

Measurement of acetic acid using a fibre Bragg grating interferometer

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 Meas. Sci. Technol. 20 125201

(<http://iopscience.iop.org/0957-0233/20/12/125201>)

[The Table of Contents](#) and [more related content](#) is available

Download details:

IP Address: 193.136.24.66

The article was downloaded on 22/12/2009 at 19:59

Please note that [terms and conditions apply](#).

Measurement of acetic acid using a fibre Bragg grating interferometer

C Jesus^{1,2}, S F O Silva^{1,3}, M Castanheira¹, G GonzálezAguilar¹,
O Frazão^{1,3}, P A S Jorge¹ and J M Baptista^{1,2}

¹ INESC Porto, Rua do Campo Alegre 687, 4169-007, Porto, Portugal

² Departamento de Matemática e Engenharias, Universidade da Madeira, Penteada, 9000-390 Funchal, Portugal

³ Faculdade de Ciências da Univ. do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

E-mail: pedro.jorge@fc.up.pt

Received 16 July 2009, in final form 25 September 2009

Published 29 October 2009

Online at stacks.iop.org/MST/20/125201

Abstract

An optical fibre sensor for determination of acetic acid is presented. The sensing probe is based on a fibre Bragg grating (FBG) Fabry–Perot cavity, coated with a thin film of sol–gel–PVP (polyvinylpyrrolidone) composite material. The polymeric thin film renders the interferometric output sensitive to the presence of carboxylic acid species. Results show that the wavelength of the interferometric peaks changes with acetic acid concentration, enabling its quantification. Coupling the fibre probe with a serrodyne modulated readout interferometer enables pseudo-heterodyne interrogation and the detection of acetic acid with a sensitivity of 92.6 deg/% L/L and a resolution of 0.2% L/L. The results demonstrate the potential of the proposed scheme to operate as a sensitive chemical sensor platform.

Keywords: optical fibre sensor, fibre Fabry–Perot cavity, acetic acid sensor

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Acetic acid and other carboxylic acid species play an important role in many food and chemical industry processes. In particular, the operation of anaerobic reactors is dependent on the balance of these chemical species. Anaerobic digesters are based on methanogenic bacteria and are highly attractive facilities for combined wastewater treatment and energy generation. However, a very careful control of temperature, pH and other process parameters is required to maintain a sustainable operation. Due to buffer effects, most of the times pH control is not a reliable indicator of the bioreactor health, whose operation can be seriously compromised by a build-up of the concentration of volatile fatty acids. Typically, the determination of such parameters is associated with expensive and time-consuming techniques, like gas–liquid chromatography, that do not provide timely feedback. In this context, simple and compact sensors capable of rapid quantification of the reactor acid content would provide the industry with a valuable tool for process control [1]. Optical fibre sensors with immunity to electromagnetic interference,

biocompatibility, remote sensing ability and miniaturization are attractive solutions to process monitoring in the food industry and environmental applications [2–4].

Some fibre optic-based solutions have been proposed for on-line detection of acetic acid. Kurauchi *et al* [5] demonstrated a colorimetric acetic acid sensor by immobilizing a sensitive dye in a poly(vinyl alcohol)-based membrane. A response time of 1 min to 5% L/L change in volume fraction with a relative standard deviation of 2% was demonstrated. Long-term stability and immunity of inorganic acids and/or non-volatile species were achieved using a protective Teflon membrane which, however, increased the response time to 5 min. In another absorption-based sensor, polyaniline films deposited in polystyrene sheets were used [6]. Acetic acid was measured in the gaseous headspace of a container with a detection limit of 5% in the 0%–100% concentration range. In a different approach, an evanescent wave sensor using a sensitive cladding layer which introduced refractive index changes in the presence of the analyte was patented by Muto and Morisawa [7]. In this case, however, etching of the fibre cladding was necessary in order to

