Infrared optical sensors for water quality monitoring

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Abstract In-situ monitoring of water quality with particular emphasis on organic pollutants is a global priority topic in water analysis. Recent developments in optical sensor technology provide advanced analytical tools for continuous assessment of pollution levels in the liquid phase and in the gas phase. Infrared sensing schemes are among the most promising concepts due to inherent molecular specificity provided by absorption patterns of fundamental molecular vibrations of organic molecules. The advent of mid-infrared transparent optical fibers and waveguides, appropriate light source technology, such as quantum cascade lasers, and the potential for the development of highly integrated analytical devices based on microfabrication technology substantiates the trend towards spectroscopic sensing techniques. Chemical modification of the waveguide surface leads to enhanced analyte recognition based on tunable properties of enrichment or (bio)chemical recognition layers. Discussion of fundamental sensing technology is complemented by recent examples, highlighting the state-of-the-art in this dynamic research field.

Keywords Chemical sensors; environmental monitoring; infrared sensors; optical sensors; organic pollutants; volatile organic compounds

Introduction
Sustained quality of the surrounding ecosystems and water resources, and resulting maintenance of public health are of central communal, political, legislative and economic interest due to steadily rising industrial activities and increasing domestic waste. Accordingly, long-term observation of the environment is nowadays considered an integral element of regulatory measures, providing continuous data for regulation enforcement and surveillance. Limited availability of drinking water and the increased appearance of global issues related to water quality, such as endocrine disrupting compounds, demand reliable, precise and efficient analytical techniques for detecting, processing and archiving a wide variety of water quality parameters.

The scope of this task translates into tremendous expenses considering merely classical laboratory analysis for continuous water quality surveillance. Furthermore, lack of (close to) real-time information and efforts and errors related to sampling foster the demand for continuously operating in-situ techniques delivering cost-effective real-time information in a field environment.

Chemical sensor technology is among the fastest growing disciplines in modern analytical chemistry (Janata et al., 1998). Besides electrochemical transducers, mass-sensitive devices and thermal sensing schemes, robust and versatile optical sensors gain increased importance for environmental monitoring, process control and in the biomedical field. Affordable technologies derived from the rapidly progressing field of telecommunications such as fiber optic waveguides and laser diodes have contributed to the advent of optical sensing devices. In particular, the application of optical fibers for signal transportation and signal transduction (transducer) enables transformation of typically bench-top optical instrumentation into portable optical sensor systems deployable at in-situ conditions in the field (Wolfbeis, 2000).
Continuous water quality surveillance requires qualitative and quantitative measurement of a wide range of adverse compounds in the liquid phase or in the gas phase. Worldwide daily use of approximately 70,000 synthetic chemicals, including approximately 700 different organic constituents (e.g. surfactants, phenols, polycyclic aromatic hydrocarbons (PAHs), pesticides, and any number of breakdown products) which may be found in drinking water shows the complexity of this task (Hennion et al., 1994). As a result, monitoring environmentally relevant pollutants represents a substantial analytical challenge for continuously operating in-situ sensing devices, due to the diversity of the sample matrix. While sophisticated analysis methods based on separation techniques with molecule specific detection enable discontinuous analysis at the trace and ultra-trace (< 1 µg/l) concentration level with high degree of speciation, sensor technology provides in-field surveillance, threshold monitoring and rapid screening capacity. Ideally, analytical strategies for water quality assessment and surveillance smartly combine sensor technologies and classical analysis in a complementary network of analytical tools.

Relevant applications of environmental sensors include but are not limited to:

1. Single point environmental analysis (e.g. regulation enforcement)
2. Continuous analysis of target compounds (e.g. sewage or industrial effluent monitoring)
3. Early warning systems and threshold monitoring (e.g. leakage detection)
4. Environmental control (e.g. remediation monitoring)
5. Protective measures (e.g. preventive monitoring)

Besides monitoring of environmentally relevant compounds increasing concern related to drinking water safety and protection at a large scale (e.g. municipal drinking water supply) with respect to biological and chemical warfare agents is gaining substantial importance.

Currently, water quality analysis focused on volatile organic compounds (VOCs) in groundwater, landfill effluents, sewages and surface waters mainly relies on discontinuous methods involving three on-site sampling, storage and transportation of the sample to a laboratory followed by sample preparation and analysis (CEN, 1997). The development of portable field screening devices, such as miniaturized field-applicable laboratory methods (“lab on a chip”) and chemical sensing systems offer the advantage of on site in-situ analysis without prior sampling procedures (Niessner, 2000). Thus, errors due to analyte evaporation and changing sample matrix conditions can be minimized. However, analysis of highly complex sample matrices containing a substantial number and variety of pollutant species present at comparable concentration levels should be considered potential limitations to some sensing systems due to matrix interferences and/or lack of discrimination power.

