
Universität Ulm
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Mid-infrared Sensors for Environmental Monitoring

DISSERTATION

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Thomas Schädle

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Amtierender Dekan: Prof. Dr. Peter Dürre
1. Gutachter: Prof. Dr. Boris Mizaikoff
2. Gutachter: Prof. Dr. Gerhard Taubmann
3. Gutachter (extern): Prof. Dr. Fiona Regan

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Abstract

The presented cumulative thesis is focused on the development of mid-infrared sensors and their application in environmental monitoring scenarios. This thesis is based on five peer-reviewed journal articles, and includes three articles published in collaboration with the *Energy* department of the Commonwealth Scientific international Research Organization (CSIRO), at the Australian Resource Research Centre (ARRC) in Perth, Western Australia. The scope of all research presented in this thesis covers contemporary applications of mid-infrared spectroscopic and sensing systems with a strong emphasis on environmental monitoring, in particular on the detection of volatile organic compounds (VOCs) and dissolved greenhouse gases (GHG).

One main focus of this thesis was the advancement of infrared attenuated total reflection (IR-ATR) methods for detecting, differentiating, and quantifying dissolved hydrocarbons, and specifically constituents derived from oil spillage by evaluating the infrared ‘fingerprint’ of VOCs generated via their dissolution pattern in water at ppb ($\mu\text{g/L}$) concentration levels. The ‘fingerprint’ of a certain VOC hereby comprises distinctive infrared absorption features in the spectral regime from $600\text{--}800\text{ cm}^{-1}$, which may be evaluated for identifying specific hydrocarbon patterns that are characteristic for different crude and refined oils.

A complementary contribution of this thesis is the development of appropriate sensor platforms enabling continuous measurements of dissolved carbon dioxide and methane, two main contributors to the release of greenhouse gases into our atmosphere. Obtaining in-situ information on greenhouse gases captured in deep sea or aquifer environments used for GHG immobilization via carbon capture and storage (CCS) mechanisms is a challenge that has not

been satisfactorily addressed to date. Hence, an IR-ATR based on-line sensor system for detecting, monitoring, and differentiating carbon dioxide and methane in dissolved and gaseous states at different pressures (up to 11 MPa) was developed and tested. Furthermore, it is demonstrated that the detection and quantification of dissolved carbon dioxide next to its isotopic analogue ($^{13}\text{CO}_2$) at pressurized conditions is enabled at relevant saline downhole conditions present within injection wells, thereby serving as an on-line/in-line monitoring tool. Consequently, such sensor systems may eliminate present problems in geosequestration scenarios related to either portability of an analyzer system, or its capability of operating reliably at harsh conditions during in-field deployment. These results are of particular importance for advancing CCS processes and fundamentally understanding the impact of stored gases on groundwater and aquifer resources.

Zusammenfassung

Die vorliegende kumulative Dissertation beschäftigt sich mit der Entwicklung von infrarotspektroskopischen Messsystemen und Sensoren für Anwendungen im Bereich der Umweltüberwachung und -analytik. Die vorgelegte Arbeit basiert auf fünf bereits veröffentlichten Artikeln in referierten Fachjournalen. Von diesen fünf Artikeln wurden drei in Kooperation mit der Abteilung für *Energie* der australischen Forschungsorganisation CSIRO (Commonwealth Scientific International Research Organization) in Perth, Westaustralien, veröffentlicht.

Der Rahmen der in dieser Dissertation dargestellten Forschung umfasst verbesserte infrarotspektroskopische Messverfahren unter Nutzung der internen Totalreflexion, mit einem besonderen Fokus auf der Bestimmung umweltrelevanter Analytspezies. Daher wurden einerseits Verfahren zur Differenzierung und quantitativen Bestimmung von in wässrigen Systemen gelösten, flüchtigen organischen Kohlenwasserstoffen (VOCs, *engl.* „volatile organic compounds“), sowie zur Bestimmung und Überwachung von gelösten Treibhausgasen (v.a. Kohlenstoffdioxid und Methan) entwickelt und getestet. Insbesondere wurden die infrarotspektroskopischen Messmethoden auf die Messbedingungen und Anforderungen für *in-situ* Feldexperimente adaptiert.

Ein wesentlicher Teil der Arbeit beschäftigt sich mit der Erfassung und Differenzierung IR-spektroskopischer „Fingerabdrücke“, die VOCs nach Lösen in wässrigem Medium z.B. durch Öl- oder Treibstoffkontaminationen in geringen Konzentrationen (ppb, bzw. µg/L) hinterlassen. Mittels Verfahren der abgeschwächten Totalreflektion konnten eindeutige

Absorptionsmuster im Spektralbereich zwischen 600-800 cm^{-1} erfasst werden, die unterschiedlichen Arten an Roh- und Raffinerieölytypen eindeutig zugeordnet werden konnten. Ein weiteres Hauptthema dieser Arbeit war darüber hinaus die Entwicklung geeigneter IR-sensorischer Verfahren zur quantitativen Erfassung von gelöstem Kohlenstoffdioxid und Methan in wässrigen Systemen, die bei der zukünftigen Sequestrierung und Speicherung derartiger Treibhausgase relevant sind. Insbesondere ist bislang der Zugang zu *in-situ* Informationen über das Verhalten dieser Gase in Salzwasserreservoirs aufgrund fehlender Sensortechnologie äußerst limitiert. Daher wurde ein portables IR-spektroskopisches on-line Sensorsystem entwickelt, das CO_2 und CH_4 in gelöstem als auch gasförmigen Zustand bei Drücken bis zu 11 MPa (110 bar) kontinuierlich erfassen, unterscheiden, und quantifizieren kann. Darüber hinaus wurde gezeigt, dass unter den zu erwartenden Speicherungsbedingungen für Treibhausgase auch $^{13}\text{CO}_2$ von $^{12}\text{CO}_2$ unterschieden und in Salzwasser simultan erfasst werden kann.

Zusammenfassend wurden im Rahmen der vorgelegte Arbeit daher infrarotspektroskopische Sensorsysteme entwickelt, die zur Erfassung und Überwachung von Umweltschadstoffen in wässrigen Systemen, insbesondere von gelösten organischen Kontaminationen und Treibhausgasen unter nur erschwert zugänglichen Messbedingungen eingesetzt werden können.

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List of Papers

The presented thesis is based on the following papers, which are published or accepted for publication in internationally peer-reviewed journals:

I. Mid-Infrared Waveguides - A Perspective.

Thomas Schädle and Boris Mizaikoff.

Applied Spectroscopy, invited manuscript, accepted for publication 2016.

II. Fingerprinting Oils in Water via Their Dissolved VOC Pattern Using MID-Infrared Sensors.

Thomas Schädle, Bobby Pejic, Matthew Myers and Boris Mizaikoff.

Analytical Chemistry, 86 (19), 2014, 9512-9517.

III. Monitoring dissolved carbon dioxide and methane in brine environments at high pressure using IR-ATR spectroscopy.

Thomas Schädle, Bobby Pejic, and Boris Mizaikoff.

Analytical Methods, 8 (4), 2016, 756-762

IV. Selecting the right tool: Comparison of the analytical performance of infrared attenuated total reflection accessories.

Thomas Schädle and Boris Mizaikoff.

Applied Spectroscopy, 0003702816641574, first published on April 18, 2016

V. Portable Mid-Infrared Sensor System for Monitoring CO₂ and CH₄ at High Pressure in Geosequestration Scenarios.

Thomas Schädle, Bobby Pejic, Matthew Myers and Boris Mizaikoff.

ACS Sensors, 1 (4), 2016, 413–419.

Featured as: 'ACS Editors' Choice'

List of Abbreviations

AgX	Silver halide
ARRC	Australian Resource Research Center
ATR	Attenuated total reflection
CCS	Carbon Capture and Storage
CSIRO	Commonwealth Scientific Research Organization
FTIR	Fourier-Transform-Infrared
GC-MS	Gas Chromatography – Mass Spectrometry
GHG	Greenhouse gas
HWG	Hollow waveguide
IPCC	Intergovernmental Panel on Climate Change
IR	Infrared
IRE	Internal reflection element
MBT	Mechanical biological treatment
MIR	Mid - infrared
ppb	Parts per billion
VOC	Volatile organic compound

Aim and Overview of the Thesis

The present thesis focuses on advancing mid-infrared sensing systems specifically for environmental monitoring scenarios at harsh application conditions. With respect to the observed climate changes during the last century, evidently at least in part attributable by anthropogenic pollution via greenhouse gas emissions or release of environmental hazardous compounds, limiting regulations and release control strategies are of increasing importance to enable at least stabilizing but potentially decrease the anthropogenic contribution to climate change on the long term. Thus, the research presented in this thesis is focused on three main topics:

- I) The analysis and identification of hazardous volatile organic compounds (VOCs), released via oil spills into the environment. The focus hereby is on the detection and identification of VOCs from different crude and refined oil types that dissolve within the aqueous phase adjacent to a dispersed oil such as the case during oil spills or oil refinery processes. An infrared spectroscopic sensor system based on the principles of attenuated total reflection has been developed for fingerprinting and identifying such contaminations. The detailed results of this research are featured in the journal article “**Fingerprinting Oils in Water via Their Dissolved VOC Pattern Using MID-Infrared Sensors**” presented in *Chapter 5, II*.
- II) Detailed studies on the dissolution behavior of greenhouse gases (i.e. carbon dioxide and methane) in greenhouse gas storage scenarios important for carbon capture and storage (CCS) programs. These studies include the discrimination and differentiation of the gases in their nature and state (i.e. gaseous, dissolved, or supercritical) during

the analysis of greenhouse gases in aqueous (e.g. brine) environments via mid-infrared attenuated total reflection (IR-ATR) spectroscopy. The results of this study are presented in *Chapter 5, III*, and have been published in the journal article **“Monitoring dissolved carbon dioxide and methane in brine environments at high pressure using IR-ATR spectroscopy”**.

- III)** The development of a portable mid-infrared sensor system capable of monitoring the sequestration process of some major greenhouse gases (here, carbon dioxide and methane) at harsh conditions (i.e. pressures up to 11 MPa), as encountered in deep well injection scenarios. The developed sensor system comprises a fully integrated FTIR spectrometer with a custom-designed ATR pressure cell. This portable sensor system features dimensions of approx. 40x35x15 cm, and may thus be used on-site at actual in-field greenhouse gas sequestration sites. The sensor system and application is described in detail in *Chapter 5, IV-V*, and was subject of the journal articles **“Selecting the right tool: Comparison of the analytical performance of infrared attenuated total reflection accessories”**, and **“Portable Mid-Infrared Sensor System for Monitoring CO₂ and CH₄ at High Pressure in Geosequestration Scenarios”**.

1. Introduction

1.1 Motivation

The need for environmental analysis is directly associated with demands on developing a more fundamental understanding on the complex interactions of the climate and ecosystems, as well as on anthropogenic contributions to changes and influences on those sensitive systems. To improve and enhance these influencing factors that industries, governments and the public perceive, researchers and scientists are collecting innovative ideas summarized under the term ‘scenarios’ since several years (Moss et al. 2010).

In these scenarios, researchers focus on predictions related to future climate and environmental situations, and aim at indicating pathways for sustainable solutions should certain predictions provide adverse perspectives (i.e. if drastic anthropogenic influences effectively unbalance the ‘circuit of nature’). A major key component of these scenarios is the evaluation of human-induced emissions, mostly focusing on the release of greenhouse gases, aerosols, and volatile chemical compounds (Kemper 2015; Moss et al. 2010; Yadugiri 2010). Not surprisingly, the quantitative evaluation of these factors in such scenarios derives a distinct impact on climate and environmental scenarios; however, uncertainty and mitigation approaches are frequently already taken into account as well.

As stated in the regularly published assessment reports by e.g. the ‘Intergovernmental Panel on Climate Change’ (IPCC), since the 1950s the atmosphere and ocean have warmed by 0.05°C on average, and the concentration of greenhouse gases has significantly increased (The Intergovernmental Panel on Climate Change (IPCC). 2013; The Intergovernmental Panel on Climate Change (IPCC). 2014; Barros & Field 2014).

Based on this nearly annually published information, the community of climate researches has established a coordinated parallel process for developing according ‘scenarios’. This process includes any kind of impact initiated by ‘radiative forcing’ (i.e. the change in balance between incoming and outgoing radiation to the atmosphere caused by changes in atmospheric constituents, such as carbon dioxide, which is usually refer to as ‘global warming’) contrasted by potential anthropogenic influence. Figure 1 illustrates the increasing temperature around the globe as a plot of time, while showing the main anthropogenic contributors to global warming listed by their respective radiative forcing.

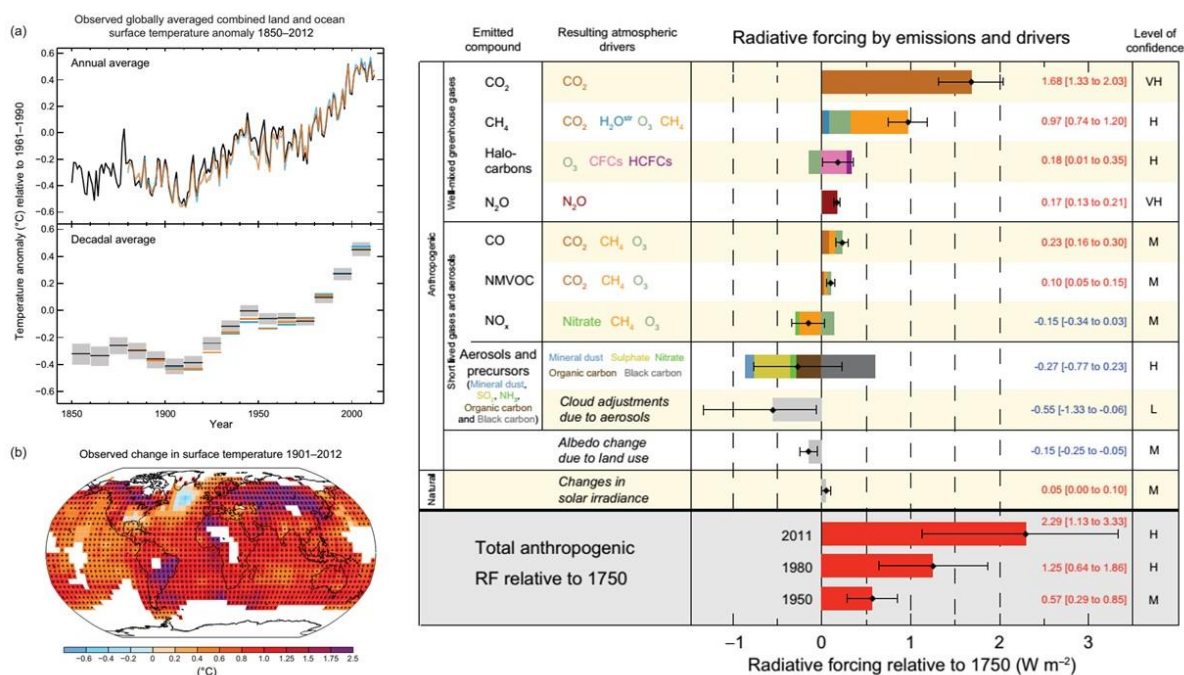


Figure 1. (Left) (a) Observed global average of atmospheric temperature indicating the rise in surface temperature from 1850 to 2012. **(b)** Mapping of the temperature changes during the last century plotted around the globe. **(Right)** Anthropogenic emitted compounds and their related radiative forcing estimates until 2011 relative to the year 1750 including uncertainty ranges (black ‘error’ bars).

Figures reproduced with permission from 'IPCC, 2013: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp 6-14.

Consequently, interdisciplinary research is clearly demanded for supporting prediction and mitigation of possible future climate conditions by closely reviewing recent climate observations and obtaining state-of-the-art molecular information on relevant processes within the climate system. Furthermore, the evaluation of strategies for reasonable mitigation options based on improvements in understanding the reasons behind larger 'climate feedbacks' (i.e, impacts like melting of permafrost and polar caps, that cause further changes in climate (Moss et al. 2010)) is required. Presently discussed climate scenarios cover mostly physical processes that are involved in radiative energy transfer through the atmosphere. Greenhouse gases (GHG) such as carbon dioxide, methane, and (halogenated) volatile compounds (VOCs) greatly affect this energy transfer. In principle, an atmosphere enriched in greenhouse gases may radiate less heat into space, and consequently inherently warms up via the molecular absorption of radiation. Hence, mitigation options involve the implementation of gaseous emission management and removal processes to avoid uncontrolled release of GHGs and volatile organic compounds into the atmosphere, as well as suggesting novel approaches for processing gaseous by-products. This is particularly true in waste treatment facilities including incineration, digestion and composting, mechanical biological treatment ('MBT'), and landfilling, whereby the implementation of appropriate technologies may comprehensively mitigate gaseous emissions into the atmosphere (Navia & Munoz 2015).

With respect to the complex and interrelated reasons for climatic impacts, the main aim of the present thesis is the development of advanced measurement principles for analytically evaluating hazardous substances - mostly anthropogenic origin - that are released into our environment. Figure

2 illustrates the relevance of the developed environmental monitoring strategies, thus outlining the structure of the research approach in this thesis:

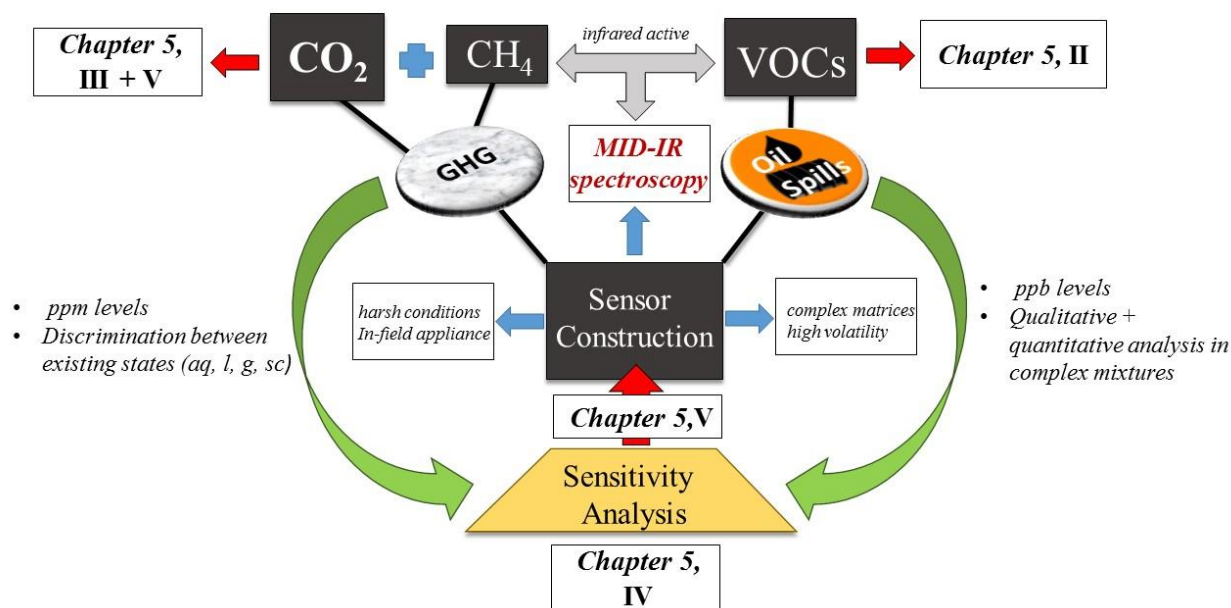


Figure 2. Relationship between the research topics investigated in this thesis and their relevance illustrating the challenges for each topic, and how each topic and subsequently published journal article addresses sensing aspects related to greenhouse gas (GHG) analysis, volatile organic compound (VOC) detection, and associated infrared sensor development.

1.1.1 Pollution and Volatile Organic Compounds Analysis

The frequent occurrence of oil spills is still among the major sources of organic contamination in marine and sedimentary environments (Peterson et al. 2015). Oil rigs and oil drilling on landsides, as well as off-shore extraction activities further contribute to the release of various hydrocarbons into the atmosphere. During recent decades, it was reported that approximately 300,000 tons of crude oil were dispersed in the Mediterranean sea alone each year (Danovaro

2003). Besides obvious pollution issues via large oil spills, problems for the ecosystem persist even after potential clean-up of the actual oil spills substantiating as long-term sedimentary contamination, thereby greatly limiting the recovery of marine ecosystem mammals and fish for decades (Peterson et al. 2015). This contamination is mostly based on the release of hazardous volatile organic compounds such as aromatic hydrocarbons including benzene, toluene, and naphthalenes (Schädle et al. 2014; Pejčic et al. 2013), as well as halogenated hydrocarbons (Mohnke & Buijten 1993) to the atmosphere. VOCs show extreme mobility due to their high vapor pressure at normal atmospheric conditions. Hence, they vaporize immediately with subsequent accumulation in the environment leading to potential long-term soil, groundwater, and atmospheric contamination. Albeit VOCs also show biogenic (i.e. from bacteria and marine organisms) origin, they are mostly released from anthropogenic sources such as fuels, solvents, adhesives, deodorants, and refrigerants just to name some of the most common sources (Peterson et al. 2015; Danovaro 2003; Zhu et al. 2009; Nikolaou et al. 2002). Furthermore, many (halogenated) VOCs are used in agriculture in the form of herbicides and fumigants (e.g. chloroform, chloroethane, benzenes, and xylenes (Nikolaou et al. 2002)). Exceedingly using such hazardous substances has caused significant enrichment levels in the environment resulting in serious health risks for the public, as they are reported among the most common contaminants found in ground waters (Pecoraino et al. 2008; Lara-Gonzalo et al. 2008).

Commonly applied VOC analysis methodologies usually involve gas chromatography coupled with mass spectrometry (GC-MS), which includes the collection of a representative sample followed by several extraction/separation steps prior to molecular characterization and quantification in laboratories (Pecoraino et al. 2008). Hence, most studies that deal with oil and hydrocarbon analysis of environmental samples are performed within laboratory environments

relying on extensive sampling, sample transportation, and sample preparation steps before the actual analytical measurement in the laboratory can be performed (Demeestere et al. 2007). Although extreme care is undertaken to ensure that representative samples are obtained, the quality and accuracy of the data will be severely affected by the chemical and biological changes that occur during sampling and storage, and especially by analyte loss due to the high vaporization potential of VOCs (Pejcic et al. 2013). Additionally, despite the promising capability and accuracy of GC-MS analysis of hydrocarbons at very low concentration levels (i.e., ppb to ppm levels), the majority of these devices struggle to separate the various signal contributions during the analysis of multi-component hydrocarbon mixtures (Pejcic et al. 2013). As a potential solution to the problems occurring during GC-MS analysis, the detection of VOCs at ppb concentration levels using infrared spectroscopy in either vapor phase (Satheeshkumar & Yang 2014; Huang et al. 2006) or liquid phase environments (Schädle et al. 2014; Stach et al. 2015; Pejcic et al. 2009) has been reported in recent years as a promising alternative for readily identifying such hazardous pollutants. In addition, the inherent molecular selectivity facilitates discriminating and fingerprinting such pollutants (i.e. especially organic components) even in complex mixtures within sweetwater as well as seawater matrices. Furthermore, besides the possibility of VOC detection and determination of their origin, for example the type of oil which caused the respective oil spill may be accomplished via IR-ATR sensing methods (Schädle et al. 2014). Detailed results for VOC detection from oil residuals using mid-infrared spectroscopy are reported in *Chapter 5, II: ‘Fingerprinting Oils in Water via Their Dissolved VOC Pattern Using MID-Infrared Sensors’*.

1.1.2 Geosequestration and Carbon Capture and Storage Scenarios

The term ‘carbon capture and storage’ (CCS) generally relates to strategies aiming at reducing emissions of CO₂ into the atmosphere mainly from anthropogenic, i.e. industrial and energy-related processes by capturing CO₂ during its formation. Subsequently, it is transferred to appropriate storage locations ideally enabling long-term retainment. CO₂ is generally considered among the major contributors to the atmospheric greenhouse gases next to methane and water vapor. Although other mitigation options to reduce atmospheric greenhouse gas concentrations exist, they mainly focus on energy efficiency improvements and alternative energy sources (i.e. renewable energy sources) as well as fine tuning industrial processes. Among the future perspectives, CCS is considered as a promising paths for the long-term reduction of atmospheric greenhouse gases (Metz et al. 2012). The principal merit of CCS is that it could act as a gateway to facilitate and strengthen carbon-reduced energy production, while renewable energy systems are improved in efficiency, reduced in cost, and expanded in scale to meet global demands (Martin Trusler 2016).

Although there is significant effort dedicated to the generation of successful strategies for a long-term stabilization of atmospheric greenhouse gas concentrations, specialists agree in counsels like the ‘Intergovernmental Panel on Climate Change’ (IPCC) that probably no single technology development will be capable to resolve all issues related to emission reduction, which must be ensured to achieve stabilization of greenhouse gas emissions. However, these panels strongly recommend that interdisciplinary processes will be needed, thereby emphasizing the importance of joint programs from research groups and stake holders around the globe (Metz et al. 2012).

Despite the concerns on climate changes via anthropogenic GHG emissions, most scenarios indicate that primary energy production will still be dominated by fossil fuels until at least the middle of this century (Kemper 2015). Hence, it is evident that the main success of CCS does not

only rely on advanced technologies, but would also require substantial socio-economic and institutional changes (Kemper 2015; Lackner & Brennan 2009). In this context, the widespread application of CCS would depend on technical maturity, costs, overall potential, diffusion and transfer of the technology to developing countries and their capacity to apply the technology, regulatory aspects, environmental issues, and public perception.

The principle benefit behind the process of capturing CO₂ is that it could be applied to large industrial point sources (i.e. general inclusion of capturing mechanisms before actual release into the environment) followed by compression and transportation of captured CO₂ to appropriate storage sites (Shiraki & Dunn 2000), as illustrated in Figure 3.

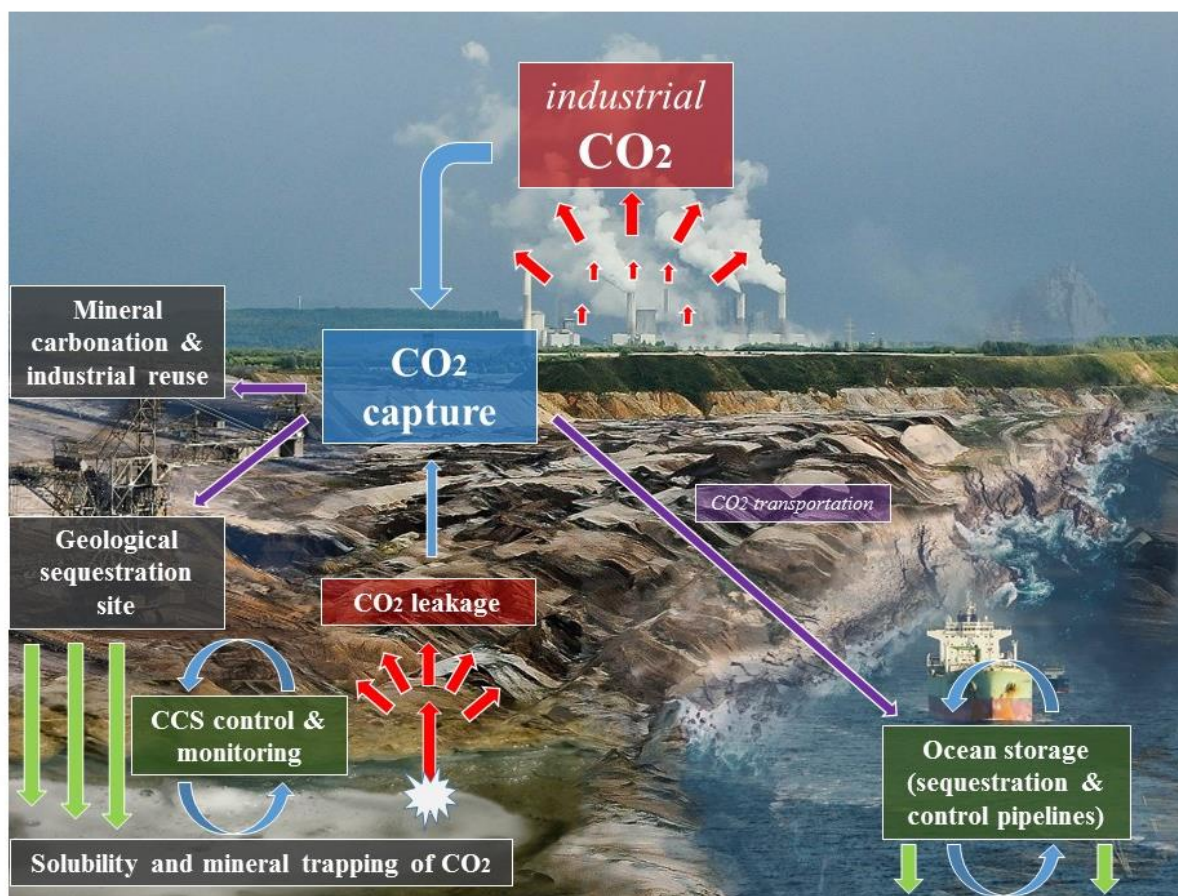


Figure 3. Schematic illustrating CCS strategies. Anthropogenically released CO₂ from industrial sites is captured and transported to various processing sites. One part is reused in specific industrial processes and artificial mineral carbonation, whereas the majority is transported to sequestration sites for carbon storage in either abandoned mining sites, other suitable geological sites or further transported for ocean storage.

Large point sources of CO₂ include large fossil fuel or biomass energy facilities, major CO₂-emitting industries, natural gas production, synthetic fuel plants, and fossil fuel-based hydrogen production plants. Potential storage methods include geological storage, storage in depleted oil and gas fields as well as abandoned coal beds and mining sites or storage in deep saline aquifers. Actually, deep saline aquifers in sedimentary basins are among the most promising sites for sequestration strategies facilitating long-term storage of CO₂ and even methane (Izgec et al. 2008),

as another critical GHG. These brine formations are among the most common fluid reservoirs within subsurface regions, and are readily available around the world. Additionally, extensive global aquifer systems are capable of accepting the required large volumes of anthropogenically produced CO₂, thereby literally rendering them the most promising depletion sites (Bachu 2015).

Regarding the options for ‘trapping’ CO₂ in downhole rock matrices (i.e. for conversion into minerals), dissolution within the contained water phase is required before long-term conversion of CO₂ into solid rock matrix could take place (Romanov et al. 2015; Soong et al. 2003). This mechanism is generally referred to as ‘solubility and/or mineral trapping’. However, one of the most critical concerns for successful solubility trapping is the potential of CO₂ leakage via imperfect or leaky confinement (Romanov et al. 2015). In mineral trapping, CO₂ is converted into carbonate minerals by a series of reactions with dissolved ions from slightly soluble minerals that are thermodynamically generated in aqueous environments. Various carbonates - i.e. mostly calcites - can be formed, which may be stored in brine for extended periods of time (Soong et al. 2003). However, this long-term carbonation process is based on temperature, pressure and brine composition, but mostly dependent on brine pH. Hence, as the dissolution of CO₂ in brine generally decreases the pH value, the conversion of CO₂ into stable carbonate minerals is expected to be quite slow and inefficient, since most carbonates are stable at pH > 7. Nevertheless, kinetic processes favor the conversion of CO₂ into mineral matrix at pH < 7. The kinetics of mineral dissolution and precipitation rates are incorporated in the general form of the ‘rate law for heterogeneous dissolution-precipitation reactions occurring at the surface of a given mineral’ initially postulated by A. Lasaga (Lasaga 1995). In conclusion, the anticipated precipitation of CO₂ as carbonates occurs on the order of magnitude of thousands of years (Bourg et al. 2015; Liu &

Maruto-Valer 2011), thus rendering mineral trapping a suitable mechanism for CO₂ storage only as a long-term perspective.

1.1.3 State-of-the-Art Sensor Technologies

For any large-scale future implementation of CCS, well-defined regulations concerning short- and long-term responsibilities for storage are needed along with economic incentives (The Intergovernmental Panel on Climate Change (IPCC). 2014). However, large-scale deployment of CCS incorporates safety and assurance of CO₂ storage integrity, as well as monitoring tools for the identification of leakage risks. During recent years, there is a growing body of literature published on the evaluation of sequestration wells (Bachu & Stewart 2002), consequences of a pressure build-up within a geologic formation (i.e. induced seismicity (Bourg et al. 2015; Lackner & Brennan 2009; Schloemer et al. 2013)), and potential human health and environmental impacts from CO₂ that migrates out of the primary injection zone (Bachu 2015). These reports are strongly focused on the development of sensing and monitoring tools that maybe implemented within CCS processes. However, only few sensor applications are reported to date, that combine all requirements desired for such in-field applications. Several studies were performed that investigate alterations of deeper mineral and ground rock formations via ‘core-flooding’ laboratory experiments carried out at simulated reservoir conditions (i.e. varying temperatures and elevated pressures). Frequently, synthetic brine compositions are used (Shiraki & Dunn 2000; Sell et al. 2013) or - in rarer instances - actual reservoir samples (Abril et al. 2006). Although a lot of simulation studies were performed to greatly improve understanding and prediction in CCS processes (Izgec et al. 2008; Liu & Maruto-Valer 2011; Bachu 2015; Bourg et al. 2015), most in-situ measurements still take place in laboratories at simulated storage conditions (Shiraki & Dunn

2000; Schädle, Pejcic & Mizaikoff 2016) lacking actual data related to on-site performance. The limiting condition is mostly the difficulty in adapting frequently delicate to operate sensor systems for in-field studies due to either lack in robustness or bulkiness of the actual analytical tool (e.g. in case GC-MS or similar laboratory instruments are used). Besides GHG monitoring, the same holds true for pollution monitoring via appropriate in-field sensing systems, e.g. for VOC detection (Zhu et al. 2009; Nikolaou et al. 2002; Pejcic et al. 2013).

To solve the ‘laboratory vs. in-field’ obstacle, advanced sensor technologies capable of handling the environmental requirements have to be introduced. Infrared-based sensor technologies have recently emerged as a promising sensing concept in a wide variety of sensing scenarios (Luzinova et al. 2012a; Chang et al. 2012; Mizaikoff 2013; Schwarz et al. 2014) combining robustness, high sensitivity, molecular selectivity, and potential for miniaturization. Hence, IR sensor systems are among the most promising candidate technologies for on-line monitoring (Mizaikoff 2003; Mizaikoff 2013; Perez-Guaita et al. 2014; Wang et al. 2012; Huang et al. 2006).

Figure 4 illustrates the requirements for developing sensor technologies for both GHG and VOC detection.

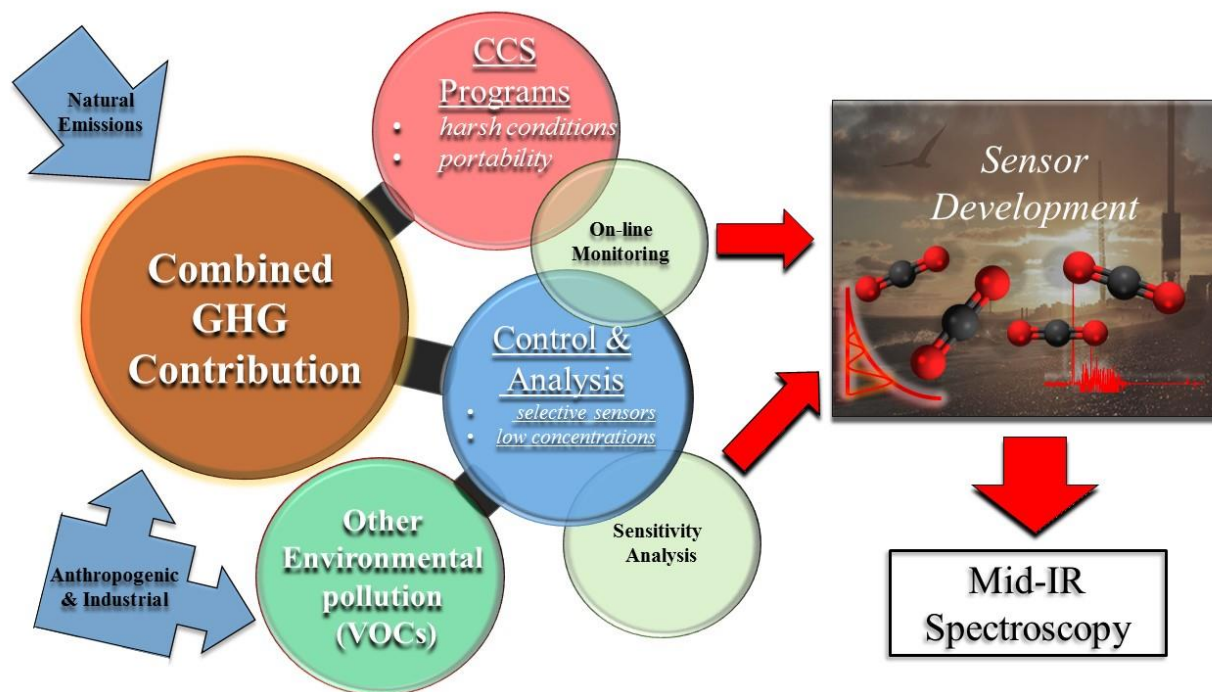


Figure 4. Schematic development path for GHG sensors including their potential for also monitoring and detecting environmentally hazardous substances. Infrared-based sensor technologies offer to potentially combine the desired requirements and specifications into a modular and versatile sensing platform.

The rapid evolution of mid-infrared based sensor technologies throughout recent decades is greatly driven by achievements in miniaturization of optical components, light sources, and detectors, as well as improvements in chemical recognition interfaces (i.e. advances in engineering of sensing layers and membranes). A major component of particular importance for in-field IR sensor technology is the availability and utility of appropriate waveguide technologies facilitating efficient photon transfer from/to the sampled site, as well as simultaneously acting as the active transducer element. Hence, a detailed report on state-of-the art applications and trends in mid-infrared spectroscopy with particular emphasis on waveguide technology has been published as an invited review article in *Chapter 5, I*, ‘**Mid-Infrared Waveguides - A Perspective.**’

1.2 Theoretical Background

1.2.1 Fundamentals of Infrared Spectroscopy

The Born-Oppenheimer approximation states that the motion of electrons and atomic nuclei can be separated due to their significant difference in mass. Consequently, the total energy of a molecule can be divided into separated energetic terms following:

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} \quad (1)$$

This leads to discrete energy eigenvalues, which the system can occupy when exposed to external energetic influences (i.e. electromagnetic radiation). Given that the introduced radiation (light) carries the energetic difference of the initial (ground) and excited molecular state, a transition via absorption of the light quantum is possible. For infrared spectroscopy covering the energetic range for vibrational and rotational transitions, this leads to a series of selection rules for the change in vibrational (v) and rotational (J) quantum numbers. Furthermore, to induce such a change of the vibrational or rotational state of a polyatomic molecule by illumination with infrared radiation, the molecule must have either a permanent dipole moment, or a dipole moment has to be generated via the excited vibration. Such vibrational modes are called IR active. As most polyatomic molecules show several vibrational modes, the number of these modes is determined by the degrees of freedom dependent on the symmetry of the respective molecule. Therefore, N -atomic molecules show $3N - 5$ vibrational modes, if they show a linear molecular structure, whereas nonlinear molecules have $3N - 6$ vibrational modes.