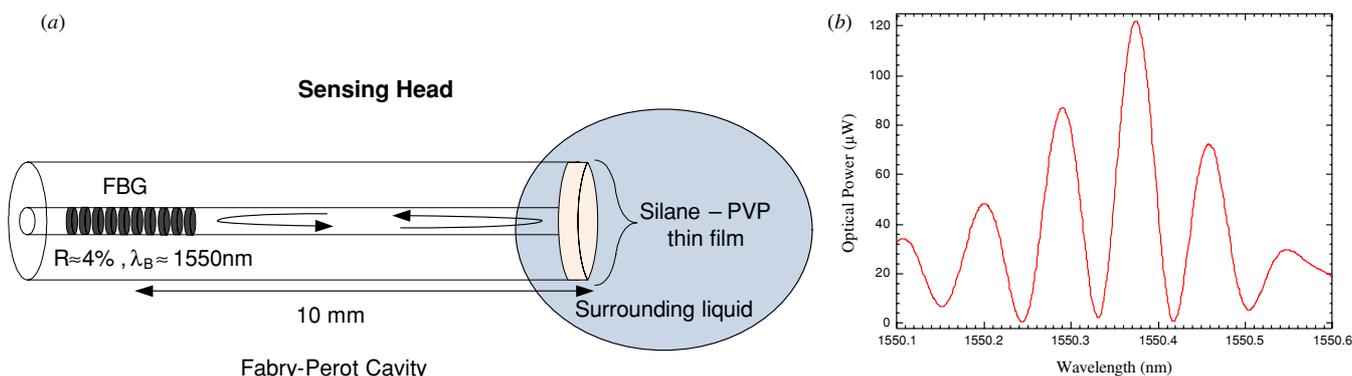


Figure 1. (a) Scheme of sensing head. (b) Interferometric output of the coated FBG Fabry-Perot cavity.

allow evanescent interaction between the guided radiation and the polymer layer, introducing complexity in the fabrication procedure and fragility to the sensing head. A variety of configurations and techniques, including fluorescence-, absorption- and reflectance-based sensors for the detection of similar volatile organic compounds, in the context of different applications, have been recently reviewed by Elosua *et al* [8]. The same authors have recently demonstrated the use of a Fabry-Perot cavity sensor fabricated by a layer-by-layer electrostatic self-assembly technique to measure volatile compounds. However, the sensor was interrogated in reflection, in an intensity-based scheme, taking little advantage of the interferometric sensitivity [9].

In this work a compact interferometric optical fibre sensor for acetic acid detection built using standard telecom optoelectronics components and a sol-gel-based sensitive layer is described and characterized.

2. Experimental setup

2.1. FBG-based Fabry-Perot cavity

The scheme of the sensing probe developed is shown in figure 1. The sensitive system is formed by a low-reflectivity fibre Bragg grating (FBG) structure ($R \approx 4\%$) with a central wavelength at 1550 nm, located 10 mm away from the tip of the fibre. SMF-28 single-mode fibre with a germanosilicate core 3% mole fraction, previously hydrogenated at 100 atm, was used. The FBG was written using a 10 mm length diffractive phase mask ($\Lambda = 1062$ nm), illuminated with a KrF laser (248 nm). In order to obtain a 4% Fresnel reflection at the tip, the fibre was cleaved perpendicular to the direction of light propagation using standard tools. In this situation, a low finesse Fabry-Perot cavity was formed between the fibre end and the low-reflectivity FBG that was shown to be a sensitive refractometer [9]. By coating the fibre tip with an analyte sensitive layer, it is expected that this configuration will allow the sensitive detection of chemical species.

2.2. Sensitive membrane

The sensitive membrane was prepared by the sol-gel method by hydrolyzing TEOS (tetraethoxysilane) dissolved in ethanol with 0.1 M HCl. During the hydrolytic procedure, a mass

fraction of 3.9% PVP (polyvinylpyrrolidone) was added for incorporation in the SiO_2 matrix. Following 1 h stirring, the extremity of the Fabry-Perot cavity was dip coated in the polymer solution and the resulting film was cured at 100 °C for a 4 h period. Both the ketone and the cycloalkyl ammonium groups of PVP are expected to interact with carboxylic species introducing refractive index changes of the membrane. These changes produce variations in the optical path of the cavity and consequently modify the phase of the interferometric pattern. Some glass slides were also coated by the same process to serve as a control. From these films a thickness of approximately 6 μm could be estimated using a needle profilometer.

