waveguides" - PBHWGs. These fibers are manufactured by Omniguide, Inc. In contrast to other hollow fibers they transmit radiation only in a rather narrow spectral range. Minimum bending radii are 4cm for fibers for 10.6 µm wavelength (core diameter 700µm) and 1cm for the fiber for 3.55 µm wavelength (core diameter 275µm).

**Gas measurements with hollow fibers**

According to literature for hollow fiber based gas measurements in the MIR around 10µm wavelength mostly glass fibers were investigated. Worrel und Gallen [10] have measured sub-ppm ethylene traces in a several meter long glass hollow fiber. They used a $CO_2$ laser as radiation source and pyrodetector / lockin amplifier detection electronics. Ethylene detection is also reported with a detection limit of 250 ppm using a quantum cascade laser (QCL) at a wavelength around 10 µm and a 43 cm long hollow glass fiber.[11] In measurements of ethylene chloride with a QCL at 10.3µm wavelength and a 1m PBHWG a detection limit of 30 ppb was reached.[12]

FTIR- measurements of volatile hydrocarbons in water were described by de Melas et al.[13] The hollow fiber absorption cell was coupled with a capillary membrane sampling unit for continuous liquid-gas-extraction. $CO_2$ -measurements with a FTIR spectrometer and hollow glass fibers are reported, too.[14] By application of an initial gas sampling stage and a thermal desorption unit atmospheric ethylene traces with a detection limit of 1ppb were reported using a FTIR spectrometer and a 47 cm long hollow glass fiber as sample cell.[15]

# 3. INVESTIGATION OF POLYMICRO- AND OMNIGUIDE- FIBERS

**Properties of investigated hollow fibers**
According to literature for application as gas absorption cell in a compact filter photometer device two types of MIR hollow fibers are selected: only Polymicro hollow glass fibers are commercially available. However, OmniGuide®-PBHWGs are very flexible with a minimum bending radius of 1 to 2cm and thus are especially attractive for compact setups.
Cross-sections of the two fiber types are shown schematically in Fig. 1 and 2 (left sides) together with the corresponding scanning electron microscope (SEM) pictures (right sides).

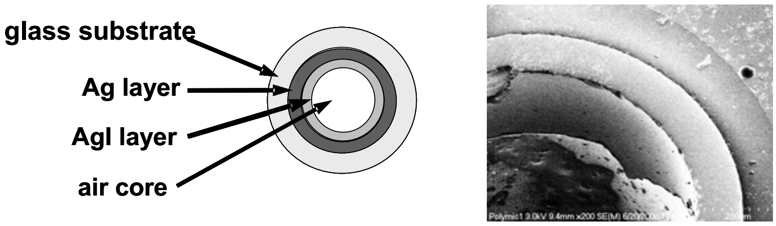


Figure 1: Design of a hollow Polymicro fiber (left) and SEM-picture of cross section (right) showing Ag layer and due to preparation partly delaminated AgI film.

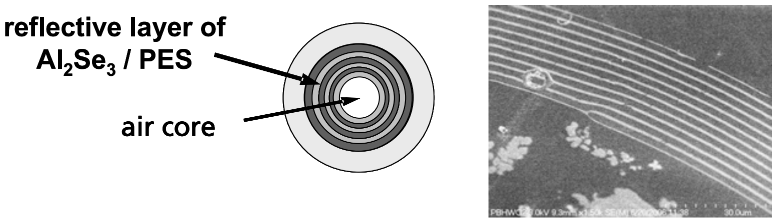


Figure 2: Design of an Omniguide® PBHWG fiber (left) and corresponding SEM cross section showing a typical stacking defect.

Important parameters for the feasibility of hollow fiber based absorption cells and the achievable degree of miniaturization are fiber attenuation, bending losses, and the coupling aperture, core diameter, fiber length and minimum bending radius of specific setup.
The low aperture of most hollow fibers is disadvantageous compared to solid core fibers for thermal radiation sources, because no refraction occurs at the entrance facet.
Starting with transmission measurements with a QCL emitting at 10.34 µm wavelength, we continued with broadband measurement with a FTIR spectrometer, an d a typical NDIR setup consisting of a thermal IR emitter, optical filters, pyrodetector, and lockin amplifier. Different lengths of straight hollow fibers were studied. 90° bends of 50 cm long fiber sections were characterized with bending radii varying from 2 to 20 cm. Inner fiber diameters were 750µm (Polymicro) and 700µm (Omniguide®).