It should be mentioned that this contribution does not provide complete review and referencing but condenses briefly recent advances in the field of infrared sensing technology for water quality analysis with highlighted examples. For additional information on chemical sensor technology and infrared sensing see (Janata et al., 1998; Mizaikoff, 1999a; Wölfbeis, 2000; Holst and Mizaikoff, 2002; Mizaikoff and Lendl, 2002).

**Optical sensor technology**

While this contribution focuses on infrared fiber optic sensor technology, general aspects of optical sensor technology shall be discussed briefly. Detailed information and examples can be found in (Wolfbeis, 1991; Holst and Mizaikoff, 2002). Two groups of fiber optic sensing systems are generally distinguished: (i) optical sensors directly detecting changes of optical analyte properties or spectral characteristics (direct sensors) and (ii) chemical optical sensors based on a variety of analyte interaction/recognition/reaction processes at
the sensor surface, by optical transduction of chemical signals upon interaction of the analyte with the recognition element (indirect sensors, indicator-based sensors). Frequently, optical sensors are also classified according to the task of the waveguide: intrinsic sensors utilize optical fibers as active signal transducers (sensor head) while extrinsic sensors use the optical fiber only for transmission of radiation and obtained signals. Combination of these concepts has been realized (physico-chemical sensors) taking advantage of both principles, e.g. sensors based on enrichment of analytes into a polymer membrane coated onto an optical fiber surface. Such sensor membranes may generate sensor response due to bulk changes of optical membrane properties (e.g. refractive index) or may act as a solid phase micro-extraction membrane for enrichment of analytes in the vicinity of the waveguide surface utilizing evanescent field analyte detection (Krska et al., 1993; Mizaikoff et al., 1995; Regan et al., 1996).

These basic principles may use a variety of optical configurations with the active sensing region of the optical fiber located at (i) the end facet of the fiber, (ii) at the side of the fiber or (iii) as an interrupting porous section inserted in the fiber. In the case of (physico)chemical sensors, the recognition element may be covalently bound to the active fiber surface or coated as membrane, polymer, gel, sol-gel or similar matrix. Biosensors are based on biorecognition elements such as enzymes, antibodies, etc. covalently attached to the sensing surface or trapped in either of the previously mentioned membranes. The latter concept will not be discussed in this contribution as only a few examples of fiberoptic infrared biosensors have been reported to date.

**Opto-chemical infrared sensors**

**Near-infrared sensors**

Robust plastic- or silica-based optical fibers derived from telecommunications technology on are nowadays available at low cost and with high optical quality, since materials have approached their theoretical attenuation limit of approximately 0.3 dB/km. Hence, fiber optic near-infrared (NIR) liquid phase sensing at wavelengths < 2.5 µm utilizing overtone vibrational modes for detection of organic compounds (e.g. C-H, N-H, O-H) is a well-established technology. Since overtone vibrations are in general 10–100 times weaker than corresponding ground vibrational modes in the mid-infrared (MIR) spectral range (3–20 µm), an active fiber/transducer length of 10–30 m is required for achieving sensitivity at the µg/l concentration level.

Examples for the application of hydrophobic polymers as a protective coating, water exclusion layer and enrichment membrane for optical waveguides in the visible and near-infrared spectral range are described by DeGrandpre and Burgess (1990) and in related subsequent publications. Applications of NIR fiber optic sensors for environmental monitoring have been extensively covered in literature, e.g. by Bück et al. (1994) and related publications. Polydimethylsiloxane (PDMS) coated multimode silica fibers with a low-OH quartz glass core (diameter 200 µm) have been coiled around a supporting rod for the determination of non-polar hydrocarbons (HCs) in aqueous solution during enrichment in the polymer coating. Combined with either a near-infrared Fourier transform infrared (FT-IR) spectrometer or with a low-cost filter photometer aromatic and aliphatic hydrocarbons as well as chlorinated hydrocarbons (CHCs) have been detected in the concentration range of mg/l down to few hundred µg/l (Sensfelder et al., 1996; Blair et al., 1997).

Response time and sensitivity depend mainly on the partition coefficients for the respective analyte between aqueous solution and polymer membrane, respectively. Hence, thorough investigation of polymer properties is required for fine-tuning and optimization of the sensor behavior. Reversibility of the sensor system is ensured since the enrichment is entirely based on diffusion without any chemical reaction inside the membrane. Hence,
concentration fluctuations resulting from variation of partition equilibrium conditions can be continuously measured.