2.3. Instrumentation and procedures

Characterization of the sensing probe properties was done using a simple setup where an erbium-doped fibre source illuminated the sensor through an optical circulator which enabled the reflected Fabry-Perot signal to be observed using an Advantest Q8384 optical spectrum analyser (OSA) with a maximum wavelength resolution of 10 pm. To avoid cross-sensitivity to temperature and strain, the sensing head was fixed to a rigid support to ensure that no strain was applied to the FBG while handling and all measurements were made at a fixed temperature. The sensor response to acetic acid (CH_3COOH) was then tested by submerging the fibre tip in a container with deionized water.

A preliminary evaluation of the sensor response showed a non-linear behaviour, where the sensitivity decreased with increasing concentration. Furthermore, due to saturation effects it was observed that above 40% L/L barely any response was observed. Therefore, in the present work, a more detailed evaluation of the sensor response was limited to selected ranges where a linear calibration could be performed.

Periodically, controlled amounts of glacial acetic acid (A6283 Sigma-Aldrich acetic acid >99%) were added to the water in order to gradually change its concentration in the 5–33% L/L range. Magnetic stirring was used to homogenize the solution and each measurement was performed after stabilization of the interferometric pattern. The refractive index of all solutions tested was measured using an Abbe refractometer.

The sensing system was also tested for dynamic response using a high-sensitivity pseudo-heterodyne interferometric

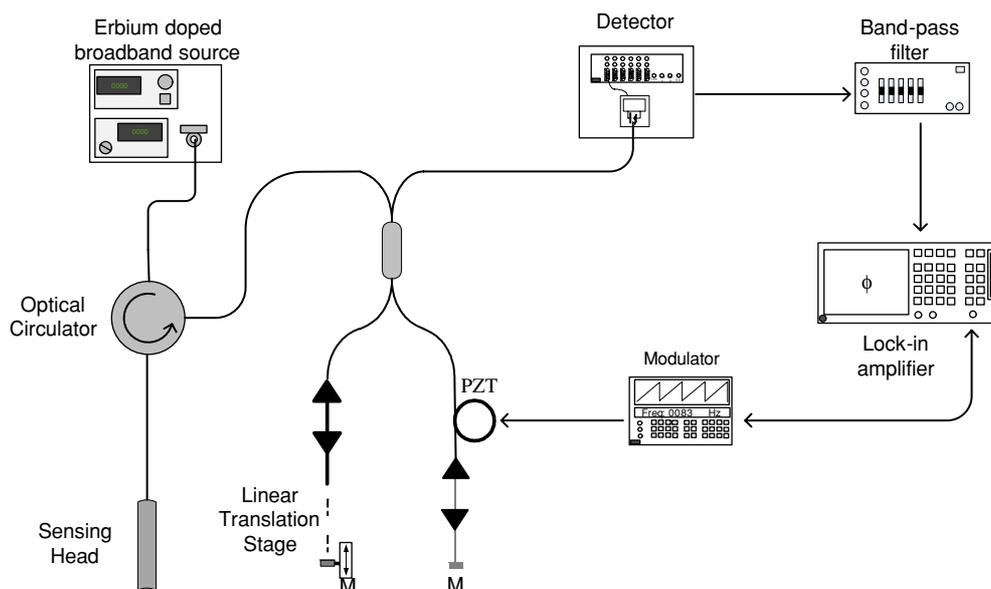


Figure 2. Setup for interferometric interrogation of the fibre probes using a pseudo-heterodyne scheme.

interrogation [10] setup that is shown in figure 2. The reflected optical signal was guided to a receptor Michelson fibre interferometer that could be tuned to match the path imbalance of the sensing head. One of the interferometer fibre arms was wound around a PZT ring, enabling sawtooth modulation of the interferometric phase. In this situation, after adequate filtering, the changes in the Fabry–Perot interferometric output arise as a phase shift on the sinusoidal carrier signal, which can be retrieved using a lock-in amplifier. To assess system sensitivity in more diluted solutions, the fibre probe was exposed to small changes in acetic acid concentration in the range 0.6–3.3% L/L.

