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A MID-INFRARED SENSOR FOR MONITORING OF CHLORINATED HYDROCARBONS IN THE MARINE ENVIRONMENT

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As part of the European research project SOFIE – “Spectroscopy using Optical Fibres in the Marine Environment”, a portable sensor system for chlorinated hydrocarbons in seawater is being developed. This novel analytical tool for real-time in-situ monitoring of a particularly important class of seawater pollutants consists of a robust, miniaturised FT-IR spectrometer in a sealed aluminium pressure vessel and a fibre optic sensor head. In a laboratory set-up using an ATR-crystal as a simplified sensor head, the effect of potentially interfering substances, both of natural and anthropogenic origin, on the sensor response was tested. It was found that the sensor readings for a specific analyte are not susceptible to aliphatic and aromatic components as well as other chlorinated hydrocarbons up to concentrations well above the average levels to be encountered in the oceans. The same applies for the parameters salinity and turbidity. Consequently, the proposed sensor system should be well suited for real-world sub-sea applications.

Keywords: Optical chemical sensor; mid-infrared evanescent wave spectroscopy; Fourier transform infrared (FTIR) spectroscopy; continuous marine monitoring; chlorinated hydrocarbons

INTRODUCTION

The increasing number of environmentally relevant marine pollutants and the limited number of methods available for continuous analysis create a considerable demand for rapid, specific and inexpensive analytical methods, preferably sensors. An important group of analytes in water analysis are chlorinated hydrocarbons (CHC's). They are toxic chemicals and generally regarded as particularly

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significant indicators for urban pollution. Consequently, they are listed in the EC council directives dealing with priority water pollutants ^[1, 2].

Currently, the determination of chlorinated organic compounds in water relies largely on chromatographic methods, mainly GC and HPLC. These methods are highly sensitive and substance specific. Common to these methods is the need for discontinuous sampling and subsequent analysis in an appropriately equipped laboratory. This imposes several disadvantages: (i) high time consumption, (ii) considerable expenses, both for instrumentation and operation, (iii) confinement to laboratory conditions and (iv) significant sampling errors due to the volatile nature of most CHC's. In addition, sampling may provide misleading results, due to the random nature of point sampling. When measuring in coastal waters with high temporal and spatial variations of concentrations, or when combining analytical results with hydrodynamic data to calculate pollution spreads, this is a key issue. Consequently, the development of continuously operating *in-situ* sensing systems aiming at specific and sensitive monitoring of CHC's has been assigned increasing importance during the last years.

Of all physico-chemical transducer principles, optical sensors are best suited for the harsh conditions to be encountered in the oceans. They remain unaffected by electric or electromagnetic interferences and are both chemically and mechanically robust.

While most optical sensors use quartz or silica fibres and (bio)chemical reactions to provide the necessary specificity, the set-up proposed here uses fibre materials transparent in the mid-infrared region of the electromagnetic spectrum ($2.5\ \mu\text{m} - 25\ \mu\text{m}$, $4000 - 400\ \text{cm}^{-1}$). Thus, it is possible to directly evaluate the strong, well-structured absorption bands caused by the excitation of fundamental vibrational states of the analyte molecules ^[3]. This results in a simple and robust sensor system with inherent molecular specificity, especially when evaluating IR absorption bands in the fingerprint region of the spectrum ($8 - 25\ \mu\text{m}$, $1250 - 400\ \text{cm}^{-1}$). During the last years, our research group developed the basics of such a sensor system for volatile organic compounds in water, based on silver halide ($\text{AgBr}_x\text{Cl}_{1-x}$) fibres ^[4, 5, 6]. Other research groups have developed a similar approach ^[7, 8, 9]. In contrast to these efforts, this work focuses on the measurement in seawater and the evaluation of possible artefacts due to seawater constituents. The development of such a ready-to-use sensor system for marine monitoring is supported by the European Union as part of the European research project SOFIE – “Spectroscopy using Optical Fibres in the Marine Environment” (MAS3-CT97-0157) ^[10, 11].

MID-INFRARED SPECTROSCOPY USING OPTICAL FIBRES IN THE MARINE ENVIRONMENT (IR-SOFIE)

Sensor principle

Fibre evanescent wave spectroscopy (FEWS) is, like attenuated total reflection (ATR), a technological application of internal reflection spectroscopy (IRS), which was first described in detail by Harrick ^[12].

Radiation hitting the interface of two dielectric media, with refractive indices n_1 and n_2 ($n_1 > n_2$), from the optically denser medium at an angle of incidence larger than the critical angle θ_c , is totally reflected back into the optically denser medium. The interaction of the incident and the totally reflected light forms an evanescent field, which to a certain extent penetrates the optically thinner medium, as schematically depicted in Figure 1.