Successful measurements of trichloroethene (TCE) at the mg/l concentration level in artificial aquifer systems and at field conditions document the applicability of NIR fiber optic sensor system for continuous environmental analysis (Bürck et al., 1998). Longterm stability has been demonstrated over a period of several weeks without recalibration.

The main advantage of NIR-based fiber optic sensor systems is the availability of virtually any length of fiber required for e.g. borehole measurements with attenuation losses at the theoretical level. Major drawbacks are limited applicability in complex matrices due to relatively unspecific absorption features and the required length of the active transducer for sufficient sensitivity.

**Mid-infrared sensors**

Chemical sensors systems based on MIR fiberoptics utilize surface modification of fibers transparent in the wavelength region 3–20 µm for transduction of a molecule-specific chemical signal into a measurable optical quantity. The rapid evolution of MIR sensing schemes in recent years is attributed to the development and commercial availability of appropriate fiber optic materials (Sanghera and Aggarwal, 1998; Lendl and Mizaikoff, 2002).

Enrichment coatings vary in selectivity from applications using molecularly imprinted polymers with selectivity close to biomreceptors (biomimetic sensors) to diffusion controlled physico-chemical enrichment of analytes in a hydrophobic polymer membrane acting as solid phase microextraction layer (Jakusch et al., 1997, 1999; Jakusch and Mizaikoff, 2001).

Only a few examples in the literature report on gas analysis based on surface modified IR fiber optics. A novel concept for gas phase VOC analysis has recently been presented by de Melas et al. (2002). A hollow waveguide (HWG) gas cell has been combined with a Fourier transform infrared (FT-IR) spectrometer. Continuous analysis of environmentally relevant compounds in the aqueous phase is achieved by coupling with a supported capillary membrane sampler (SCMS) probe. Carrier gas flow inside the thin-walled capillary membrane enables permeation of VOC from aqueous solution into the gas phase and facilitates continuous and quantitative detection in the HWG IR gas cell. Sensitivities at the µg/l concentration level and response times of a few minutes have been achieved for individual components and mixtures of e.g. benzene, toluene, xylene isomers, chloroform, methanol and various other hydrocarbon species.

Direct liquid phase detection of aliphatic, aromatic and/or halogenated hydrocarbons in water via MIR optic chemical sensor systems has been intensively investigated during the last decade (Mizaikoff et al., 1995; Regan et al., 1996; Walsh et al., 1996; Mizaikoff, 1999a; and others).

Applications include coupling IR radiation of an FT-IR spectrometer into silver halide fibers simultaneously acting as both waveguide and active transducer. The active sensing area is coated with a thin hydrophobic polymer layer, such as ethylene/propylene copolymer, Teflon AF, polybutadiene, etc., enriching organic pollutants. Water is effectively excluded from the measurement, since the selected polymer layer thickness is larger than the penetration depth of the evanescent field guided outside the optical fiber. Based on this fiber optic evanescent wave sensor (FEWS) scheme, qualitative and quantitative determination of a wide variety of organic analytes in the mg/l to the low µg/l concentration range has been demonstrated (see e.g. Jakusch et al., 1997). The first application of molecularly selective membranes created by molecular imprinting in a mid-infrared sensing application was recently demonstrated for the herbicide 2,4 dichlorophenoxyacetic acid (Jakusch et al., 1999).
A novel field of application for IR spectroscopic sensing systems is the area of pollution monitoring in a subsea environment, e.g. deep sea, lake or river. Based on a Bruker Vector 22 FT-IR spectrometer the first marine FT-IR sensing system has been developed and successfully tested in simulated real-world conditions. The feasibility of this approach has been demonstrated by multicomponent analysis of aliphatic and aromatic hydrocarbons in seawater (Mizaikoff, 1999b; Kraft and Mizaikoff, 2000).

Outlook
Progress in the field of mid-infrared sensing is mainly focused on technological improvement of components required for MIR sensor systems. Significant miniaturization of light sources and optics has been achieved, featuring advanced techniques such as microfabrication and microelectronics. In combination with smart chemical recognition schemes a new generation of molecule specific optical sensors can be envisaged.