**QCL transmission measurements**
For measurements with a quantum cascade laser (QCL) at an emission wavelength of 10.34µm modules of QCL-gas measurement system [16] were adapted. The lasers were operated with usual parameters (150-200ns pulse length, 10 kHz repetition rate). To investigate different polarization directions (with respect to the plane of fiber bending) the laser platform was rotated with respect to the input fiber mount.
Fig. 3 shows the input and output fiber platforms with fiber mounts and a 90° bent hollow fiber. For adjustment and reference measurements both platforms were joined and the radiation was focused through a pinhole located between the input and output collimating mirror optics.

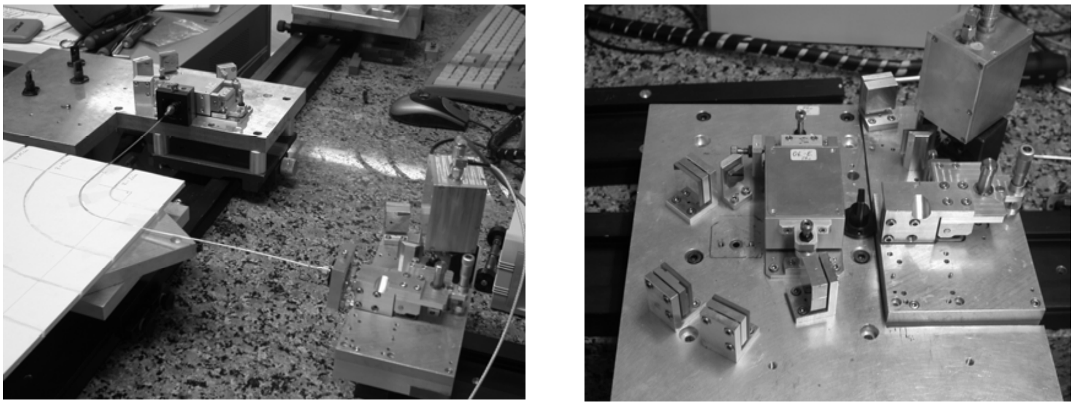

Figure 3: Setup for fibre characterisation with QCL. Between the platforms with reflective optics for in- and out coupling of radiation a 90° bent hollow fibre is displayed (left). For comparison the radiation is focused into a pinhole between the platforms (right). The collimated QCL radiation enters from the left side.

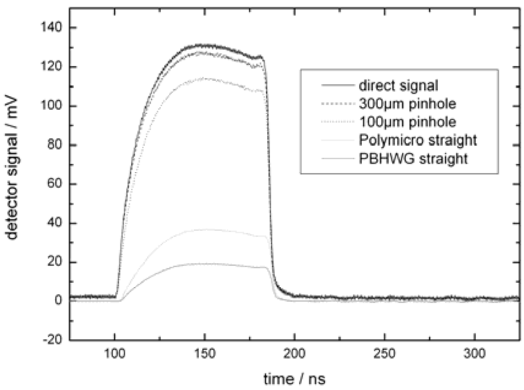


Figure 4: QCL measurements of 50 cm long hollow fibers from Polymicro and Omniguide® (Photonic bandgap-hollow waveguide PBHWG).

Referencing to measurements without fiber and pinhole (top curve in Fig. 4) a transmission of 20.8% (Polymicro) and 9.3% (Omniguide®) respectively fiber attenuations of 13.6 dB/m (Polymicro) and 20.6 dB/m (Omniguide®) were obtained. These values are much larger than the available datasheet information. Bending losses were determined from measurements of a bent 50 cm long fiber referring to the straight fiber. Only 90° bends were used. Bending radii of the Polymicro fibers were 20 cm to 5 cm, and 20 cm to 2 cm for the OmniGuide® fibers. Corresponding laser pulses are shown in Fig. 5.