The energy of vibrational transitions is frequently described as an approximation by the energy of a harmonic oscillator following:

$$E_{vibrational} = \hbar\omega(v + \frac{1}{2}) \quad (2)$$

including the constant $\omega = \sqrt{\frac{k}{\mu}}$, with the reduced mass μ and the force constant k . However, when calculating the vibrational energy of a diatomic molecule more precisely, factors such as anharmonicity of the oscillation model need to be considered. The energy levels in the harmonic oscillator are equally spaced, unlike the energy levels in anharmonic oscillator. This anharmonicity leads to a modified expression of $E_{vibrational}$ following (excluding vibro-rotational energies):

$$E_{vibrational} = \hbar\omega \left(v + \frac{1}{2}\right) - \hbar\omega\chi \left(v + \frac{1}{2}\right)^2 \quad (3)$$

As already stated above, a molecule that is infrared active needs to provide a change in dipole moment as a result of the vibration that occurs when infrared radiation is absorbed. The dipole moment is a vector quantity, and depends on the orientation of the molecule, the electric vector of the photon, and is proportional to the intensity of the resulting infrared signature:

$$I_{vib} \propto \left(\frac{\partial\mu}{\partial Q}\right)^2 \quad (4)$$

with I_{vib} as the intensity of the infrared signature, the dipole moment μ , and Q as the vibrational coordinate. Further, we need to keep in mind that $\left(\frac{\partial\mu}{\partial Q}\right) \neq 0$ (i.e. there must be a change in dipole moment), which leads to $\Delta v = 1$ as the selection rule for $E_{vibrational}$. Despite the mentioned anharmonicity, this holds only precisely true for the vibrational energy of harmonic oscillations. However, given the typical energy of infrared radiation, most vibrational excitations involve the first (i.e. ‘fundamental’ vibration) or second excited state (i.e. ‘overtone’ vibration), for which a harmonic oscillation represents a sufficiently accurate model to describe the energetic transitions without the need to account for inequivalent energy spacing (i.e. since anharmonicity for the first transition would only be a minute deviation) or dissociation via vibrational excitation of the molecules, which are included in the anharmonic oscillator model (i.e. via the so-called ‘Morse

potential'). Nevertheless, transitions with $\Delta v = 1$ are equally allowed for the anharmonic potential, but I_{vib} will become smaller with higher number of v .

The term mid-infrared ('MIR' will be further used as abbreviation for mid-infrared from here on) generally covers the spectral region from 4000 cm^{-1} to 400 cm^{-1} ($2.5 - 25\text{ }\mu\text{m}$). MIR spectroscopy provides inherently discriminatory information due to the excitation of fundamental vibrational (including rotational, and vibro-rotational) transitions. These excitations result in a characteristic spectrum for a given molecular species and can be applied to most molecular species in either liquid/dissolved, solid or vapor state. In particular, due to their pronounced resonances organic molecules are characterized by distinctive MIR spectra, thus rendering infrared spectroscopy a routine analysis technique for identifying and structurally characterizing different molecular species, which will be further illustrated in the following chapters.

1.2.2 Transmission-Absorption Spectroscopy

Probably the most straight forward configuration of an infrared absorption experiment can be realized as a beam of IR radiation that is passed directly through a transparent sample container while being absorbed by analyte molecules, if the energy of the incident beam is equal to the energy needed to excite a vibrational transition of the respective species. The IR beam (now with lower intensity) is then detected by an infrared detector. A schematic fundamental measurement setup for transmission absorption spectroscopy is shown in Figure 5.

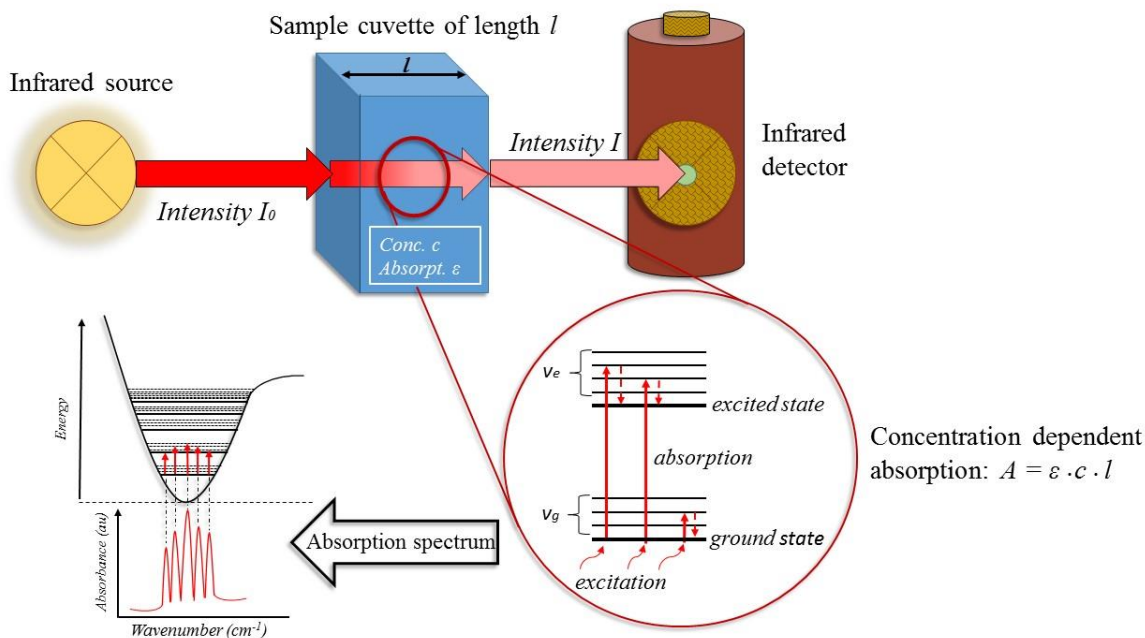


Figure 5. (Top) Schematic principle of a transmission absorption spectroscopy. **(Bottom)** Schematic of the absorption process via irradiation. Molecules absorbing infrared energy via vibrational transitions that are described by an oscillator-like potential generating distinctive infrared absorption signatures also termed ‘molecular fingerprint’.

In simple transmission-absorption spectroscopy, infrared radiation with an intensity I_0 from an infrared source (e.g. global, black body, infrared laser, etc.) passes through a sample cuvette of a certain length l , containing an analyte at a given concentration c with a molar absorptivity ϵ , and is partially absorbed by analytes and surrounding matrix resulting in light with decreased intensity I after the sample cuvette to be detected by an appropriate infrared detector. The absorption properties can be described by the following relationship, if the sample solution can be defined as homogeneous (i.e. molecularly disperse), and the analyte concentration is relatively low (i.e. highly diluted samples thereby reducing the probability of inter-molecular interactions):

$$A = \log \frac{I_0}{I} = \epsilon \cdot c \cdot l \quad (5)$$

with A as the absorbance, ε the molar absorptivity, c the concentration of the analyte, and l the optical pathlength (a.k.a. absorption pathlength) through the transmission cell. This relation is generally referred to as the ‘Lambert-Beer law’. However, this equation only precisely describes absorbance in transmission-absorption spectroscopy, i.e. if the absorbance of all absorbing molecules inside the sample cell appear independent of each other and radiation may be described as monochromatic parallel rays without taking any scattering or similar light-medium interactions into account.

1.2.3 Internal Reflection Spectroscopy and Optical Waveguides

The analysis of particularly opaque or highly scattering samples strongly limits spectroscopy in transmission-absorption mode, due to significant intensity losses if the infrared beam is passed directly through the sample. As an alternative, internal reflection spectroscopy propagates light inside a MIR transparent material serving as a waveguide, thereby probing samples adjacent to the waveguide surface via radiation leaking from the waveguide at the waveguide/sample interface (a.k.a. evanescent field). Total internal reflection occurs if light is reflected at the interface between an optically denser material (with refractive index n_1) and an optically rarer (with refractive index n_2) material at an incidence angle exceeding the critical angle ϕ following *Snell’s law*:

$$\phi = \sin^{-1} \frac{n_2}{n_1} \quad (6)$$

Radiation guided along a MIR transparent material via internal reflections thereby generates an evanescent field propagating along the waveguide/sample interface. The leaky component of this electromagnetic field extends beyond the waveguide surface and penetrates into the adjacent medium with an exponentially decaying field intensity characterized as the so-called penetration depth (d_p). For a given wavelength λ , d_p can be approximated as (Harrick 1979):

$$d_p = \frac{\lambda}{2\pi \sqrt{n_1^2 \sin^2 \theta - n_2^2}} \quad (7)$$

where d_p is the penetration depth, λ is the wavelength of the incoupled radiation, n_1 is the refractive index of the waveguide, n_2 is the refractive index of the surrounding medium, and θ is the incoupling angle. Absorbing species present within the penetration depth of the evanescent field may interact with the evanescently guided radiation similar to conventional transmission absorption spectroscopy resulting in specific attenuation (i.e., ‘attenuated total reflection’, *ATR*) at frequencies where resonant energy transfer to vibrational or rotational transitions may occur. Absorption spectroscopy via evanescent field sensing is schematically illustrated in Figure 6.

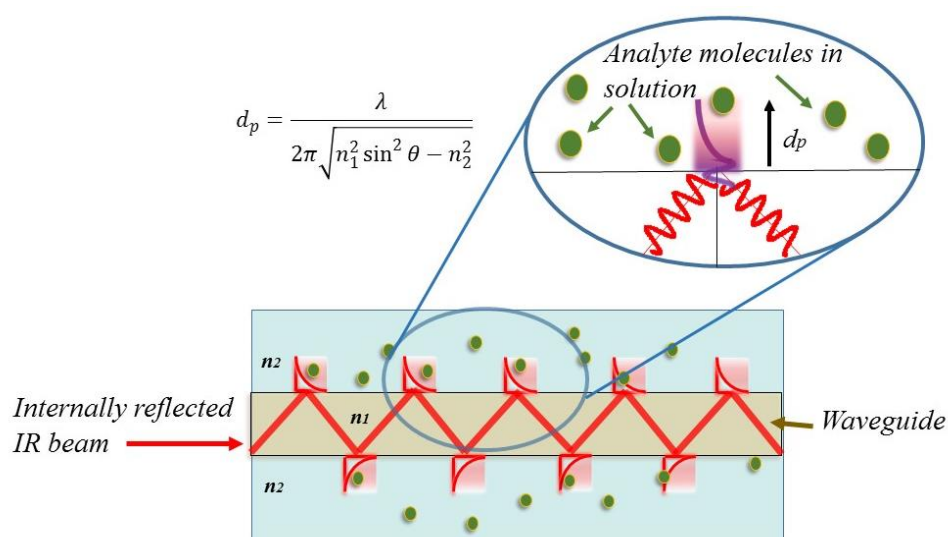


Figure 6. Schematic of the principle of internal reflection spectroscopy via evanescent field absorption. IR-absorbing molecules within the penetration depth d_p of the evanescent field may frequency-specific absorb IR radiation, thereby giving rise to evanescent field absorption spectra of the probed molecular species.

Consequently, the development of MIR transparent materials and specifically of optical fibers was particularly relevant for the advancement of MIR sensor technology resulting in advanced generations of waveguide-based infrared sensing systems. Typically, IR-ATR sensing elements in the MIR are fabricated from materials such as zinc selenide (ZnSe) or germanium (Ge), and feature geometries like trapezoidal prisms or solid core cylindrical rods. Further materials available for MIR transparent ATR rod or prism fabrication include thallium bromide-iodide (KRS-5), thallium bromide-chloride (KRS-6), and silicon (Si). Such ATR-configurations are usually referred to as ‘internal reflection elements’ (IREs), and were already introduced in the 1960s (*see Chapter 5, I*). However, the introduction of MIR transparent optical fibers marked a major milestone for the development of IR-ATR based sensor platforms during the 1980s. Such MIR transparent fiber optics are typically made from materials such as polycrystalline silver halides, crystalline sapphires or chalcogenide glasses, and have emerged as a viable alternative to conventional IREs in absorption spectroscopy taking advantage of optical fibers as both waveguide and actual sensing element. A strong driving force in the development process of advanced MIR waveguides is increasing the intensity of the evanescent field, which directly affects the obtainable signal-to-noise ratio (SNR) during an absorption measurement, and therefore directly enhances the sensitivity of the corresponding measurement. Consequently, the intensity of the evanescent field depends on the dielectric constant as well as the geometries and dimensions of the involved waveguide materials. In conclusion, tailoring the waveguide thickness, structure, and geometry leads to a variety of possible configurations, finally marked by the advent of thin-film waveguide structures that feature dimensions down to the order of magnitude of the incident wavelength. Detailed principles of state-of-the-art internal/attenuated total reflection spectroscopy and evanescent field absorption spectroscopy are described in *Chapter 5, I*, within the invited review article ‘**Mid-Infrared**

Waveguides - A Perspective'. Analytical results using IR-ATR spectroscopy and sensing are presented in *Chapter 5* within the published papers II-V.

2. Results and Conclusions

The present thesis features the development of advanced mid-infrared sensor technologies for addressing relevant environmental monitoring scenarios. It is shown that mid-infrared sensing strategies provide a promising toolbox of innovative sensing technologies featuring high robustness, high sensitivity, molecular selectivity, and the potential for remote sensing applications. Hence, the development of advanced mid-infrared sensors may finally close the gap between in-field analysis and sampling strategies requiring laboratory-based analysis without sacrificing sensitivity and efficiency. In the following, a brief summary of the most relevant results achieved within this thesis and published in the corresponding journal articles is provided.

The first journal article '**Mid Infrared Waveguides - A Perspective**' is an invited review article, which investigates the evolution of MIR waveguides along with associated state-of-the-art technologies facilitating next-generation MIR chem/bio sensors introducing a classification scheme that historically defines three 'generations' of MIR waveguides: (i) conventional internal reflection elements as '1st generation' waveguides, (ii) MIR-transparent optical fibers as '2nd generation' waveguides, and (iii) thin-film waveguide structures as '3rd generation' waveguides. Furthermore, utility and perspectives for waveguide-based MIR spectroscopy and sensing systems are highlighted.

The utility of waveguide-based MIR sensor technologies in environmental analysis is elucidated in the second article '**Fingerprinting Oils in Water via Their Dissolved VOC Pattern Using**

MID-Infrared Sensors', which was resulting from a research collaboration with CSIRO, Perth, Western Australia. This article demonstrates the detection of VOCs in aqueous environments, and how VOC analysis may be used to retrace their origin of release particularly in terms of oil spills – i.e. fingerprinting different types of oils via the VOC pattern dissolved in the aqueous environment. During a research stay at CSIRO, different oil types were interfaced with an aqueous phase – i.e., a laboratory simulation of an oil spill – and the dissolution of VOCs from the oil phase into the aqueous phase was studied. By using an adapted IR-ATR method, the evaluation of the so-called 'VOC fingerprint' in the water phase was enabled. In the MIR regime, a distinctive 'VOC fingerprint' was identified via the infrared signatures of the dissolved hydrocarbons (here, benzene, toluene, xylenes, and naphthalene) from different crude oils (i.e. types 'Barrow', 'Goodwyn', and 'Saladin') and refined oils (i.e. 'Petrol' and 'Diesel'). These hydrocarbons provide specific absorption features, which may be used to identify distinctive hydrocarbon patterns that are characteristic for the different crude and refined oils. However, the concentration of such hydrocarbons in water usually does not exceed ppb ($\mu\text{g/L}$) concentration levels, thus representing a challenge for reliable quantification. Paired with their high volatility, sampling procedures required for e.g., GC-MS analysis are tedious, and are frequently accompanied with losses of analyte. On the other hand, ppb levels in water matrices may be challenging for infrared spectroscopy, due to the strong infrared absorption of the water matrix. As a solution, a thin hydrophobic layer of poly(ethylene-co-propylene) was coated onto the IRE surface for minimizing interferences of the surrounding water matrix and to amplify the VOC signatures by enrichment into the polymer membrane. Consequently, the establishment of suitable calibration functions for the quantification of characteristic concentration patterns of the detected VOCs was enabled, as well as a first study on the discriminating power offered by multivariate statistics. However,

directly deriving the original oil type from the VOC fingerprint requires more calibration/classification examples, and potentially more sophisticated multivariate algorithms. In a next step, it is anticipated that real world scenarios at in-field conditions will be tested. As demonstrated, extensive sampling and transportation steps may potentially be avoided using the proposed method, thereby proposing a strategy towards in-field monitoring devices. Last but not least, this study corroborates the potential of mid-infrared sensing at trace concentration levels for identifying, fingerprinting, and potentially quantifying oil-based contaminants in aqueous environments.

Following the trace level detection of hydrocarbon contaminations in water, the potential of mid-infrared sensors for analyzing dissolved greenhouse gases was demonstrated in the articles ‘**Monitoring dissolved carbon dioxide and methane in brine environments at high pressure using IR-ATR spectroscopy**’ and ‘**Portable Mid-Infrared Sensor System for Monitoring CO₂ and CH₄ at High Pressure in Geosequestration Scenarios**’. These two publications investigate in detail the utility of infrared spectroscopy for greenhouse gas monitoring in geosequestration scenarios – both focusing on two main greenhouse gases, carbon dioxide and methane. These two gases show distinctive infrared signatures readily enabling side-by-side detection and quantification of both species after dissolution in the aqueous phase. Paper III particularly focuses on the observation and identification of various representations of these species (i.e. dissolved, gaseous, supercritical) when introduced to aqueous – and specifically brine - environments. The obtained *in-situ* information on the behavior of greenhouse gases in such scenarios reveals remarkable changes in the infrared signatures of the dissolved gases at pressurized conditions simulating e.g. deep aquifer or deep sea environments. Gathering such information at pressure ranges from 6-11 MPa is a challenge that has not been satisfactorily resolved to date, although it is

required in order to improve fundamental understanding of the molecular behavior at proposed storage conditions. Consequently, it was demonstrated that the detection of dissolved CO₂ (and its isotopic species ¹³CO₂) besides methane at pressurized conditions is enabled via IR-ATR sensing techniques, and that furthermore the gaseous and dissolved states (including clearly observable changes in the infrared signatures during the dissolution processes that also have not been reported to date) of both gases may be differentiated using infrared sensors. Even though the results of this paper are performed and reported using a laboratory-based conventional FTIR spectrometer and a high-pressure commercial ATR-accessory, the results clearly indicate the utility for studying GHG storage mechanisms and to derive fundamental information for the development of a portable sensor system, which has been reported in the follow-up article '**Portable Mid-Infrared Sensor System for Monitoring CO₂ and CH₄ at High Pressure in Geosequestration Scenarios**'. In addition, during the development process of the portable sensor system a strategy for evaluating and comparing the sensitivity achieved by various available waveguide materials as well as different optical ATR configurations was devised, which was crucial for the design of the pressure sample cell used in the portable system. The article '**Selecting the right tool: Comparison of the analytical performance of infrared attenuated total reflection accessories**' (*Chapter 5, IV*) investigates and normalizes the sensitivity obtained from various IR-ATR accessories in an innovative way. In particular, by comparing dissolved analyte species (i.e. carbonates and carbon dioxides were selected to yield useful results for geosequestration scenarios), as well as acetate as an easy-to-identify molecule providing generically relevant information of interest to a wider field of spectroscopists working with aqueous solutions. In this study, the majority of commercially available ATR-accessories and waveguide/IRE materials was exhaustively investigated. The comparison of four ATR-systems showed that significant differences in analytical performance

(i.e. sensitivity and efficiency) are evident among the various ATR configurations and IRE materials, and were further evaluated by normalizing noise, number of internal reflections and sensor efficiency enabling a detailed comparison. Given that the combination of a diamond ATR disc combined with a zinc selenide optical coupling element provides the highest sensitivity, the dissolved greenhouse gas sensor configuration was based on a similar design leading to a portable analyzer system presented in Paper V (*Chapter 5, V*).

Consequently, the article **‘Portable Mid-Infrared Sensor System for Monitoring CO₂ and CH₄ at High Pressure in Geosequestration Scenarios’** presents a portable in-field deployable infrared sensor system to finally close the gap between simulated laboratory studies and actual on-site GHG monitoring. This infrared-based online sensor system proved suitable for monitoring, detecting, and differentiating carbon dioxide and methane at high pressures (i.e. up to 11 MPa) in saline aquifer and/or synthetic brine environments. In addition, robust and reproducible calibration functions were established enabling the quantification of CO₂ and CH₄ concentrations at downhole conditions, which was not available for *in-situ* analysis to date. The analyzer system is currently being tested at CSIRO, Perth, Western Australia, and will be applied during field experiments once the test well at the currently established GHC storage site is activated.

It should be noted that the article **‘Portable Mid-Infrared Sensor System for Monitoring CO₂ and CH₄ at High Pressure in Geosequestration Scenarios’** was selected as ‘ACS Editors’ Choice Publication’, and was subject of a ‘first reaction comment’ in *ACS Central Science* (Gabriel 2016) upon release of the article.

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5. Journal Articles

5.1 Paper I. Mid-Infrared Waveguides - A Perspective

The scope of the paper was determined in close communication with B. Mizaikoff and P. Griffiths. T. Schädle wrote the manuscript. B. Mizaikoff edited the manuscript for the final version.

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Mid-Infrared Waveguides – A Perspective

Thomas Schädle¹ and Boris Mizaikoff^{1*}

¹ Institute of Analytical and Bioanalytical Chemistry (IABC), Ulm University, Ulm, Germany

* Corresponding author: boris.mizaikoff@uni-ulm.de

Abstract

Significant advancements in waveguide technology in the mid-infrared regime (MIR) during recent decades have assisted in establishing mid-infrared spectroscopic and sensing technologies as a routine tool among non-destructive analytical methods. In this review, the evolution of MIR waveguides along with state-of-the-art technologies facilitating next-generation MIR chem/bio sensors will be discussed introducing a classification scheme defining three ‘generations’ of MIR waveguides: (i) conventional internal reflection elements as ‘1st generation’ waveguides, (ii) MIR-transparent optical fibers as ‘2nd generation’ waveguides, and – most recently introduced – (iii) thin-film structures as ‘3rd generation’ waveguides. Selected application examples for these each waveguide category along with future trends will highlight utility and perspectives for waveguide-based MIR spectroscopy and sensing systems.

Index Terms – *mid-infrared, optical sensors, infrared sensors, waveguides, attenuated total reflection, internal total reflection, chem/bio sensing, waveguide classification, thin film waveguides, optical fibers*

Why Mid-Infrared?

The term mid-infrared (MIR) generally covers the spectral region from approx. 4000 cm⁻¹ to 400 cm⁻¹ (2 - 25 μm). This spectral region allows for qualitative and quantitative spectroscopy providing chemical, structural, and compositional information on molecular constituents. MIR

spectroscopy may be applied for gas/vapor, liquid, and solid samples. Inherently discriminatory information is obtained owing to the excitation of fundamental vibrational, rotational, and vibro-rotational transitions resulting in a characteristic spectrum for a given molecular species (a.k.a., molecular fingerprint). In particular, due to their pronounced resonances, organic molecules are characterized by particularly distinctive MIR spectra, thus rendering infrared spectroscopy a routine analysis technique for identifying and structurally characterizing such molecular species. While conventional waveguide-based spectroscopic techniques – internal total reflection and attenuated total reflection spectroscopy – were introduced by Harrick and Fahrenfort already in the 1960s^{1,2}, it was the introduction of MIR transparent optical fibers in particular since the late 1980s, including materials such as chalcogenide glasses, polycrystalline silver halides (AgX), single-crystalline sapphire, and hollow waveguide (HWG) structures, that have laid the foundation for transitioning classical infrared spectroscopic techniques into fiberoptic MIR chem/bio sensing technologies³. Due to the inherent molecular selectivity, MIR spectroscopy naturally lends itself as a viable approach for direct label-free analysis, which is particularly attractive for establishing optical chem/bio sensors. Real-world sensing and monitoring scenarios have been reported in medical settings⁴⁻⁵, for industrial and material sciences⁶⁻⁹, and in environmental analysis, including most recently monitoring of greenhouse gases¹⁰⁻¹⁵. Until fairly recently, MIR spectroscopy has been largely considered as a rather bulky instrumental technique confined to laboratory usage with limited utility for in-field applications in real-world scenarios. However, with increasing adoption of micro- and nanofabricated optical components (e.g., light sources, waveguides - also serving as the active sensing element (a.k.a., transducer), photodetectors, etc.), conventional instrumentation and MIR sensing devices may significantly be scaled down in physical dimensions without sacrificing their robustness, reliability, sensitivity, and selectivity¹⁶⁻¹⁸. Given the progress in waveguide technology, this focal point review will predominantly consider advanced MIR sensing technologies that take advantage of waveguide-based measurement principles, as specifically the direct analysis of strongly absorbing samples or of selected constituents in matrices (e.g., water) that limit the use of conventional MIR spectroscopic techniques in the transmission mode¹⁹. Infrared attenuated total reflection spectroscopy (IR-ATR) is considered among the most suitable routine measurement techniques for addressing such complex analytical scenarios¹, and particularly benefits from the evolution in MIR waveguide technology discussed herein.

Optical Components for MIR Spectroscopy and Sensing

Regardless of whether they are installed in commercially available Fourier transform infrared (FT-IR) based laboratory systems or state-of-the-art on-chip IR sensing devices, waveguide-based (most recently termed ‘waveguide-enhanced’²⁰) IR instrumentation generally comprises three main components: (i) an IR light source; (ii) a waveguide-based IR transducer (a.k.a., sensing element) frequently also used for propagating MIR radiation from the light source to the sample, and – after photon-sample interaction to (iii) a detection device.

i) MIR Light Sources

Among the currently established and available MIR radiation sources – usually ‘broadband’ sources - recent advancements in MIR laser technology have led to an increasing adoption of laser light sources in MIR spectroscopy, and even more so in MIR sensor technology. Sophisticated solid-state lasers^{21–23}, quantum cascade lasers (QCLs)^{24–26} and interband cascade lasers (ICLs)^{27,28} are considered ‘the revolution in MIR light source technology’, in particular for highly integrated and on-chip MIR devices^{10,14,16–18}. In contrast to conventional heterostructure laser diodes generating MIR radiation via electron-hole recombination between the conduction and the valence band of appropriate semiconductors or semiconductor mixtures, QCLs and ICLs emit MIR radiation from cascaded structures of alternating ultra-thin layers of semiconductor materials (i.e., quantum well heterostructures) utilizing subband or interband transitions, respectively. In brief, such quantum heterostructures are organized as a superlattice composed of periodic series of semiconductor layers with different electric potentials leading to different electron occupation throughout the superlattice. As a consequence, these one-dimensional potential wells are characterized by splitting of the band of permitted energies into a number of discrete electronic subbands. By precisely engineering the layer sequence and nature of the semiconductor materials (a.k.a., bandstructure engineering), the emission wavelength and lasing conditions may be widely tuned throughout the MIR up to THz emission frequencies in pulsed and continuous wave (cw) operation. Hence, QCLs are tailorable MIR light sources with miniature dimensions featuring high output power while covering a widespread spectral regime.^{16,17,20} Coupling QCLs to an external cavity and a movable grating enables tuning of the emission wavelength nowadays across a band of 2-3 μm , thereby rendering such devices miniature IR spectrometers from an analytical

perspective^{25,29,30}. Albeit to date limited to the shorter wavelengths in the MIR, ICLs are of increasing interest in particular for mobile sensing applications due to their high voltage efficiency (i.e., low power consumption) resulting from interband transitions at type-II heterointerfaces.³¹

ii) MIR Waveguides & Transducers

In IR-ATR spectroscopy, the sampling performance and achievable sensitivity is largely determined by the physical and optical properties of the actual sensing element, i.e., the internal reflection element (IRE), fiberoptic evanescent wave (FEWS) probe, or the planar waveguide structure in on-chip MIR photonics. Conventional IREs are most frequently made from MIR-transparent crystalline materials such as zinc selenide (ZnSe), zinc sulfide (ZnS), diamond, germanium (Ge), thallium bromo-iodide (KRS-5), and silicon (Si) shaped into multi-reflection ATR rods, trapezoids or similar parallelograms, or single-reflection hemispheres at macroscopic (i.e., mm-cm) dimensions^{15,32}. These ATR crystal materials are complemented by a range of optical fibers transparent at MIR wavelengths including e.g., chalcogenide glasses or polycrystalline silver halides^{20,33}. These optical fibers are available at a length of several meters with diameters < 1 mm down to few hundreds of micrometers. Thin-film waveguides facilitate a waveguide thickness of the order of magnitude of the wavelength (i.e., few micrometers), thus offering the potential on-chip integration, utilizing readily established microfabrication processes for deposition and structuring, and single-mode operation ideally matching the emission characteristics of laser light sources such as QCLs and ICLs. Figure 1 summarizes the MIR transparency of commonly applied waveguide materials prevalent throughout all three generations of MIR waveguides.

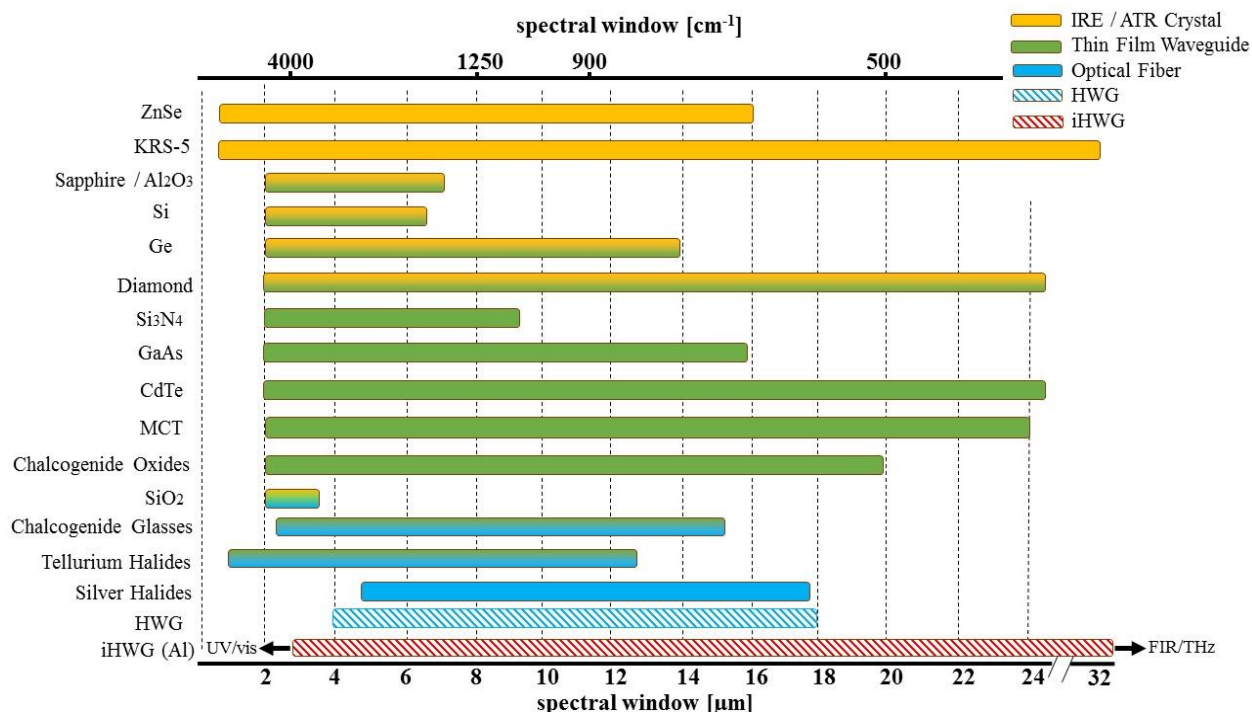


Figure 1. Overview of the most prevalent MIR transmitting waveguide materials color coded as conventional IREs, optical fibers, and thin-film waveguides along with their approximate MIR transmission window. Multi-colored materials have been used in two or more configurations (i.e., IRE and/or optical fiber and/or thin-film waveguide or hollow waveguides (fiberoptic and integrated types).

Given their MIR transmission window, it is evident why thallium bromo-iodide (albeit nowadays rarely used due to toxicity of the material)), zinc selenide, silicon, and germanium are among the most commonly used IRE materials, and in particular among commercially available IR-ATR laboratory accessories. However, besides the accessible spectral window, material parameters including the refractive index, the resulting evanescent field intensity, and potential propagation losses when using extended waveguide geometries have to be taken into account. The most prevalent MIR waveguide materials currently used in evanescent field spectroscopy are color-coded in Figure 1 according to their typical application either as conventional IRE mostly in combination with FT-IR-based spectroscopy (yellow), as optical fiber in fiberoptic evanescent field spectroscopy and sensing (FEWS; blue), as thin-film and/or on-chip waveguide material (green), as hollow-core optical fiber (dashed blue) or as ‘substrate integrated hollow waveguide (iHWG)’ (i.e., fabricated within an aluminum substrate) with some materials occurring in two or more representations. iHWGs were most recently introduced by the group of Mizaikoff³⁴ featuring

radiation-reflective hollow waveguide channels enabling transmission from the UV/vis to the FIR/THz regime.

iii) MIR Detectors

Probably the most commonly applied detector technology in MIR spectroscopy and sensing utilizes room-temperature, thermoelectrically cooled or liquid nitrogen cooled (increasing order of detectivity) photoconductive semiconductor detectors comprising detector materials such as indium antimonide (InSb), mercury-cadmium telluride (HgCdTe; MCT) and the like^{35–37}. Alternatively, thermal or pyroelectric detectors are of current interest as they are usually significantly cheaper, operated without cooling, provide a spectral response over a possibly broad MIR wavelength band, and may readily be miniaturized^{38,39}. Adopting the strategy used for QCLs, the same quantum heterostructures may in fact be used as so-called quantum cascade detectors (QCDs) operated without applying a bias voltage⁴⁰ which enables further miniaturization and integration of MIR sensing platforms⁴¹. QCDs are therefore interesting alternatives serving as a photovoltaic version of quantum well infrared photodetectors^{42,43}. Given the fact that QCDs are passive devices only generating a response signal by propagating incident photons via cascading quantum wells, a significantly reduced power budget of the final sensor system is anticipated.

Focus on MIR Waveguides: Fundamentals & Classification

i) Fundamentals of Evanescent Field Spectroscopy and Sensing

IR-ATR spectroscopy is nowadays considered a routine measurement technique when analyzing strongly absorbing films, pastes, gels, powders, and liquids taking advantage of radiation leaking from the waveguide into the adjacent sample environment (a.k.a., evanescent field) upon total internal reflection at the waveguide/sample interface. Total internal reflections occurs if light is reflected at an incidence angle exceeding the critical angle ($\theta_c = \sin^{-1}(n_2/n_1)$, i.e., Snell's law) at the interface between a high-refractive-index (n_1 or n_{wg}) waveguiding element and a low(er)-refractive-index (n_2 or n_c) cladding, environment or sample matrix⁴⁴. The leaky component of the electromagnetic field (from here on referred to as 'evanescent field') penetrates into the adjacent

medium with an exponentially decaying field intensity characterized as the so-called penetration depth (d_p). For a given wavelength λ , d_p can be approximated as⁴⁴:

$$d_p = \frac{\lambda}{2\pi\sqrt{n_{wg}^2 \sin^2 \theta - n_c^2}}$$

Molecules present within the evanescent field generated at the waveguide/sample may resonantly interact with this evanescent field interface leading to evanescent field absorption spectrum, a.k.a., ATR spectrum, as a result of the attenuation of the propagating radiation at analyte-specific frequencies. Absorption within the evanescent field essentially follows a Beer-Lambert relationship according to:

$$A = (\varepsilon cl)r = r \log\left(\frac{I_0}{I}\right)$$

with I_0 as the light intensity before attenuation, I as the intensity after molecular absorption, ε as the molar absorptivity, c as the concentration, and r as the fraction of light power residing outside the waveguide.^{3,20} More precisely, absorbance within the evanescent field depends on the square of the product $[E(\partial\mu/\partial q)]^2$, whereby μ is the transition dipole, q a coordinate normal to the incident plane, and E the electric field amplitude in the outer medium. Additionally, the absorbance is proportional to the so-called effective penetration depth (d_e) defined as^{2,45}:

$$d_e = \frac{n_{21}}{\cos \theta} \int_0^\infty E^2 dz = \frac{n_{21}E^2 d_p}{2 \cos \theta}$$

with $n_{21}=(n_2/n_1)$, E as the electric field amplitude, d_p as the penetration depth, and z the distance from the waveguide/sample interface. Furthermore, the reflectivity R for a single reflection is given as⁴⁶:

$$R = 1 - \alpha d_e$$

whereby α describes the absorption coefficient at a given wavelength. Consequently, any number of N multiple internal reflections would result in:

$$R = (1 - \alpha d_e)^N$$

Since usually αd_e is $\ll 1$, it may be safely assumed that the absorbance for N reflections approximately equals N -times the absorption of a single reflection^{20,45,47}. Using such basic geometric considerations when generating an evanescent field, one may readily derive the first generation of MIR waveguides termed ‘internal reflection elements (IREs)’.

ii) 1st Generation MIR Waveguides: Internal Reflection Elements (IREs)

Considering the propagation of radiation inside a waveguide for waveguide dimensions significantly larger than the wavelength at the conditions of internal total reflection conditions (i.e., as is the case for conventional IREs), conventional geometric optics result in the emergence of evanescent field spots at each reflection along the IRE surface (Figure 2).