3. Results

The interferometric nature of the bare FBG cavity could be confirmed by the observation of the typical channelled spectrum (figure 1(b)). In addition; the comparison of the output spectra before and after polymer deposition revealed only very small changes in visibility ($\sim 1\%$), indicating that the film produced had a good optical quality and a refractive index close to that of the fibre core. When submerged in deionized water a clear decrease in the visibility was observed due to the increase in the external refractive index ($n_{\text{water}} \sim 1.33$). Nevertheless, the visibility observed (44%) was adequate for the interferometric measurements undertaken.

The addition of acetic acid resulted in small changes in the solution refractive index (from $n = 1.3365$ to $n = 1.3540$, which corresponds to 0.018 RIU for the full range of acid concentration tested 0.6–33% L/L). However, the interaction of the analyte with the sol–gel–PVP film strongly impacted the phase of the interferometric pattern. This can be seen in figure 3 where the output spectra for two distinct acetic acid concentrations, 5.26% L/L and 14.29% L/L, can be compared. These results indicate that the presence of the analyte created a change in the refractive index of

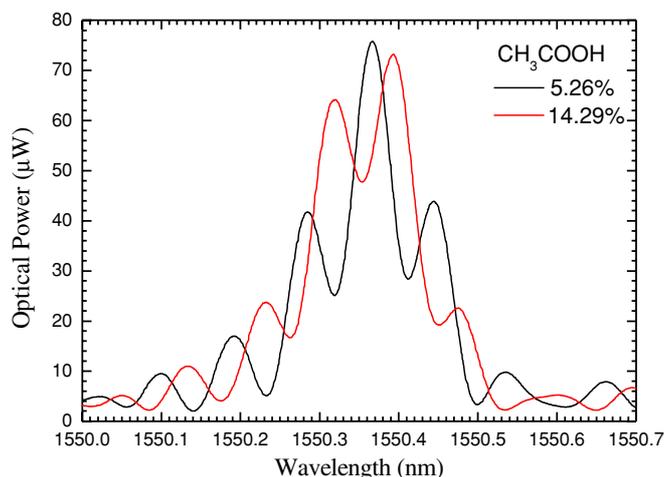


Figure 3. Interferometric output spectra for two different acetic acid concentrations.

the sensing membrane, introducing changes in the optical path of the cavity and consequently modifying the phase of the interferometric pattern. It was verified that exposure to ethanol and ethylene glycol did not impact the spectral pattern significantly, indicating selectivity towards volatile fatty acids. Nevertheless, a more thorough evaluation of cross-sensitivity to other chemicals will be carried out with the aim of using the sensor in practical applications.

An approximately linear relation ($R^2 = 0.990$) was found between the acid concentration and the relative position of the interferometric peaks in the concentration range 5–33% L/L. A sensitivity of 2.71 pm/% L/L acid was estimated for this operation range. Due to the limited resolution of the OSA (10 pm), a limit of detection of approximately 4% L/L was established. Even with high-resolution spectrometers, the resolution is typically in the range of 1 pm. Therefore, direct spectral interrogation would impose a limit of detection of