For measurements of parallel and perpendicular polarization directions with respect to fiber bending no significant difference was observed for the Polymicro hollow fiber as expected. For the OmniGuide®-fiber a larger attenuation was found with the plane of fiber bending parallel to the polarization direction ("high loss plane"). Because for a single 90° bend the fiber length is changing by variation of the bending radius, the bending loss was first determined by the ratio of pulse heights for 90° bent and straight fibers, then normalized with the number of coils for 1 m coiled fiber length, and is depicted in Fig. 6 (left) versus the inverse bending radius.

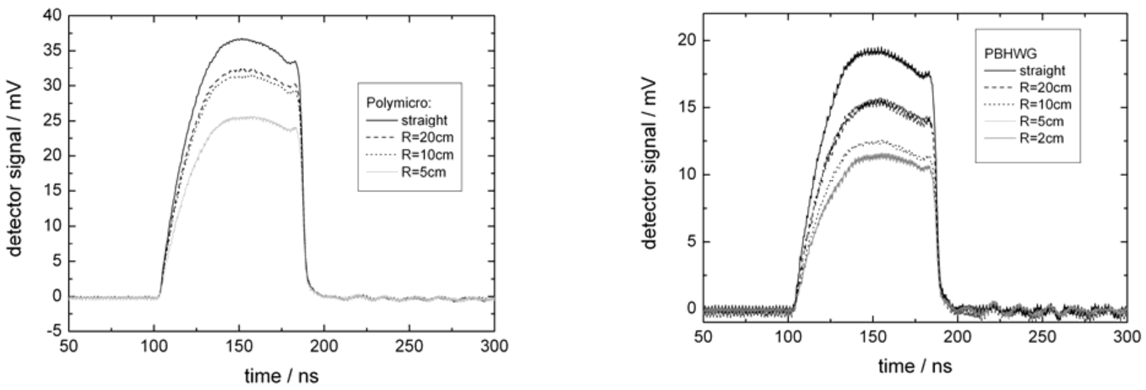


Figure 5: QCL measurement with a 90° bent Polymicro fiber (left) and an Omniguide® PBHWG-fiber with linear polarization perpendicular to fiber bending (low loss plane).

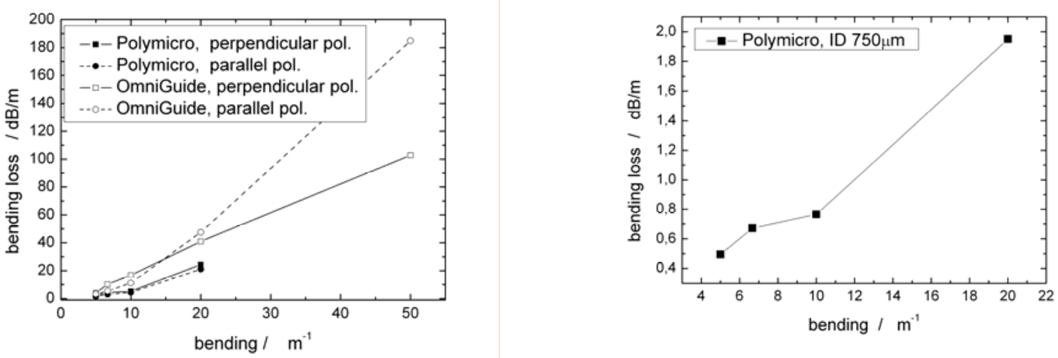


Figure 6: Calculated bending loss for QCL measurements for 1m coiled hollow fibers. The Omniguide® fiber shows higher bending loss for polarization parallel to fiber bending and small bending radii (left). Bending loss with thermal emitter for 1m coiled Polymicro fibers at different curvatures (right).