The application of laser light sources for optical sensing devices has the advantage of coherent radiation with high spectral density. While the predominant laser light source in the mid-infrared spectral region is the CO2 laser, significantly smaller semiconductor lead salt lasers made from materials such as Pb1–xCd0.5xS, Pb1–xS2xSe or Pb1–xSn0.5xSe provide access to the MIR band, but still require accurate cryogenic cooling (Tacke, 1995). The introduction of quantum cascade lasers (QCL) based on intersubband transitions significantly extends the possibilities of laser spectroscopy in the mid-infrared range and can be considered as current state-of-the-art semiconductor light sources in the MIR (Faist et al., 1994). The development of unipolar lasers using intersubband transitions, so-called quantum cascade lasers, made from InGaAs/InAlAs/InP, GaAs/AlGaAs and similar heterostructures has attracted substantial attention as novel light sources for mid-infrared sensor technology. Their main feature is the option to design semiconductor lasers emitting at selected frequencies within the entire mid-infrared spectrum. Emission characteristics of such optoelectronic devices are controlled by semiconductor layer thickness rather than material composition using band-structure engineering techniques. Since each injected electron generates multiple photons due to a cascaded active region, output power > 200 mW and emission wavelengths reaching into the far-infrared region are achievable, while operation of the device is at room temperature. Since QCLs are manufactured as “on chip” devices with extremely small physical dimensions, highly integrated sensing systems for target analysis in the liquid- and gas-phase can be foreseen.

Besides miniaturized light sources optical components can be scaled down using microfabrication techniques. Recently, a miniature single-pass Fourier transform spectrometer integrated on a 10 × 5 cm optical bench has been presented. Based upon a classical Michelson interferometer design, all components are microfabricated from silicon, including dovetailed bearing surfaces for precise translation of the moving mirror (Collins et al., 1999). With a spectral resolution of 0.1 cm−1 optical performance comparable to benchtop-style instrumentation is demonstrated. Combining such miniaturized interferometers with MIR fiber optic sensor technology leads to a new generation of multicomponent analyzer systems, particularly applicable in environmental monitoring.

Enhancement of the chemical recognition step using optical sensor systems is based on appropriate coatings for selective enrichment of analyte molecules. With the recent demands for accurate speciation of the determined pollutants and analyzer systems operating in increasingly complex matrices, such as industrial effluents, new strategies towards “smart” transducer mechanisms in combination with more selective recognition membranes have to be developed.

Molecularly imprinted polymers are among the most promising approaches to enhance the performance of optical chemical sensors, enabling the formation of molecule specific...
recognition sites in an appropriate polymer matrix. The polymerization process is performed in the presence of the target analyte (“template”) using functional monomers, which form pre-polymerization complexes with template molecules in solution. Due to a high degree of crosslinking, “imprinted” recognition sites are formed, which are complementary to the template in shape and position of the functional groups. The general applicability of this procedure for a wide variety of template substances is extensively described in the literature and a recently published book on molecular imprinting technology (Sellergren, 2000). Using this technology, MIPs effectively mimicking the recognition properties of antibodies have been developed, while at the same time exhibiting much better chemical and physical stability. Recently, our research group has introduced the first step towards mid-infrared chemical sensors based on planar MIP layers combined with evanescent wave spectroscopy, demonstrating selective enrichment for the herbicide 2,4-dichlorophenoxyacetic acid (Jakusch et al., 1999). These results encourage the development of novel selective sensing schemes for environmental monitoring, particularly in combination with current progress in optical microtechnology as outlined above.

**Conclusion**

Infrared chemical sensor technology is among the most promising concepts for continuous *in-situ* assessment of water quality, if high molecular specificity is required. Current trends for analysis of organic pollutants particularly demand a high degree of speciation. Differentiated analysis enables accurate tracing of pollution sources and supports implementation of appropriate regulatory measures. Whilst being more sensitive, conventional water quality surveillance relies mainly on discontinuous laboratory analysis. In contrast, rapid response to pollution events, effluent screening and water treatment plant or estuary monitoring requires on-line analytical tools. Ideally, a network of analytical strategies for water quality surveillance spans from *in-situ* alarm sensors to automated sampling and subsequent laboratory analysis of selected samples with high precision. While the latter technology is well established, accurate long-term surveillance of environmentally relevant compounds at trace levels requires improved sensor technology.

Development of near- and mid-infrared sensor technology is rapidly progressing, providing the technological basis for optical sensing schemes with high molecular specificity. Multicomponent analysis using fully featured broadband spectrometers, as well as target analyzers based on diode laser technology, have successfully been demonstrated and tested in simulated and real field conditions. Current efforts are focused on improved detection limits for volatile organic compounds towards the low µg/l concentration range, long-term stability, system prototyping and validated field tests.

Considering the versatility, robustness and molecular specificity of spectroscopic sensing concepts extended application for a wide range of continuous pollution monitoring situations, threshold surveillance, effluent monitoring and drinking water analysis can be envisaged. Smart interfacing with existing analytical techniques will expand the information/data space, while decreasing associated analysis costs, working towards complete and accurate water quality assessment on a global basis.

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