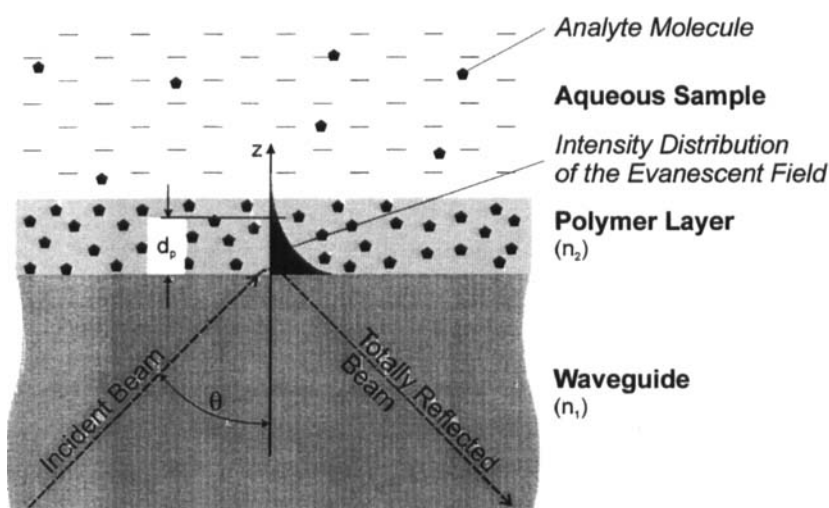


FIGURE 1 Polymer coated ATR crystal for evanescent wave measurements. The hydrophobic analytes are enriched inside the polymer layer and therefore interact with the evanescent field, while water and hydrophilic components are excluded. (n_1 : refractive index of the waveguide, n_2 : refractive index of the adjacent medium, $E(z)$: intensity distribution of the evanescent field perpendicular to the interface, θ : angle of incidence, d_p : penetration depth)

In a simplified way, all molecules within the information depth of the evanescent wave are able to absorb light from the evanescent field at their specific absorption wavelengths. Consequently, the radiation detected at the end of the

optical waveguide shows an absorption spectrum very similar to standard absorption spectra. Differences occur in the relative band intensities, as the penetration depth d_p is dependent on the wavelength of the incident light, as well as on the refractive indices n_1 and n_2 and the angle of incidence θ , according to Equation 1. The penetration depth is typically in the order of magnitude of the wavelength of the incident light.

$$d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2 \theta - n_2^2}} \quad (1)$$

The key value characterising IRS based sensors is the so-called cumulative penetration depth. This value is directly proportional to the penetration depth d_p , the number of total internal reflections per length unit and the length of the sensing fibre. In order to maximise the sensitivity, these parameters have to be optimised.

For sensing applications of trace components, especially in strongly IR absorbing matrices like water, it is essential to coat the sensor surfaces with (chemo)selective layers. In the present case, a thin layer of a hydrophobic polymer, as shown in Figure 1, fulfils this role.

The thickness of the polymer approximately matches the information depth of the evanescent field. While the hydrophobic CHC's readily enrich in the polymer, water is effectively excluded. Simultaneously, the waveguide is protected from corrosive components of the sample. The application of such a polymer coating on the waveguide enhances the sensitivity of the sensor by several orders of magnitude in comparison to non-coated sensors. However, a longer response time due to the introduction of a diffusion layer has to be taken into account.

Sub-sea instrumentation

The main obstacle for sensor applications in the marine environment is the severely limited possible length of the mid-IR waveguides. The high attenuation of silver halide fibres (0.5 – 1 db/m @ 10.6 μm) effectively prohibits the utilisation of fibres with lengths of several 100 metres, as would be necessary for marine monitoring and profiling. Hence, the FT-IR spectrometer must be modified to make it operational under marine conditions, both in costal waters and on the high seas down to depths of 300 metres.

The spectrometer prototype developed for this purpose is depicted in Figure 2. All parts are contained inside a sealed cylindrical pressure body made from hard-anodised aluminium. The design is based on a Bruker Vector 22 FT-IR spectrometer, which, by virtue of its design, is able to withstand rocking movements.

All spectrometer parts are mounted on one optical bench, which is connected to the hull via vibration damping elements. An optical glass-fibre telemetry system between the spectrometer and the on-board or on-shore computer station has been implemented for bi-directional data transfer and operation control.