**Transmission measurements with thermal emitters**

With both fiber types the IR transmission was measured with a FTIR spectrometer and a filter photometer setup using thermal radiation sources. FTIR measurements were performed with a Bruker Equinox 55 using the external port and an external HgCdTe Detector. Details of the measurements are described elsewhere.[17]

Caused by the photonic structure the Omniguide®- fiber is only transmitting between 900 - 1050 $cm^{-1}$. To compare with the QCL measurements the attenuations were determined at 10.34µm, and 50cm long straight fiber sections were used. Values of 13.5 dB/m (Polymicro) and 35,4 dB/m (Omniguide®) were obtained. Because of the strong attenuation of the Omniguide® fiber a reliable determination of the bending losses was not possible with the FTIR. For the Polymicro-fiber however a determination similar to the QCL measurements could be performed. For the smallest radius of 5 cm the bending loss of the Polymicro fiber at 10.34µm was 2.8 dB/m.

Both fiber types were characterized using basic components of a compact filter photometer, i.e. IR radiation source and pyrodetector with an optical filter at 10.34µm.

The radiation of an IR source ((Intex, Inc., Tucson, AZ, USA) electrically modulated with 10 Hz is coupled into the hollow fiber using 2 90° off-axis parabolic mirrors. The transmitted radiation is detected by a sufficiently large pyrodetector closely placed at the fiber end. The fiber end with detector can be moved together in case of the fiber bending experiments. Again the fiber transmission for straight fibers and the bending losses for 90° bends of Polymicro and OmniGuide® fibers were determined for different bending radii. Obtained attenuation values were 12.9 dB/m (Polymicro) and 34.0 dB/m (OmniGuide®), the bending loss for the Polymicro fiber was 2.0 dB/m for 5cm radius. Reliable bending losses could only be obtained for the Polymicro hollow fibers (see Fig. 6 right), because the signals obtained with the OmniGuide®- fiber were too close to the noise level of the setup.

## 4. NDIR SYSTEM CONCEPT AND ETHANOL MEASUREMENT RESULT

**System concept and components**

Based on the measurement results for the Polymicro hollow fibers a system concept for a filter photometer with coiled hollow fiber was developed and the detection limit for an ethanol measurement was estimated. Schematically the setup is shown in Fig. 7. The IR radiation is coupled into the fiber without any optics and is detected behind the fiber with a relatively large pyrodetector with an optical filter.

The following components and data were used:

- IR- emitter (Intex, Inc.); 0.5mm thick $CaF_2$ window, emission area 1.7x1.7 $mm^2$
- Polymicro hollow fiber, inner diameter 750µm, different lengths, 3cm and 5cm bending radii
- pyrodetector (Infratec GmbH, type LME-541-X001), sensor area 3x3 $mm^2$ ,
- filter for ethanol: center wavelength 9.48µm / bandwidth 610nm

The $CaF_2$- window in front of the IR emitter is needed because the ethanol interference filter is not blocked for longer wavelengths than 600 $cm^{-1}$.

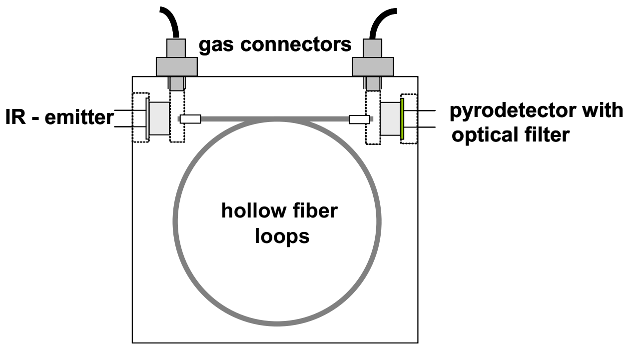


Figure 7: Schematic setup of a NDIR photometer with coiled hollow fiber gas cell.

**Detection limit calculations**

The emission power of the IR-emitter (10 Hz modulation 0-6V) was measured with spectral filtering behind a 700µm pinhole. A corresponding value of 3.46 µW in front of a 750µm fiber was calculated. Then the output power behind different fiber lengths and for bending radii of 3cm and 5 cm were determined. Values for fiber attenuation and bending losses were taken from section 3.3.