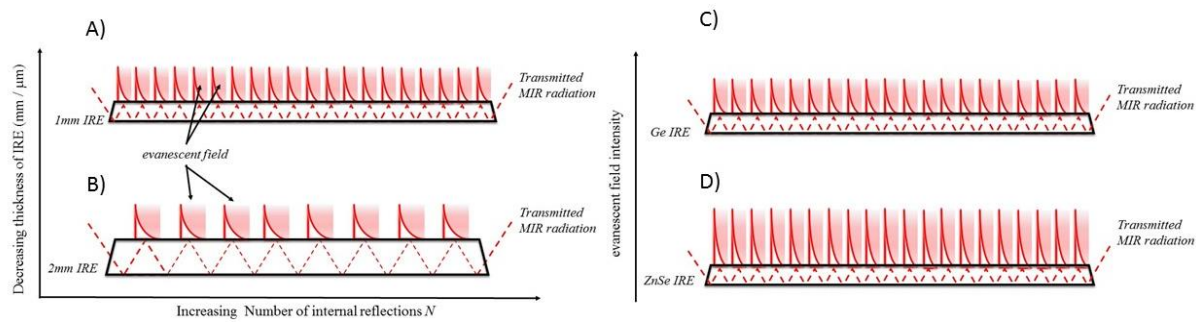


Figure 2. (Left) Schematic representation of radiation propagation inside and the evanescent field at the surface of an IRE featuring A) a macroscopic multi-reflection IRE (e.g., trapezoid with 1 mm thickness), and B) an IRE twice the thickness (2 mm) at the same angle of incidence. Albeit not to scale, the increase in density of evanescent field spots responsible for generating the analytical signal (i.e., absorbance) with decreasing IRE thickness is immediately evident. **(Right)** Schematic increase in penetration depth, and thus, intensity of the evanescently guided radiation at similar optical conditions for C) a germanium IRE with a refractive index of 4.06, and D) a zinc selenide IRE with a refractive index of 2.44. Note that for clarity the evanescent field is only shown at the the upper surface of the IRE.

Figure 2 schematically illustrates the influence of the thickness and material choice of the IRE. Considering the IRE thickness (Figure 2 A-B), the number of internal reflections scales with the waveguide dimensions for obvious geometric reasons, which should increase the sensitivity of the measurement with decreasing waveguide thickness. However, while reducing the IRE thickness positively affects the sensitivity, the decreasing optical aperture adversely decreases, usually resulting in less photons coupled into the IRE; likewise, more internal reflections may lead to

increased reflection losses. Hence, the signal-to-noise ratio (SNR) will be negatively affected usually requiring more sensitive detectors for compensation.

Conversely, Figure 2 C-D schematically illustrates how the selected IRE material (i.e., its refractive index or, more generally, dielectric constant) may affect the penetration depth and intensity of the evanescent field. Decreasing the refractive index of the waveguide material (i.e., the leaky component) increases the penetration depth, and thus increases the interaction volume with molecules at the waveguide/sample interface, which positively affects the SNR during absorption measurements.

In summary, it is immediately evident that optimizing the waveguide structure, dimensions, and geometry (i.e., number of internal reflections), along with the optical properties of the waveguide material (i.e., penetration depth of the evanescent field) are major parameters for maximizing the performance and sensitivity in waveguide-based MIR spectroscopy and sensing concepts.

iii) 2nd Generation MIR Waveguides: Optical Fibers

During the past three decades, fiberoptic evanescent wave spectroscopy and sensing schemes have emerged as a viable alternative to conventional IREs in absorption spectroscopy taking advantage of MIR transparent optical fibers as waveguide and actual sensing element⁴⁸. Evidently, using optical fibers enables extended separation of the actual active sensing interface from the light source and detector, thus facilitating the design of fiberoptic sensor for in-situ experiments. Given the length of optical fibers (i.e., several meters for MIR fibers at acceptable attenuation losses) and their mechanical flexibility, the main advantage vs. 1st generation waveguides is the opportunity of robust light guiding and sensing in remote application scenarios (i.e., ‘guiding photons to the sample rather than bringing the sample to the spectrometer’). Next to fine-tuning of the fiber thickness, surface, and radiation in-/out-coupling facets, the active sensing region of the fiber (where the fiber serves as evanescent field sensing element interacting with sample molecules upon immersion) may be tailored. For example, the interaction length may be significantly extended vs. conventional IREs (e.g., ‘spiraling’ of the fiber; see Figure 3 B) or the fiber geometry may be designed for maximizing the number of internal reflections within the sample interaction length by symmetrically tapering (e.g., etching, pulling, or thinning a cylindrical segment) or flattening the fiber core (see Figure 3 C). Furthermore, due to its rotational symmetry (Figure 3 A), usually the

entire evanescent field surrounding the fiber is used for generating the absorption signal as the fiber may readily be sealed as a suspended IRE within a flow-through cell, whereas conventional IREs usually utilize only one side of the waveguide for the actual measurement (i.e., with the exception of macroscopic ATR rods).

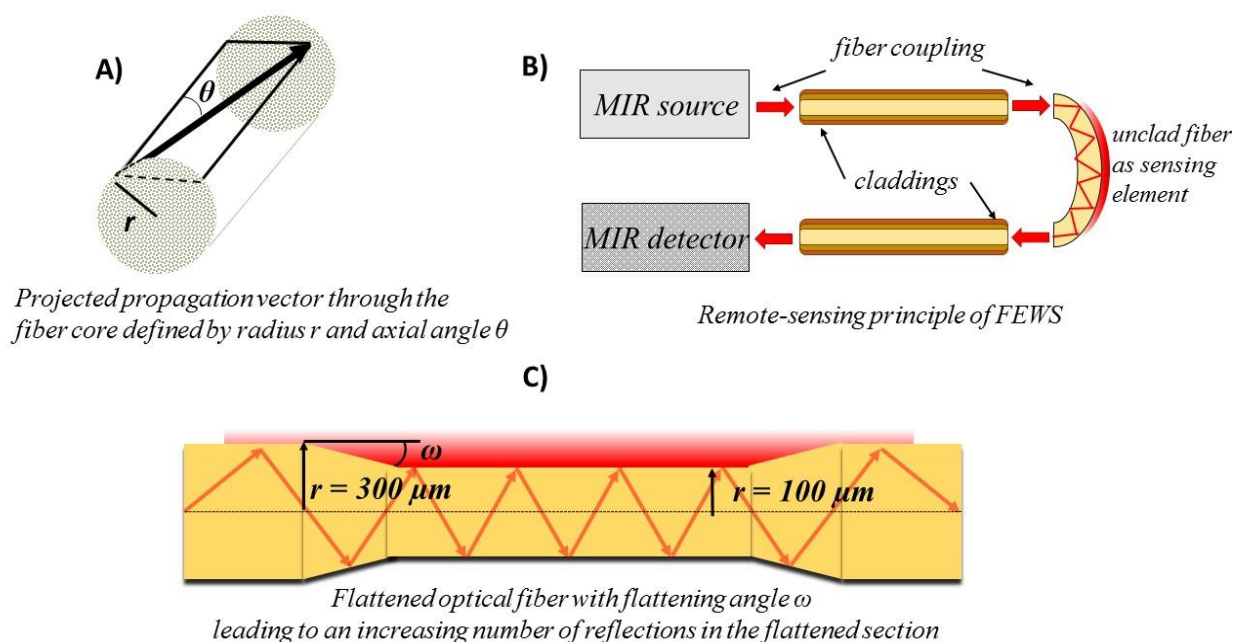


Figure 3. Schematic examples for fiberoptic evanescent field sensing concepts. **A)** Vector representation of radiation propagation inside a fiberoptic waveguide. Here, the evanescent field is generated along the propagation vector throughout the fiber core (in all three dimensions). **B)** Remote sensing via FEWS with MIR radiation propagating e.g., along core-clad optical fibers generating an analytically useful evanescent field (i.e., accessible by sample molecules) only along the unclad active sensing region at a distance from light source or spectrometer and detector. **C)** Tapering or flattening of the fiber core within the active sensing region leads to an increased number of internal reflections as a consequence of the reduced waveguide thickness and the tapering angle ω .

A variety of theoretical models based on simple geometric optics or advanced electromagnetic field theory have been used for describing radiation propagation along fiberoptic waveguide structures in great detail⁴⁹. The advances of FEWS in terms of portability and the potential for remote sensing applications constitutes the main breakthrough of fiberoptic-based spectroscopic sensors vs. the application of conventional IRE-based devices with applications ranging from determining

chemical reaction rates⁵⁰, to gas detection⁵¹ and biosensors⁵². However, to date such transducers remain predominantly coupled to commonly applied FT-IR spectrometer systems.

In order to improve the achievable sensitivity, tapering and flattening of fiberoptic waveguides has been applied, albeit limited to a thickness of usually few tens of micrometers of the tapered active sensing element, as the thinned section is of increasing mechanical fragility. Hence, real-world application scenarios usually abstain from using tapered fibers in chem/bio sensing. Likewise, while in principle possible, it is of little practical value to taper fibers to a thickness on the order of magnitude of the wavelength (i.e., $< 20\ \mu\text{m}$) for achieving single-mode radiation propagation behavior. Consequently, the advent of advanced MIR laser light sources such as QCLs and ICLs demanded for a 3rd generation of MIR waveguides – thin-film planar waveguiding structures.

iv) 3rd Generation MIR Waveguides: Thin-film Waveguides

As discussed so far, the thickness of most conventionally applied waveguides significantly exceeds the order of magnitude of the propagated wavelength. As the number of reflections is inversely proportional to the thickness of the IRE, thinning the waveguide to dimensions corresponding to the wavelength increases the effective absorption path length until ultimately a uniform evanescent field is obtained extending along the surface of such core-only waveguide structures, which may lead to substantial sensitivity enhancements.⁵³

Since light propagation within such thin-film waveguides may no longer be adequately described via a series of internal reflections, the generated continuous evanescent fields are represented via more sophisticated models based on wave analysis. Waveguides realized at these dimensions are commonly referred to as thin-film waveguides or integrated optical waveguides (IOWs).

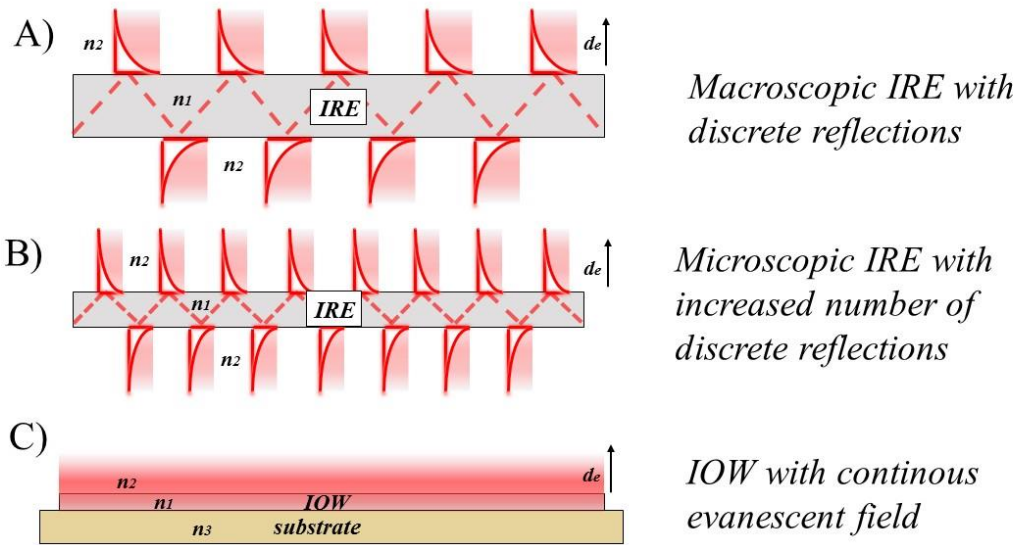


Figure 4. Schematic representation of evanescent wave/field and radiation propagation with decreasing thickness of the IRE (A-B) leading to integrated optical waveguides IOW providing a continuous evanescent field leaking into the adjacent environment (C).

Hence, without being discussed here in detail rather focusing on the analytical and applied spectroscopic aspects, parameters such as mode confinement, lateral distribution of the radiation in various modes (i.e., TE, TM, etc.), etc. lead to the fact that IOWs facilitate significant increases enhancements of the evanescently guided field intensity and penetration depth, thereby enabling specifically tailoring waveguide structures to selected applications. However, it should be noted that most commonly such thin-film waveguide structures are deposited at and mechanically supported by suitable (i.e., refractive index matched) substrate materials - with the possible exception of sufficiently robust free-standing thin-film diamond waveguides - thus providing only one surface of the waveguide for active sensing purposes.

Recent Trends and Selected Applications

Given that extensive literature has been published on conventional IREs and MIR transparent optical fibers – and applications thereof^{3,20}, this review focuses predominantly on recent trends in

both waveguide technology and applications that have emerged during the last decade. Most condensed materials by nature of their inherent structure reveal vibrational transitions limiting their MIR transparency. Hence, semiconductors of different compositions appear most suitable for providing sufficient transmittance in the electromagnetic spectrum of interest, and for establishing tailorable waveguiding platforms. Among the fabrication techniques, drawing or growing optical fibers next to chemical vapor deposition (CVD) for planar waveguide structures (i.e., IREs) remain among the most commonly applied fabrication processes for MIR transparent waveguides⁵⁴.

With the emergence of 3rd generation thin-film waveguides and integrated MIR optics, techniques initially developed predominantly for silicon-based microfabrication are increasingly being adopted for the development of miniaturized MIR sensing platforms (a.k.a., MIR on-chip device technology). Processing techniques including UV photolithography, electron beam patterning, (hot) embossing, etc. facilitate rapid and straightforward processing even of sophisticated optical device designs⁵⁵. Simple IOWs comprise strip or rib waveguide structures of a higher refractive index n_1 - most commonly semiconductor - material are locally deposited on top of a suitable substrate (i.e., usually wafer-based substrates with any number of strain and/or refractive index matching additional interface layers) with a lower refractive index n_2 . Alternatively, previously deposited waveguide films are etched after lithographic structuring (e.g., wet etching, reactive ion etching, etc.) readily creating 3-dimensional linear waveguide structures or more sophisticated optical geometries (e.g., ring-, disc- or racetrack-shaped resonators) with precise control on the desired dimensions.

Evidently, current trends in waveguide-based MIR applications increasingly take advantage of waveguides as an active transducer, rather than merely serving as a radiation propagation conduit. From an analytical spectroscopy perspective, this is an essential – if not the most essential - function, as the transducer plays the major role within optical sensor systems in generating the actual analytical signal by ensuring reproducible intimate interaction between photons and sample constituents (i.e., conversion of chemical, biochemical, or biological processes or recognition events into changes of optical properties). While nowadays optical chemosensors increasingly take advantage of the distinctive molecular signatures generated in the MIR regime, only few representative examples of optical biosensors operating in the MIR have been published. This may be attributed to the fact– with few recent exceptions – that the sensitivity of 1st generation

waveguides (i.e., conventional IREs) and even 2nd generation fiberoptic-based liquid phase MIR sensors remains insufficient for detecting (i) small quantities of relevant biomolecules such as e.g., proteins or DNA, and (ii) in appreciable small volumes (i.e., microliter regime). In contrast, limited sensitivity of MIR chemosensors is readily mitigated by using, e.g., solid phase enrichment schemes via immobilization of appropriate polymer, sol-gel or similar membranes directly at the waveguide surface acting as in-situ enrichment membranes; a strategy applicable for conventional IREs, fiberoptic transducers, and IOWs. Thereby, detection levels in the ppb (i.e., $\mu\text{g/L}$) concentration range have been realized in a true chemical physico-chemical sensing format (i.e., diffusion of analyte molecules into and out the solid phase membrane in lieu of chemical reactions). Using such membranes, IR-ATR-based chemosensors have been developed serving for environmental contaminant monitoring^{32,56}, in pollutant analysis^{11,57,58}, and even in microbiological applications⁵⁹, as exemplarily illustrated for detection of volatile organic components (VOCs) towards dissolved oil fingerprinting in aqueous/marine environments (Figure 5).

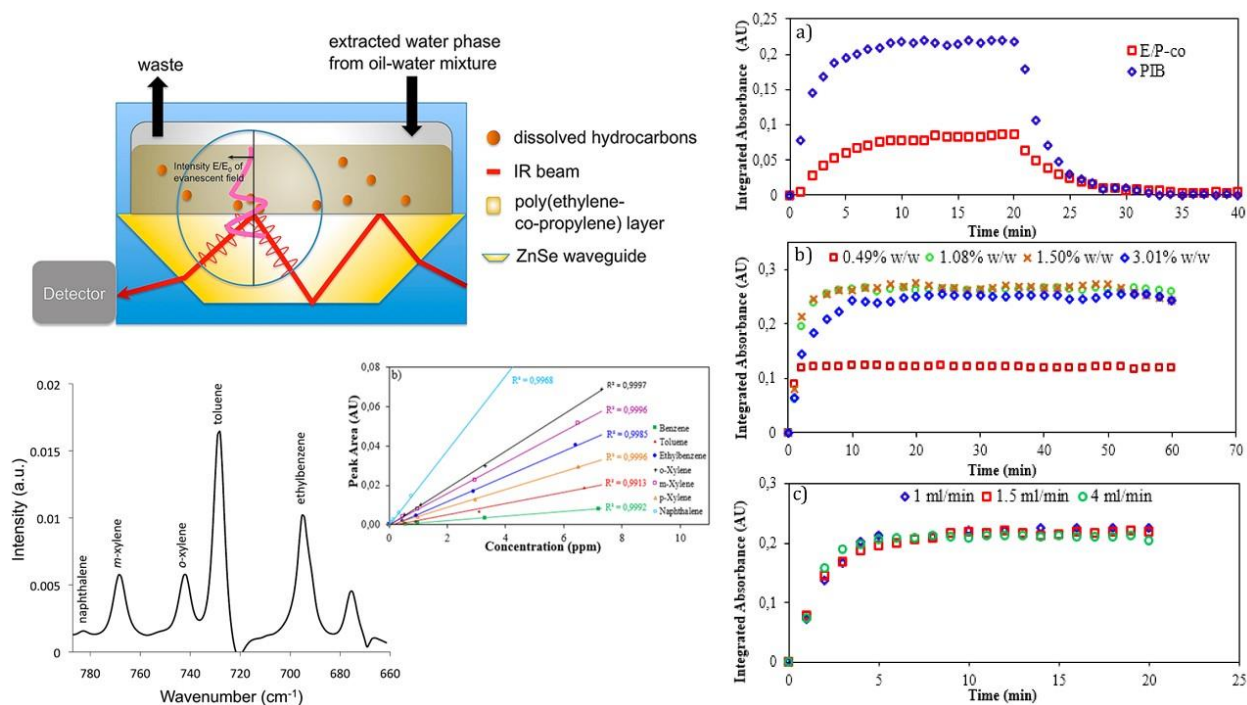


Figure 5. (Top Left) Schematic of IR-ATR system comprising a macroscopic ZnSe IRE coated with a polymeric enrichment membrane for detecting organic pollutants in marine environments (i.e., dissolved oil fingerprinting via characteristic VOC patterns dissolved in the aqueous phase). **(Bottom left)** Characteristic absorption patterns of dissolved hydrocarbons detected via IR-ATR evanescent field absorption spectroscopy after enrichment within a

suitable polymer membrane. **(Right)** Analytical response of a polymer-coated diamond IRE in aqueous solution at a contaminant concentration of 50 ppm (p-xylene). Adopted and reprinted with permission from ACS Publishing. Copyright 2014/2015.^{32,57}

After optimization, the application of conventional IR-ATR techniques using membrane-coated macroscopic IREs revealing characteristic concentration patterns of dissolved VOC fractions assignable to different oil contaminations at trace levels has been shown^{32,56}. Obtaining such low detection limits for relevant pollutants supports the potential of MIR sensors for in-situ analyses and monitoring purposes. Nevertheless, in-field applications require a significant scaling of involved instrumentation for facilitating, e.g., on-ship studies. Given ongoing progress in miniaturized MIR waveguide technology, light sources, and detectors it is anticipated that waveguide-based IR sensing systems for in-situ and in-field monitoring (e.g., in marine environments) are within reach.

As a consequence, more compact MIR sensor systems utilizing ATR sensing concepts are predominantly focusing on miniaturizing the actual MIR transducer as well as the entire instrument, yet maintaining the sensitivity via improved chem/bio recognition architectures. Giammarco et al. proposed a method combining an innovative multi-layered coating with ATR waveguide technology.⁶⁰ The established enrichment polymer film had a thickness of only 27 nm, and was capable of extracting a variety of constituents for determination via the evanescent field emanating at an IRE surface (Figure 6).

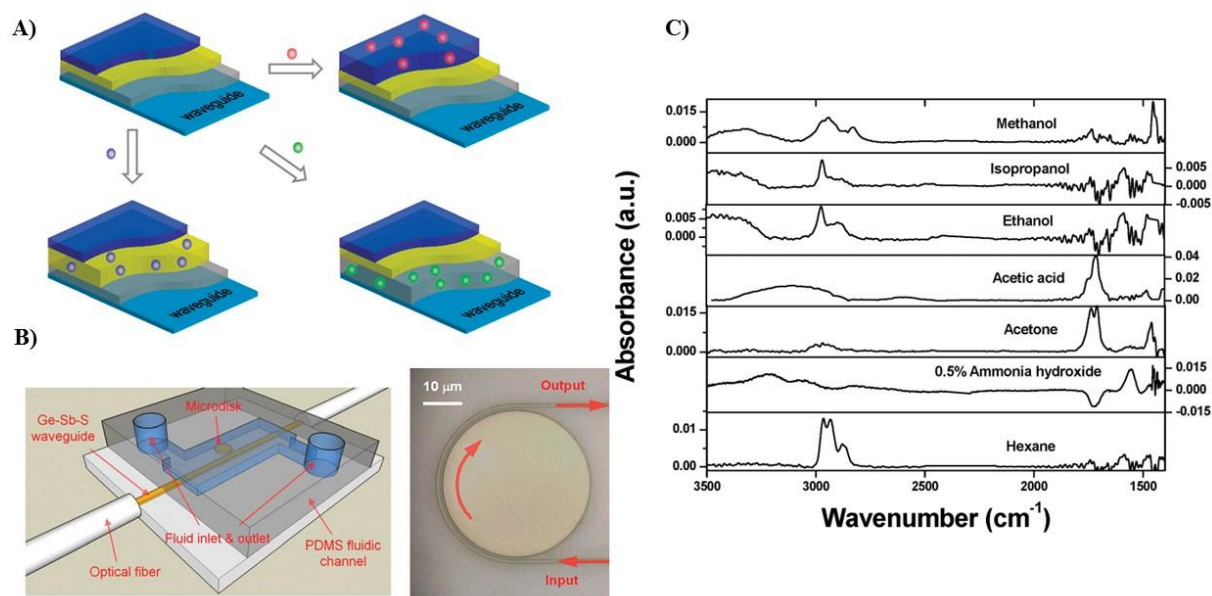


Figure 6. A) Schematic illustrating the interaction of a multi-layered enrichment coating with various analytes. B) Schematic of the micro-disc-on-chip system (left), and top view image of a micro-disc resonator in a pulley-coupler configuration (right). C) IR-ATR spectra of various analyte vapors detected using the multi-layered enrichment coating deposited at a Si crystal waveguide surface. Reprinted with permission from RSC Publishing. Copyright 2011.⁶⁰

Here, an advanced architecture that comprised a multi-layer nanostructured polymer film was immobilized at the surface of the MIR transducer, which represents a straightforward and robust approach for the fabrication of nanocoatings at IR-ATR waveguide surfaces. Due to the multi-layer nature of the membrane, a variety of components may be enriched from aqueous and vapor phase samples directly at the waveguide surface facilitating analysis via evanescent field absorption.

In FEWS, the group of A. Katzir and Y. Raichlin is among the pioneers of evanescent wave spectroscopy using silver halide (AgClBr in various compositions) optical fibers. These polycrystalline fibers are mechanically flexible and malleable materials with a wide MIR transmission window, and therefore lend themselves for various tapering procedures. For example, a central section of the fiber may be flattened to a thickness of approx. 100 μm at a length of 1–5 cm width of several millimeters⁶¹. By adjusting the length and angle of the section leading into the flat tapered segment, the angle of incidence during propagation of the radiation within the fiber core may be tailored such that maximum penetration depth and number of reflections is achieved,

thus maximizing the achievable analytical sensitivity of such fiberoptic transducers. Raichlin et al. recently reported evanescent wave spectroscopy using flattened fibers for detecting micrograms of insoluble hormones and explosives (Figure 7). Following their increasing usage in medication, contraceptives, agriculture, etc., hormones are considered among the most relevant emerging microcontaminants of environmental concern, due to their adverse effects on animal and human health (e.g., endocrine disrupting effects, etc.). Forensic applications⁶¹ of MIR FEWS are increasingly adopted via detecting explosive residues at crime scenes, and for implementing potential screening strategies in airport security.

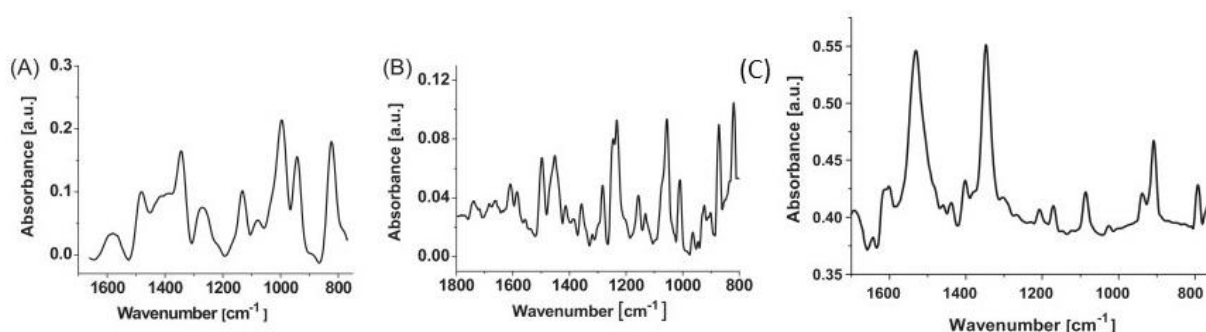


Figure 7. **A)** Exemplary spectrum of β -estradiol obtained via a silver halide fiberoptic sensor system. **B)** Spectrum of dry powder β -estradiol determined via a commercial IR-ATR (i.e., diamond IRE) system and a FT-IR spectrometer. The dry powder was pressed onto the prism-shaped diamond ATR element. **C)** FEWS measurement of an explosive (TNT)⁶¹. Reprinted with permission from Elsevier, Copyright 2014.

For biological applications, the group of N. Pleshko recently reported a fiberoptic method quantifying collagen and elastin at an in-vitro model of extracellular matrix degradation processes in aorta samples⁶². The extracellular matrix is a key component and regulator within a wide variety of biological tissues. The aorta is the major blood vessel responsible for blood circulation, and aortic diseases have emerged among the leading causes of death in developed countries. A custom-made optical fiber probe based on a silver halide sampling tip mounted at the end of a 1-m long silver halide fiber was connected to a commercial spectrometer, thereby generating an ATR sampling tip with a length of 15 cm and a diameter of 3 mm, as illustrated in Figure 8.

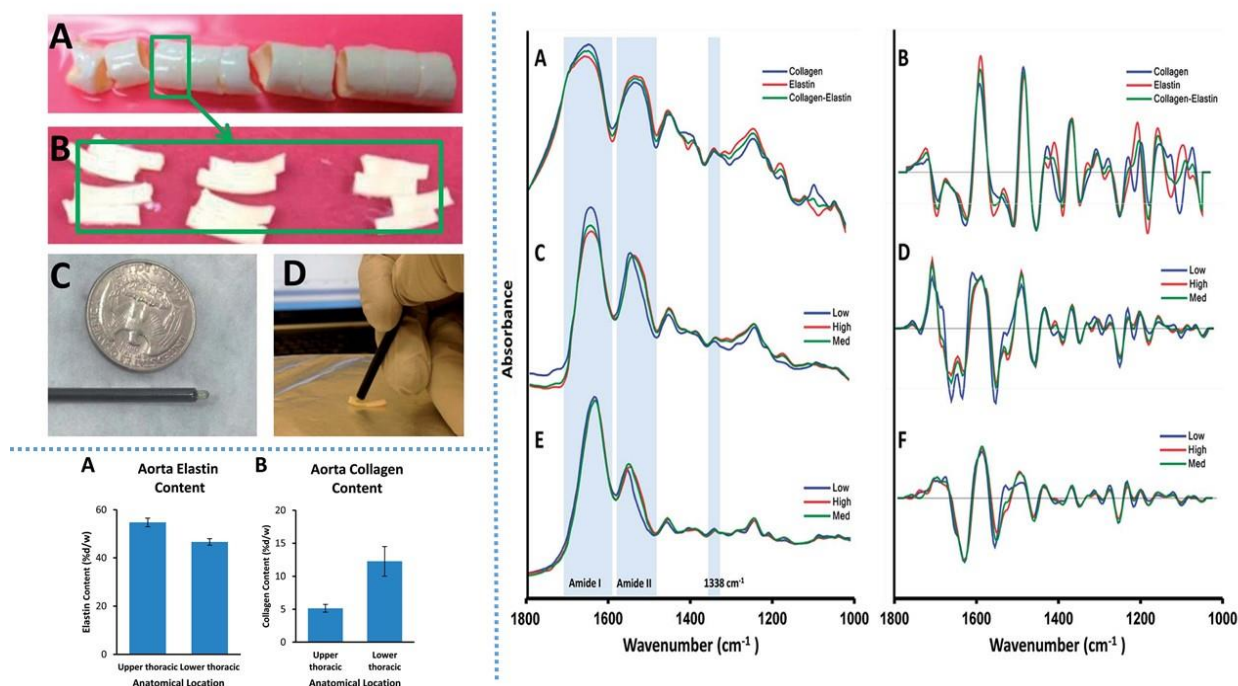


Figure 8. (Top left) (A-B) Aorta samples prepared as open rings of a few centimeters in length. (C) Custom fiberoptic sampling tip for IR-ATR data collection next to a US quarter dollar coin for size comparison. (D) Actual data collection from an aorta sample. **(Bottom left)** Elastin and collagen content within aorta samples at different anatomical locations. **(Right)** Average spectra of samples with low, medium, and high elastin content. (A) Reference spectra of collagen–elastin recorded via conventional transmission spectroscopy. (C-E) Fiberoptic spectra of collagen-elastine and their 2nd derivatives (B, D, F)⁶². Reprinted with permission from RSC Publishing, Copyright 2014.

This methodology enabling identifying collagen or elastin in aortic tissue is an interesting and promising approach for studying changes of extracellular matrices in different aortic diseases with minimal preparation compared to common histological or immunohistochemical methods. In addition, a multivariate calibration model was presented for automatically quantifying elastin within intact aortic tissue via the MIR fiber optic probe.

Such studies clearly illustrate that - besides the development of advanced thin-film MIR waveguide technologies - MIR transparent optical fibers remain of substantial utility for identifying and quantifying organic, inorganic or biological constituents and their chemical properties. Hence, FEWS methods remain a viable alternative in IR-ATR spectroscopy and sensing due to usually straightforward optical configurations, reduced cost vs. conventional IREs, a minimal requirements on sample preparation and processing. In addition, small sample quantities and areas may be

addressed, which is of particular interest in biomedical applications, whereas the sensitivity of such fiberoptic probes lends itself to applications in environmental protection/monitoring, drug enforcement, and homeland safety/security.

Among the already limited set of MIR transmitting materials applicable for fabricating fiberoptic waveguides, there is an even more limited selection of materials useful for establishing on-chip thin-film waveguide structures. In addition, using semiconductor materials for chem/bio sensors has to consider their chemical robustness in terms of, e.g., high (or low) pH values, elevated temperatures, mechanical stress, etc. Yet, the emergence of advanced QCL and ICL light sources demands for frequency-matched waveguide layers and structures for fully unlocking the potential of these almost ideal light sources.

Therefore, besides the rather excellent transparency throughout a broad wavelength window, diamond has emerged as a most interesting option also for MIR waveguide structures. Nowadays, diamond fabrication is predominantly performed via chemical vapor deposition (CVD)⁶³ at low-pressure-high-temperature conditions (LPHT), because of the metastable transition of diamond to graphite at high temperatures. However, LPHT requires expensive equipment and experience in the fabrication process, lacks in reproducibility when processing of large numbers of samples. As a result, LPHT annealing remains a unique technique available only at few laboratories and companies for research and small-scale production.⁶⁴ Yet, methods for thermally etching diamond have been reported in recent years⁶⁵, which facilitate processing of miniaturized of diamond structures. An example of thus established free-standing diamond strip waveguides (DSWGs) and their potential utility for chemical sensing is illustrated in Figure 9.

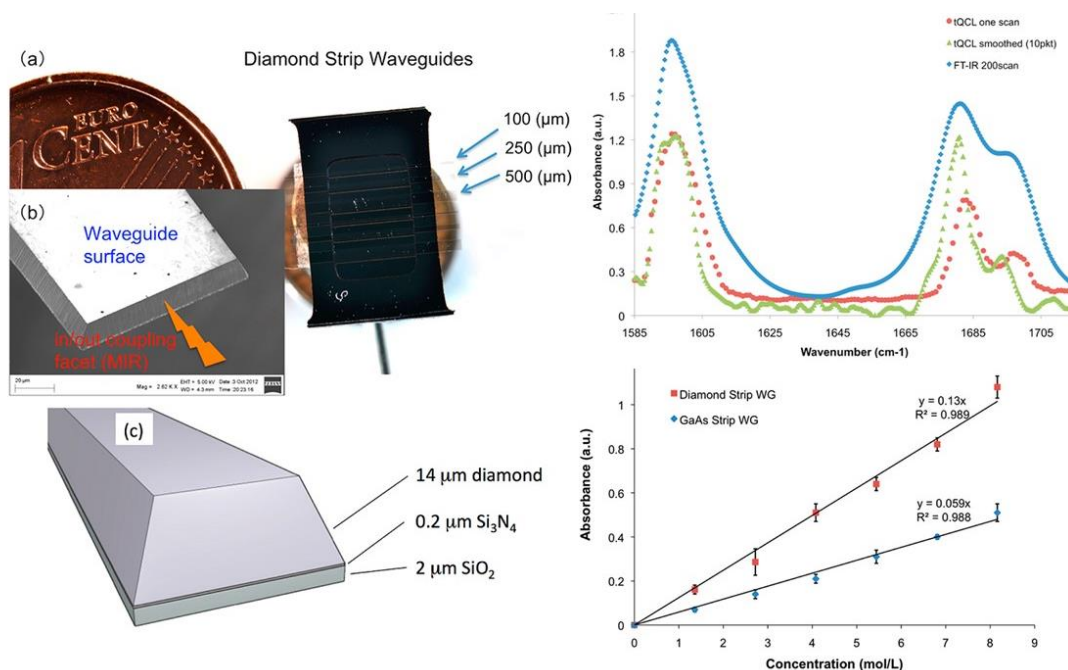


Figure 9. (Left) Diamond strip waveguides (DSWs) grown at a passivated silicon wafer substrate. (a) microfabricated free-standing diamond waveguides with a series of strip widths (100 –500 μm) compared in size to a Euro one cent coin. (b) SEM image at the in/out-coupling end facet for a 100-μm-wide waveguide with a thickness of 14 μm representing the actual free-standing waveguiding strip. (c) Schematic of the thin-film diamond waveguide structure on top of the substrate layers. **(Right)** Infrared absorption spectra of anisaldehyde and chemical response of the sensor recorded with a tunable QCL after deposition at the surface of a thin-film diamond waveguide and comparison of the IR-ATR spectrum recorded using a conventional FT-IR spectrometer averaging 200 spectra is shown. Reprinted with permission from ACS Publishing. Copyright 2014.

This sensing application clearly demonstrates the potential optical/analytical performance for evanescent field sensing using diamond as an advanced waveguiding layer, which might be among the key developments for enabling highly miniaturized MIR optical sensing platforms in combination with appropriate tunable QCLs or ICLs. Considering the generally already achieved level of miniaturization/integration of other wavelength optical devices (i.e., in the NIR and UV-vis wavelength regime), the opportunities for MIR chemical sensors/biosensors upon appropriate miniaturization are immediately evident towards molecularly selective MIR diagnostics. Following this route, further structured waveguides offer opportunities for further miniaturizing and integrating optical components into possibly small devices, yet offering comparable results in terms of analytical sensitivity and reproducibility vs. laboratory-based spectroscopic MIR analyzer

systems. For example, a three-times higher SNR value was shown by the research group of Mizaikoff⁶⁶ using diamond strip waveguides combined with QCL light sources vs. commercial FT-IR spectrometers. Because of the outstanding robustness of diamond even at harsh environmental conditions, as well as its intrinsic biocompatibility, diamond has excellent prospects to emerge as the most interesting material for next-generation on-chip MIR chem/bio sensors combined with QCL and ICL light source technologies.

Another promising group of materials for thin-film-based MIR sensors are the chalcogenides, i.e., mixtures containing S, Se, As, and Te, which are commonly known for their broad optical transparency and high refractive index in optical fiber technology (i.e., 2nd generation waveguides). Several chalcogenide material compositions are also being applied for fabricating thin-film waveguides taking advantage of the high refractive index contrast between the chalcogenide layer and a suitable substrate. For example, using GeTe₄ as a waveguiding core layer at a ZnSe substrate with respective refractive indices of 3.34 and 2.43 (at 3.5 μ m), a suitable optical density contrast can be generated between core and substrate, thus increasing the intensity of the evanescent field yielding high surface sensitivity at the waveguide/analyte interface. Using these materials channel waveguide structures have been realized in the 2.5–3.7 and 6.4–7.5 μ m spectral region.⁶⁷ The research group of Mittal et al. recently reported a convenient fabrication method for such waveguide structures using sputtering and lift-off techniques to realize GeTe₄ waveguides on ZnSe substrates later applied in evanescent field sensing (Figure 10).

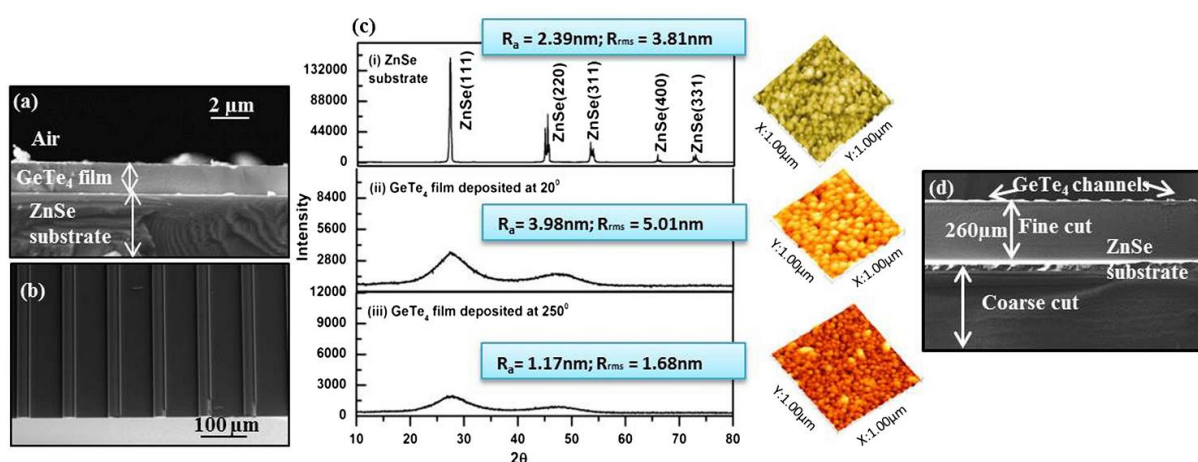


Figure 10. (a) SEM image of a cleaved cross-section of GeTe₄ film as deposited; (b) top view of GeTe₄ channels fabricated by lift-off techniques; (c) XRD pattern and AFM image of the ZnSe substrate and the GeTe₄ films. (d) Distal

coupling facet of the waveguide cut by ductile dicing.⁶⁷ Reprinted with permission from The Optical Society Publishing. Copyright 2015.