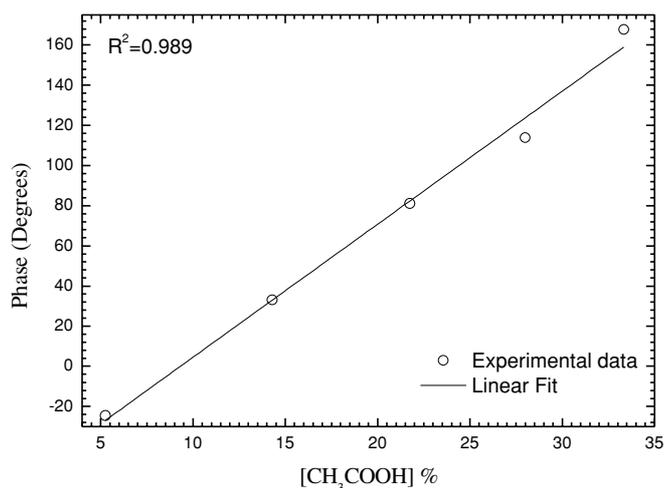


Figure 4. Response of the interferometric phase to changes in acetic acid concentration in the range 5–33% L/L.

roughly 0.4% L/L. Nevertheless, the nature of the sensing mechanism is compatible with high-sensitivity interferometric readout schemes. In fact, the use of the pseudo-heterodyne system described above was tested in different concentration ranges.

Figure 4 shows the phase response of the readout interferometer when the sensor was submitted to acetic acid concentration changes in the range 5–33% L/L. The data obtained showed a linear response ($R^2 = 0.989$) and allowed us to estimate a sensitivity of 6.6 deg/% L/L. Considering that the output of the readout interferometer showed a standard deviation, σ , around 4° , and considering a minimum detectable signal of 2σ , means that with the heterodyne system the minimum detectable acetic acid concentration would be of approximately 1% L/L, which represents a fourfold increase as compared with spectral interrogation with the OSA. Nevertheless, it should be mentioned that, in its present configuration, the readout interferometer suffered from some vibration- and thermal-induced instability which limited its resolution.

Because the phase of the interferometer depends on these parameters, its output phase results from the sum of the analyte-induced phase shift and the interferometer quasi-static phase. Therefore, the system measures relative phase shifts, performing relative concentration measurements. In operational terms this means that the measurement of an absolute concentration value will require that an initial measurement at a known concentration, using a reference solution, is made.

Additional tests were performed in a lower concentration range of acetic acid. The results obtained are shown in figure 5 where it can be seen that the phase output depends linearly on the acid concentration ($R^2 = 0.999$) in the range 0.6–3.3% L/L. From these data a sensitivity of 92.6 deg/% L/L could be estimated. These results show that the sensing membrane is intrinsically very sensitive to the analyte in a low concentration range and that the sensitivity is reduced as the concentration increases. Such behaviour

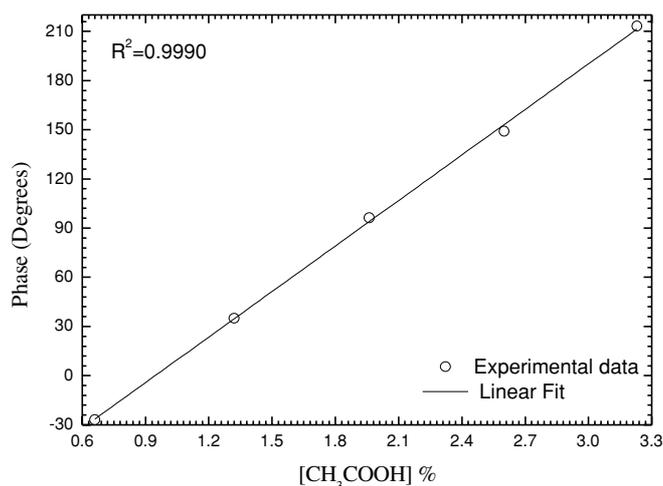


Figure 5. Response of the interferometric phase to changes in acetic acid concentration in the range 0.6–3.3% L/L.