In Fig. 8 (left) the resulting power behind a coiled Polymicro fiber is shown for fibers with 10 to 70 cm length and two bending radii of 3 and 5 cm. The transmission is much stronger reduced by (straight) attenuation than by bending.

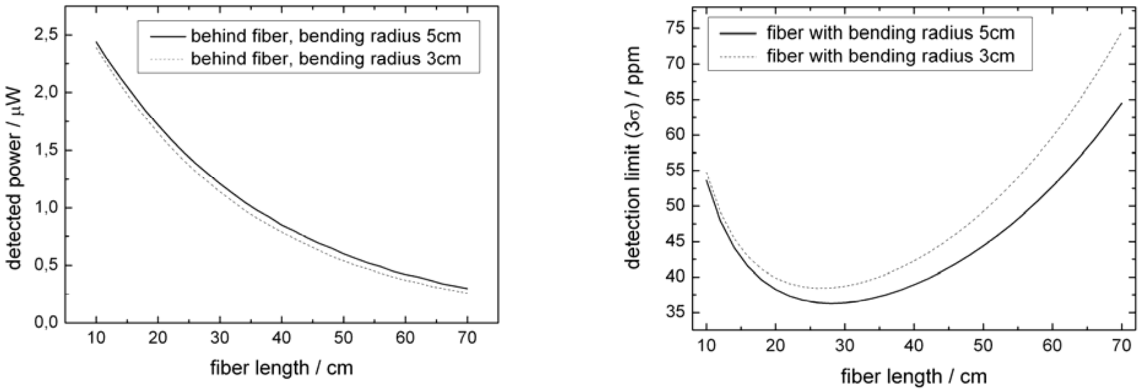


Figure 8: Radiation power behind coiled Polymicro fibers vs. fiber length for bending radii of 5 and 3 cm (left). Corresponding detection limits (3σ) for ethanol vs. fiber length (right).

To calculate the signal change by IR absorption FTIR spectra of 500 ppm gaseous ethanol in $N_2$ were measured for optical path lengths of 35 and 50 cm together with the $CaF_2$ and 9.48µm spectral filter.
By integration the spectra and referencing to the pure $N_2$ signal relative transmission changes were calculated, which are multiplied with the output emission power of Fig. 8 (left) to determine the relative signal change depending on the fiber length. A maximum value of some 35nW at 30cm fiber length was obtained.
The detection limit for ethanol detection is limited by detector noise and thus can be estimated using the datasheet information which gives a noise equivalent power NEP = 0.89 nW (10Hz chopper modulated radiation from blackbody at 500°C, bandwidth 1Hz). The detection limit (3σ) obtained in a linear approximation from three times the NEP divided by the detector signal change of 500 ppm ethanol is displayed in Fig. 8 (right).
For fiber loops an optimum length of 27 to 31 cm and corresponding minimum detection limits (3σ) between 38 and 33ppm are determined. A straight fiber has a corresponding detection limit of 31 ppm at an optimum length of 33 cm.

**Experimental results**
Following the theoretical considerations an ethanol measurement with a 50 cm long straight Polymicro fiber was performed. Without optical elements the IR emitter was directly coupled into the fiber and the transmitted radiation was measured by a pyrodetector with an interference filter at 9.48 µm. A digital lockin amplifier (Signal Recovery, Mod. 7265) was used for registration. Fig. 9 shows the measurement results of 500 ppm ethanol vapor in $N_2$ with time constants of 1s and 2s. From noise analysis detection limits (3σ) of 45 ppm (τ = 1s) resp. 34 ppm (τ = 2s) are obtained. These values agree very well with the calculated value of 33 ppm for a 50 cm long straight fiber.