The reported thin-film waveguides were found to be amorphous in nature with an average surface roughness <4 nm providing MIR transparency in the spectral range of 2–20 μm , while actual waveguiding was demonstrated in the 2.5–3.7 μm and 6.4–7.5 μm regime. While single-mode behavior is desired for most biochemical sensing experiments, the reported GeTe_4 channels revealed multimode behavior for the given wavelength ranges. However, the authors state that a multimode waveguide design was selected on purpose in order to establish waveguiding also at longer wavelengths (i.e., up to 12 μm) ensuring sufficient coupling efficiency via commercially available single-mode fibers. In future, the applied materials and fabrication techniques may readily be adapted to achieve single-mode behavior.⁶⁷ Incidentally, the combination of thin-film channel waveguides and MIR optical fibers as coupling elements also highlights that these waveguide technologies are not mutually exclusive, but may even be combined to the advantage of the selected application scenario.

Conclusions and Future Perspectives

Classifying mid-infrared waveguide technologies into three generations facilitates documenting the evolution and progress in waveguide technology towards compact, robust, and portable MIR analyzer systems and sensors. The coexistence of these waveguide technologies – now and in future – is certainly a result of the fact that broadband emitters (e.g., as used in conventional (FT)IR spectrometers) as well as highly collimated laser light sources (e.g., QCLs, ICLs) enable and facilitate complementary measurement scenarios, and will therefore continue to be developed in parallel rather than replacing each other. Hence, it is anticipated that IR-ATR measurements based on conventional macroscopic IREs will remain prevalent next to thin-film waveguide based sensing systems addressing analyses in minute sample volumes and at exceptionally low concentrations. Clearly, innovative optical approaches and advancements in integrated optics and photonics will lead to further miniaturized, more versatile, and ideally – but not necessarily – to more efficient and sensitive MIR spectroscopic, sensing, and diagnostic platforms operated at in-field conditions and with trace-to-ultratrace detection limits.

Hence, the major breakthrough in MIR sensor technology during the past two decades is certainly attributed to the introduction of advanced laser light sources including QCLs and ICLs, it is the actual development of matching waveguide technologies serving as MIR transducers that has been the major driving force towards the analytical applicability of advanced IR sensors and measurement systems. With the recent emergence of on-chip semiconductor waveguides the path towards integrated MIR photonic systems - i.e., 'IR-lab-on-a-chip' systems – is evidently paved, and promises a wide variety of innovative label-free sensing and assay concepts. Finally, with the introduction of more sophisticated optical structures for on-chip waveguides and waveguide-linked technologies including optical resonators, optical couplers, and optical amplifiers along with increasingly complex chem/bio recognition schemes, it is clearly evident that with the advancements discussed herein we are only seeing the beginning of an entire generation of MIR chem/bio sensing and assay devices that will continue to push the envelope in terms of size, cost, and sensitivity.

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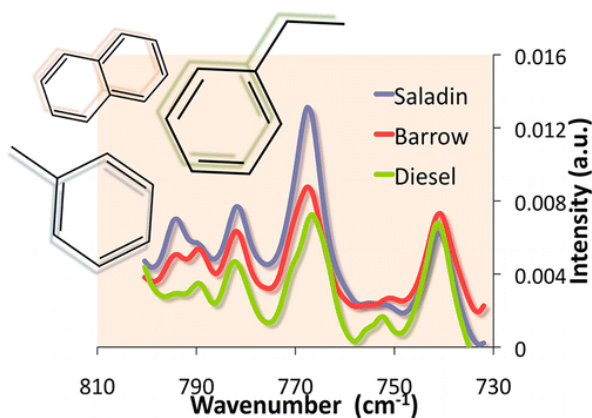
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5.2 Paper II. Fingerprinting Oils in Water via Their Dissolved VOC Pattern Using MID-Infrared Sensors

T. Schädle performed all measurements, analyzed the data, and established the analytical conclusions in agreement with all co-authors. B. Pejčic and B. Mizaikoff supervised the associated project during the research stay at CSIRO, ARRC, Perth, WA, Australia. B. Pejčic, M. Myers, and B. Mizaikoff contributed with revisions to the final manuscript.

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Fingerprinting Oils in Water via Their Dissolved VOC Pattern Using Mid-Infrared Sensors

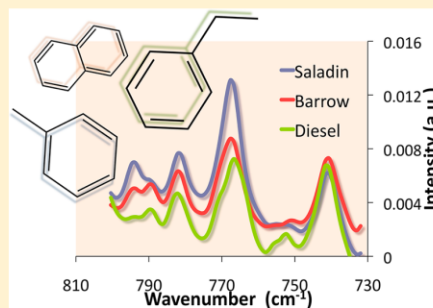
Thomas Schädle,^{†,‡} Bobby Pejčić,[‡] Matthew Myers,[‡] and Boris Mizaikoff^{*,†}

[†]University of Ulm, Institute of Analytical and Bioanalytical Chemistry, Albert-Einstein-Allee 11, 89081 Ulm, Germany

[‡]CSIRO, Earth Science and Resource Engineering, Wealth from Oceans Flagship and Energy Flagship, Kensington, WA 6151, Australia

Supporting Information

ABSTRACT: An infrared attenuated total reflection (IR-ATR) method for detecting, differentiating, and quantifying hydrocarbons dissolved in water relevant for oil spills by evaluating the “fingerprint” of the volatile organic compounds (VOCs) associated with individual oil types in the mid-infrared spectral range (i.e., 800–600 cm^{-1}) is presented. In this spectral regime, these hydrocarbons provide distinctive absorption features, which may be used to identify specific hydrocarbon patterns that are characteristic for different crude and refined oils. For analyzing the “VOC fingerprint” resulting from various oil samples, aqueous solutions containing the dissolved hydrocarbons from different crude oils (i.e., types “Barrow”, “Goodwyn”, and “Saladin”) and refined oils (i.e., “Petrol” and “Diesel”) were analyzed using a ZnSe ATR waveguide as the optical sensing element. To minimize interferences from the surrounding water matrix and for amplifying the VOC signatures by enrichment, a thin layer of poly(ethylene-co-propylene) was coated onto the ATR waveguide surface, thereby enabling the establishment of suitable calibration functions for the quantification of characteristic concentration patterns of the detected VOCs. Multivariate data analysis was then used for a preliminary classification of various oil-types via their VOC patterns.



Given recent events, the general public has become increasingly aware of the problems associated with the contamination of ground and surface water resources that are globally occurring due to oil spill events.¹ From such oil spills, volatile organic compounds (VOCs)—and especially benzene, toluene, and the xylenes (also called “BTX”)—are able to dissolve to a certain extent into the surrounding water phase, thereby causing contamination at concentration levels ranging from ppb ($\mu\text{g/L}$) to ppm (mg/L) levels; notwithstanding, VOCs are among the most commonly detected organic contaminants in water.²

For the detection of contaminants derived from crude oil or refined products in the aqueous environment, various hydrocarbon sensors have been developed that are suitable for marine monitoring and surveys.^{3,4} However, for efficient environmental monitoring and water quality control, enhanced real-time measurement capabilities facilitating the in situ determination of dissolved hydrocarbons are preferred.⁵

To obtain effective analytical data, IR spectroscopy has recently emerged among the most promising analytical and sensing techniques currently available in this domain.^{6,7} By taking advantage of mid-infrared frequencies (2–20 μm), transmission-absorption spectroscopy is the most commonly applied measurement technique for analyzing solid, liquid, or gas phase samples.⁸ However, the direct analysis of liquid-phase samples using conventional Fourier-transform infrared (FTIR) spectroscopy

in transmission-absorption mode is frequently limited by strong background absorptions of the matrix (i.e., solvent)—which is particularly pronounced in aqueous samples—and usually requires the application of thin-film transmission cells.⁹ Yet, attenuated total reflectance (ATR) spectroscopy, which is based on the fundamental principles of internal total reflection,¹⁰ offers a useful alternative measurement strategy¹¹ capable of reliable hydrocarbon identification and quantification in geochemically relevant fluids.^{12–14} Due to the inherent molecular selectivity and robustness of the measurement scheme, IR-ATR spectroscopy and sensing techniques have successfully been used for the detection of a wide variety of organic constituents,^{13,15} as well as for the analysis of oil-in-water and water-in-oil.^{1,16} Among other parameters, the detection performance and achievable sensitivity of IR-ATR systems is largely determined by the properties of the ATR waveguide. Today, a wide variety of commercial ATR crystals are available, with the most commonly used ones made from zinc selenide (ZnSe).¹⁷

In the present study, we describe an IR-ATR-based method for detecting, quantifying, and fingerprinting hydrocarbons that partition into the water phase from oil e.g., generated via spill events. By evaluating the so-called “fingerprint region” (600–800

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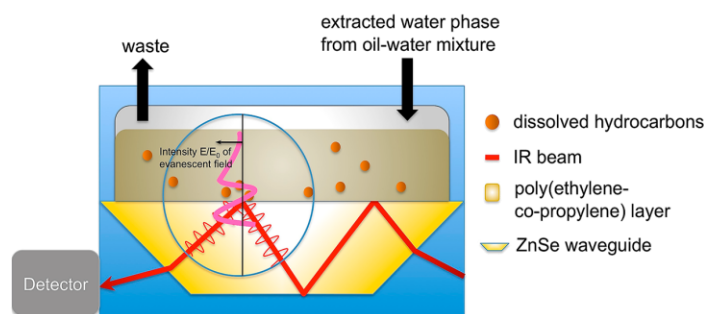


Figure 1. Schematic of the measurement principle. The water phase from the respective oil–water mixture containing the associated dissolved hydrocarbons at a characteristic concentration pattern is flown across a polymer-coated ZnSe IR-ATR waveguide, and the hydrocarbons are detected via evanescent field absorption spectroscopy after enrichment within the polymer membrane.

cm^{-1}), every hydrocarbon component is characterized by a distinctive pattern of absorption features, which may readily be used to identify specific constituents even in complex mixtures comprising a variety of organic species.^{18,19}

■ EXPERIMENTAL SECTION

Materials and Reagents. Toluene (99.8%), *m*-xylene (99%), *o*-xylene (97%), ethylbenzene (99.8%), naphthalene (99%), and *n*-hexane were all obtained from Sigma–Aldrich, and were used as purchased. All organic solvents were of AR grade, and were used without further purification. Poly(ethylene-co-propylene) (60:40) was supplied by Scientific Polymer Products, Inc. (Ontario, NY, U.S.A.).

As the sensing element, a trapezoidal ($80 \times 10 \times 4$ mm) ZnSe-crystal with beveled end facets (45°) was used as a multireflection ATR waveguide. The ZnSe ATR crystal was mounted into an attenuated total reflection (ATR) unit comprising a stainless steel flow cell (Pike Technologies, Madison, WI, U.S.A.).

Crude oils (types “Barrow”, “Goodwyn” and “Saladin”, Australia, western offshore shelves) and refined oils (“Petro”, “Diesel”) were used without further preparation.

Seawater was collected from South Fremantle Beach (South Fremantle, Western Australia, Australia), filtered using a $0.45 \mu\text{m}$ filter, and used without further treatment or purification.

Film Preparation. A 23.5-mg portion of poly(ethylene-co-propylene) was dissolved into 5 mL *n*-hexane. A thin polymer film was deposited by drop-coating $500 \mu\text{L}$ of the solution directly onto the ZnSe waveguide surface. For complete evaporation of the solvent, the ZnSe crystal was kept in the fumehood for at least 3 h. The obtained reconstituted polymer film thickness was determined at $5 \pm 0.5 \mu\text{m}$ via differential weighting, which corresponds to approximately twice the penetration depth of the IR evanescent field at these optical conditions, ensuring optimum performance.^{18,19} To equilibrate the deposited polymer membrane and to ensure removal of residual solvent molecules, the coated ZnSe crystal was soaked in deionized water by flowing water through the cell at a constant rate of 5 mL/min for 24 h prior to usage using an Ismatec peristaltic pump (IDEX Corporation, Lake Forest, IL, U.S.A.). IR spectra of the water-equilibrated and solvent-free coated waveguide were used as background spectra for all further IR-measurements.

Solution Preparation. In order to analyze which constituents of the different crude (types “Barrow”, “Goodwyn” and “Saladin”) and refined oils (“Petro”, “Diesel”) partition into the adjacent aqueous phase, two scenarios were tested: (a) using

deionized water and (b) using filtered seawater (South Fremantle Beach, Western Australia, Australia).

Crude and Refined Oil Solutions in Deionized Water.

Hydrocarbon solutions were prepared by layering 30 mL of the respective oil onto the top of 900 mL of deionized water, followed by stirring using a glass stir bar for 48 h at a constant rotation speed of 350 rpm. The sample silica glass bottle was capped and wrapped with aluminum foil to avoid the exposure of crude oil to ambient light. Subsequently, the water phase of the oil–water mixtures was collected for further analysis.

Crude and Refined Oil Solutions in Seawater. Similarly to the oil-in-water solutions, one example each of a crude oil (type “Barrow”; 30 mL) and a refined oil (type “Diesel”; 30 mL) were layered on top of 900 mL of filtered ($0.45 \mu\text{m}$ filter) seawater and treated identically to the deionized water extracts above (i.e., 48 h stirring at 350 rpm).

Hydrocarbon Calibration Solutions. Single analyte calibration curves were established by dissolving *m*-xylene, *o*-xylene, toluene, ethylbenzene and naphthalene in deionized water in the concentration range between 50 and 1000 ppb. All analytical calibration curves were generated using at least four standard solutions. Since the VOC concentration in water may vary considerably during solution preparation and storage, it is recommended that the calibration standards are prepared in headspace-free sealed glass containers and analyzed almost immediately.

Instrumentation and Calibration. IR-ATR measurements were performed using a Fourier transform infrared spectrometer (Bruker Vertex 70, Bruker Optics, Ettlingen, Germany) equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector.

For the analysis of the dissolved VOCs associated with different oils, the previously prepared hydrocarbon solutions were flowed across the polymer coated ZnSe surface at a constant flow rate of 5 mL/min. Data were recorded in the spectral range of $4000\text{--}650 \text{ cm}^{-1}$ at a spectral resolution of 2 cm^{-1} averaging 100 scans per spectrum. All experiments were performed at room temperature ($21 \pm 1^\circ\text{C}$).

Data Processing. Infrared absorption features were evaluated by peak area analysis using the software package OPUS (Bruker Optics, Ettlingen, Germany). Each enrichment study was independently performed three times, and the peak areas from each spectral region were averaged (OPUS program feature, integration borders: $790\text{--}775 \text{ cm}^{-1}$ for naphthalene; $773\text{--}757 \text{ cm}^{-1}$ for *m*-xylene, $748\text{--}731 \text{ cm}^{-1}$ for *o*-xylene, $729\text{--}722 \text{ cm}^{-1}$ for toluene and $702\text{--}690 \text{ cm}^{-1}$ for ethylbenzene).

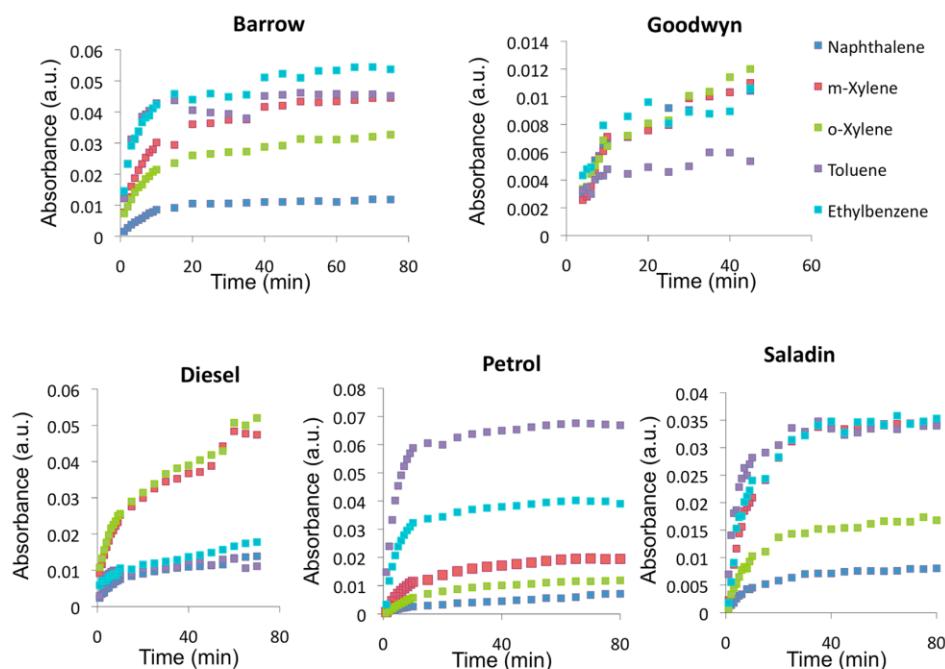


Figure 2. Enrichment curves revealing the partitioning behavior of selected oil-relevant VOCs after evaluating distinctive absorption bands in the fingerprint region of the IR spectrum. Each oil-relevant component is readily identified within the water matrix including naphthalene at 781 cm^{-1} , *m*-xylene at 767 cm^{-1} , *o*-xylene at 741 cm^{-1} , toluene at 727 cm^{-1} , and ethylbenzene at 696 cm^{-1} .

Experimental Set-Up. To analyze the “VOC fingerprint” resulting from and attributed to distinctive oil samples, an aqueous solution containing the dissolved hydrocarbons was flowed across the polymer-coated ZnSe waveguide, while continuously recording IR-ATR spectra of the VOCs partitioning into the polymer film. Next to the enrichment of VOCs, using a hydrophobic polymer membrane has the additional effect that water is effectively excluded from the analytically probed volume, which is defined by the exponentially decaying evanescent field (i.e., over a few micrometers) generated at the waveguide/polymer interface (Figure 1).

RESULTS AND DISCUSSION

Analysis of Oil Fingerprints in Water. Enrichment Curves. In order to minimize spectral interferences by water absorptions, poly(ethylene-co-propylene) was applied as a suitable hydrophobic polymer coating (see the Supporting Information, SI) to enrich VOCs such as toluene, ethylbenzene, xylenes, and naphthalene at the waveguide surface.² It has previously been shown that the sensitivity of a polymer film coated sensor system is not considerably affected by the water exposure time,¹² which is an important aspect considering long-term monitoring of hydrocarbons (e.g., environmental applications). IR-ATR measurements were executed in aqueous solutions containing different concentration levels of hydrocarbons. Figure 2 shows exemplary enrichment curves for the characteristic dissolved hydrocarbons of five different oil–water–mixtures partitioning into the polymer film coated onto the surface of the ZnSe waveguide.

From the enrichment studies shown in Figure 2, it is evident that each oil type is characterized by differences in the VOC enrichment patterns in terms of the absorbance intensities of the

respective hydrocarbons, thereby providing a distinct “VOC fingerprint”. Regan et al. (2003) observed that the diffusion and enrichment profiles of certain hydrocarbon compounds are affected by the presence of more than one component within a BTX mixture.²⁰ However, a partition equilibrium is achieved for each of the dissolved hydrocarbons enriching into the poly(ethylene-co-propylene) film after approximately 20 min of exposure time, which is in accordance with previously observed diffusion times of BTX into poly(ethylene-co-propylene) membranes.² Infrared spectra extracted during the enrichment process for *Saladin* crude oil are shown in Figure 3 showing good separation between the various absorbance bands. Baseline artifacts at lower wavenumbers (e.g., 720 cm^{-1}) occur from dynamically changing absorption bands of the polymer coating given the continuously shifting equilibrium of water with the polymer membrane, which may cause differences of the instantaneous water absorption spectrum vs the previously recorded background.

VOC Fingerprints. Figure 4 shows the “VOC fingerprint” of *Petrol* in water. The spectra were collected after an enrichment time of 100 min to ensure equilibrium conditions. IR absorption peaks referring to C—H bending vibration patterns were readily identified as naphthalene at 781 cm^{-1} , *m*-xylene at 767 cm^{-1} , *o*-xylene at 741 cm^{-1} , toluene at 727 cm^{-1} , and ethylbenzene at 696 cm^{-1} . On the basis of these characteristic patterns the quantification of the dissolved hydrocarbon species via multivariate data evaluation was enabled.

VOC Fingerprints in Seawater. A study was performed to determine if the absorption peaks identified in deionized water (Figures 3 and 4) are readily identified in seawater. Figure 5 clearly reveals that the detected absorption peaks in the seawater spectrum (see the SI) after partitioning into the polymer

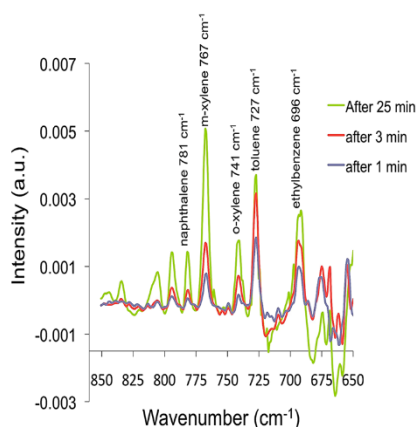


Figure 3. IR-spectra of the aqueous phase from a *Saladin*–water mixture using a polymer coated ZnSe waveguide after enrichment periods of 1, 3, and 25 min exposure/partitioning time. (a.u. ... absorbance units).

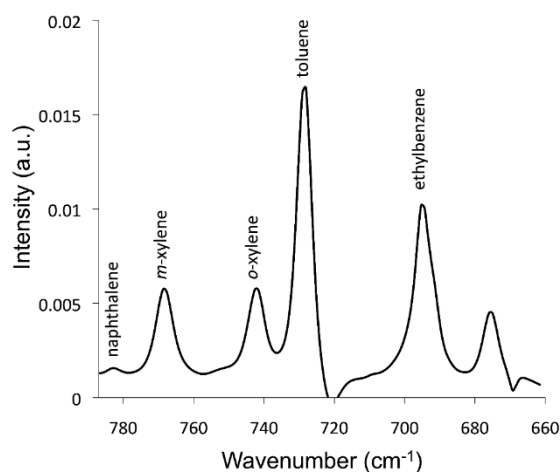


Figure 4. “VOC fingerprint” of *Petrol* in water recorded using a poly(ethylene-co-propylene) coated ZnSe waveguide after an exposure/partitioning period of 100 min.

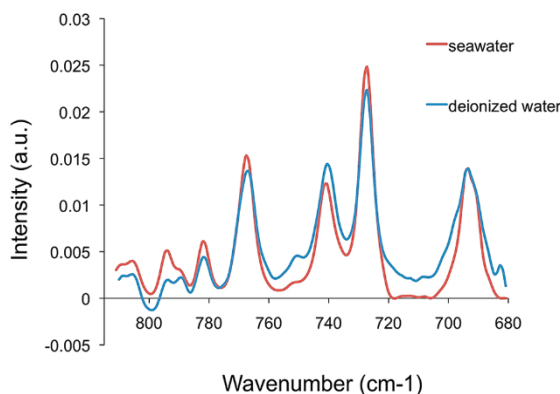


Figure 5. Comparison of *Barrow* “VOC fingerprint” in seawater and deionized water after 25 min of enrichment time.

membrane are consistent in frequency position with those obtained using deionized water as the matrix. Hence, the specific “VOC fingerprint” associated with each oil may be used for the identification of the oil type in real world scenarios without matrix interference, as the comparison of the IR-signature in deionized water and real seawater confirms.

Sensor Calibration and VOC Quantification. A mixture of toluene, *m*-xylene, *o*-xylene, ethylbenzene, and naphthalene was dissolved in deionized water in the concentration range of each 50 to 1000 ppb (i.e., all analytes at the same concentration). The solutions were prepared with little to no headspace, and immediately analyzed to prevent evaporative loss of the volatiles. Calibration functions were generated from the mixtures by integrating the characteristic absorption peaks of each species. Figure 6 summarizes the obtained linear calibration functions for each VOC dissolved in deionized water.

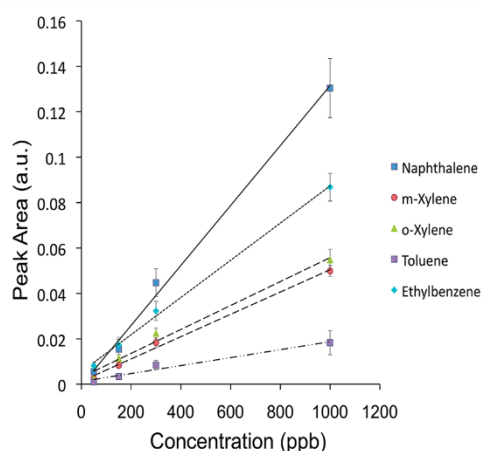


Figure 6. Calibration functions derived from the associated IR-ATR spectra recorded after enrichment at a poly(ethylene-co-propylene) coated ZnSe ATR waveguide exposed to various hydrocarbon mixtures dissolved in water. All absorbance values were plotted after 1.5 h of exposure time ensuring equilibrium conditions. The error bars were calculated as the standard deviation of 5 independent measurements.

The associated parameters of the linear fits are summarized in Table 1. The R^2 values (goodness of the fit) for the obtained calibration functions indicate that polymer coated ATR-waveguides can be used to reliably quantify BTX concentrations at these levels. The limits of detection (LOD) and quantification (LOQ) were calculated according to IUPAC using the $3\sigma/10\sigma$ criteria (i.e., 3-times/10-times standard deviation of the smallest concentration value measured)^{2,17} as 38 ppb (LOD) and 126 ppb (LOQ) for naphthalene, 55 ppb (LOD) and 183 ppb (LOQ) for *m*-xylene, 59 ppb (LOD) and 196 ppb (LOQ) for *o*-xylene, 61 ppb (LOD) and 202 ppb (LOQ) for toluene, and 53 ppb (LOD)/175 ppb (LOQ) for ethylbenzene. Using these linear calibrations, all dissolved hydrocarbons were readily quantified in the aqueous phase of different oil–water mixtures. Thus, derived concentrations for the relevant VOCs associated with the different types of oils are given in Table 2.

From these calculated VOC concentrations, it is evident that all examined oil types vary in the composition of these oil-relevant constituents. Concentrations given in square brackets are below the LOQ, yet, still above the calculated LOD. Hence, a distinctive IR “VOC fingerprint” for each oil-type is obtained after

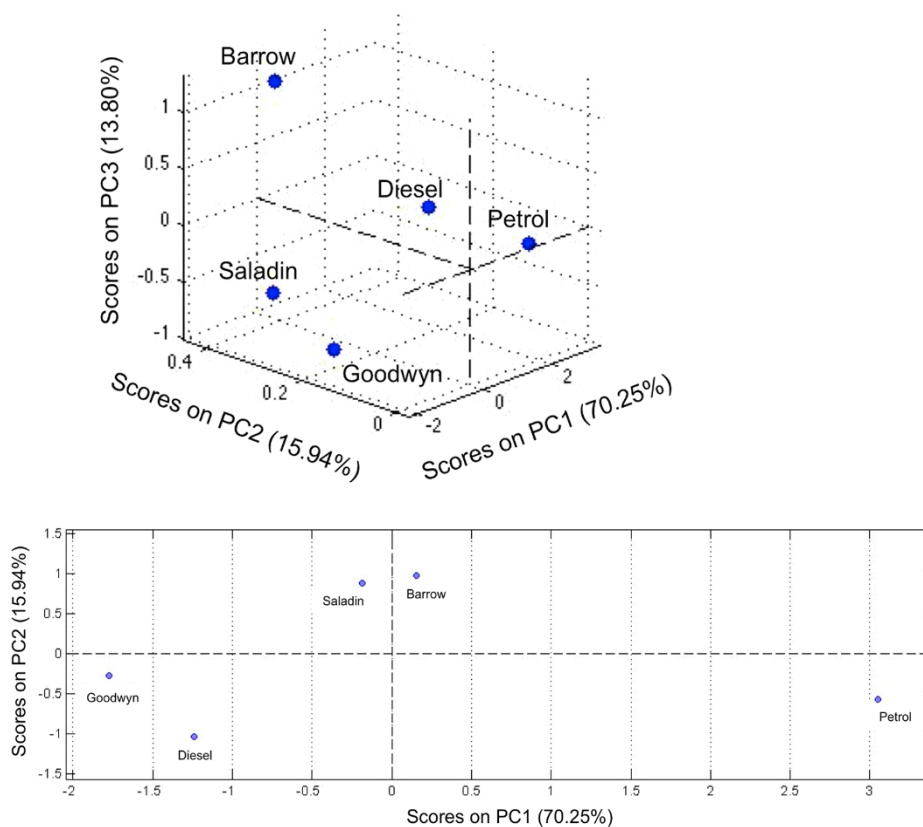
Table 1. Calibration Functions Derived from IR-ATR Spectra and R^2 -Values for the Established Calibration Graphs Shown in Figure 6 over the Studied Concentration Range of 50–1000 ppb

molecule	wavenumber (cm^{-1}) of evaluated absorption band	linear fit (AU/ppb)	R^2	LOD (ppb)	LOQ (ppb)
naphthalene	781	$y = 0.0001x - 0.0004$	0.995	38	126
<i>m</i> -xylene	761	$y = 0.00005x + 0.0013$	0.9946	55	183
<i>o</i> -xylene	741	$y = 0.00005x + 0.0031$	0.9851	59	196
toluene	727	$y = 0.00002x + 0.0012$	0.9688	61	202
ethylbenzene	696	$y = 0.00008x + 0.0055$	0.9979	53	175

Table 2. Dissolved VOC Concentrations (ppb) in the Aqueous Phases Associated with the Respective Oil Types Derived via the Calibration Functions Given in Table 1^a

oil	hydrocarbon concentration (ppb)				
	naphthalene	<i>m</i> -xylene	<i>o</i> -xylene	toluene	ethylbenzene
Barrow	123 (± 22)	865 (± 23)	592 (± 30)	2249 (± 60)	612 (± 88)
Goodwyn	108 (± 14)	194 (± 30)	[178 (± 12)]	240 (± 32)	[64 (± 20)]
Diesel	143 (± 5)	941 (± 19)	979 (± 22)	597 (± 31)	[153 (± 13)]
Petrol	[75 (± 4)]	3896 (± 120)	2274 (± 119)	3743 (± 70)	496 (± 23)
Saladin	[83 (± 8)]	667 (± 14)	285 (± 13)	1679 (± 90)	379 (± 20)

^aThe variance was determined from three independent measurements performed at similar conditions.

**Figure 7.** PCA scores plot for the evaluated oil types. The data are spreading mainly along the PC1 axis, accounting for 70% of the total variance within the data set.

dissolution in water, which can be used for the unambiguous identification of oil types.

Preliminary Multivariate Classification of Oil Types via their VOC Fingerprint. Despite the limitations of a rather small data set accessible during the current study, principal components

analysis (PCA) was performed, taking advantage of the characteristic fingerprint patterns, i.e., the oil-relevant VOC composition after dissolution in the aqueous phase. The resultant root-mean-square error in probability (RMSEP) plot indicates that the model fits the data well with 3 PCs describing 99% of the

total variance. The resulting scores plots (PC1 vs PC2 vs PC3) obtained from the calculated dissolved hydrocarbon concentration of the 5 oils (Table 2) is shown in Figure 7. Each data point in the graph corresponds to one oil type.

The scores plot displays that the difference in VOC composition of *Goodwyn*-, *Diesel*-, and *Petrol*-type oils is sufficient to identify each type of oil. While *Saladin*- and *Barrow*-type oils are not clearly separable with this low number of example spectra along the PC1 and PC2 axis, they are readily separated along the PC3 axis from the other 3 oil types. Hence, despite the rather low number of samples accessible to the present study, the obtained distribution suggests that oils dissolved in water may readily classify into types of parent oils based on quantitative “VOC fingerprints” obtained by IR-ATR spectroscopy/sensing of their associated water extracts using polymer-coated ATR waveguides.

CONCLUSIONS

After establishing appropriate calibration functions for selected oil-relevant hydrocarbons, quantification of characteristic “VOC fingerprints” in the water phase after interaction with crude oil samples was enabled. In addition, it was demonstrated for the first time that after enriching characteristic concentration patterns of the detected VOCs via polymer-coated IR-ATR waveguides, the obtained IR-ATR spectra may be used for the in situ analysis, quantification, and classification of the associated parent oils. Preliminary results using multivariate data evaluation methods revealed that the classification of oil types via their IR-fingerprint pattern is possible, and may be readily refined using more spectra from an expanded library of different oil types. Finally, it is anticipated that using waveguide-based and miniaturized IR sensing systems^{21–25} for in situ oil fingerprinting in marine environments is within reach.

ASSOCIATED CONTENT

Supporting Information

Additional characterization data on the polymer coating as well as a full spectrum of a seawater sample. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: boris.mizaikoff@uni-ulm.de.

Notes

The authors declare no competing financial interest.

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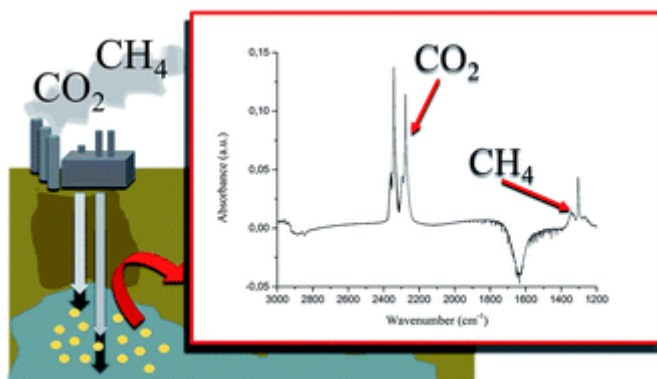
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5.3 Paper III. Monitoring dissolved carbon dioxide and methane in brine environments at high pressure using IR-ATR spectroscopy

T. Schädle performed all measurements, analyzed the data, and developed the measurement setup used in this study. The scope of the paper was selected in agreement with all co-authors. B. Pejic and B. Mizaikoff contributed with revisions to the final manuscript.

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Monitoring dissolved carbon dioxide and methane in brine environments at high pressure using IR-ATR spectroscopy

Thomas Schädle,^a Bobby Pejic^b and Boris Mizaikoff^{*a}

Obtaining *in situ* information on greenhouse gases arising from deepwater environments is a challenge that has not been satisfactorily resolved to date. An infrared attenuated total reflection (IR-ATR) based on-line sensor system for detecting, monitoring, and differentiating carbon dioxide and methane in dissolved and gaseous states at different pressures (*i.e.*, up to 6 MPa) in saline aquifer and/or synthetic brine environments is presented. It is demonstrated that the detection of dissolved CO₂ next to ¹³CO₂ and methane under pressurized conditions is possible under saline downhole conditions, and that gaseous vs. dissolved states of methane and CO₂ in aqueous environments may be differentiated using IR-ATR sensing techniques. Finally, it is shown for the first time that there are observable changes associated with distinctive infrared signatures of methane under the conditions of greenhouse gas storage mechanisms. These are of particular importance for advancing carbon capture and storage processes and fundamentally understanding the impact of emissions during the extraction of fossil-based fuels (*i.e.*, shale, petroleum, etc.) from offshore environments.

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Introduction

In natural or artificial reservoirs, gases such as carbon dioxide or methane are usually in contact with aqueous environments.¹ The solubility of such gases in water is an important issue from an environmental perspective due to regulatory restrictions imposed on the hydrocarbon content in surface and ground waters. However, gas solubility data for most relevant reservoir gases as well as for volatile hydrocarbons under elevated pressure conditions and low temperatures ($T \leq 298.15$ K) have been scarcely reviewed to date. Consequently, the influence of such greenhouse gases and contaminants on ground water resources and aquifer systems is a topic of increasing global awareness.

The ocean plays an important role in exchanging and regulating gas levels in the biosphere. Recently, artificial reservoirs particularly in the tropics have been identified as significant contributors of CO₂ and CH₄ in the atmosphere.^{2–4} The Petit Saut hydroelectric reservoir at the Sinnamary River in French Guiana is a typical example of a human-induced modification of the continental surface that has significantly changed the CO₂ and CH₄ exchange with the atmosphere.⁴ Due to the microbial decomposition of flooded biomass primarily composed of tropical forest, this reservoir emits substantial amounts of CO₂ and CH₄ into the atmosphere.⁵ Hence, various strategies including carbon capture and storage (CCS) aim at preventing

a more widespread dissemination of such gases. In order to decrease such human-induced contributions to atmospheric pollution, while at the same time potentially facilitating oil recovery, CCS or core flooding methods are investigated based on gas injection into saline reservoirs.^{6,7} As these sequestration strategies aim at reducing greenhouse gas emissions by capturing and diverting them to a secure storage location, CO₂ is predominantly sequestered into geological formations *via* solubility trapping into the water phase of the otherwise solid formation.⁸

These storage mechanisms lead to the inclusion of gaseous CO₂ trapped within pore spaces, dissolution within the water phase, and long-term conversion of CO₂ into solid rock matrices.⁹ Deep saline aquifers in sedimentary basins are potential sites for such sequestration strategies for CO₂. Such brine formations are the most common fluid reservoirs in the subsurface region prevalent around the world. Flow systems that involve water, CO₂, and dissolved ions have been extensively studied in geothermal reservoir engineering.^{10,11} Hence, the development of robust on-line monitoring technologies facilitating advanced understanding on subsurface fluid and dissolution behaviour related to injected and stored gases in aqueous environments is demanded.

To date, various sensor technologies have been developed enabling monitoring of marine and downhole environments.¹² Concurrently, such sensing concepts are potentially equally suited as promising monitoring tools for gas dissolution monitoring scenarios. However, most sensor technologies reported to date are based on conventional laboratory equipment

^aUlm University, Institute of Analytical and Bioanalytical Chemistry, Albert-Einstein-Allee 11, 89081 Ulm, Germany. E-mail: boris.mizaikoff@uni-ulm.de

^bCSIRO, Energy Flagship, 26 Dick Perry Avenue, Kensington, WA 6151, Australia

and analysis strategies rather than providing reliable devices suitable for in-field monitoring under the injection conditions of such gases into adequate storage compartments.