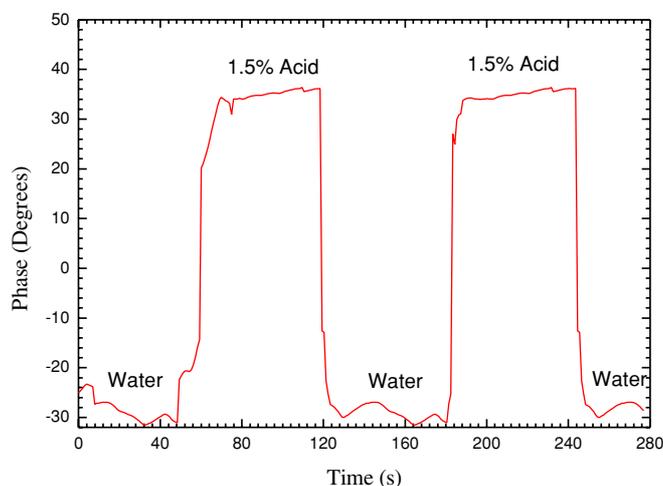


Figure 6. Sensor dynamic behaviour showing the reversibility of the phase response when the sensor is subjected to step changes in acetic acid concentration.

indicates that the sensing mechanism relies on diffusion-based processes, where the higher concentration range is typically associated with lower concentration gradients and lower availability of receptor sites to the analyte, resulting therefore in reduced sensitivity as concentration increases. Nevertheless, linear responses could be observed in limited concentration ranges.

The sensor dynamic response was tested in the lower concentration range. Figure 6 shows the response of the sensor to alternate exposure to distilled water and 1.5% L/L acetic acid solutions. The results obtained demonstrate the reversibility and repeatability of the sensor response. From these data a resolution of 0.2% L/L could be estimated. Also response and recovery times of approximately 6 s and 4 s were measured, respectively. In the present scheme, system resolution was hindered due to some instability in the interferometric interrogation system due to poor acoustic and thermal isolation. Nevertheless a reduction in phase noise and vibration-induced noise should allow us to improve the system performance by at least one order of magnitude, enabling

high-sensitivity chemical measurements. A coarse evaluation of the sensor response time was made in the full range tested and it was verified that the response time increased slightly with concentration due to longer diffusion times, going from 9 s at 10% L/L to 11 s at 33% L/L.

Potential problems of the presented sensing system include cross-sensitivity to strain, temperature and other chemical species. Proper packaging of the FBG can be used to stabilize temperature and strain without compromising the chemical sensitivity of the tip. In fact, considering that FBG-based sensors typically exhibit a temperature sensitivity of around $10 \text{ pm } ^\circ\text{C}^{-1}$, a fluctuation in temperature of $0.25 \text{ }^\circ\text{C}$ is expected to produce an effect similar to a 1% variation in acid (when the range 5–33% is considered). Therefore, because in the present experiments temperature was controlled to $\pm 0.5 \text{ }^\circ\text{C}$ the resolution obtained ($2.71 \text{ pm}/\% \text{ L/L}$) is probably a limitation imposed by temperature fluctuations. Several solutions are possible to avoid temperature interference, either its simultaneous measurement followed by signal processing, or by using an athermal FBG or a differential detection scheme. In any case, the sensor resolution is expected to be improved substantially. The cross-sensitivity to chemical parameters depends strongly on the environment in which the sensor is to be applied and must be dealt with either by chemical modification of the sensing layer or by the use of protective/selective membranes. Some preliminary assessments of cross-sensitivities were performed. It was verified that in the presence of non-acidic species such as ethanol and ethylene glycol the sensor phase output did not change significantly. In addition, some tests were made where the sensor response was tested in different pH buffers. Although some small fluctuations could be observed in the sensor output, no correlation could be made with the pH value. Therefore, a preliminary evaluation seems to indicate that the membrane is selective towards short-chain carboxylic acids, such as acetic acid, and is little influenced by more complex species. Nevertheless, a more detailed study of cross-sensitivity is necessary if the aim is to use the sensor in complex samples. These studies, along with the optimization of the membrane response range, are the subject of ongoing work.