## 5. QCL SYSTEM CONCEPT AND TATP MEASUREMENT

An important application of sensitive small gas volume measurement is explosive detection. Fast and effective detection of explosives is a key security issue against possible terrorist attacks. The current ‘gold standards’ for sensors are gas chromatography chemo luminescence (GC-CL) used in forensic applications and ion mobility spectrometry (IMS) deployed in field applications e.g. for carry-on baggage screening at airports. However, these techniques have some drawbacks: insensitivity to some key compounds, masking by interferents, practical deployment concerns etc. The nature of the threat from explosives is also increasing by the developments in improvised explosive devices (IEDs) which use explosives manufactured from common domestic chemicals rather than those produced commercially. One example is TATP( triacetone triperoxide) which was used in the London transport bombings. TATP is a high vapor pressure compound with a characteristic IR spectrum (see Fig. 10). Hence trace detection in the gas phase is a potential method. During sampling trace amounts of TATP in the nanogram range could be evaporated and introduced in a low volume IR gas cell. Dilution by carrier gas etc. should be kept at a minimum, which could be solved using a hollow fiber setup.

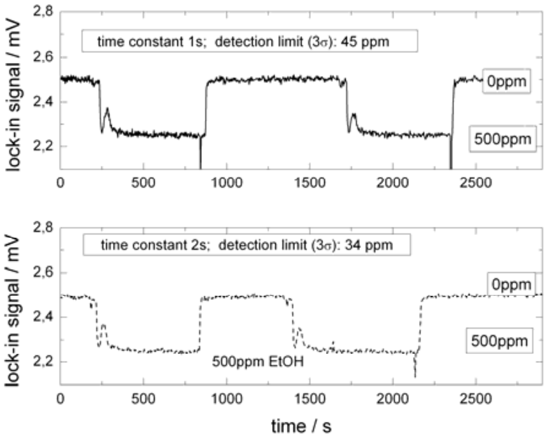


Figure 9: Measurement of 500ppm ethanol in $N_2$ using a 50 cm long straight hollow fiber and time constants of 1s and 2s.

To increase the sensitivity we use a QCL from Fraunhofer IAF emitting at 1200 $cm^{-1}$ instead of the thermal radiation source in Fig. 7 and a reference detector to monitor the fiber input power. Though broad absorption bands as of TATP are not really suitable for QC laser spectroscopy the high power of a multimode QCL is advantageous. The first investigations which are reported here are focused on sensitivity. In a later stage selectivity can be achieved by using broadly tunable external cavity QCL which recently became commercially available (Daylight Solutions, Inc., Poway, CA, USA).

The setup shown in Fig. 11 consists of a sample chamber, where a small amount of TATP is heated and equilibrium vapor pressure values are approximately obtained. By slightly pressurizing with $N_2$ part of the chamber gas is introduced into the hollow fiber. The Polymicro fiber is heated to approximately 90°C to prevent condensation at the fiber walls. The result of a measurement is shown in Figure 12.

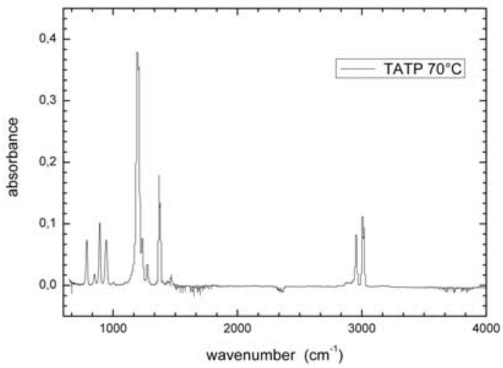


Figure 10: FTIR (Fourier transform infrared) spectrum of 0.15g/l TATP in the gaseous phase at 70°C shows a characteristic absorption at 1190 $cm^{-1}$.

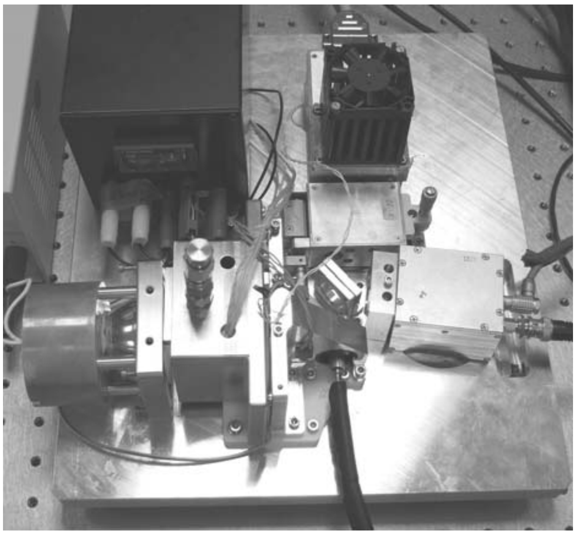

Figure 11: Setup showing desorption cell with heating elements and power supply (left), QCL module and collimation optics (top), beam splitter (middle), reference detector (right), and hollow fiber in heating hose (bottom).