Mid-infrared (MIR) spectroscopy takes advantage of molecular vibration patterns at distinctive frequencies providing unique fingerprints of organic and inorganic molecules. Especially, infrared attenuated total reflection (IR-ATR) sensing techniques that are significantly less affected by interferences due to background absorptions of, *e.g.*, water appear ideally suited for studies in such aqueous environments, and have therefore recently emerged among the most promising in-field sensor technologies for the detection of volatile organic constituents (VOCs) resulting from crude oil or refined product spillage¹³ and chemical tracer molecules.¹⁴ Moreover, spectroscopic techniques are particularly suited for investigating dynamic processes, which enable additional insight into potentially relevant molecular interactions.^{15,16}

In the present study, we have developed an IR-ATR on-line sensor system for detecting and differentiating carbon dioxide in dissolved and gaseous states at different pressures (*i.e.*, up to 6 MPa), which simultaneously facilitates methane detection. It is demonstrated that the quantitative detection of dissolved CO₂ next to ¹³CO₂ as well as dissolved methane under pressurized conditions is possible, and that gaseous *vs.* dissolved states of such gases in water may be differentiated. Using IR-ATR sensing techniques provides the basis for particularly robust and highly miniaturizable sensing techniques that are readily adaptable for in-field applications under harsh environmental conditions. The geothermal studies performed to date mostly address higher temperatures and lower CO₂ pressures than would be encountered during aquifer disposal of sequestered CO₂. Consequently, the present work focuses on temperature and pressure ranges above and beyond these reported values, as they have not been covered by previous work to the best of our knowledge.

Instrumentation and data processing

A high pressure IR-ATR setup was realized combining a Jet-Stream Circle Cell (Pike Technologies, Cottonwood, United States) with a Swagelok® connection to a gas-mixing/inlet system that is capable of handling 6 MPa of pressure. The pressure cell containing the ATR setup is made of stainless steel. A cylindrical ZnSe rod (approx. 82 × 6.4 mm in dimensions) providing 12 internal reflections with an incident angle of 45° was used as the internal reflection element (IRE). The IRE is sealed with nitric butadiene rubber o-rings to the end caps of the pressure cell and is fully surrounded by the brine matrix (Fig. 1).

The examined gases (CO₂, ¹³CO₂, and CH₄) were directly injected into the sample chamber filled with the artificial saline solution (1.5 mL sample volume) *via* the inlet valves of the gas mixing system. IR spectra were immediately recorded after opening the inlet valves in order to monitor the entire dissolution process of the gases, until equilibrium of the dissolution process was reached (*i.e.* no further changes in the IR signatures observable). Equilibrium conditions at elevated pressures were

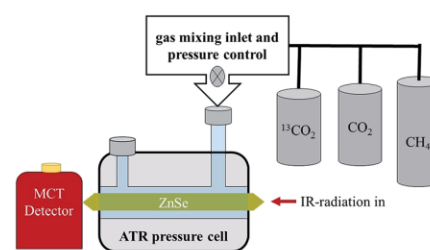


Fig. 1 Schematic of the experimental setup including a high pressure IR-ATR system combined with a gas-mixing/inlet system.

typically reached after a time period of 10 min. No further pumping system was needed to observe the dissolution process of these gases until equilibrium conditions.

IR-ATR spectra were recorded using a Bruker Vertex 70 FTIR spectrometer (Bruker Optics, Ettlingen, Germany) equipped with a liquid nitrogen cooled mercury-cadmium-telluride detector (MCT, Infrared Associates, Stuart/FL, United States). Spectral data were processed using the 'Essential FTIR' software package. Infrared absorption features were evaluated *via* peak area analysis. For each measurement, 100 spectra were averaged at a spectral resolution of 0.5 cm⁻¹.

Results and discussion

Monitoring of CO₂, ¹³CO₂, and CH₄ dissolved in synthetic brine

To successfully monitor the behaviour of different gases in aqueous environments, it is anticipated that the respective IR absorption signatures are clearly discernible and spectrally sufficiently separated, thereby avoiding interferences among their individual gas absorption signatures and the background matrix. Fig. 2 shows an example of the absorption signatures of

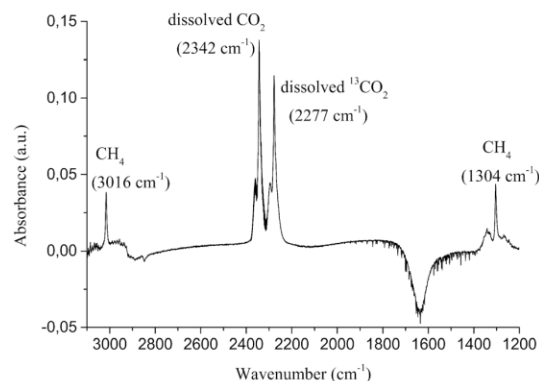


Fig. 2 IR-ATR spectra of dissolved greenhouse gases in the aqueous environment (*i.e.*, synthetic brine). The recorded spectrum shows the characteristic absorption features of CH₄ next to CO₂ and ¹³CO₂ dissolved in water recorded at 4 MPa of pressure and with 1 cm⁻¹ spectral resolution, and an estimated concentration of 900 ppm (CH₄) and 5000 ppm (CO₂).

CO₂, ¹³CO₂, and CH₄ in water after the dissolution process of these gases has reached equilibrium between gaseous and dissolved states. The spectra were recorded against the synthetic brine matrix as the background at 4 MPa of pressure with all gas valves opened simultaneously.

From the recorded IR spectra it is evident that the IR signatures of dissolved CO₂ at 2343 cm⁻¹, dissolved ¹³CO₂ at 2277 cm⁻¹, and methane at either 3016 cm⁻¹ or 1304 cm⁻¹ are clearly evident and sufficiently separated for enabling simultaneous detection and quantification of all three components side-by-side within the same sample solution. This is of particular importance for directly monitoring the behaviour and solution states of the different gases in saline water and downhole environments where carbon capture and storage are of interest and monitoring of several relevant constituents is required. The negative absorbance of the water band at 1620 cm⁻¹ results from changes in the background spectrum due to injection of yet undissolved gases that were not present in the background spectra, therefore causing negative absorbances by pushing water away from the IRE surface prior to dissolution. Water also usually shows a strong absorption feature at around 3000 cm⁻¹, which may lead to interferences with the methane 3016 cm⁻¹ signature during long term monitoring of such dynamic processes. This is the reason why the methane absorbance at 1304 cm⁻¹ is used for further examination in this study.

Dissolved CO₂ and ¹³CO₂ in saline environments at elevated pressures

The typical absorption signature of gaseous CO₂ (2365 cm⁻¹ and 2333 cm⁻¹) shifts to 2343 cm⁻¹, if CO₂ dissolves in water. Since the solubility of CO₂ in water is pressure dependent, more CO₂ will dissolve at higher pressures. At slightly increased pressures (*i.e.*, up to approx. 0.6 MPa), the dissolution process from CO₂(g) to CO₂(aq) can actually be directly observed *via* the IR signatures of CO₂, as indicated by the arrows in Fig. 3.

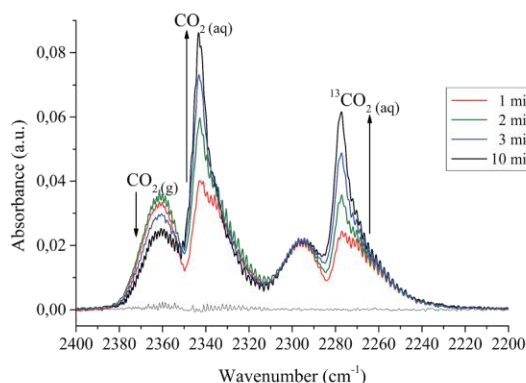


Fig. 3 Dissolution of CO₂ and ¹³CO₂ in water over a period of 10 min. IR-ATR spectra were recorded at 0.5 cm⁻¹ spectral resolution and at a pressure of 0.6 MPa.

Increasing the pressure from ambient conditions (0.1 MPa) to 0.6 MPa to dissolve more CO₂ in water results in a distinct increase of the absorption bands from CO₂(aq) at 2343 cm⁻¹, as evident in Fig. 3. The light grey line represents the background absorption prior to the CO₂ injection into the IR-ATR sample cell. After 1 min (red line) of CO₂ injection at 0.6 MPa, both the CO₂(g) and CO₂(aq) signatures are already evident and clearly discernible. After 2 minutes (green line), a small increase in CO₂(g) is observable until all CO₂(g) according to the respective pressure value is evenly distributed within the sample chamber. Already after 3 minutes (green to blue line), the CO₂(g) signature decreases in intensity, whereas the intensity of the CO₂(aq) absorption band at 2343 cm⁻¹ increases until saturation is reached (black line). After 10 minutes, no more changes in signal intensities could be observed leading to the assumption of equilibrium conditions within the sample cell.

Similar to dissolved CO₂ at 2343 cm⁻¹, its naturally occurring isotope ¹³CO₂ shows a distinctive absorption feature, if dissolved in water. However, the absorption feature of dissolved ¹³CO₂ appears in the spectral range around 2277 cm⁻¹, thereby revealing a significant shift to a lower wavenumber of 65 cm⁻¹ compared to the absorption signature of dissolved CO₂ located at 2343 cm⁻¹. This readily enables the direct evaluation – and discrimination – of dissolved ¹³CO₂ next to ¹²CO₂, which is particularly relevant for monitoring the behaviour of CO₂ under extreme conditions when injected together with ¹³CO₂ used, for example, as a tracer molecule for carbon capture and storage processes.¹⁷ The increase in absorption intensity with increasing pressure for ¹³CO₂ is shown in detail in Fig. 4. The spectra represent the absorption signature of ¹³CO₂ after reaching equilibrium conditions (10–15 min) at the respective pressures.

Methane dissolved in water at elevated pressures

The solubility of methane in water is a function of temperature and pressure. Under ambient conditions, methane dissolves only slowly in water. Hence, by simply bubbling gaseous methane through water a less-than-measurable amount of

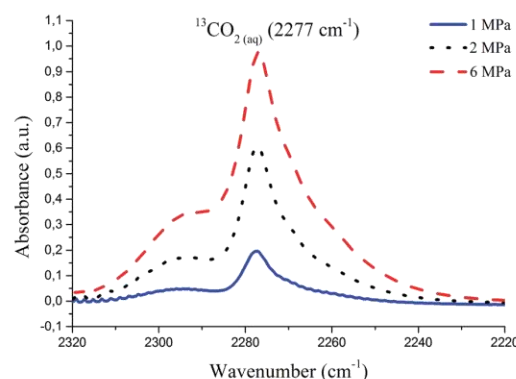
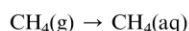


Fig. 4 IR spectra of ¹³CO₂ dissolved in water at different pressures. Dissolved ¹³CO₂ shows a distinctive absorption feature at 2277 cm⁻¹.

methane (<20 ppm at 20 °C) is dissolved under ambient conditions.¹⁸

However, with temperatures approaching 0 °C, higher salinity, and increasing pressure as present in deep sea environments, the solubility of methane is significantly increased.¹⁷ Using the high pressure IR-ATR sensing system herein, methane in water was clearly detectable when increasing the pressure from 0.1 MPa (ambient conditions) to 0.4 MPa after manual baseline correction in the spectral region from 1320–1280 cm⁻¹. During the change of the pressure conditions, methane shows a minute shift to lower wavenumbers (approx. 2.5 cm⁻¹) of its absorbance maximum in the MIR, as shown in Fig. 5. At low pressures (*i.e.*, 0.4 MPa), the maximum of the methane absorption feature appears at 1305.5 cm⁻¹, with a second local maximum evident as a shoulder peak at 1303 cm⁻¹. With increasing pressure, the absorption maximum is shifted to 1303 cm⁻¹. This shift may indicate the solution process of methane in water, as a shift of a vibrational absorption feature in the IR spectrum is usually related to a change of the force constant of the observed bond, which may be attributed to the formation of a hydration shell during the dissolution process



However, the critical pressure for methane is 4.6 MPa, and close to this pressure regime the solubility of methane in water no longer follows a linear behavior,¹⁹ which is reflected in the non-linear absorbance intensity changes evident in the spectra recorded >4 MPa (orange and violet lines).

For a more precise examination of this effect occurring during the dissolution process, an experiment was performed with the sample chamber of the IR-ATR system filled only with gaseous methane for comparing the IR signatures of gaseous and dissolved methane under similar conditions (*i.e.*, 21 °C, 4 MPa of pressure). The resulting IR spectra are illustrated in Fig. 6.

The IR spectra of CH₄(g) (black line) and CH₄(aq) (red line) clearly reveal the difference in absorption maxima of methane

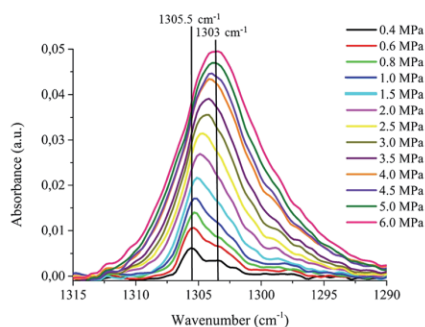


Fig. 5 Wavenumber shift of the main methane absorption under increasing pressure conditions covering a concentration range of approx. 200–1000 ppm. The spectra were recorded by averaging 100 scans at a spectral resolution of 0.5 cm⁻¹.

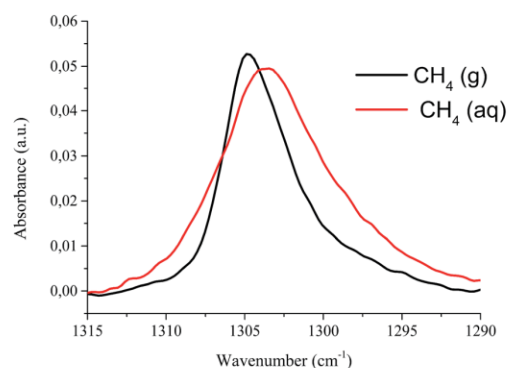


Fig. 6 IR spectra of dissolved (red line) and gaseous (black line) CH₄ in water. The spectra were recorded at 4.5 MPa averaging 100 scans at a spectral resolution of 0.5 cm⁻¹.

in gaseous and dissolved states close to the critical pressure point. Gaseous methane shows no shift in peak intensity at pressures beneath the critical pressure, as compared to methane dissolved in a saline water matrix. Since the critical temperature for methane is set at 190 K, methane becomes supercritical beyond this limit and no discernible changes of the absorption features are evident. The IR signature of CH₄ in the supercritical state is provided in Fig. 7.

Fig. 7 clearly discriminates the different states of methane in aqueous environments *via* their IR signatures. The solid black line refers to dissolved CH₄, whereas the dashed lines refer to supercritical CH₄ in water with the absorption maximum at 1303 cm⁻¹. Hence, this shift in peak maximum enables the determination whether CH₄ may be stored in the supercritical or dissolved state, if injected into saline reservoirs under high pressure conditions, which is of particular relevance for on-line monitoring purposes.

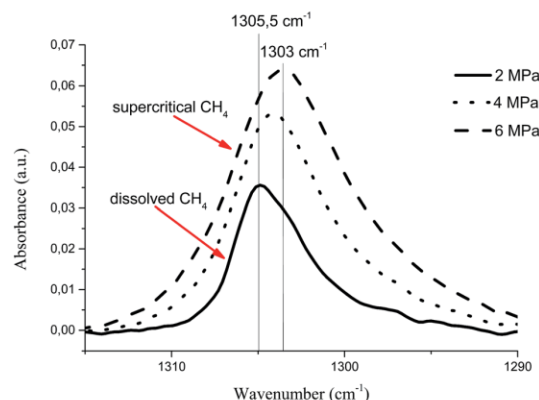


Fig. 7 IR spectra of dissolved and supercritical CH₄ in brine. The spectra were recorded averaging 100 scans at a spectral resolution of 0.5 cm⁻¹.

Multivariate data analysis and sensor calibration

Various models have been established for determining the dissolution processes of gases in aqueous environments. Most of these models are highly sophisticated and combine approximations of different theoretical models for simulating the physics that is involved in such complex gas–liquid systems. To date, there is no physical equation established that covers multi-component dissolution processes at high pressures, which renders quantitative calibrations for such scenarios an intricate task.

As a potential solution for datasets with a variety of potentially unknown changes during the measurements, multivariate data analysis strategies based on multicomponent regression methods appear suitable. Chemometric data evaluation approaches take advantage of statistical algorithms for maximizing the chemical information derived from, *e.g.*, multi-wavelength spectroscopic data recorded under highly variable and frequently unpredictable measurement conditions. Hence, in the present study multivariate regression models based on partial least squares (PLS) were established for deriving robust calibration models of the investigated multicomponent systems. Four latent variables (LVs) were selected, which captured 99% of the variance within the calibration dataset. Applying mean-centering and cross-validation as data preprocessing steps, the spectra used for calibration resulted in sufficiently robust quantitative calibration models. The influence of selected variables such as absorbance, relative pressure and relative wavelength within the calibration model may be evaluated using the so-called selectivity ratios, *i.e.*, the larger the value of the selectivity ratio, the more relevant the associated wavelength contributes to the prediction. Consequently, wavelengths with low selectivity ratios will be excluded for calculating the regression function for the calibrations. The selectivity ratios shown in Fig. 8 correlate well with the investigated analytes, *i.e.*, the highest values match up with the methane signature at 1305 cm^{-1} and the region of the carbon dioxide species from 2260–2350 cm^{-1} . Hence, the PLS model weights the wavelengths of the gas absorbance signatures highest, which corresponds to the most relevant contributions within the spectral datasets.

The calibration set used herein comprised three independent IR spectra recorded at four different pressures (0.6, 1.2, 2, and 4 MPa) covering the linear range of dissolution of the investigated gases. From these calibration samples, a linear regression model was established, as shown in Fig. 9.

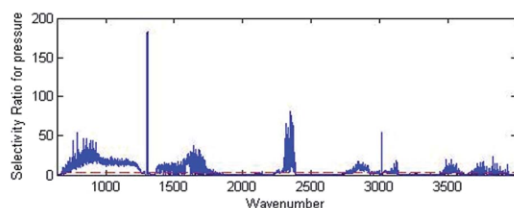


Fig. 8 Selectivity ratio for establishing a multivariate regression model. The highest ratios match up with the relevant IR signatures of the dissolved molecules within the water matrix.

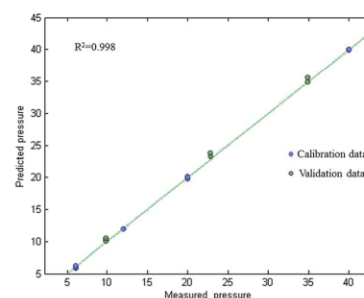


Fig. 9 Calibration model for the investigated greenhouse gas mixtures in brine solution. The calibration dataset included 3 independent spectra containing CO_2 , $^{13}\text{CO}_2$, and CH_4 recorded at 4 different pressures resulting in a $R^2 = 0.998$.

The calibration model reveals a goodness-of-the-fit of $R^2 = 0.998\%$, and suitably predicts the associated pressures. A set of spectra, which were recorded at different pressures (*i.e.*, 1, 2.4, and 3.5 MPa), which were not included in the calibration model were used as quasi unknowns for validating the established model. As anticipated, the predicted pressure values matched the actual pressure values very well, thereby confirming the robustness of the regression model. Fig. 10 shows that the integrated peak areas of both the methane absorption band at 1305 cm^{-1} and the carbon dioxide absorption band at 2343 cm^{-1} linearly correlate with both (i) the estimated concentration, and (ii) the ambient pressure at which the spectra were recorded. This correlation confirms that the direct evaluation of the methane and carbon dioxide absorption at relevant concentration levels reported in the literature^{17,25–27} may be performed *via* direct peak area integration taking variable pressure conditions accurately into account. Although both signatures show a linear behavior at the estimated concentrations, it is evident that methane is likely to appear at concentrations at least one order of magnitude lower than carbon dioxide in such mixtures, thus revealing significantly lower peak areas at the respective pressures.

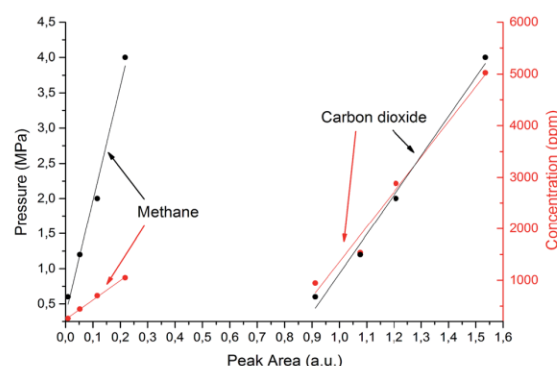


Fig. 10 Integrated peak areas of the methane and carbon dioxide signatures. The red scale refers to the peak area against the estimated dissolved gas concentration^{19,27} at different pressure values (black line).

Table 1 Composition of synthetic brine solution

	g L ⁻¹	wt%
MgSO ₄	12	4.9
Na ₂ SO ₄	1.3	0.5
CaCl ₂	14.8	6
KCl	0.7	0.3
NaCl	215	88.3

Considering the linear relationship between the pressure and peak area, the multivariate calibration model for predicting pressure conditions meets the desired requirements for monitoring such constituents under elevated pressure conditions in saline environments. Consequently, the predictions derived from the calibration model may be directly related to the linear behaviour of pressure *vs.* the dissolvable amount of gas in these pressure ranges.

Experimental

Sample processing

Carbon dioxide (99.5%) and methane (99.5%) were purchased from MTI IndustrieGase AG (Neu-Ulm, Germany). ¹³CO₂ (99.9%) was purchased from CAMPRO Scientific GmbH (Berlin, Germany). The JetStream Circle Cell IR-ATR accessory was purchased from Pike Technologies (Pike Technologies, Cottonwood, United States).

MgSO₄, Na₂SO₄, CaCl₂, KCl, and NaCl were purchased from VWR International GmbH (Darmstadt, Germany). Deionized water was used as the solvent for the salts to simulate saline environments.¹¹

The synthetic brine environment used as the background matrix in this study was established by dissolving MgSO₄, Na₂SO₄, CaCl₂, KCl, and NaCl in deionized water following the composition given in Table 1.

The compositions of saline aquifers around the world differ slightly in the concentration of dissolved salt, rock and/or sediment content. The composition used herein was adapted from Sell *et al.* (2013) for creating a representative brine environment.¹¹

Conclusions

Using a synthetic brine solution as a surrogate for real-world saline aquifer matrices, it was shown that IR-ATR spectroscopy is a useful analytical tool for on-line monitoring of changes in the gaseous, dissolved or supercritical states of greenhouse gases present in saline aquifers. This unique measurement concept ideally lends itself to applications in energy-related environmental monitoring scenarios aiming at capture and storage of such gases. To the best of our knowledge, the present study demonstrates for the first time that changes of the characteristic methane IR signature in saline environments are detectable using IR-ATR spectroscopy in a wide range of relevant pressure conditions. Furthermore, a multivariate data

evaluation strategy was developed establishing a robust calibration model for simultaneously quantifying CO₂, ¹³CO₂, and CH₄ in brine matrices. Taking advantage of thin-film IR waveguide technology^{20–22} in combination with advanced infrared light sources such as quantum cascade lasers^{22–24} promises robust, portable, and highly miniaturized IR analyzers deployable under harsh in-field conditions present in downhole and deep sea scenarios for monitoring of storage gases.

Acknowledgements

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5.4 Paper IV. Selecting the right tool: Comparison of the analytical performance of infrared attenuated total reflection accessories

The general concept of the paper was established by B. Mizaikoff during the contribution of T. Schädle to the project that included the research scope of paper III and V. All measurements and data analysis were performed by T. Schädle, who also established the analytical and scientific conclusions after data analysis in close communication with B. Mizaikoff, and wrote the final paper.

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Selecting the Right Tool: Comparison of the Analytical Performance of Infrared Attenuated Total Reflection Accessories

Thomas Schädle and Boris Mizaikoff

Abstract

The analytical performance of four commercially available infrared attenuated total reflection (IR-ATR) accessories with various ATR waveguide materials has been analyzed and evaluated using acetate, CO₂, and CO₃^{2−} solutions. Calibration functions have been established to determine and compare analytically relevant parameters such as sensitivity, signal-to-noise ratio (SNR), and efficiency. The obtained parameters were further analyzed to support conclusions on the differences in performance of the individual IR-ATR accessories.

Keywords

Attenuated total reflection, ATR, infrared spectroscopy, mid-infrared, MIR, Fourier transform infrared spectroscopy, FT-IR, sensor performance

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Introduction

Within the optical analytical techniques, mid-infrared (MIR) spectroscopy has emerged as a routine analysis as well as a promising sensing tool.^{1,2} Consequently, transmission spectroscopy in the 2.5–25 μm regime is among the most commonly applied measurement techniques for analyzing solid, liquid, or gas phase samples.³ However, the direct analysis of opaque samples using conventional Fourier transform infrared (FT-IR) spectroscopy in transmission mode is, in particular, frequently limited by strong background absorption of the solvent/matrix, which is particularly pronounced for aqueous samples.⁴ Attenuated total reflection (ATR) spectroscopy, which is based on the fundamental principle of total internal reflection,⁵ offers a useful alternative measurement strategy.⁶ Consequently, IR-ATR spectroscopy is commonly applied to a wide range of samples, including biomedical and environmental applications.^{7–9} As a result of increasing academic and industrial demand, a variety of ATR accessories are currently commercially available for any kind of FT-IR spectrometer. Among other parameters, the sampling performance and achievable sensitivity of IR-ATR accessories is largely determined by the properties of the ATR waveguide. Although such waveguides are most frequently made from zinc selenide (ZnSe) or silicon (Si),¹⁰ a variety of materials suitable for the MIR spectral window are available, including germanium (Ge), thallium bromide (KRS-5), and diamond; in addition, materials suitable

for fiber optic ATR waveguide applications such as chalcogenide glasses or polycrystalline silver halides may be used.^{11–13}

Given such a broad selection, it is increasingly difficult to choose the right device from the available accessories and waveguide materials to most appropriately serve a specific application. In general, any sampling accessory should provide high analytical sensitivity next to a robust sampling performance, ease of implementation, and enable state-of-the-art qualitative and quantitative figures of merit. While the literature certainly contains a large number of references containing ATR as a measurement concept along with a variety of equipment configurations, a comprehensive strategy for comparing absolute performance parameters including sensitivity and signal-to-noise ratio (SNR) for comparing available ATR accessories remains absent.

With the present study, we aim at (1) providing a strategy for sample preparation that ensures comparability between different optical set-ups (i.e., minimizing sample variance); and (2) providing a first comparison on a selection of commonly used and commercially available ATR

Institute of Analytical and Bioanalytical Chemistry, University of Ulm, Ulm, Germany

Corresponding author:

Boris Mizaikoff, Ulm University, Institute of Analytical and Bioanalytical Chemistry, Albert-Einstein-Allee 11, Ulm 89081 Germany.
Email: boris.mizaikoff@uni-ulm.de

accessories with a main focus on deriving, on an objective basis, the differences in analytical performance. During this initial study, four different IR-ATR accessories comprising several internal reflection elements (IREs) were investigated via recording IR-ATR spectra of identical solutions containing sodium acetate dissolved in water as easy-to-prepare and readily available species along with more sophisticated analytes (in terms of their IR signatures) including CO₂ and carbonate in aqueous solution.

Description of ATR Accessories

A schematic drawing for each investigated ATR unit type is illustrated in Figure 1, briefly indicating the IRE configuration.

JetStream Cylindrical Cell (Type I)

The Pike Technologies Jet Stream (JSCC) (Pike Technologies) is an ATR accessory designed exclusively for liquid phase analysis at operating pressures up to 1500 psi. The liquid sample surrounds a cylindrical 82 × 6.4 mm ATR rod (Ge or ZnSe) providing a sample chamber volume of 1.3 mL. The ATR rod provides for 12 reflections of the IR beam along the crystal surface.

Bruker/Harrick BioATR II (Type II)

The Bruker/Harrick BioATR II system (BioATR) (Bruker Optics, Ettlingen, Germany) offers a multi-reflection ATR module (seven to eight internal reflections) based on a 400 μm thick silicon waveguide that is specifically suited for studies on biological samples due to a temperature-controlled environment and the minute sample volume (a few hundreds of microliters). A dual-crystal system (DCT); (i.e., a ZnSe cone-shaped crystal optically coupled to a thin silicon disk (6 mm in diameter) serving as the actual ATR element) is used for generating an evanescent field at the Si

waveguide surface. A few hundred microliters of liquid phase samples are sufficient to cover the active measurement area.

Harrick ConcentratIR2 (Type II)

The ConcentratIR2 (CoIR) (Harrick Inc.) is designed for micro-liquid samples similar to the BioATR II, featuring interchangeable diamond and silicon ATR sampling plates with a diameter of 6 mm. Both ATR configurations use the same DCT coupling mechanism, as described for the BioATR II system. The silicon configuration features either 12 or 23 internal reflections depending on the thickness (either 350 μm or 250 μm) of the selected IRE with a nominal incidence angle of 30°, whereas the diamond configuration provides ten internal reflections (250 μm thickness) with a nominal angle of incidence of 45° for the incoupling radiation. Again, a minimal sample volume of a few hundred of microliters is required to cover the actively sampled area of the IRE.

Bruker Horizontal ATR Accessory (Type III)

The Bruker horizontal-ATR accessory (HATR) (Bruker Optics, Ettlingen, Germany) features a trapezoidal ZnSe crystal serving as the sensing element. Infrared radiation is coupled into the 45° facet of the crystal and guided along the trapezoid via 10 internal reflections. The active area of the IRE is approximately 6 cm × 1 cm, and approximately 0.1 mL of sample is required to cover the entire crystal surface with a liquid film extending beyond the penetration depth of the evanescent field. This is of particular importance for ensuring comparable and reproducible quantitative measurements.

Experimental

Materials and Reagents

Carbon dioxide (99.5%) was purchased from MTI IndustrieGase AG. Potassium carbonate and sodium acetate were purchased from VWR International GmbH. De-ionized water was used as the solvent for CO₂ and the salts.

Solution Preparation

Preparation of Saturated CO₂ Solutions. The CO₂ solutions were prepared by passing gaseous CO₂ through a capped 500 mL bottle of de-ionized water for 2 h until saturation was reached. Preliminary studies revealed that 2 h is perfectly sufficient for saturating 500 mL of de-ionized water with CO₂ at ambient conditions of $T = 21\text{ }^{\circ}\text{C}$ and $p = 1.013\text{ bar}$ (i.e., no further changes in signal intensity of the dissolved CO₂ IR spectrum were observed). At ambient

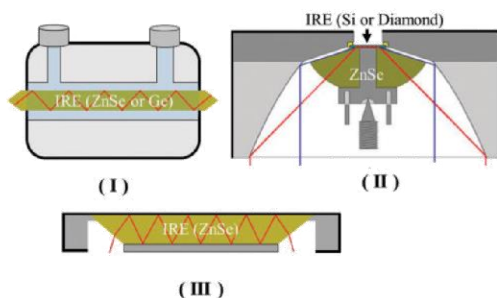


Figure 1. Schematics of the investigated IR-ATR accessories. (a) Type I: JSCC with either ZnSe or Ge IRE rod; (b) Type II: CoIR and BioATR DCT system with different IRE wafers on top of the ZnSe rod as the main difference; (c) Type III: Bruker HATR ZnSe sampling plate.

conditions, this corresponds to 1.7 g/L (1700 ppm) as saturation value.¹⁴ During concentration series, the saturated CO₂ solution was further diluted 1:2, 1:3, and 1:4.

Preparation of CO₃²⁻ Solutions. Carbonate solutions were prepared by dissolving 5 g of K₂CO₃ in 1 L of de-ionized water (i.e., 5000 ppm) at ambient conditions with $T = 21\text{ }^{\circ}\text{C}$, which were then diluted 1:2, 1:3, and 1:4 for providing a concentration series.

Preparation of Acetate Solutions. Diluted with the same concentration series as the other constituents, 10 g of sodium acetate was dissolved in 100 mL of de-ionized water (i.e., 100 000 ppm) at ambient conditions ($T = 21\text{ }^{\circ}\text{C}$).

The analytical performance of the ATR accessories was analyzed using the same analyte solution for each unit. For each measurement, the solution was deposited onto the surface of the ATR waveguide ensuring entire surface coverage and a liquid layer thickness $>100\text{ }\mu\text{m}$, thereby exceeding the penetration depth of the evanescent field multiple times.

Instrumentation and Data Processing

Infrared attenuated total reflection spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer (Bruker Optics, Ettlingen, Germany) equipped with a liquid nitrogen-cooled wide-band mercury–cadmium–telluride (MCT) detector (Infrared Associates). Spectral data were processed using the Bruker OPUS software package. Infrared absorption features were evaluated via peak area analysis using the OPUS software package. Each measurement was independently performed three times using a separately deposited liquid phase sample, albeit each from the same stock solution, and the peak areas were subsequently averaged. For each measurement, 100 spectra were averaged at a spectral resolution of 2 cm^{-1} . All CO₂ measurements were performed against air as background, whereas water was used as the background for recording the spectra of the carbonate solutions. Since the absorption signature of dissolved CO₂, which readily differentiates from vapor phase CO₂, was evaluated, no further atmospheric correction was required during data processing.

Results and Discussion

As performance evaluation of the ATR units should be performed using reproducible measurement conditions, analytes (i.e., the salt solutions) were selected that ensure a rapid, robust, and easily reproduced sample preparation across laboratories while providing distinct and readily discernible IR signatures. This is of particular importance for studies in aqueous solutions. The preparation of salt solution samples such as dissolved acetate and carbonate in the g/L concentration range is robust and reproducible due to

the solubility of these salts in water; in addition, de-ionized water is readily available in any laboratory. Furthermore, saturating a given sample volume of de-ionized water with soluble gases such as readily available CO₂ at ambient laboratory conditions (1.013 bar, $21\text{ }^{\circ}\text{C}$) may be more time-consuming and sophisticated; however, results in the same concentration of dissolved analyte regardless of the surrounding environment (i.e., if temperature and pressure can be kept constant). Moreover, the IR signature of dissolved CO₂ (at 2343 cm^{-1}) is distinctly shifted when compared with gaseous carbon dioxide, and readily separates from the salt signatures (carbonate at 1390 cm^{-1} , acetate at 1550 cm^{-1} and 1413 cm^{-1}). The latter are the two strongest absorption signatures of acetate, thus providing an analyte absorbing in the higher wavenumber region without substantial interference from water absorption. Hence, these simple and readily available analytes facilitate evaluation of the performance of ATR units at different wavelength regimes within the mid-infrared spectral window, and therefore represent quasi-ideal samples for performance comparison among different ATR units.

Performance Evaluation

The performance of the ATR accessories was evaluated regarding sensitivity, SNR, noise (peak-to-peak noise ratio), and efficiency E_f (i.e., $E_f = \text{sensitivity/noise}$). All measurements were performed in triplicate. For dissolved CO₂ studies, the solutions were freshly prepared ensuring that evaporative loss of analyte with time was avoided; equal concentration levels were confirmed for each solution by comparing the absorption intensities to previously recorded IR spectra at the same ATR module. Figure 2 shows the IR-ATR spectra of the four different IR signatures that were used for data evaluation (2343 cm^{-1} for dissolved CO₂, 1550 cm^{-1} and 1413 cm^{-1} for acetate, and 1390 cm^{-1} for carbonate) recorded using the ATR accessories investigated and IRE materials. The intensity variation of the absorption features for each analyte confirms a remarkable difference among the investigated ATR accessories, and, furthermore, if different ATR materials are used within the same ATR system.

From the IR spectra of the carbonate solutions (Figure 2b), it is evident that the noise level in the region of the carbonate signature (1390 cm^{-1}) is significantly higher compared to the CO₂ and acetate signals, which is explained by the background water absorption that significantly reduces the overall energy throughput. It was therefore necessary to analyze the carbonate signal against water as background at the given concentrations of carbonate, in order to illustrate that the results at low concentrations follow the same trend established for the higher acetate concentrations. Calibration functions were generated via peak integration (OPUS Software, Inc., integration boundaries: $2347\text{--}2333\text{ cm}^{-1}$ for CO₂, $1570\text{--}1505\text{ cm}^{-1}$ and

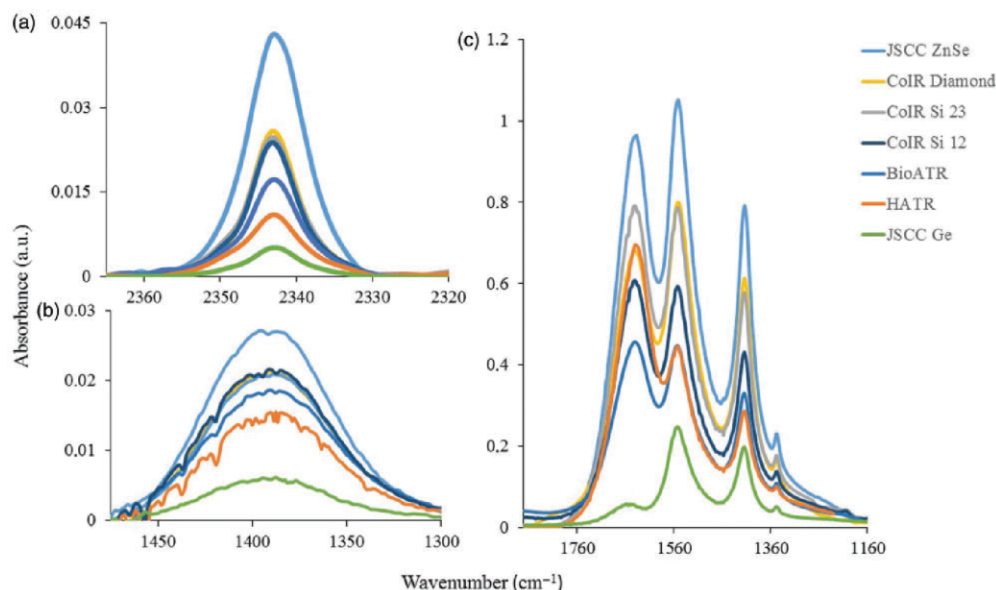


Figure 2. Infra-red spectra of (a) CO_2 , (b) CO_3^{2-} and (c) sodium acetate dissolved in water after manual baseline correction recorded with the evaluated ATR accessories and waveguide materials. Each spectrum is an average of 100 scans at a resolution of 2 cm^{-1} . Absorbance spectra were calculated against air as the background, except for carbonate with water as the background for better visibility of the IR signature at low carbonate concentrations.

$1458\text{--}1366\text{ cm}^{-1}$ for acetate, $1465\text{--}1310\text{ cm}^{-1}$ for carbonate) to determine the sensitivity (i.e., slope of the calibration function) of each ATR unit (Figure 3).