4. Conclusions

An interferometric optical fibre sensor for the detection of acetic acid based on a FBG-based Fabry–Perot cavity and a sensitive sol–gel–PVP coating was demonstrated. The system showed a linear and reversible response and short response times with adequate reproducibility and repeatability. A sensitivity of $96.2 \text{ deg}/\% \text{ L/L}$ and a resolution of $0.2\% \text{ L/L}$ were obtained, in the $0.6\text{--}3.3\% \text{ L/L}$ concentration range, using a pseudo-heterodyne interrogation scheme. The response and recovery times of the sensor were 6 s and 4 s, respectively, for the lower concentration range. Cross-sensitivity to temperature and strain can be dealt with by some well-established referencing strategies. Some preliminary results showed that the membrane was selective towards short-chain

carboxylic species, showing no response to more complex acids and to non-acidic species. Nevertheless, in order to use the sensor in real samples, a more complete assessment of the interference of other chemical species is yet to be made.

The configuration presented has potential advantages such as the fact that it operates spectrally on the telecommunication window (1550 nm) and it does not use physically entrapped colorimetric or luminescent indicators, thus avoiding the problems associated with leaching and bleaching. Also, the sensor is addressed in reflection and can be multiplexed, enabling sensor networks. The sensitive layer is placed at the very tip of the fibre, avoiding complex etching processes necessary to promote evanescent interaction. Furthermore, the chemical modification of the sensitive layer will allow the same sensing scheme to be applied to a variety of chemical parameters, enabling the implementation of multiparameter/multipoint sensing networks.

Acknowledgments

Carlos de Jesus acknowledges the financial support given by FCT—Fundação para a Ciência e Tecnologia, Portugal (Project—OPTIC-ALGAE, PTDC/BIO/71710/2006).

References

- [1] Cooney M, Maynard N, Cannizzaro C and Benemann J 2007 Two-phase anaerobic digestion for production of hydrogen–methane mixtures *Bioresource Technol.* **98** 2641–51
- [2] Wolfbeis O S 2008 Fiber-optic chemical sensors and biosensors *Anal. Chem.* **80** 4269–83
- [3] Narayanaswamy R and Wolfbeis O S (eds) 2004 *Optical Sensors—Industrial Environmental and Diagnostic Applications (Springer Series on Chemical Sensors and Biosensors)* ed O S Wolfbeis (Berlin: Springer)
- [4] Holst G and Mizaikoff B 2002 Fiber optic sensors for environmental applications *Handbook of Optical Fibre Sensing Technology* (New York: Wiley) pp 729–55
- [5] Kurauchi Y, Ogata T, Egashira N and Ohga K 1996 Fiber-optic sensor with a dye-modified chitosan poly(vinyl alcohol) cladding for the determination of organic acids *Anal. Sci.* **12** 55–9
- [6] Asijati E, Kuswandi B, Arifah N F, Kurniawati Y I and Gani A A 2005 Non-invasive optical chemical sensor based on polyaniline films for detection of ammonia and acetic acid solutions *Proc. 2005 Asian Conf. on Sensors and the Int. Conf. on New Techniques in Pharmaceutical and Biomedical Research* pp 111–4
- [7] Muto S and Morisawa M 2006 Acetic acid concentration detector sensor for use in e.g. foodstuff application, has sensitive cladding layer which swells in presence of acetic acid around core of optical fiber JP2008076195-A
- [8] Elosua C, Matias I R, Barriain C and Arregui F J 2006 Volatile organic compound optical fiber sensors: a review *Sensors* **6** 1440–65
- [9] Elosua C, Matias I R, Barriain C and Arregui F J 2006 Development of an in-fiber nanocavity towards detection of volatile organic gases *Sensors* **6** 578–92
- [10] Jackson D A, Kersey A D, Corke M and Jones J D C 1982 Pseudoheterodyne detection scheme for optical interferometers *Electron. Lett.* **18** 1081–3