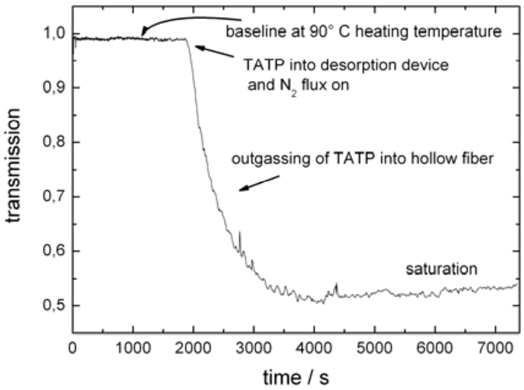


Figure 12: QCL based infrared transmission measurement of 1.5 mg TATP introduced into desorption stage and vapor extraction through hollow fiber cell.

The detection limit can be estimated in the following way: at 90°C the saturation vapor pressure of TATP is 110 hPa.[18] Thus in the desorption chamber a maximum TATP volume concentration of 11 % is reached. With a fiber length of 50 cm roughly a 50% transmission change is obtained. A transmission change of $10^{-3}$ is detectable for such an instrument without much effort, which corresponds to some 160 ppm concentration change. Thus, taking a sensitive fiber volume of 0.2 ml (neglecting dead volumes of fittings etc.), an estimate of the TATP density in the gas phase of 10g/l, this translates to a detection limit of roughly 240 ng.

By improvements in the system transmission changes in the $10^{-4}$ range are feasible, and the fiber parameters may be further optimized. Hence detection limits in the 10 ng range are within reach. Using a fast desorption stage a measurement time of e few seconds is possible, too.

## 6. CONCLUSION AND OUTLOOK

The feasibility of compact optical gas sensors based on hollow fibers was investigated. Calculated and experimentally determined detection limits agree quite well. The detection limit is basically limited by the rather high fiber attenuation. By winding up the fiber with bending radii ≥3 cm the detection limit is only increased by a small amount. If compact IR-sources, detectors, electronics, and housing components (gas fittings etc.) are selected, a compact gas sensor with approximate dimensions $\leq 10x10<1cm^3$ for small gas volumes below 1 ml is feasible.

However, the detection limit is not lower than with conventional setups (i.e. multireflection cells). Thus for applications where a sufficient supply of sample gas exists, the established solutions will be preferred. Main reasons are the lack of information on lifetime, possible degradation mechanisms, sensitivity to humidity etc.

On the other hand we expect that by technological improvements the fiber attenuation can be further reduced which results immediately in a lower detection limit. The reported fiber losses still include coupling losses. They depend very much on the properties of the radiation sources and coupling optics. Even small improvements at this point could greatly enhance the sensitivity.

If only very limited sample masses are available, which is the case for trace explosive detection, hollow fibers could offer a promising solution. As an example TATP vapor detection was demonstrated with a QCL setup. With hollow fibers volatile explosive quantities far below 1µg will be detectable within a few seconds.

Though quite promising because of their flexibility photonic bandgap hollow waveguide (PBHWG) fibers turned out to be not suitable for the anticipated application using incoherent thermal radiation sources. However, if their attenuation could be greatly reduced, such fibers may offer integrated spectral filtering and, via an optimized dispersion control, the possibility of enhanced absorption due to the reduced group velocity in photonic crystals.[1]

Because fiber technology in the MIR is still at the beginning, and many practical details are unknown, substantial effort to develop new hollow fibers in this spectral range would be greatly appreciated.


## ACKNOWLEDGEMENTS

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