From the calibration functions, it is immediately evident that the different ATR units and waveguide materials (i.e., ZnSe, Ge, diamond, and Si) widely vary in sensitivity. The sensitivity was calculated as $S = \Delta I_{(\text{intensity})} / \Delta C_{(\text{concentration})}$, i.e., representing the slope of the calibration functions listed in Table I. Evidently, the achievable sensitivity largely varies not only between different IRE materials using the same accessory, but also among the different ATR units. The sensitivity for CO_2 measured with the JSCC appears nearly three times that of the sensitivity of the HATR when equipped with a ZnSe ATR rod, yet provides only half the sensitivity when using a Ge rod as the ATR element. The sensitivity of the BioATR and the CoIR units is in between the HATR and the JSCC, yet providing the anticipated, albeit minute, increase in sensitivity with an increasing number of internal reflections, if the silicon IRE is thinner or changed to diamond. This increase in sensitivity may reliably be related to the waveguide material and the associated increase in internal reflections, as these two units use the same DCT configuration for coupling the IR radiation into the actual waveguide.

Regarding the CO_3^{2-} results, the JSCC system equipped with the germanium ATR waveguide revealed only half of the sensitivity compared to the other ATR accessories, which are all located in the range 0.3063 to 0.3505.

The ZnSe-ATR-equipped JSCC again revealed the highest sensitivity at 0.8416. For investigation of the acetate bands, the same unambiguous result for both of the stronger absorptions has been observed with a sensitivity starting from 0.0457 (JSCC, Ge) to 0.1923 (JSCC, ZnSe), and all other units and IREs in between. Overall, the observed trends are similar among all the investigated species and absorbance intensities, thereby enabling averaging the sensitivities for each analyte for further calculations. An overview summarizing all parameters derived from the sensitivity analysis is given in Table I.

Considerations on Multiple Reflections and Effective Penetration Depths

Absorbance within the evanescent field depends on the square of the product $[E(\partial\mu/\partial q)]^2$ where μ is the transition dipole, q a coordinate normal to the incident plane, and E the electric field amplitude in the rarer medium.¹⁴ Additionally, it can be shown that the absorbance is proportional to the so-called effective penetration depth defined as¹⁵

$$d_e = \frac{n_{2,1}}{\cos \theta} \int_0^\infty E^2 dz = \frac{n_{2,1} E^2 d_p}{2 \cos \theta} \quad (1)$$

where $n_{2,1} = (n_2/n_1)$, E is the electric field amplitude, d_p is the penetration depth, and z is the distance from the

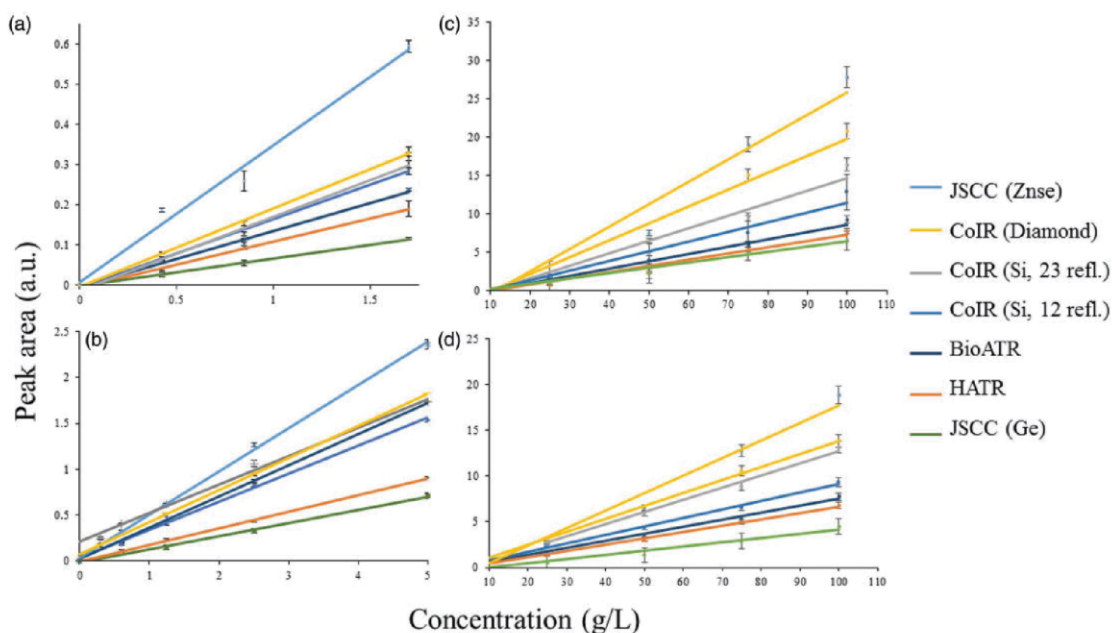


Figure 3. Calibration functions for determining the sensitivity of the dissolved analytes: (a) CO_2 at 2343 cm^{-1} ; (b) carbonate at 1390 cm^{-1} ; (c) acetate at 1550 cm^{-1} ; (d) acetate at 1413 cm^{-1} using peak area integration. Each measurement was performed in triplicate using separate samples from the same stock solution.

interface. Furthermore, the reflectivity R for a single reflection is given as

$$R = 1 - \alpha d_e \quad (2)$$

where α describes the absorption coefficient at a given wavelength. Consequently, n multiple reflections would result in

$$R = (1 - \alpha d_e)^n \quad (3)$$

Because αd_e is usually $\ll 1$, it may be assumed that the absorbance for n reflections approximately equals n times the absorption of a single reflection.¹⁴ However, this relation could not be observed using the CoIR ATR unit with two different silicon IREs, i.e., 12 or 23 reflections, or for the BioATR unit (Si IRE with seven to eight reflections). As the theoretical calculations would suggest, the absorbance intensity using the 23 reflection silicon IRE should be approximately two to three times higher than the band intensities obtained from the thicker silicon IREs. However, the band intensities and the established sensitivities do not confirm linearity of these theoretical considerations. As a result, two hypotheses are postulated.

1. The modulation of the absorbance intensities in the spectra is dependent on the geometry and quality of

the IRE, as well as on the optical throughput and alignment of the unit as a whole, rather than solely dependent on the number of internal reflections. This assertion is supported by the differences in intensities obtained from the HATR (trapezoidal ZnSe IRE) compared to the JSCC (cylindrical ZnSe IRE), yet, still providing roughly the same number of internal reflections (10 versus 12). Theoretical calculations usually consider macroscopically scaled and mostly trapezoidal IREs, and may not directly apply to dual-crystal systems using thin wafers as actual IREs. Additionally, the in-coupling aperture apparently decreases in dimension with decreasing thickness of the IRE, consequently propagating less light through the IRE.

2. The obtained absorption spectra are predominantly influenced by the effective depth of penetration d_e reducing the sensitivity increase anticipated by multiple reflections. However, Eq. 3 may still be appropriate when comparing single reflection and multiple reflection spectra. Consequently, the IRE material, along with its effective penetration depth, may be the more relevant factor affecting the absorption spectrum intensity of a specific analyte.

Optical properties for the investigated IRE materials are given in Table 2.

Table 1. Sensitivities derived from the slope of the calibration functions for the investigated ATR accessories and IREs. The systems are ranked in order of sensitivity from lowest to highest.

ATR	Sensitivity (CO ₂)	Sensitivity (CO ₃ ²⁻)	Sensitivity (acetate at 1550 cm ⁻¹)	Sensitivity (acetate at 1413 cm ⁻¹)	Sensitivity (average)	Number of reflections
JSCC (Ge)	0.0694 $y = 0.0694x - 0.0029$	0.143 $y = 0.143x - 0.0189$	0.0689 $y = 0.0689x - 0.5159$	0.0457 $y = 0.0457x - 0.4172$	0.0817	12
HATR (ZnSe)	0.1147 $y = 0.1147x - 0.006$	0.3063 $y = 0.3063x + 0.0336$	0.0689 $y = 0.0689x - 0.5159$	0.069 $y = 0.069x - 0.208$	0.1397	10
BioATR (Si)	0.1384 $y = 0.1384x - 0.0038$	0.3375 $y = 0.3375x + 0.12$	0.0946 $y = 0.0946x - 0.9429$	0.0767 $y = 0.0767x - 0.1721$	0.1618	7-8
ColR (Si, 12 reflections)	0.1714 $y = 0.1714x - 0.0064$	0.3015 $y = 0.3015x + 0.2484$	0.1262 $y = 0.1262x - 1.1733$	0.092 $y = 0.092x - 0.1006$	0.1727	12
ColR (Si, 23 reflections)	0.1841 $y = 0.1841x - 0.0141$	0.3206 $y = 0.3206x + 0.0693$	0.1626 $y = 0.1626x - 1.6227$	0.1338 $y = 0.1338x - 0.6073$	0.2001	23
ColR (diamond)	0.1954 $y = 0.1954x - 0.0036$	0.3505 $y = 0.3505x - 0.0135$	0.2212 $y = 0.2201x - 2.2793$	0.1418 $y = 0.1418x - 0.3353$	0.2272	10
JSCC (ZnSe)	0.3412 $y = 0.3405x + 0.0071$	0.8416 $y = 0.8416x + 0.2247$	0.2914 $y = 0.2914x - 3.364$	0.1923 $y = 0.1923x - 1.4911$	0.4166	12

From the optical properties given in Table 2, it is evident that the effective penetration depth shows the highest value (6.17) for diamond versus ZnSe and silicon, and with germanium providing the lowest value (0.74). This ranking is, in fact, in agreement with the sensitivities established from the absorption spectra and therefore corroborates that the effective depth of penetration may be the single most relevant parameter affecting the absorption intensity.

Considerations on Noise Levels and Efficiency

Besides sensitivity, the noise of the system (peak-to-peak) and the SNR are among the most important factors considering sensor performance. For determining the noise of the systems, two single-beam spectra of water were measured consecutively with each accessory in place and converted to absorbance. The peak-to-peak ratios in the spectral regions of interest (2500–2300 cm⁻¹ and 1600–1300 cm⁻¹) were then calculated and averaged to obtain the noise of the system. The established parameters for averaged peak-to-peak noise at the analytical wavelengths, SNR, and efficiency are summarized in Table 3.

Regarding the noise ratios, the investigated ATR accessories follow the inverse trend of the sensitivity, as anticipated. This is in particular true for decreasing thickness and thereby increasing number of internal reflections of the IRE using the same configuration (i.e., BioATR and ColR with silicon IREs). For the two ZnSe configurations (i.e., HATR and JSCC) providing similar internal reflections, the noise levels are also quite similar (2.953 versus 3.021), thereby supporting the assumption of increasing noise with increasing number of internal reflections.

For the SNR, the ATR accessories appear to follow the same trend established for the sensitivity in descending order, i.e., from the JSCC (ZnSe) revealing the highest SNR (14.8 cm⁻¹ at 2500–2300 cm⁻¹ and 35.6 at 1600–1300 cm⁻¹), via the ColR (diamond) to the JSCC with the Ge ATR rod (1.43 at 2500–2300 cm⁻¹ and 9.2 at 1600–1300 cm⁻¹). Although noise ratios follow the inverse trend of sensitivity, SNR and efficiency confirm the previously established trend of sensor performance.

Table 2. Optical properties for the different IRE materials investigated within this study.

IRE	n_i (5 μm)	Transmission range (cm ⁻¹)	d_e (μm)	d_p (μm)
Silicon	3.4	4000–1000	4.32	1.17
ZnSe	2.4	4000–650	5.29 (θ = 45°) 1.86 (θ = 60°)	1.22
Germanium	4	4000–830	0.74	0.40
Diamond	2.35	4000–2200; 1900–400	6.17	1.35

Since the sensitivity should increase with the number of internal reflections, which is inversely proportional to the thickness of the IRE, it should be considered that also the optical aperture decreases with decreasing IRE thickness. Hence, less light propagates through the IRE, thereby leading to an increase in noise in the absorbance spectra. A more in depth explanation of this behavior is provided when calculating the efficiency parameter E_f for each ATR unit as

$$E_f = S_{(\text{averaged sensitivity})} / n_{(\text{averaged noise})} \quad (4)$$

which leads to a more useful descriptor of the overall performance, rather than merely taking the sensitivity into

account. Figure 4 illustrates that the efficiency is directly correlated to the number of internal reflections within the same ATR configuration (i.e., BioATR and ColR as the only systems providing a different number of reflections for the same configuration), yet, as previously discussed, the sensitivity or absorbance intensity does not necessarily show this correlation.

Conclusions

Using robust, reproducible, and easy-to-prepare standard samples, i.e., aqueous solutions of acetate, as well as more sophisticated analyte solutions including saturated aqueous CO₂ solutions and aqueous solutions of carbonate, enables the establishment of calibration functions for comparing and ranking the performance of IR-ATR accessories and different IRE materials in terms of achievable sensitivity, SNR, and a newly established parameter termed efficiency (E_f). By comparing four ATR systems and several IRE materials, it was shown that significant differences in performance are evident. These performance parameters facilitate the selection of the appropriate ATR accessory for a given analytical problem based on analytically relevant analysis. Of course, additional parameters such as ease of use, required sample volume, robustness of a particular IRE material, availability of additional accessories such as flow cells, etc., may be additional criteria for particular preferences. It is anticipated that expanding such studies will provide a growing data set for applied spectroscopists, thereby assisting the selection of the most appropriate sampling accessory on a comparative basis for a particular measurement scenario.

Table 3. Noise parameters and efficiency for the investigated ATR accessories.

	Noise (pp)	SNR	Efficiency (E_f)
		(2500–2300 cm ⁻¹ / 1600–1300 cm ⁻¹)	
JSCC (Ge)	3.144	1.43/8.2	0.026
HATR (ZnSe)	3.021	3.3/14	0.046
BioATR (Si)	3.167	5.37/14.2	0.051
ColR (Si, 12 reflections)	3.344	6.9/17.3	0.053
ColR (Si, 23 reflections)	3.522	7.1/22.1	0.056
ColR (diamond)	3.368	7.72/23.7	0.067
JSCC (ZnSe)	2.953	14.8/35.6	0.141

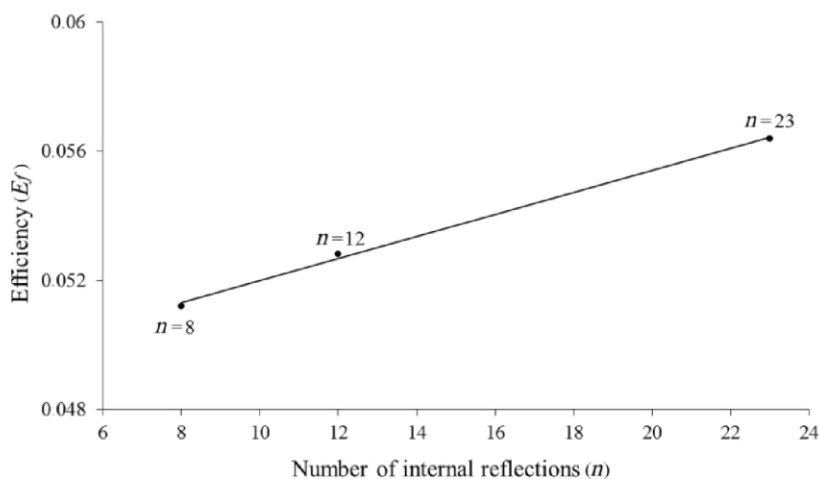


Figure 4. Efficiency versus number of internal reflections within the same ATR configuration (BioATR ($n=8$) and ColR with silicon IRE ($n=12$ and 23)).

Conflict of Interest

The authors report there are no conflicts of interest.

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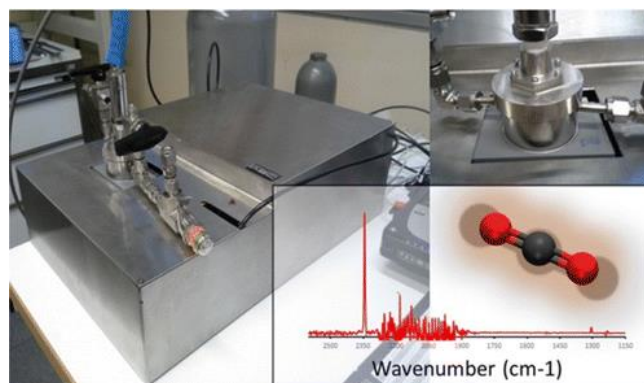
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5.5 Paper V. Portable Mid-Infrared Sensor System for Monitoring CO₂ and CH₄ at High Pressure in Geosequestration Scenarios

T. Schädle designed and built the pressure cell, developed the sensor setup, and performed all measurements. M. Myers contributed to the on-line sequestration simulation studies during a research stay of T. Schädle at CSIRO, ARRC, Perth, WA, Australia. M. Myers, B. Pejic, and B. Mizaikoff contributed with revisions to the final manuscript.

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Article

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Portable Mid-Infrared Sensor System for Monitoring CO₂ and CH₄ at High Pressure in Geosequestration Scenarios

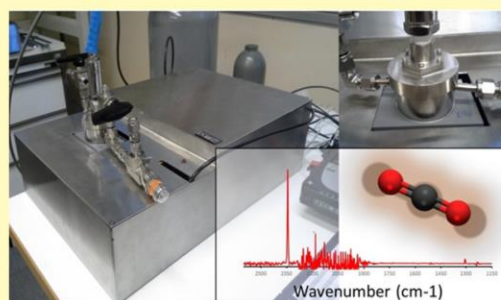
Thomas Schädle,[†] Bobby Pejic,[‡] Matthew Myers,[‡] and Boris Mizaikoff^{*,†}

[†]University of Ulm, Institute of Analytical and Bioanalytical Chemistry, Albert-Einstein-Allee 11, 89081 Ulm, Germany

[‡]CSIRO, Energy, 26 Dick Perry Avenue, Kensington, Western Australia 6151, Australia

ABSTRACT: A portable infrared attenuated total reflection (IR-ATR) spectrometer was developed for analyzing CO₂ and CH₄ in geosequestration scenarios. This infrared-based online sensor system is suitable for monitoring, detecting, and differentiating carbon dioxide and methane at different pressures (i.e., up to 11 MPa) in saline aquifer and/or synthetic brine environments. The design of the sensor system eliminates the present problems in such measurement scenarios of either portability or capability operating at harsh conditions, and especially at elevated pressures for in-field deployment of current available IR systems. It is demonstrated that the detection and quantification of dissolved CO₂ and CH₄ at pressurized conditions is feasible at relevant saline downhole conditions present within the piping of the present injection wells serving as an online/in-line monitoring tool.

KEYWORDS: environmental monitoring, infrared spectroscopy, mid-infrared, attenuated total reflection, ATR, carbon capture and storage



The global uptake of anthropogenic CO₂ by the oceans induces fundamental changes in seawater chemistry that could result in dramatic impacts on biological ecosystems. The main greenhouse gas from combustion of fossil fuel is carbon dioxide, which is therefore considered among the major contributors to global warming.¹ Recently, artificial reservoirs have also been identified as significant contributors of CO₂ and CH₄ in the atmosphere,^{2–5} as such human-induced modifications of continental surfaces may significantly change the CO₂ and CH₄ exchange with the atmosphere.⁵ Due to the microbial decomposition of flooded biomass primarily composed of organics and plants, reservoirs emit substantial amounts of CO₂ and CH₄ into the adjacent environment.⁶ In addition, procedures such as gas-well drilling and hydraulic fracturing are likely causing groundwater contamination within part hazardous volatile organics including, e.g., methane.⁷ Consequently, the influence of greenhouse gases and volatile contaminants on groundwater resources and aquifer systems is evolving into a globally relevant topic.

Hence, various strategies including carbon capture and storage (CCS) approaches aim at reducing the release of such gases into the atmosphere. For example, CCS methods are investigated based on the sequestration and injection of constituents contributing to global warming into saline reservoirs.^{8,9} As these sequestration methods aim at reducing greenhouse gas emissions via appropriate capturing mechanisms diverting them to secure storage locations, CO₂ is nowadays predominantly sequestered into the water phase of deep rock formations.¹⁰ These storage mechanisms lead to the

inclusion of gaseous CO₂ trapped within the rock formations, dissolution within the contained water phase, and long-term conversion of CO₂ into solid rock matrix.¹¹ These mechanisms are generally summarized using the expression “solubility and/or mineral trapping”. The most critical concern during solubility trapping is the potential of CO₂ leakage via imperfect or leaky confinement.¹² In mineral trapping, CO₂ is converted into carbonate minerals by a series of reactions with aqueous ions found in aquatic environments. Various carbonates, i.e., mostly calcites, can be formed, and are then stored in the brine for extended periods of time.¹⁰ However, as dissolution of CO₂ in water decreases the pH value, the conversion of CO₂ to stable carbonate minerals is expected to be slow. The calculated periods for the precipitation of various carbonates is on the order of hundreds of years,¹² thus suggesting that mineral trapping is a potential mechanism that significantly aids in reducing atmospheric CO₂ concentrations, however, only via long-term geochemical processes.

Deep saline aquifers in sedimentary basins are potential sites for such sequestration strategies trapping CO₂ and/or methane. These brine formations are among the most common fluid reservoirs within subsurface regions, and are in existence around the world. Among the variety of geological CO₂ sequestration options, injection into saline aquifer formations is considered among the most promising opportunities, as

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extensive global aquifer systems are capable of accepting sizable volumes of anthropogenically produced CO₂ without the need for extensive transportation pathways.

Nowadays, an increasing number of experimental studies on carbon capture and storage with a particular focus on geosequestration are executed.¹² As carbon dioxide is mostly sequestered into various geological formations, these natural or artificial reservoirs end up as a mixture of gas and aqueous phase environments. The solubility of such gases in water is therefore an important issue from an environmental perspective due to regulatory restrictions imposed, e.g., on the hydrocarbon content in surface and ground waters. However, gas solubility data for most relevant reservoir fluids, as well as for volatile hydrocarbons at elevated pressure conditions and low temperatures ($T \leq 298.15\text{K}$), are scarcely reviewed; extensive laboratory studies directed at the sequestration of CO₂ in brine aquifers are largely absent to date. Downhole geochemical measurements are an important component of any CCS monitoring and verification program; yet, current methods usually involve U-tube shaped sampling systems for acquiring fluid samples subject to analysis.¹³ Hence, the development of robust online/in-line monitoring technologies facilitating advanced understanding on subsurface fluid and dissolution behavior related to injected and stored gases in aqueous environments is needed. Additionally, as atmospheric methane is considered to contribute up to 20% to the greenhouse effect,¹⁴ the accurate determination of dissolved methane concentrations is equally vital for analyzing methane dynamics in a variety of natural aqueous environments.

CH₄ emissions from aquatic ecosystems (e.g., lakes, rivers, deep oceanic waters, surface seawater, etc.) are currently not continuously analyzed over extended time periods in the field. Hence, the aqueous phase or the atmosphere are usually sampled at discrete locations, and thus collected samples are then processed and analyzed in the laboratory.¹⁴ This procedure limits considerably the estimation of aquatic ecosystem contributions to the global release of CH₄ and CO₂.¹⁵

To date, various sensor technologies have been developed enabling monitoring of marine and downhole environments, which are potentially suitable for the detection of volatile organic constituents (i.e., VOCs including CH₄)¹⁶ resulting, e.g., from oil spillage into aqueous environments.^{17,18} Concurrently, such sensing concepts are potentially equally suited as monitoring tools for dissolved gas monitoring scenarios.¹⁶ However, most sensor technologies reported to date are based on conventional laboratory equipment and analysis strategies, rather than providing reliable devices suitable for in-field application at injection conditions of such gases into adequate storage compartments.

Mid-infrared (MIR) spectroscopy takes advantage of molecular vibration patterns at distinctive frequencies providing unique fingerprints of organic and inorganic molecules. Especially, infrared attenuated total reflection (IR-ATR) sensing techniques are significantly less affected by interferences from background absorptions (e.g., water), and thus, appear ideally suited for studies in aquatic environments. Hence, evolving conventional IR spectroscopy and sensing techniques into field-deployable analyzer platforms is considered an emerging in-field optical sensing technique. Moreover, spectroscopic techniques are particularly suited for investigating dynamic processes, which facilitates additional insight on potentially relevant molecular interactions.^{19–21}

In the present study, we have developed a portable IR-ATR online/in-line sensor system for detecting and differentiating carbon dioxide and methane in dissolved states at elevated pressures (i.e., up to 11 MPa). It is demonstrated that the quantitative detection of dissolved CO₂ next to CH₄ at pressurized conditions is indeed feasible at relevant CCS conditions. Since the analysis of dissolved gases such as CO₂ or CH₄ is usually performed by collecting water samples in appropriate sample containers followed by a gas-extraction step and detection via gas chromatographic (GC) analysis, a main goal of the technology presented herein is avoiding sampling and sample preparation steps prior to the analysis. Both headspace and purge-and-trap extraction techniques are highly efficient; however, they require procedures of up to a few hours for sampling, sample transportation, and sample preparation for obtaining quantitative results.^{22,23}

Consequently, IR-ATR sensing techniques are particularly robust and readily adaptable for a wide variety of in-field deployment scenarios such as the harsh environmental conditions, as discussed in the present study. As most CCS-related injection wells provide connection and control lines for accessing subsurface fluid compartments, the monitoring setup developed herein may bypass time-consuming sampling, transportation, and preparation procedures by directly linking into such injection or control lines at or close to the actual sequestration site. Additionally, currently reported studies address elevated temperatures and lower CO₂ pressures, but usually do not cover the entire relevant pressure range up to 11 MPa. Consequently, the present study particularly aims at covering the entire relevant pressure range, which to the best of our knowledge has not been reported via IR-ATR spectroscopy to date. Finally, it is anticipated that the developed IR analyzer technology will be of particular importance for fundamentally advancing CCS processes by providing readily applicable and adaptable online monitoring technologies for in-field usage.

■ EXPERIMENTAL SECTION

Portable Sensor System. The MIR sensor system developed herein comprise two main components, (i) a replaceable pressure cell (stainless steel) containing the ATR waveguide (here, diamond; also, Si, GaAs, or other waveguide materials may be used), and (ii) a Fourier transform infrared (FT-IR) based analyzer unit packaged along the required control electronics, optics, a DTGS IR-detector, and the power supply into a compact stainless steel housing (dimensions: 45 × 35 × 13 cm³) designed for in-field applications. Both parts are manufactured of stainless steel. The pressure cell is equipped with Swagelok fittings ensuring connectivity to most downhole pressure lines. A schematic of the IR sensor systems is given in Figure 1.

The replaceable ATR pressure cell developed by our research team has a sample volume of approximately 5 mL. It was designed to withstand a maximum pressure of up to 14 MPa. Nevertheless, 11 MPa is actually sufficient for matching the requirements of most geosequestration scenarios. From an optical perspective, the cell utilizes a dual-crystal ATR system comprising (i) a thin diamond wafer (250 μm thickness, 6 mm diameter), which serves as the actual internal reflection element (IRE) (i.e., 10 internal reflections), and (ii) a ZnSe crystal, which is in optical contact with the diamond IRE to couple IR radiation from the spectrometer into the thin diamond wafer. The diamond wafer is directly sealed to the bottom of the stainless steel cell body using an epoxy adhesive (Polytec 653). Furthermore, the pressure cell is equipped with p/T sensors embedded into the top plate of the pressure cell. A cross-sectional schematic indicating the optical elements located at the bottom compartment of the ATR cell is shown in Figure 2.

By locating sensitive optical elements at the bottom part of the pressure cell, only the actual diamond IRE requires adequate pressure

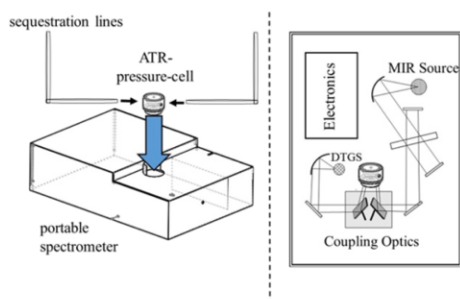


Figure 1. Schematics of the portable IR sensor system. (Left) Dimensions of the entire system are approximately $45 \times 35 \times 13 \text{ cm}^3$ including all optical and electrical components. The ATR pressure cell will be connected to sequestration lines via Swagelok fittings, and the cell may directly be inserted into the spectrometer top plate and/or replaced as indicated (blue arrow), thereby optically connecting to the radiation coupling mirrors. (Right) Top-view layout of the sensor system indicating the main components, the optical path, and the coupling optics.

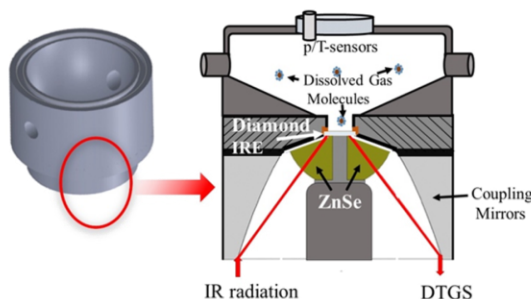


Figure 2. (Left) Schematic of the ATR pressure cell (full rendering). (Right) Cross-sectional view of the entire ATR cell assembly with coupling optics. The red line represents the IR beam coupling through the thin diamond wafer serving as the IRE.

sealing. An appropriate epoxy material provided strong bonding of metal surface to diamond at high pressures (Shore D > 80). However, due to the thickness of the diamond IRE, support against the liquid phase pressure at the top from beneath is required for preventing fracturing. Hence, the ZnSe coupling-crystal not only provides IR radiation coupling, but also serves as support structure for the IRE.

Prior to manufacturing, modeling of the anticipated flow conditions and pressure distribution inside the cell was executed (@ 14 MPa) using the COMSOL Multiphysics software package and CAD-files of the cell design (Figure 3).

The simulations of the anticipated flow velocity distribution (A) revealed a primarily laminar flow through the pressure cell; however, promoted by the hemispherical shape of the sample chamber the injected fluid will still pass the bottom of the cell (i.e., flow across the IRE) at a velocity of approximately 18–22 m/s. Therefore, a constant, rapid, and representative sample transport across the surface of the diamond IRE located at the bottom of the cell is ensured. Furthermore, the pressure simulations (B) inside the cell indicate a highly uniform pressure distribution throughout the entire volume of the sample chamber volume, thus ensuring compliance with the required maintenance of the injection conditions relevant for sequestration scenarios inside the pressure cell.

For high pressure experiments conducted at CSIRO, a 1.6 L high pressure vessel was loaded with water. A high pressure syringe pump was used to inject CO_2 mixtures into the aqueous phase at the desired

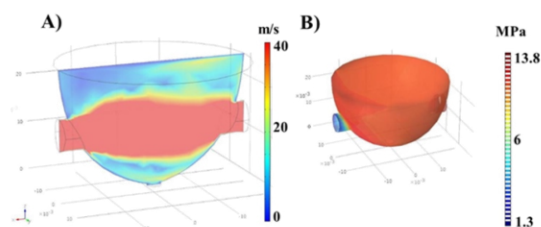


Figure 3. Calculations representing (A) the anticipated flow velocities inside the cell in m/s @ 14 MPa, and (B) the pressure distribution in MPa within the ATR pressure cell.

pressure. An appropriate piston-type circulation pump was used to circulate the fluids from the bottom of the vessel to the top, while the IR-ATR sensor was placed in-line with the circulation pump. All experiments were conducted at room temperature.

Sample and Data Processing. Carbon dioxide (99.5%) and methane (99.5%) were purchased from MTI IndustrieGase AG (Neu-Ulm, Germany). Polytec 653 was purchased from Polytec PT GmbH (Waldbrunn, Germany). cMgSO_4 , Na_2SO_4 , CaCl_2 , KCl , and NaCl were purchased from VWR International GmbH, (Darmstadt, Germany). Deionized water was used as solvent for the salts to simulate saline environments.²⁴ The brine environment used as background matrix in this study was simulated by dissolving MgSO_4 , Na_2SO_4 , CaCl_2 , KCl , and NaCl in deionized water following the composition given in Table 1. The examined gases (CO_2 , CH_4) were

Table 1. Composition of Synthetic Brine

	g/L	wt %
MgSO_4	12	4.9
Na_2SO_4	1.3	0.5
CaCl_2	14.8	6
KCl	0.7	0.3
NaCl	215	88.3

directly injected into the sample chamber filled with the artificial saline solution (5 mL sample volume). IR spectra were recorded after gas injection until equilibrium was reached (i.e., no further changes in the IR spectra were evident) between gas and liquid/dissolved states.

The composition of saline aquifers around the world differs slightly in the amounts of salt, rock, and sediment content. The composition used herein for creating synthetic brine environments was adapted from Sell et al.²⁴

IR-ATR spectra were recorded using the developed IR sensing system, which was equipped with a room-temperature DTGS detector. Spectral data were processed using the “Essential FTIR” software package. Infrared absorption features of CO_2 and CH_4 were evaluated via peak area analysis. For each measurement, 100 spectra were averaged at a spectral resolution of 4 cm^{-1} . All measurements were performed at room temperature (i.e., $20 \pm 1^\circ \text{C}$).

RESULTS AND DISCUSSION

Monitoring Storage of Greenhouse Gases. Both CO_2 and CH_4 show distinctive infrared absorption features (i.e., 2342 cm^{-1} for CO_2 , 1304 cm^{-1} for methane) when dissolved in water. Their respective infrared absorption signatures are clearly evident without spectral overlap including the aqueous background matrix. For instance, Figure 4 shows the absorption signatures of CO_2 and CH_4 dissolved in saline solution. The spectra were recorded using the ATR pressure cell filled with synthetic brine serving also as the background spectrum at 11 MPa, and after reaching equilibrium (i.e., after approximately 20 min) following the injection of both gases.

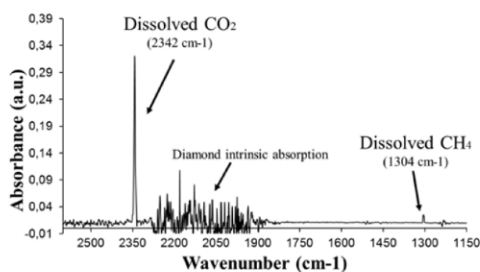


Figure 4. Simultaneous detection of dissolved CO₂ and CH₄ via IR-ATR spectroscopy using a diamond IRE (100 scans at 4 cm⁻¹ resolution) and the ATR pressure cell developed herein (@ 11 MPa).

From the IR spectrum it is immediately evident that the signatures of dissolved CO₂ at 2342 cm⁻¹, and of dissolved methane at 1304 cm⁻¹, are not only identifiable, but are also sufficiently separated from intrinsic diamond absorptions resulting from lattice bands (2000–2280 cm⁻¹) to enable simultaneous detection of both constituents without the need of multivariate statistics. Although the absorbance of CH₄ (approximately 0.017 au) in aqueous solution is weak compared to CO₂ (approximately 0.32 au), the methane signature is still clearly discernible against the brine background. Hence, direct monitoring in downhole and/or saline aquifer environments appears entirely feasible at relevant in-field pressure conditions.

Dissolved Gas Sensing and Sensor Calibration. The sensor performance was characterized by measuring IR-spectra of (i) CO₂ and (ii) methane dissolving in water under increasing pressure. The peak areas of the IR signatures of the dissolved gases have been evaluated to generate calibration functions. The resulting peak areas at the respective pressure steps have been correlated to theoretical solubility values (based on ECO2N module for TOUGH2 developed by Spycher et al.²⁵) to established concentration-dependent calibration functions. These calculated solubilities of CO₂ and CH₄ in water are given in Figure 5.

From the solubility behavior of the gases under investigation it is evident that the correlation between solubility and pressure is not linear. Hence, calibrating the IR sensor system via peak area evaluation would require a nonlinear calibration model,

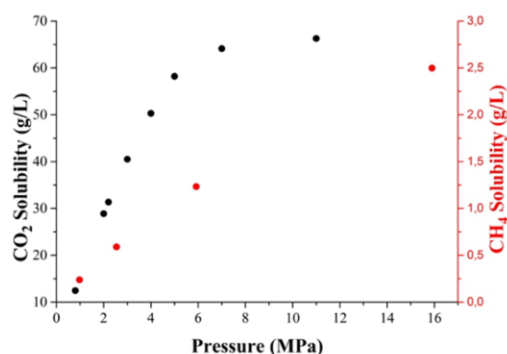


Figure 5. Solubility for CO₂ (black) and CH₄ (red) in water vs pressure.

which may be less convenient for the direct quantification of dissolved gas concentrations during online monitoring scenarios. A reciprocal transformation of the data sets (i.e., using reciprocal values of pressure and solubility) leads to a linear relationship facilitating simple linear regression model for both CO₂ and CH₄, as shown in Figure 6.

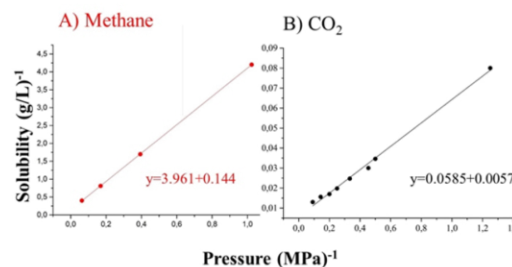


Figure 6. Gas solubility of (A) CH₄ and (B) CO₂ represented as a linear regression function of the pressure after reciprocal transformation.

For dissolved gas detection, IR spectra of both gases were recorded at increasing pressure conditions. Peak integration was used for both carbon dioxide (integration boundaries: 2310–2365 cm⁻¹) and methane (integration boundaries: 1300–1310 cm⁻¹) signatures after equilibrium was reached in the ATR pressure cell (i.e., no more changes in signal intensity were observed). Equilibrium between gas and liquid phase after CO₂ injection was reached after approximately 10–15 min when increasing the pressure stepwise. Infrared spectra of CO₂ and the associated peak areas are illustrated in Figure 7A). Accordingly, for the quantification of CO₂ dissolved in saline solution thus obtained peak areas were converted into CO₂ concentrations using the equation shown in Figure 6B). The resulting increase in peak area after integration of the dissolved CO₂ signature is in accordance with the trend shown in Figure 5 when related to pressure.

For methane sensing, the evaluation of the spectral signatures of CH₄ in aqueous solution (i.e., @ 1304 cm⁻¹) was performed similarly to the CO₂ studies. Methane shows a significantly lower solubility, and therefore a less pronounced IR signature compared to CO₂ in water. In addition, the equilibration of methane between brine and the gas phase is slower than for CO₂, and was reached after approximately 20 min for each pressure interval. Yet, the evaluated data clearly indicates that methane may quantitatively be detected at elevated pressures relevant to CCS scenarios, as illustrated in Figure 7B).

The resulting peak areas—after integration of the methane signature—show the same trend as for CO₂. Likewise, the calibration function for methane was established by the relation of the respective peak area to the expected concentration of methane in aqueous environments at increasing pressures calculated via the equation given in Figure 6. As the solubility at increasing pressures (in the range of 6–11 MPa for CO₂ and 2–11 MPa for CH₄) is evidently nonlinear, all data was treated using the reciprocal transformation discussed above for finally establishing linear calibration model to predict the dissolved gas concentration across the entire CCS-relevant pressure regime, as shown in Figure 8.

From Figure 8 it is evident that a straight line regression model fits the transformed spectral data with an $R^2 = 0.991$ for

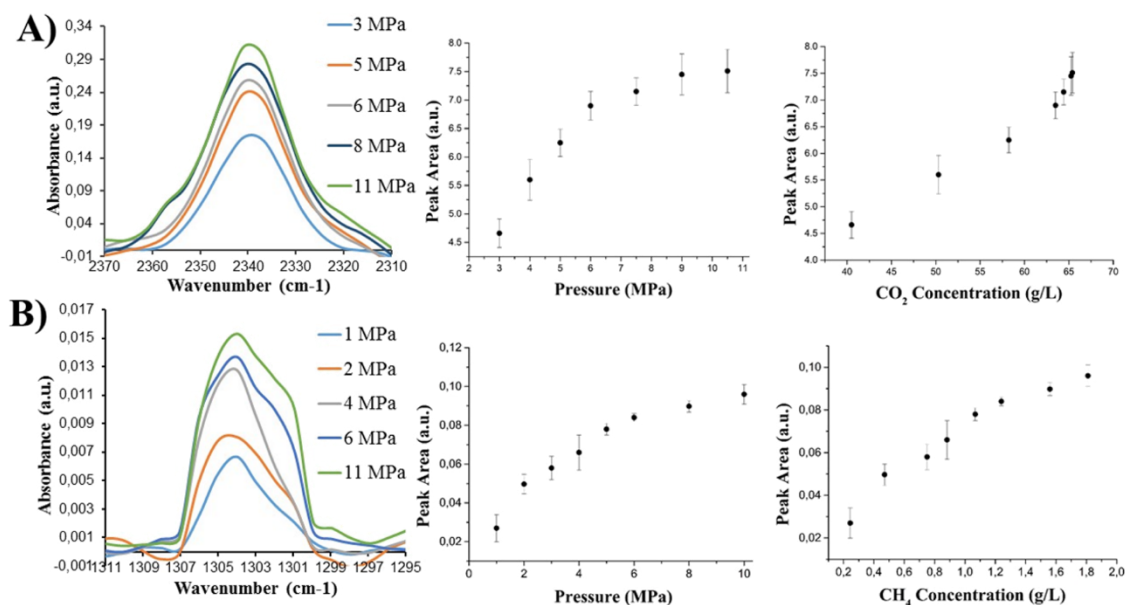


Figure 7. IR spectra of the dissolved gases at elevated pressures up to 11 MPa recorded by averaging 100 spectra at a spectral resolution of 4 cm⁻¹. (A) Exemplary infrared spectra of CO₂ (at 2342 cm⁻¹), the integrated peak area vs pressure from the IR spectra, and the peak area vs the calculated concentration after dissolution of CO₂. (B) Exemplary infrared spectra of methane recorded at similar conditions evaluating the IR band at 1304 cm⁻¹.

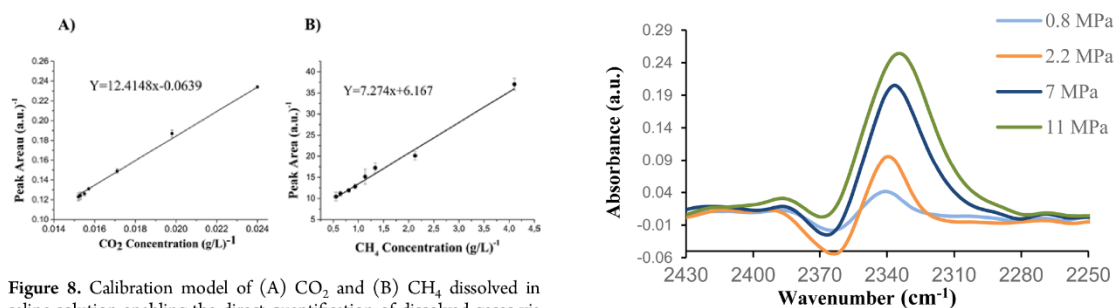


Figure 8. Calibration model of (A) CO₂ and (B) CH₄ dissolved in saline solution enabling the direct quantification of dissolved gases via peak area evaluation after an appropriate linear transformation. Here, the reciprocal value of Y equals the respective concentration of the dissolved gas.

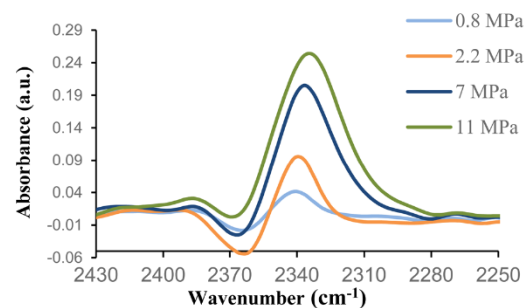


Figure 9. IR spectra of liquefied CO₂/water mixtures at different field-relevant pressures. The spectra were recorded during constant flow through the ATR pressure cell developed during the present study at spectral resolution of 4 cm⁻¹ averaging 100 scans per spectrum.

CO₂, and $R^2 = 0.987$ for CH₄, thus proving this method suitable for the direct quantification of dissolved gases in brine environments.

Simulation Online Sequestration Scenario. As a preliminary study prior to an actual in-field deployment, the in-line scenario of a CO₂ sequestration tube was simulated at ARRC CSIRO, (Perth, WA) using a high pressure piston pump system providing mixtures of liquefied CO₂ and water at different pressures relevant to this study. The IR sensor system developed herein was in-line connected via Swagelok fittings to the pressurized pump circuit, thus providing a constant flowthrough scenario of liquefied CO₂–water mixtures in the ATR cell emulating a real-world CCS scenario. Exemplary IR spectra obtained in this simulated in-field measurement situation are given in Figure 9.

It is immediately evident that the infrared signature of liquefied/dissolved CO₂ was unambiguously observable across the entire pressure range of interest for the geosequestration scenarios studied herein, i.e., from minute pressure increases of only 0.8 MPa up to a maximum of 11 MPa. From the previously obtained calibration functions a concentration comparison at the highest operating pressure (11 MPa) was derived with the analytical figures-of-merit summarized in Table 2. The achievable sensitivity was calculated as $S = \Delta I_{(\text{intensity})} / \Delta C_{(\text{concentration})}$, and the limits of detection (LOD) and quantification (LOQ) were calculated according to IUPAC using the $3\sigma/10\sigma$ criteria (i.e., three-times/ten-times the standard deviation of the smallest concentration value determined within the calibration data sets).

Table 2. In-Line Performance Parameters of the IR Sensor System

	CO ₂	CH ₄
Calculated concentration (g/L)	66.04 (11 MPa)	1.8 (11 MPa)
Sequestration simulation (g/L)	64.87 (± 0.75) (11 MPa)	N/A
LOD/LOQ (ppm)	60/208	142/432
Sensitivity S (ppm)	80.5	137
Calibration function	$Y^{-1} = 12.415x - 0.0639$	$Y^{-1} = 7.27x + 6.167$

The concentration obtained during the laboratory-simulated sequestration scenario testing was close to the theoretically calculated concentration of CO₂ in water. The minute underestimation may result from either a remaining unsaturated mixture of water and liquid CO₂ or a contribution from gaseous CO₂ to the IR signature of dissolved CO₂, even though usually distinct spectral signatures are observable for both species; however, a slightly negative absorption around 2365 cm⁻¹ was observed in the spectra. Notwithstanding, the relevant analytical figures-of-merit including LOD and LOQ, as well as the sensitivity of the IR sensor for both CO₂ and CH₄, are all within the anticipated range relevant to geosequestration applications.

CONCLUSIONS

A field-deployable IR-ATR sensor system has been developed, calibrated, and tested enabling the qualitative and quantitative determination of dissolved greenhouse/storage gases in brine environments relevant to carbon capture and sequestration scenarios. It was shown that IR-ATR spectroscopy is a promising analytical tool that can fill the current gap of online/in-line monitoring systems for operation at harsh environmental conditions including elevated pressures (up to 11 MPa) and aggressive media such as brine solutions, while showing robustness against temperature or similar drift sources. The development of such portable devices is crucial to facilitate a major step forward in environmental monitoring and control scenarios for carbon capture and sequestration scenarios in general, and specifically for gas storage and atmospheric greenhouse gas reduction. Furthermore, the developed method may be extended beyond the discussed gases facilitating the determination of additional critical greenhouse sources that are currently difficult to detect via online monitoring methods including, e.g., ammonia,³¹ which shows various infrared signatures in the spectral regime of 1000 cm⁻¹ to 1600 cm⁻¹. To the best of our knowledge, the present analyzer system for the first time enables in situ and on-site IR-ATR spectroscopy at elevated pressure conditions (i.e., >10 MPa) packaged into a compact, portable, and field-deployable system. Moreover, by using emerging thin-film IR waveguide technologies combined with advanced infrared light sources such as broadly tunable quantum cascade lasers,^{26–30} such sensor systems may be further improved in analytical performance at yet reduced dimensions. Hence, it is anticipated that based on the developments presented herein, the more widespread adoption of mid-infrared spectroscopy and sensing technologies in geologically and geochemically relevant application scenarios ranging from online monitoring to downhole greenhouse gas storage will be evident in the near future.

AUTHOR INFORMATION

Corresponding Author

*E-mail: boris.mizaikoff@uni-ulm.de.

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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5.6 Commentary article associated with Paper V: First reaction comment: A Promising Portable Tool for the Continuous, Online, and Field Monitoring of Pressured Processes (Gabriel 2016)

This article represents a ‘first reaction comment’ in the journal *ACS Central Science* written by J. P. Gabriel (Gabriel 2016) discussing the topic and results presented in Paper V: ‘**Portable Mid-Infrared Sensor System for Monitoring CO₂ and CH₄ at High Pressure in Geosequestration Scenarios**’ (Schädle, et al. 2016) in context of the present situation in geosequestration and groundwater monitoring. This comment provides a consistent outlook on the future perspective and potential of the research presented in this thesis.

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A Promising Portable Tool for the Continuous, Online, and Field Monitoring of Pressured Processes

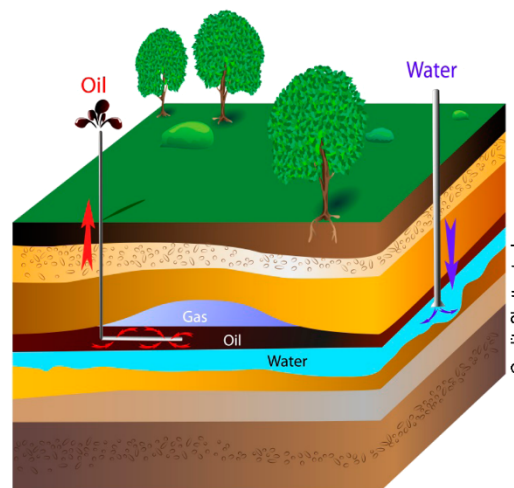
Jean-Christophe P. Gabriel

CEA, 17 Avenue des Martyrs, 38000 Grenoble, France

As exemplified by the recent massive gas leak at Porter Ranch California, hydraulic fracking¹ or other human activities,² their impacts on our ground-water and other deep water reservoirs (brines) could be significant and should be monitored on a continuous basis. But, unfortunately, this is not always the case for all pollutants, especially when field operations and high pressure measurements are required. Hence, in the largest sample pool and most cited study on the pollution associated with hydraulic fracking,¹ water analyses were performed in the laboratory by mass spectrometry on samples taken in a one-off manner at water wells. Therefore, being able to monitor, in real time (online), and over a long time period, the composition of ground waters is yet a challenge which, once solved, has the potential to lead to significant societal impact. Therefore, it is a very promising solution that is being brought to the scientific community in the article of the Mizaikoff group.³

Indeed, this month, the Mizaikoff group reports their studies of CO₂ and CH₄ concentration measurements when dissolved under harsh conditions (high pressure in simulated deep saline aquifers). This is done using a portable infrared spectrometer equipped with a specifically designed attenuated total reflection (ATR) cell (Figure 1), enabling

We need better, faster, and *in situ* tools, like that of Mizaikoff et al., to track ground water quality (ACS Sensors).



As we continue to manipulate our groundwater reserves through drilling, fracking, and other activities, it becomes ever more important to be able to monitor these reserves in real time.

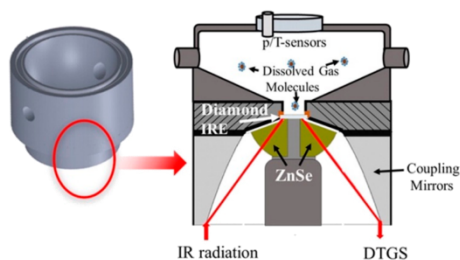


Figure 1. Schematic of the ATR pressure cell (red line represents the IR beam). Figure reproduced with permission from ref 3. Copyright 2016 American Chemical Society.

reproducible measurements to be performed in such conditions as can be found underground (especially high pressures, up to 14 MPa). It is shown that stable, linear and reproducible calibration curves can be obtained enabling the

calibration of the sensor and therefore the measurement of CO₂ and CH₄ concentrations in simulated downhole conditions.

This study is paramount to enable the understanding, modeling, and eventual usage of such aquifers for the deployment of CO₂ and CH₄ sequestration strategies. The compact FTIR that has been developed to do so can

This study is paramount to enable the understanding, modeling, and eventual usage of such aquifers for the deployment of CO₂ and CH₄ sequestration strategies.



be fitted to most downhole pressure lines and therefore is suitable for permanent and online/in-line monitoring (note that it also measures temperature and pressure, which are key for real life measurements and calibrations). But beyond sequestration, measuring concentrations of molecules in the reservoir's conditions will enable a much better understanding of their chemistries.

What is clear from the data presented is that this approach could be used for many other purposes and chemical mixtures, since fairly large functioning windows exist in the IR spectra of the ATR cell (Figure 2), including other

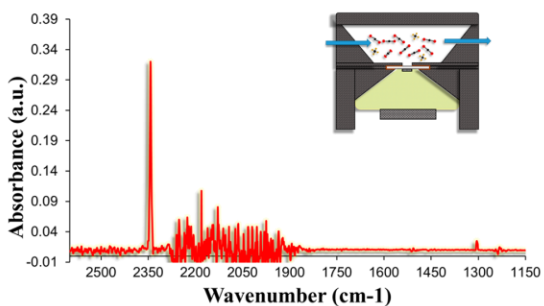


Figure 2. Typical FT-IR-ATR spectrum obtained showing simultaneous detection of CO₂ and CH₄ as well as the wide available wavenumber range available for more complex mixtures studies. Figure provided by T. Schaedle and B. Mizaikoff.

alkanes, ammonia, nitrates, and other chemicals of interest. Ammonia is especially important as its impact on the environment is too seldom studied currently due to the lack of adequate ammonia sensors.^{4,5}

For all these reasons, we suspect that, if such a cell could quickly be made available to the research community, it would become a standard for online, in field, studies in the harsh conditions of ground waters. We therefore look forward to future reports from this group using this device on more complex mixtures, including ammonia and other alkanes, not to mention the study of carbonate's chemistry in real such environments and their reaction kinetics.⁶ Such kinetics will indeed play a key role in enabling or disabling industrial CO₂ sequestration, just as it did to enable multicellular life thanks to the carbonic anhydrase enzyme.^{7,8} The influence of the temperature on the calibration's stability will also have to be studied.

Finally, it would be interesting to benchmark the ATR cell developed here with the remote analytical capability made possible with chalcogenide or silver halide IR fibers used in evanescent wave spectroscopy.^{9,10}

Author Information

E-mail: jean-christophe.gabriel@cea.fr. Fax: +33 438 782 626.

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Curriculum Vitae

Persönliche Daten

Name: Thomas Fabian Schädle

Adresse: Tokajerweg 13
89075 Ulm
Deutschland

Geburtsdatum: 02.06.1988 in Ulm

Schulische Bildung

1998-2007 Abitur am Schubart-Gymnasium, Ulm

Studium

2007-2010 Studium an der Universität Ulm, Chemie
Abschluss: Bachelor

2010-2012 Studium an der Universität Ulm, Chemie
Abschluss: Master

07-08 / 2012 Forschungsaufenthalt TAU, Tel-Aviv, Israel.

2012-2016 Doktorand am Institut für Analytische und Bioanalytische Chemie, Universität Ulm. Titel Der Dissertation: *Mid-infrared Sensors for Environmental Monitoring*. Doktorvater/Betreuer: Prof. Dr. Boris Mizaikoff

03-09/2013 Forschungsaufenthalt CSIRO, ARRC, Perth, WA

06/2015 Forschungsaufenthalt CSIRO, ARRC, Perth, WA

Lehrtätigkeiten

04/2010-08/2012	<u>Tutor/Assistent in studentischen Praktika, Universität Ulm:</u>
SS 2010-WS2011	Grundpraktikum Bachelor Chemie, Institut für Anorganische Chemie I
SS 2012	Grundpraktikum Bachelor Biochemie, Institut für Anorganische Chemie I
WS 2012	Fortgeschrittenenpraktikum Physikalische Chemie, Institut für Elektrochemie
12/2012-04/2016	Betreuung von diversen wissenschaftlichen Arbeiten und Praktika von Bachelor-, Master- und Projektstudenten der Universität Ulm, Institut für Analytische und Bioanalytische Chemie.

Beruflicher Werdegang

10/2010-03/2011	Wissenschaftliche Hilfskraft der Universität Ulm, Institut für Anorganische Chemie II.
12/2012-04/2016	Wissenschaftlicher Mitarbeiter der Universität Ulm, Institut für Analytische und Bioanalytische Chemie.

Spachen und besondere Kenntnisse

Deutsch (Muttersprache)
Englisch (fließend)
Französisch (Grundkenntnisse)
Sehr gute EDV Kenntnisse aller gängigen Office-Programme sowie Kenntnisse in verschiedener CAD- und Visualisierungssoftware.

Außerberufliche Interessen

Musik (Bands, Kreation und Produktion)
Reisen, Kunst und Kultur
Sport & Fitness
Mitglied der Gesellschaft Deutscher Chemiker (GdCh)

Publikationen

Schädle, T.; Katzir, A.; Raichlin, Y. Mizaikoff, B. Mid-infrared planar silver halide waveguides with integrated grating couplers. *Applied spectroscopy*, 2013, 67(9), pp.1057–63.

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Schädle, T.; Mizaikoff, B. Mid-Infrared Waveguides - A Perspective. *Applied Spectroscopy*, invited manuscript, accepted for publication 2016.

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Ulm, März 2016

Eidesstaatliche Erklärung

Hiermit erkläre ich, dass ich die vorliegende Dissertation selbständig angefertigt und keine anderen als die in der Arbeit angeführten Hilfsmittel verwendet habe.

Mid-Infrared Waveguides: A Perspective

Thomas Schädle and Boris Mizaikoff

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Abstract

Significant advancements in waveguide technology in the mid-infrared (MIR) regime during recent decades have assisted in establishing MIR spectroscopic and sensing technologies as a routine tool among nondestructive analytical methods. In this review, the evolution of MIR waveguides along with state-of-the-art technologies facilitating next-generation MIR chem/bio sensors will be discussed introducing a classification scheme defining three “generations” of MIR waveguides: (1) conventional internal reflection elements as “first generation” waveguides; (2) MIR-transparent optical fibers as “second generation” waveguides; and most recently introduced (3) thin-film structures as “third generation” waveguides. Selected application examples for these each waveguide category along with future trends will highlight utility and perspectives for waveguide-based MIR spectroscopy and sensing systems.

Keywords

Mid-infrared, MIR, optical sensors, infrared sensors, waveguides, attenuated total reflection, internal total reflection, chem–bio sensing, waveguide classification, thin film waveguides, optical fibers

Date received: 9 May 2016; accepted: 10 May 2016

Why Mid-Infrared?

The term mid-infrared (MIR) generally covers the spectral region from approximately 4000 cm^{-1} to 400 cm^{-1} ($2.5\text{--}25\text{ }\mu\text{m}$). This spectral region allows for qualitative and quantitative spectroscopy providing chemical, structural, and compositional information on molecular constituents. Mid-infrared spectroscopy may be applied for gas/vapor, liquid, and solid samples. Inherently discriminatory information is obtained owing to the excitation of fundamental vibrational, rotational, and vibro-rotational transitions resulting in a characteristic spectrum for a given molecular species (a.k.a. molecular fingerprint). In particular, due to their pronounced resonances, organic molecules are characterized by particularly distinctive MIR spectra, thus rendering IR spectroscopy a routine analysis technique for identifying and structurally characterizing such molecular species. While conventional waveguide-based spectroscopic techniques, internal reflection and attenuated total reflection spectroscopy (ATR), were introduced by Harrick and Fahrenfort already in the 1960s,^{1,2} it was the introduction of MIR transparent optical fibers in particular since the late 1980s, including materials such as chalcogenide glasses, polycrystalline silver halides (AgX), single-crystalline sapphire, and hollow waveguide (HWG) structures, that have laid the foundation for transitioning classical IR spectroscopic techniques into fiber optic MIR chem/bio sensing technologies.³ Due to its inherent molecular

selectivity, MIR spectroscopy naturally lends itself as a viable approach for direct label-free analysis, which is particularly attractive for establishing optical chem/bio sensors. Real-world sensing and monitoring scenarios have been reported in medical settings,^{4,5} for industrial and material sciences,^{6–9} and in environmental analysis, including most recently monitoring of greenhouse gases.^{10–15} Until fairly recently, MIR spectroscopy has been largely considered as a rather bulky instrumental technique confined to laboratory usage with limited utility for in-field applications in real-world scenarios. However, with increasing adoption of micro- and nanofabricated optical components (e.g., light sources, waveguides—also serving as the active sensing element (a.k.a. transducer), photodetectors, etc.), conventional instrumentation and MIR sensing devices may significantly be scaled down in physical dimensions without sacrificing their robustness, reliability, sensitivity, and selectivity.^{16–18} Given the progress in waveguide technology, this focal point review will predominantly consider advanced MIR sensing technologies that take advantage of waveguide-based measurement principles, as specifically the

Institute of Analytical and Bioanalytical Chemistry (IABC), Ulm University, Ulm, Germany

Corresponding author:

Boris Mizaikoff, Albert-Einstein-Allee 11 Ulm 89081 Germany.
Email: boris.mizaikoff@uni-ulm.de

direct analysis of strongly absorbing samples or of selected constituents in matrices (e.g., water) that limit the use of conventional MIR spectroscopic techniques in transmission mode.¹⁹ Infrared attenuated total reflection spectroscopy (IR-ATR) is considered among the most suitable routine measurement techniques for addressing such complex analytical scenarios,¹ and particularly benefits from the evolution in MIR waveguide technology discussed herein.

Optical Components for Mid-Infrared Spectroscopy and Sensing

Regardless of whether they are installed in commercially available Fourier transform infrared (FT-IR) based laboratory systems or state-of-the-art on-chip IR sensing devices, waveguide-based (most recently termed “waveguide-enhanced”²⁰) IR instrumentation generally comprises three main components: (1) an IR light source; (2) a waveguide-based IR transducer (a.k.a. sensing element) frequently also used for propagating MIR radiation from the light source to the sample; and—after photon-sample interaction—to (3) a detection device.

Mid-Infrared Light Sources

Among the currently established and available MIR radiation sources—usually “broadband” sources—recent advancements in MIR laser technology have led to an increasing adoption of laser light sources in MIR spectroscopy, and even more so in MIR sensor technology. Sophisticated solid-state lasers,^{21–23} quantum cascade lasers (QCLs)^{24–26} and interband cascade lasers (ICLs)^{27,28} are considered “the revolution in MIR light source technology,” in particular for highly integrated and on-chip MIR devices.^{10,14,16–18} In contrast to conventional heterostructure laser diodes generating MIR radiation via electron-hole recombination between the conduction and the valence band of appropriate semi-conductors or semi-conductor mixtures, QCLs and ICLs emit MIR radiation from cascaded structures of alternating ultra-thin layers of semi-conductor materials (i.e., quantum well heterostructures) utilizing sub-band or interband transitions, respectively. In brief, such quantum heterostructures are organized as a superlattice composed of periodic series of semi-conductor layers with different electric potentials leading to different electron occupation throughout the superlattice. As a consequence, these one-dimensional potential wells are characterized by splitting of the band of permitted energies into a number of discrete electronic sub-bands. By precisely engineering the layer sequence and nature of the semi-conductor materials (a.k.a. band-structure engineering), the emission wavelength and lasing conditions may be widely tuned throughout the MIR down to THz emission frequencies in pulsed and continuous wave (cw) operation. Hence, QCLs are tailorable MIR light sources with miniature dimensions featuring high

output power while covering a widespread spectral regime.^{16,17,20} Coupling QCLs to an external cavity and a movable grating enables tuning of the emission wavelength nowadays across a band of 2–3 μm , thereby rendering such devices miniature IR spectrometers from an analytical perspective.^{25,29,30} Albeit to date limited to the shorter wavelengths in the MIR, ICLs are of increasing interest in particular for mobile sensing applications due to their high voltage efficiency (i.e., low power consumption) resulting from interband transitions at type-II heterointerfaces.³¹

Mid-Infrared Waveguides and Transducers

In IR-ATR spectroscopy, the sampling performance and achievable sensitivity is largely determined by the physical and optical properties of the actual sensing element, i.e., the internal reflection element (IRE), fiber optic evanescent wave (FEWS) probe, or the planar waveguide structure in on-chip MIR photonics. Conventional IREs are most frequently made from MIR-transparent crystalline materials such as zinc selenide (ZnSe), zinc sulfide (ZnS), diamond, germanium (Ge), thallium bromo-iodide (KRS-5), and silicon (Si) shaped into multi-reflection ATR rods, trapezoids or similar parallelograms, or single-reflection hemispheres at macroscopic (i.e., mm–cm) dimensions.^{15,32} These ATR crystal materials are complemented by a range of optical fibers transparent at MIR wavelengths including, for example, chalcogenide glasses or polycrystalline silver halides.^{20,33} These optical fibers are available at a length of several meters with diameters < 1 mm down to few hundreds of micrometers. Thin-film waveguides facilitate a waveguide thickness of the order of magnitude of the wavelength (i.e., few micrometers), thus offering the potential on-chip integration, utilizing readily established microfabrication processes for deposition and structuring, and single-mode operation ideally matching the emission characteristics of laser light sources such as QCLs and ICLs. Figure 1 summarizes the MIR transparency of commonly applied waveguide materials prevalent throughout all three generations of MIR waveguides.

Given their MIR transmission window, it is evident why thallium bromo-iodide (albeit nowadays rarely used due to toxicity of the material), zinc selenide, silicon, and germanium are among the most commonly used IRE materials, and in particular among commercially available IR-ATR laboratory accessories. However, besides the accessible spectral window, material parameters including the refractive index, the resulting evanescent field intensity, and potential propagation losses when using extended waveguide geometries have to be taken into account. The most prevalent MIR waveguide materials currently used in evanescent field spectroscopy are color-coded in Figure 1 according to their typical application either as conventional IRE mostly in combination with FT-IR-based spectroscopy (yellow), as optical fiber in fiber optic evanescent field

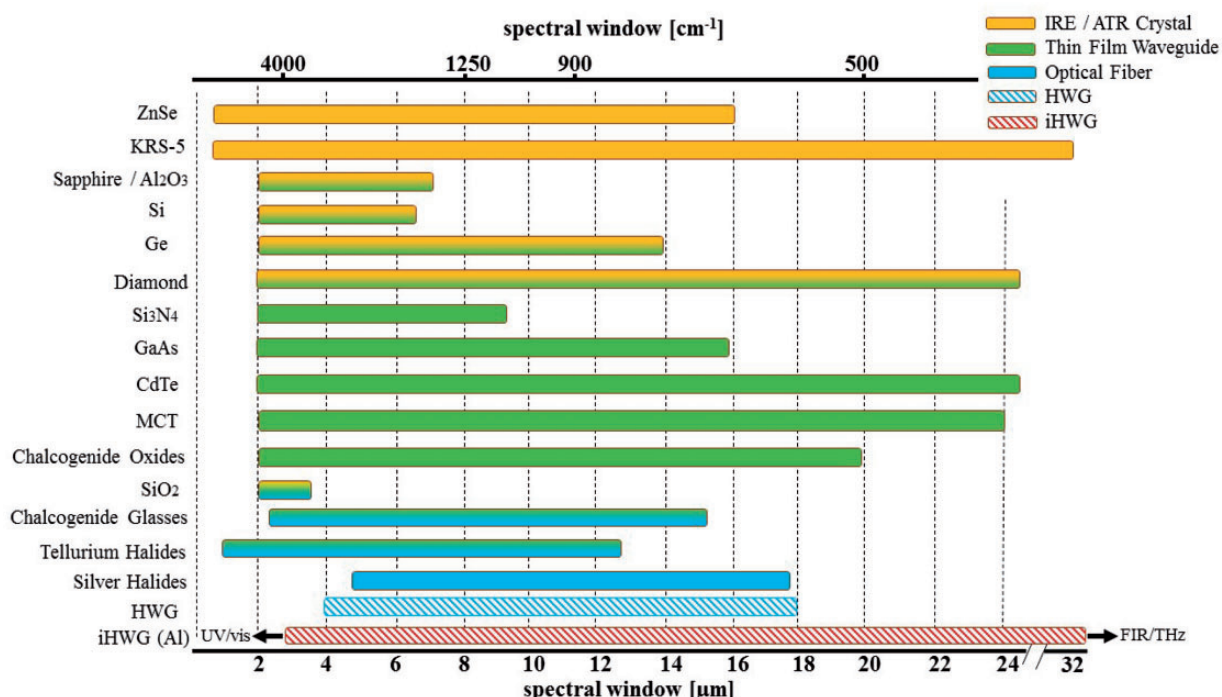


Figure 1. Overview of the most prevalent MIR transmitting waveguide materials color coded as conventional IREs, optical fibers, and thin-film waveguides along with their approximate MIR transmission window. Multicolored materials have been used in two or more configurations (i.e., IRE and/or optical fiber and/or thin-film waveguide or hollow waveguides (fiber optic and integrated types)).

spectroscopy and sensing (FEWS; blue), as thin-film and/or on-chip waveguide material (green), as hollow-core optical fiber (dashed blue), or as “substrate integrated hollow waveguide (iHWG)” (i.e., fabricated within an aluminum substrate) with some materials occurring in two or more representations. Integrated hollow waveguides were most recently introduced by the group of Mizaikoff,³⁴ featuring radiation-reflective hollow waveguide channels enabling transmission from the ultraviolet–visible (UV-Vis) to the FIR-THz regime.

Mid-Infrared Detectors

Probably the most commonly applied detector technology in MIR spectroscopy and sensing utilizes room-temperature, thermoelectrically cooled, or liquid nitrogen cooled (increasing order of detectivity) photoconductive semiconductor detectors comprising detector materials such as indium antimonide (InSb), mercury-cadmium telluride (HgCdTe; MCT), and the like.^{35–37} Alternatively, thermal or pyroelectric detectors are of current interest as they are usually significantly cheaper, operated without cooling, provide a spectral response over a possibly broad MIR wavelength band, and may readily be miniaturized.^{38,39} Adopting the strategy used for QCLs, the same quantum heterostructures may in fact be used as so-called quantum cascade detectors (QCDs) operated without applying a bias voltage⁴⁰ which enables further miniaturization and integration of

MIR sensing platforms.⁴¹ Quantum cascade detectors are therefore interesting alternatives serving as a photovoltaic version of quantum well IR photodetectors.^{42,43} Given the fact that QCDs are passive devices only generating a response signal by propagating incident photons via cascading quantum wells, a significantly reduced power budget of the final sensor system is anticipated.

Focus on Mid-Infrared Waveguides: Fundamentals and Classification

Fundamentals of Evanescent Field Spectroscopy and Sensing

Infrared attenuated total reflection spectroscopy is nowadays considered a routine measurement technique when analyzing strongly absorbing films, pastes, gels, powders, and liquids taking advantage of radiation leaking from the waveguide into the adjacent sample environment (a.k.a. evanescent field) upon total internal reflection at the waveguide–sample interface. Total internal reflection occurs if light is reflected at an incidence angle exceeding the critical angle ($\theta_c = \sin^{-1}(n_2/n_1)$, i.e., Snell’s law) at the interface between a high-refractive-index (n_1 or n_{wg}) waveguiding element and a low(er)-refractive-index (n_2 or n_c) cladding, environment, or sample matrix.⁴⁴ The leaky component of the electromagnetic field (hereon referred to as “evanescent field”) penetrates into the adjacent medium

with an exponentially decaying field intensity characterized as the so-called penetration depth (d_p). For a given wavelength λ , d_p can be approximated as:⁴⁴

$$d_p = \frac{\lambda}{2\pi\sqrt{n_{wg}^2 \sin^2 \theta - n_c^2}} \quad (1)$$

Molecules present within the evanescent field generated at the waveguide/sample may resonantly interact with this evanescent field interface leading to evanescent field absorption spectrum, a.k.a. ATR spectrum, as a result of the attenuation of the propagating radiation at analyte-specific frequencies. Absorption within the evanescent field essentially follows a Beer–Lambert relationship according to:

$$A = (\epsilon cl)r = r \log\left(\frac{I_0}{I}\right) \quad (2)$$

with I_0 as the light intensity before attenuation, I as the intensity after molecular absorption, ϵ as the molar absorptivity, c as the concentration, and r as the fraction of light power residing outside the waveguide.^{3,20} More precisely, absorbance within the evanescent field depends on the square of the product $[E(\partial\mu/\partial q)]^2$, whereby μ is the transition dipole, q is a coordinate normal to the incident plane, and E is the electric field amplitude in the outer medium. Additionally, the absorbance is proportional to the so-called effective penetration depth (d_e) defined as:^{2,45}

$$d_e = \frac{n_{21}}{\cos \theta} \int_0^\infty E^2 dz = \frac{n_{21} E^2 d_p}{2 \cos \theta} \quad (3)$$

with $n_{21} = (n_2/n_1)$, E as the electric field amplitude, d_p as the penetration depth, and z the distance from the waveguide–sample interface. Furthermore, the reflectivity R for a single

reflection is given as:⁴⁶

$$R = 1 - \alpha d_e$$

whereby α describes the absorption coefficient at a given wavelength. Consequently, any number of N multiple internal reflections would result in:

$$R = (1 - \alpha d_e)^N \quad (4)$$

Since usually $\alpha d_e < 1$, it may be safely assumed that the absorbance for N reflections approximately equals N -times the absorption of a single reflection.^{20,45,47} Using such basic geometric considerations when generating an evanescent field, one may readily derive the first generation of MIR waveguides termed “internal reflection elements (IREs)”.

First Generation Mid-Infrared Waveguides: Internal Reflection Elements

Considering the propagation of radiation inside a waveguide for waveguide dimensions significantly larger than the wavelength at the conditions of IRE conditions (i.e., as is the case for conventional IREs), conventional geometric optics result in the emergence of evanescent field spots at each reflection along the IRE surface (Figure 2).

Figure 2 schematically illustrates the influence of the thickness and material choice of the IRE. Considering the IRE thickness (Figure 2a and b), the number of internal reflections scales with the waveguide dimensions for obvious geometric reasons, which should increase the sensitivity of the measurement with decreasing waveguide thickness. However, while reducing the IRE thickness positively affects the sensitivity, the decreasing optical aperture adversely decreases, usually resulting in fewer photons coupled into the IRE; likewise, more internal reflections

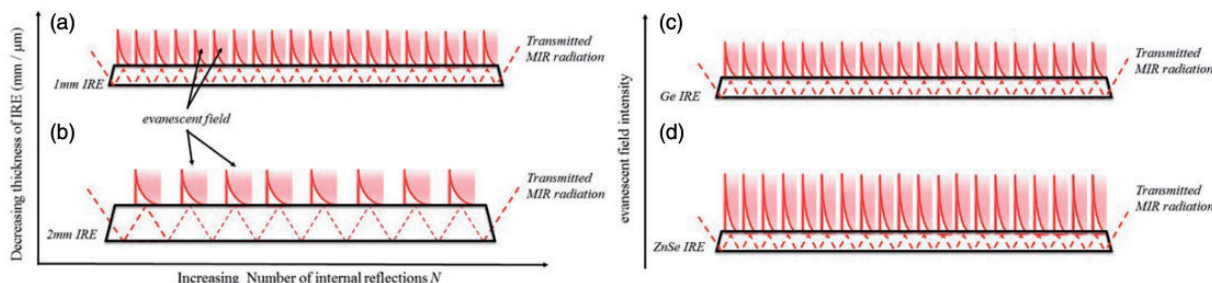


Figure 2. (Left) Schematic representation of radiation propagation inside and the evanescent field at the surface of an IRE featuring (a) a macroscopic multi-reflection IRE (e.g., trapezoid with 1 mm thickness) and (b) an IRE twice the thickness (2 mm) at the same angle of incidence. Albeit not to scale, the increase in density of evanescent field spots responsible for generating the analytical signal (i.e., absorbance) with decreasing IRE thickness is immediately evident. (Right) Schematic increase in penetration depth and thus intensity of the evanescently guided radiation at similar optical conditions for (c) a germanium IRE with a refractive index of 4.06, and (d) a zinc selenide IRE with a refractive index of 2.44. Note that for clarity the evanescent field is only shown at the upper surface of the IRE.

may lead to increased reflection losses. Hence, the signal-to-noise (S/N) ratio will be negatively affected usually requiring more sensitive detectors for compensation.

Conversely, Figure 2c and d schematically illustrates how the selected IRE material (i.e., its refractive index or, more generally, dielectric constant) may affect the penetration depth and intensity of the evanescent field. Decreasing the refractive index of the waveguide material increases the penetration depth, and thus, increases the interaction volume with molecules at the waveguide-sample interface, which positively affects the SNR during absorption measurements.

In summary, it is immediately evident that optimizing the waveguide structure, dimensions, and geometry (i.e., number of internal reflections), along with the optical properties of the waveguide material (i.e., penetration depth of the evanescent field) are major parameters for maximizing the performance and sensitivity in waveguide-based MIR spectroscopy and sensing concepts.

Second Generation Mid-Infrared Waveguides: Optical Fibers

During the past three decades, fiber optic evanescent wave spectroscopy and sensing schemes have emerged as a viable alternative to conventional IREs in absorption spectroscopy, taking advantage of MIR transparent optical fibers as waveguide and actual sensing element.⁴⁸ Evidently, using optical fibers enables extended separation of the actual active sensing interface from the light source and detector, thus facilitating the design of a fiber optic sensor for in-situ experiments. Given the length of optical fibers

(i.e., several meters for MIR fibers at acceptable attenuation losses) and their mechanical flexibility, the main advantage versus first generation waveguides is the opportunity of robust light guiding and sensing in remote application scenarios (i.e., “guiding photons to the sample rather than bringing the sample to the spectrometer”). Next to fine-tuning of the fiber thickness, surface, and radiation in-/out-coupling facets, the active sensing region of the fiber (where the fiber serves as evanescent field sensing element interacting with sample molecules upon immersion) may be tailored. For example, the interaction length may be significantly extended versus conventional IREs (e.g., “spiraling” of the fiber; see Figure 3b) or the fiber geometry may be designed for maximizing the number of internal reflections within the sample interaction length by symmetrically tapering (e.g., etching, pulling, or thinning a cylindrical segment) or flattening the fiber core (see Figure 3c). Furthermore, due to its rotational symmetry (Figure 3a), usually the entire evanescent field surrounding the fiber is used for generating the absorption signal as the fiber may readily be sealed as a suspended IRE within a flow-through cell, whereas conventional IREs usually utilize only one side of the waveguide for the actual measurement (i.e., with the exception of macroscopic ATR rods).

A variety of theoretical models based on simple geometric optics or advanced electromagnetic field theory have been used for describing radiation propagation along fiber optic waveguide structures in great detail.⁴⁹ The advances of FEWS in terms of portability and the potential for remote sensing applications constitutes the main breakthrough of fiber optic-based spectroscopic sensors versus the application of conventional IRE-based devices with

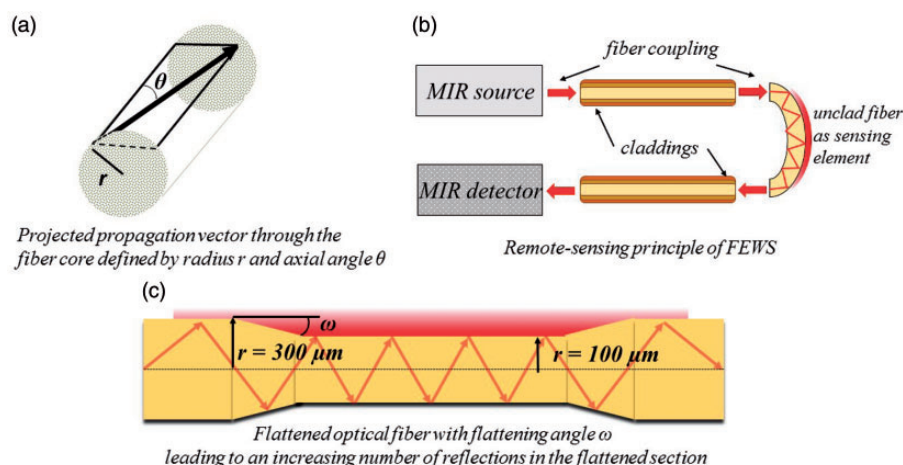


Figure 3. Schematic examples for fiber optic evanescent field sensing concepts. (a) Vector representation of radiation propagation inside a fiber optic waveguide. Here, the evanescent field is generated along the propagation vector throughout the fiber core (in all three dimensions). (b) Remote sensing via FEWS with MIR radiation propagating, e.g., along core-clad optical fibers generating an analytically useful evanescent field (i.e., accessible by sample molecules) only along the unclad active sensing region at a distance from light source or spectrometer and detector. (c) Tapering or flattening of the fiber core within the active sensing region leads to an increased number of internal reflections as a consequence of the reduced waveguide thickness and the tapering angle ω .

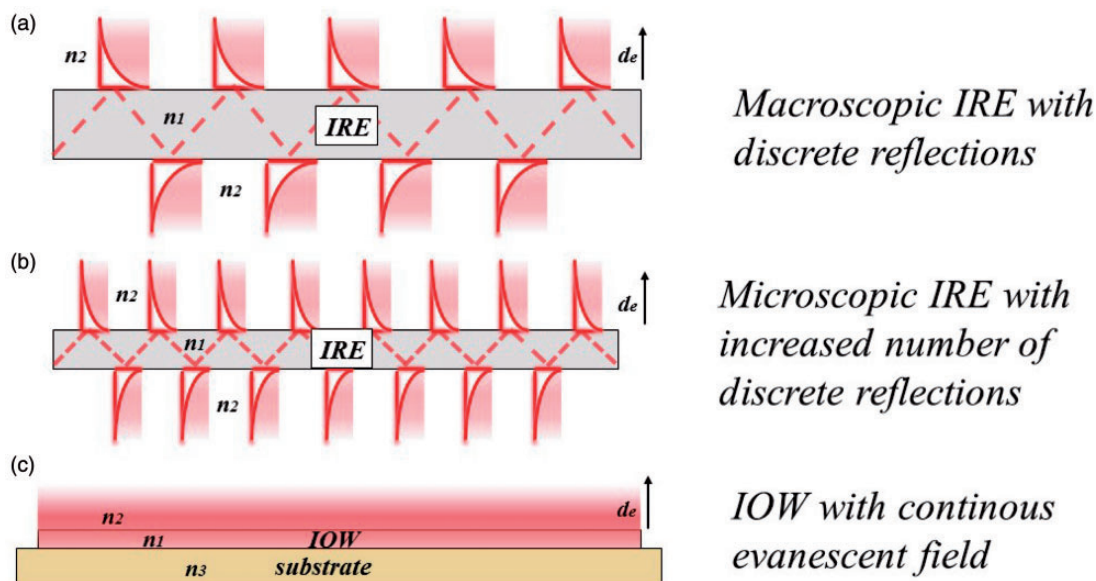


Figure 4. Schematic representation of evanescent wave/field and radiation propagation with decreasing thickness of the IRE (a, b) leading to integrated optical waveguides (IOW) providing a continuous evanescent field leaking into the adjacent environment (c).

applications ranging from determining chemical reaction rates,⁵⁰ to gas detection⁵¹ and biosensors.⁵² However, to date such transducers remain predominantly coupled to commonly applied FT-IR spectrometer systems.

In order to improve the achievable sensitivity, tapering and flattening of fiber optic waveguides has been applied, albeit limited to a thickness of usually few tens of micrometers of the tapered active sensing element, as the thinned section is of increasing mechanical fragility. Hence, real-world application scenarios usually abstain from using tapered fibers in chem/bio sensing. Likewise, while in principle possible, it is of little practical value to taper fibers to a thickness on the order of magnitude of the wavelength (i.e., $<20\ \mu\text{m}$) for achieving single-mode radiation propagation behavior. Consequently, the advent of advanced MIR laser light sources such as QCLs and ICLs demanded a third generation of MIR waveguides: thin-film planar waveguiding structures.

Third Generation Mid-Infrared Waveguides: Thin-Film Waveguides

As discussed so far, the thickness of most conventionally applied waveguides significantly exceeds the order of magnitude of the propagated wavelength. As the number of reflections is inversely proportional to the thickness of the IRE, thinning the waveguide to dimensions corresponding to the wavelength increases the effective absorption path length until ultimately a uniform evanescent field is obtained extending along the surface of such core-only waveguide structures, which may lead to substantial sensitivity enhancements.⁵³

Since light propagation within such thin-film waveguides may no longer be adequately described via a series of internal reflections, the generated continuous evanescent fields are represented via more sophisticated models based on wave analysis. Waveguides realized at these dimensions are commonly referred to as thin-film waveguides or integrated optical waveguides (IOWs).

Hence, without being discussed here in detail, rather focusing on the analytical and applied spectroscopic aspects, parameters such as mode confinement, lateral distribution of the radiation in various modes (i.e., TE, TM, etc.), etc. lead to the fact that IOWs facilitate significant increases enhancements of the evanescently guided field intensity and penetration depth, thereby enabling specifically tailoring waveguide structures to selected applications. However, it should be noted that most commonly such thin-film waveguide structures are deposited at and mechanically supported by suitable (i.e., refractive index matched) substrate materials, with the possible exception of sufficiently robust free-standing thin-film diamond waveguides, thus providing only one surface of the waveguide for active sensing purposes.

Recent Trends and Selected Applications

Given that extensive literature has been published on conventional IREs and MIR transparent optical fibers, and applications thereof,^{3,20} this review focuses predominantly on recent trends in both waveguide technology and applications that have emerged during the last decade. Most condensed materials by nature of their inherent structure reveal vibrational transitions limiting their MIR transparency.

Hence, semi-conductors of different compositions appear most suitable for providing sufficient transmittance in the electromagnetic spectrum of interest and for establishing tailorable waveguiding platforms. Among the fabrication techniques, drawing or growing optical fibers next to chemical vapor deposition (CVD) for planar waveguide structures (i.e., IREs) remain among the most commonly applied fabrication processes for MIR transparent waveguides.⁵⁴

With the emergence of third generation thin-film waveguides and integrated MIR optics, techniques initially developed predominantly for silicon-based microfabrication are increasingly being adopted for the development of miniaturized MIR sensing platforms (a.k.a. MIR on-chip device technology). Processing techniques including UV photolithography, electron beam patterning, (hot) embossing, and so on facilitate rapid and straightforward processing even of sophisticated optical device designs.⁵⁵ Simple IOWs comprising strip or rib waveguide structures of a higher refractive index n_1 , most commonly semi-conductor, material are locally deposited on top of a suitable substrate (i.e., usually wafer-based substrates with any number of strain and/or refractive index matching additional interface layers) with a lower refractive index n_2 . Alternatively, previously deposited waveguide films are etched after lithographic structuring (e.g., wet etching, reactive ion etching, etc.) readily

creating three-dimensional linear waveguide structures or more sophisticated optical geometries (e.g., ring-, disc-, or racetrack-shaped resonators) with precise control on the desired dimensions.

Evidently, current trends in waveguide-based MIR applications increasingly take advantage of waveguides as an active transducer, rather than merely serving as a radiation propagation conduit. From an analytical spectroscopy perspective, this is an essential—if not the most essential—function, as the transducer plays the major role within optical sensor systems in generating the actual analytical signal by ensuring reproducible intimate interaction between photons and sample constituents (i.e., conversion of chemical, biochemical, or biological processes or recognition events into changes of optical properties). While nowadays optical chemosensors increasingly take advantage of the distinctive molecular signatures generated in the MIR regime, only few representative examples of optical biosensors operating in the MIR have been published. This may be attributed to the fact that, with few recent exceptions, the sensitivity of first generation waveguides (i.e., conventional IREs) and even second generation fiber optic-based liquid phase MIR sensors remains insufficient for detecting: (1) small quantities of relevant biomolecules such as, for example, proteins or DNA; and (2) in

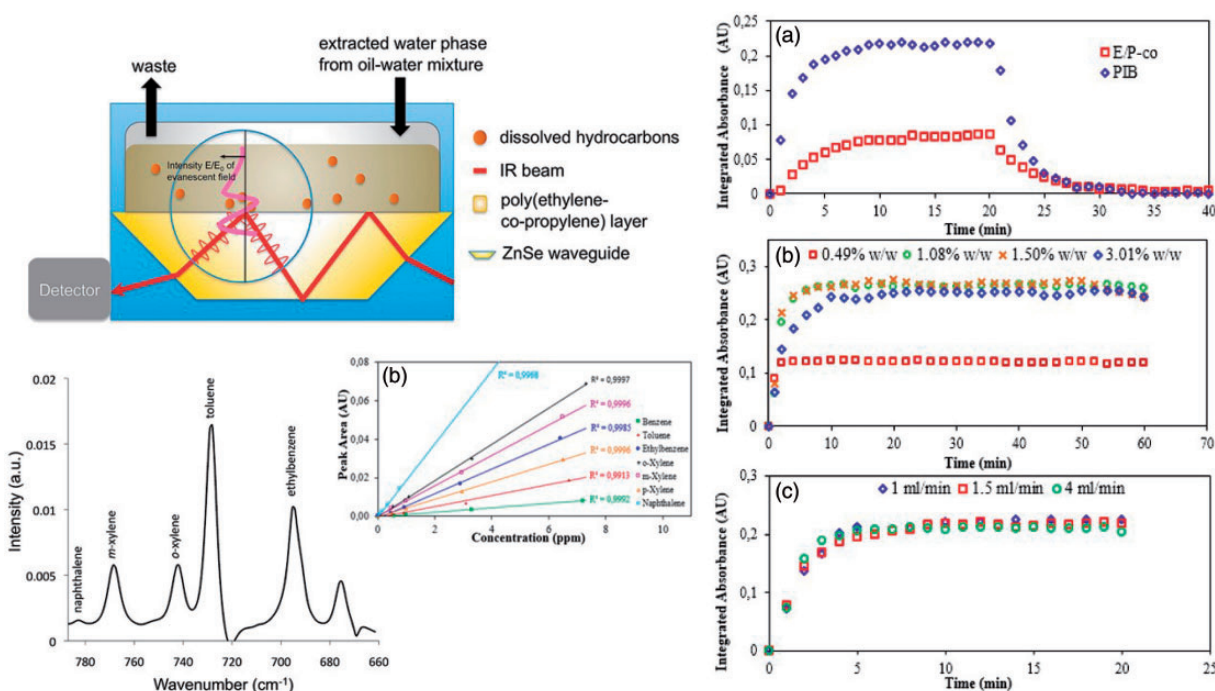


Figure 5. (Top left) Schematic of IR-ATR system comprising a macroscopic ZnSe IRE coated with a polymeric enrichment membrane for detecting organic pollutants in marine environments (i.e., dissolved oil fingerprinting via characteristic VOC patterns dissolved in the aqueous phase). (Bottom left) Characteristic absorption patterns of dissolved hydrocarbons detected via IR-ATR evanescent field absorption spectroscopy after enrichment within a suitable polymer membrane. (Right) Analytical response of a polymer-coated diamond IRE in aqueous solution at a contaminant concentration of 50 ppm (p-xylene). Adopted and reprinted with permission from ACS Publishing, 2014/2015.^{32,57}

appreciable small volumes (i.e., microliter regime). In contrast, limited sensitivity of MIR chemosensors is readily mitigated by using, for example, solid phase enrichment schemes via immobilization of appropriate polymer, sol-gel, or similar membranes directly at the waveguide surface acting as in-situ enrichment membranes; a strategy applicable for conventional IREs, fiber optic transducers, and IOWs. Thereby, detection levels in the parts per billion (i.e., $\mu\text{g/L}$) concentration range have been realized in a true chemical physico-chemical sensing format (i.e., diffusion of analyte molecules into and out the solid phase membrane in lieu of chemical reactions). Using such membranes, IR-ATR-based chemosensors have been developed serving for environmental contaminant monitoring,^{32,56} in pollutant analysis,^{11,57,58} and even in microbiological applications,⁵⁹ as exemplarily illustrated for detection of volatile organic components (VOCs) towards dissolved oil fingerprinting in aqueous/marine environments (Figure 5).

After optimization, the application of conventional IR-ATR techniques using membrane-coated macroscopic IREs revealing characteristic concentration patterns of dissolved VOC fractions assignable to different oil contaminations at trace levels has been shown.^{32,56} Obtaining such low detection limits for relevant pollutants supports the potential of MIR sensors for in-situ analyses and monitoring purposes. Nevertheless, in-field applications require a significant scaling of involved instrumentation for facilitating, for example, on-ship studies. Given ongoing progress in miniaturized MIR waveguide technology, light sources, and

detectors, it is anticipated that waveguide-based IR sensing systems for in-situ and in-field monitoring (e.g., in marine environments) are within reach.

As a consequence, more compact MIR sensor systems utilizing ATR sensing concepts are predominantly focusing on miniaturizing the actual MIR transducer as well as the entire instrument, yet maintaining the sensitivity via improved chem/bio recognition architectures. Giammarco et al. proposed a method combining an innovative multi-layered coating with ATR waveguide technology.⁶⁰ The established enrichment polymer film had a thickness of only 27 nm, and was capable of extracting a variety of constituents for determination via the evanescent field emanating at an IRE surface (Figure 6).

Here, an advanced architecture that comprised a multi-layer nanostructured polymer film was immobilized at the surface of the MIR transducer, which represents a straightforward and robust approach for the fabrication of nanocoatings at IR-ATR waveguide surfaces. Due to the multi-layer nature of the membrane, a variety of components may be enriched from aqueous and vapor phase samples directly at the waveguide surface facilitating analysis via evanescent field absorption.

In FEWS, the group of Katzir and Raichlin is among the pioneers of evanescent wave spectroscopy using silver halide (AgClBr in various compositions) optical fibers. These polycrystalline fibers are mechanically flexible and malleable materials with a wide MIR transmission window and therefore lend themselves for various tapering

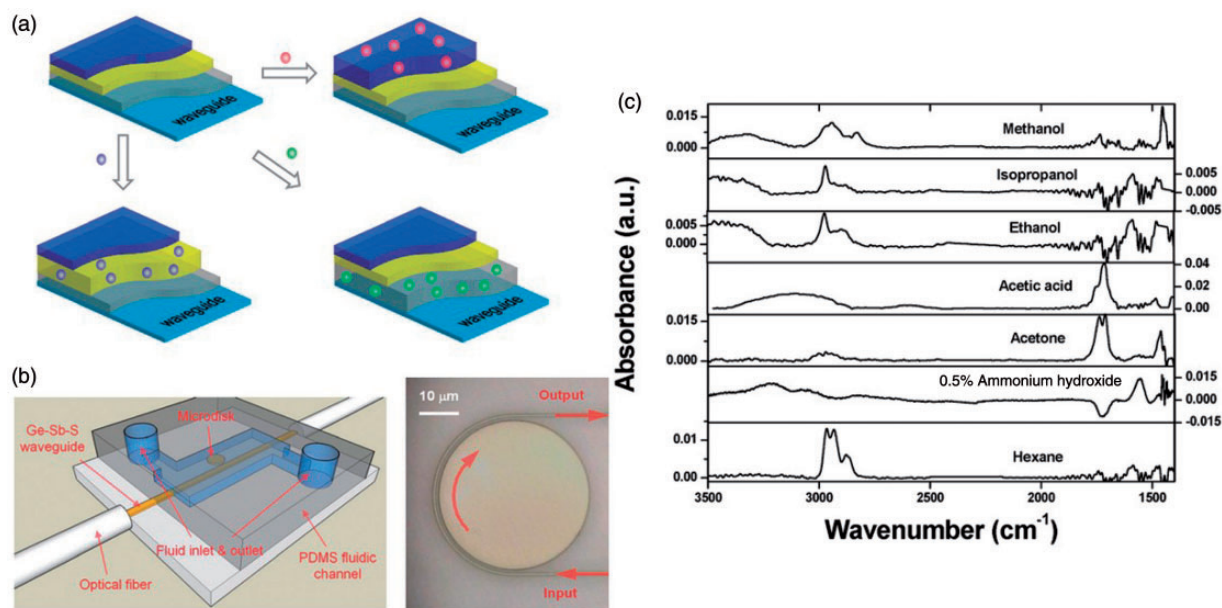


Figure 6. (a) Schematic illustrating the interaction of a multi-layered enrichment coating with various analytes. (b) Schematic of the micro-disc-on-chip system (left), and top view image of a micro-disc resonator in a pulley-coupler configuration (right). (c) Infrared attenuated total reflection spectra of various analyte vapors detected using the multi-layered enrichment coating deposited at a Si crystal waveguide surface. Reprinted with permission from RSC Publishing, 2011.⁶⁰

procedures. For example, a central section of the fiber may be flattened to a thickness of approximately 100 μm at a length of 1–5 cm width of several millimeters.⁶¹ By adjusting the length and angle of the section leading into the flat tapered segment, the angle of incidence during propagation of the radiation within the fiber core may be tailored such that maximum penetration depth and number of reflections

is achieved, thus maximizing the achievable analytical sensitivity of such fiber optic transducers. Raichlin et al. recently reported evanescent wave spectroscopy using flattened fibers for detecting micrograms of insoluble hormones and explosives (Figure 7). Following their increasing usage in medication, contraceptives, agriculture, and so on, hormones are considered among the most relevant emerging

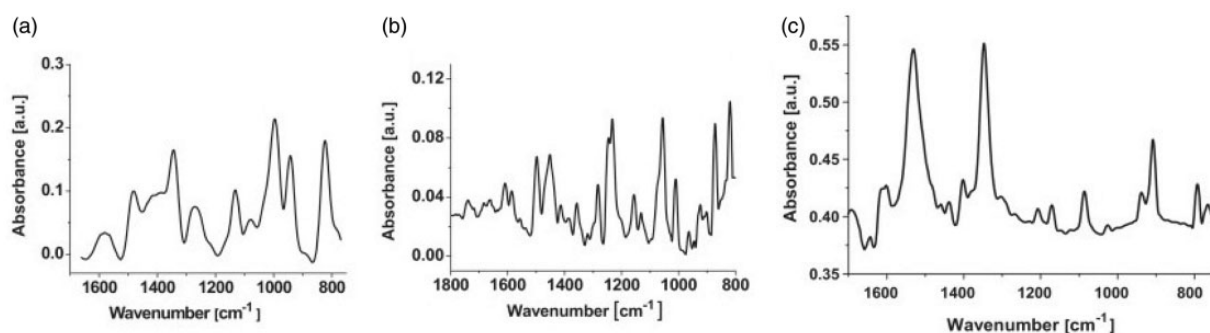


Figure 7. (a) Exemplary spectrum of β -estradiol obtained via a silver halide fiber optic sensor system. (b) Spectrum of dry powder β -estradiol determined via a commercial IR-ATR (i.e., diamond IRE) system and a FT-IR spectrometer. The dry powder was pressed onto the prism-shaped diamond ATR element. (c) Fiber optic evanescent wave measurement of an explosive (TNT).⁶¹ Reprinted with permission from Elsevier, 2014.

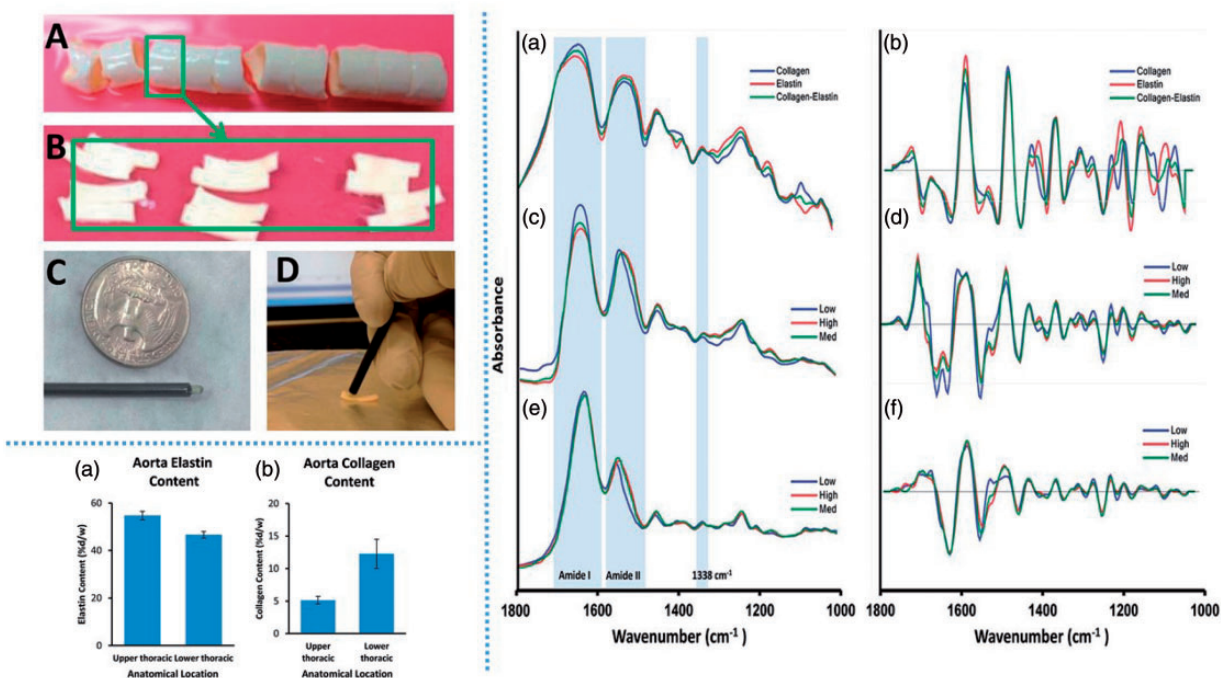


Figure 8. (Top left) (a, b) Aorta samples prepared as open rings of a few centimeters in length. (c) Custom fiber optic sampling tip for IR-ATR data collection next to a US quarter dollar coin for size comparison. (d) Actual data collection from an aorta sample. (Bottom left) Elastin and collagen content within aorta samples at different anatomical locations. (Right) Average spectra of samples with low, medium, and high elastin content. (a) Reference spectra of collagen–elastin recorded via conventional transmission spectroscopy. (c–e) Fiber optic spectra of collagen–elastine and their second derivatives (b, d, f).⁶² Reprinted with permission from RSC Publishing, 2014.

microcontaminants of environmental concern, due to their adverse effects on animal and human health (e.g., endocrine disrupting effects, etc.). Forensic applications⁶¹ of MIR FEWS are increasingly adopted via detecting explosive residues at crime scenes and for implementing potential screening strategies in airport security.

For biological applications, the Pleshko group recently reported a fiber optic method quantifying collagen and elastin at an in-vitro model of extracellular matrix degradation processes in aorta samples.⁶² The extracellular matrix is a key component and regulator within a wide variety of biological tissues. The aorta is the major blood vessel responsible for blood circulation, and aortic diseases have emerged among the leading causes of death in developed countries. A custom-made optical fiber probe based on a silver halide sampling tip mounted at the end of a 1 m long silver halide fiber was connected to a commercial spectrometer, thereby generating an ATR sampling tip with a length of 15 cm and a diameter of 3 mm, as illustrated in Figure 8.

This methodology enabling identifying collagen or elastin in aortic tissue is an interesting and promising approach for studying changes of extracellular matrices in different aortic

diseases with minimal preparation compared to common histological or immunohistochemical methods. In addition, a multivariate calibration model was presented for automatically quantifying elastin within intact aortic tissue via the MIR fiber optic probe.

Such studies clearly illustrate that, besides the development of advanced thin-film MIR waveguide technologies, MIR transparent optical fibers remain of substantial utility for identifying and quantifying organic, inorganic, or biological constituents and their chemical properties. Hence, FEWS methods remain a viable alternative in IR-ATR spectroscopy and sensing due to usually straightforward optical configurations, reduced cost versus conventional IREs, a minimal requirement on sample preparation and processing. In addition, small sample quantities and areas may be addressed, which is of particular interest in biomedical applications, whereas the sensitivity of such fiber optic probes lends itself to applications in environmental protection/monitoring, drug enforcement, and homeland safety/security.

Among the already limited set of MIR transmitting materials applicable for fabricating fiber optic waveguides, there is an even more limited selection of materials useful

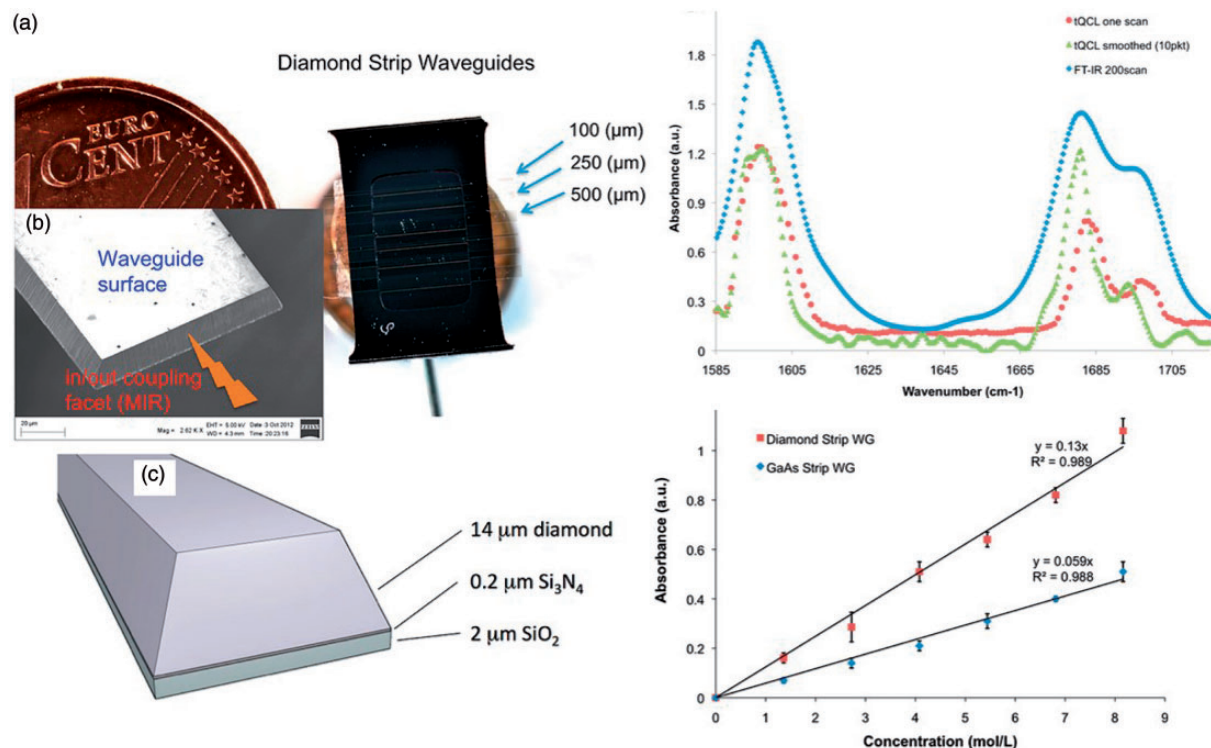


Figure 9. (Left) Diamond strip waveguides (DSWGs) grown at a passivated silicon wafer substrate. (a) Microfabricated free-standing diamond waveguides with a series of strip widths (100–500 μm) compared in size to a Euro one cent coin. (b) Scanning electron microscopy image at the in/out-coupling end facet for a 100-μm wide waveguide with a thickness of 14 μm representing the actual free-standing waveguiding strip. (c) Schematic of the thin-film diamond waveguide structure on top of the substrate layers. (Right) Infrared absorption spectra of anisaldehyde and chemical response of the sensor recorded with a tunable QCL after deposition at the surface of a thin-film diamond waveguide and comparison of the IR-ATR spectrum recorded using a conventional FT-IR spectrometer averaging 200 spectra is shown. Reprinted with permission from ACS Publishing, 2014.

for establishing on-chip thin-film waveguide structures. In addition, using semi-conductor materials for chem/bio sensors has to consider their chemical robustness in terms of, for example, high (or low) pH values, elevated temperatures, mechanical stress, and so on. Yet, the emergence of advanced QCL and ICL light sources demands for frequency-matched waveguide layers and structures for fully unlocking the potential of these almost ideal light sources.

Therefore, besides the rather excellent transparency throughout a broad wavelength window, diamond has emerged as a most interesting option also for MIR waveguide structures. Nowadays, diamond fabrication is predominantly performed via chemical vapor deposition (CVD)⁶³ at low-pressure-high-temperature conditions (LPHT), because of the metastable transition of diamond to graphite at high temperatures. However, LPHT requires expensive equipment and experience in the fabrication process, lacks in reproducibility when processing of large numbers of samples. As a result, LPHT annealing remains a unique technique available only at few laboratories and companies for research and small-scale production.⁶⁴ Yet, methods for thermally etching diamond have been reported in recent years,⁶⁵ which facilitate processing of miniaturized diamond structures. An example of these established free-standing diamond strip waveguides (DSWGs) and their potential utility for chemical sensing is illustrated in Figure 9.

This sensing application clearly demonstrates the potential optical/analytical performance for evanescent field sensing using diamond as an advanced waveguiding layer, which might be among the key developments for enabling highly miniaturized MIR optical sensing platforms in combination with appropriate tunable QCLs or ICLs. Considering the generally already achieved level of miniaturization/integration of other wavelength optical devices (i.e., in the NIR and UV-Vis wavelength regime), the opportunities for MIR

chemical sensors/biosensors upon appropriate miniaturization are immediately evident towards molecularly selective MIR diagnostics. Following this route, further structured waveguides offer opportunities for further miniaturizing and integrating optical components into possibly small devices, yet offering comparable results in terms of analytical sensitivity and reproducibility versus laboratory-based spectroscopic MIR analyzer systems. For example, a three-times higher SNR value was shown by the research group of Mizaikoff⁶⁶ using diamond strip waveguides combined with QCL light sources versus commercial FT-IR spectrometers. Because of the outstanding robustness of diamond even at harsh environmental conditions, as well as its intrinsic biocompatibility, diamond has excellent prospects to emerge as the most interesting material for next-generation on-chip MIR chem/bio sensors combined with QCL and ICL light source technologies.

Another promising group of materials for thin-film-based MIR sensors are the chalcogenides, i.e., mixtures containing S, Se, As, and Te, which are commonly known for their broad optical transparency and high refractive index in optical fiber technology (i.e., second generation waveguides). Several chalcogenide material compositions are also being applied for fabricating thin-film waveguides taking advantage of the high refractive index contrast between the chalcogenide layer and a suitable substrate. For example, using GeTe₄ as a waveguiding core layer at a ZnSe substrate with respective refractive indices of 3.34 and 2.43 (at 3.5 μm), a suitable optical density contrast can be generated between core and substrate, thus increasing the intensity of the evanescent field yielding high surface sensitivity at the waveguide/analyte interface. Using these materials, channel waveguide structures have been realized in the 2.5–3.7 and 6.4–7.5 μm spectral region.⁶⁷ The research group of Mittal et al. recently reported a convenient fabrication method for

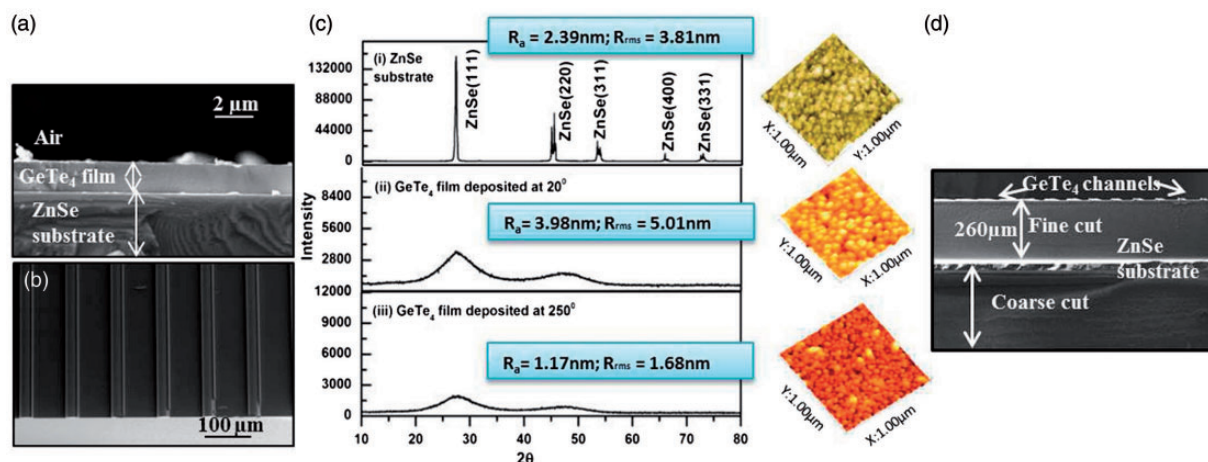


Figure 10. (a) SEM image of a cleaved cross-section of GeTe₄ film as deposited ; (b) top view of GeTe₄ channels fabricated by lift-off techniques; (c) X-ray diffraction pattern and atomic force microscopy image of the ZnSe substrate and the GeTe₄ films. (d) Distal coupling facet of the waveguide cut by ductile dicing.⁶⁷ Reprinted with permission from The Optical Society Publishing, 2015.

such waveguide structures using sputtering and lift-off techniques to realize GeTe₄ waveguides on ZnSe substrates later applied in evanescent field sensing (Figure 10).

The reported thin-film waveguides were found to be amorphous in nature with an average surface roughness <4 nm providing MIR transparency in the spectral range of 2–20 μm , while actual waveguiding was demonstrated in the 2.5–3.7 μm and 6.4–7.5 μm regime. While single-mode behavior is desired for most biochemical sensing experiments, the reported GeTe₄ channels revealed multimode behavior for the given wavelength ranges. However, the authors state that a multimode waveguide design was selected on purpose in order to establish waveguiding also at longer wavelengths (i.e., up to 12 μm) ensuring sufficient coupling efficiency via commercially available single-mode fibers. In future, the applied materials and fabrication techniques may readily be adapted to achieve single-mode behavior.⁶⁷ Incidentally, the combination of thin-film channel waveguides and MIR optical fibers as coupling elements also highlights that these waveguide technologies are not mutually exclusive, but may even be combined to the advantage of the selected application scenario.

Conclusions and Future Perspectives

Classifying MIR waveguide technologies into three generations facilitates documenting the evolution and progress in waveguide technology towards compact, robust, and portable MIR analyzer systems and sensors. The coexistence of these waveguide technologies—now and in future—is certainly a result of the fact that broadband emitters (e.g., as used in conventional FT-IR spectrometers) as well as highly collimated laser light sources (e.g., QCLs, ICLs) enable and facilitate complementary measurement scenarios, and will therefore continue to be developed in parallel rather than replacing each other. Hence, it is anticipated that IR-ATR measurements based on conventional macroscopic IREs will remain prevalent next to thin-film waveguide-based sensing systems addressing analyses in minute sample volumes and at exceptionally low concentrations. Clearly, innovative optical approaches and advancements in integrated optics and photonics will lead to further miniaturized, more versatile, and ideally, but not necessarily, to more efficient and sensitive MIR spectroscopic, sensing, and diagnostic platforms operated at in-field conditions and with trace-to-ultratrace detection limits.

Although the major breakthrough in MIR sensor technology during the past two decades is certainly attributed to the introduction of advanced laser light sources including QCLs and ICLs, it is the actual development of matching waveguide technologies serving as MIR transducers that has been the major driving force towards the analytical applicability of advanced IR sensors and measurement systems. With the recent emergence of on-chip semi-conductor waveguides, the path towards integrated MIR photonic

systems (i.e., “IR-lab-on-a-chip” systems) is evidently paved and promises a wide variety of innovative label-free sensing and assay concepts. Finally, with the introduction of more sophisticated optical structures for on-chip waveguides and waveguide-linked technologies including optical resonators, optical couplers, and optical amplifiers along with increasingly complex chem/bio recognition schemes, it is clearly evident that with the advancements discussed herein we are only seeing the beginning of an entire generation of MIR chem/bio sensing and assay devices that will continue to push the envelope in terms of size, cost, and sensitivity.

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Conflict of Interest

The authors report there are no conflicts of interest.

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