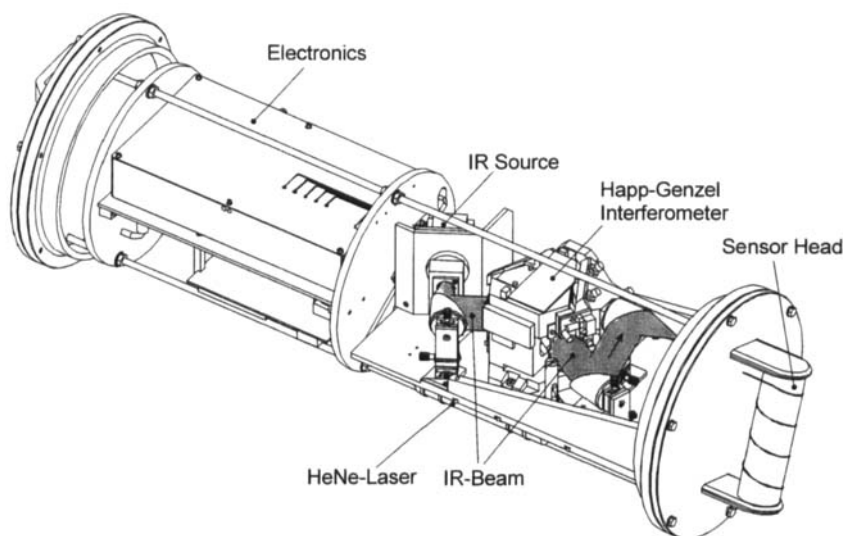


FIGURE 2 Design drawing of the underwater FT-IR spectrometer with parts of the pressure body removed. (technical data: inner tube diameter: 250 mm, maximum outer diameter: 308 mm; overall length: 1060 mm; power supply: 230 V AC, 50 Hz, < 0.6 A; glass fibre telemetry system)

EXPERIMENTAL

While a number of different sensor head geometries are currently under investigation ^[13], an ATR crystal as the simplest available geometry for evanescent wave spectroscopy was chosen for the laboratory experiments.

Chemicals

Artificial seawater (ASW) was prepared by dissolving 28.0 g NaCl, 7.0 g MgSO₄·7H₂O, 5.0 g MgCl₂·6H₂O, 2.4 g CaCl₂·6H₂O and 0.2 g NaHCO₃ (all analytical grade) in 985 ml of deionised water ^[14]. Alternatively, a standard salt mixture for seawater aquaria (*Instant Ocean*[®] by Aquarium Systems) was used, dissolving 30.0 g of the salt mixture in 1000 ml deionised water.

Polyformazine *turbidimetric standard solutions* were prepared by mixing 5 ml of hydrazine sulphate solution (1 g in 100 ml deionised water) with 5 ml hexamethylenetetramine solution (10 g in 100 ml deionised water) in a 100 ml volumetric flask, according to the routine recipe for nephelometric standards ^[15]. After a reaction time of 24 h at 25 °C and filling up with deionised water to 100 ml, a solution with a turbidity value of 400 nephelometric turbidity units (NTU) is gained. By adding the required amount of the freshly prepared solution to the CHC samples, the required turbidity values were obtained.

Chloroform (CF), 1,2-dichlorobenzene (DCB), n-pentane, tetrachloroethylene (TeCE), toluene (Tol) and trichloroethylene (TCE) were all of analytical grade and obtained from Merck. Chlorobenzene (CB), n-hexane (Hex), Methanol (MeOH), hydrazine sulphate and hexamethylenetetramine were of analytical grade and acquired from Fluka. Ethylene/propylene (60:40) copolymer (E/PCo) was obtained from Sigma/Aldrich.

Measurement parameters

All measurements were made using a laboratory FTIR spectrometer of the same type as the submerged one, equipped with a LN₂-cooled mercury-cadmium-telluride (MCT) detector. One hundred scans were averaged per spectrum at a spectral resolution of 4 cm⁻¹. A low-pass filter with a cut-off wavenumber of 1400 cm⁻¹ was used in order to enhance the signal-to-noise ratio in the relevant part of the IR spectrum (1400 cm⁻¹ – 700 cm⁻¹).

The ATR measurements were performed with trapezoidal ZnSe-ATR-crystals (50 × 20 × 2, 45°), mounted in a specially designed flow-through cell (sample volume: 280 µl, contact area: 5.5 cm²) made of stainless steel. The cell was connected with stainless steel tubes to the sample container and a peristaltic pump respectively. The pump was positioned behind the cell, thus avoiding losses due to absorption of the lipophilic analytes in the polysiloxane tubing of the peristaltic pump. Figure 3 shows the experimental set-up. A flow rate of 1.1 ml/min was chosen throughout the experiments.

Sample preparation

E/PCo layers

A 3% (w/v) solution of ethylene/propylene copolymer was prepared by dissolving the granular polymer in a 1:1 mixture of n-pentane and n-hexane under reflux. The clear, hot solution was applied to the surface of the ATR-crystal using a Pasteur pipette. The crystal was kept at room temperature for 24 h to let the sol-

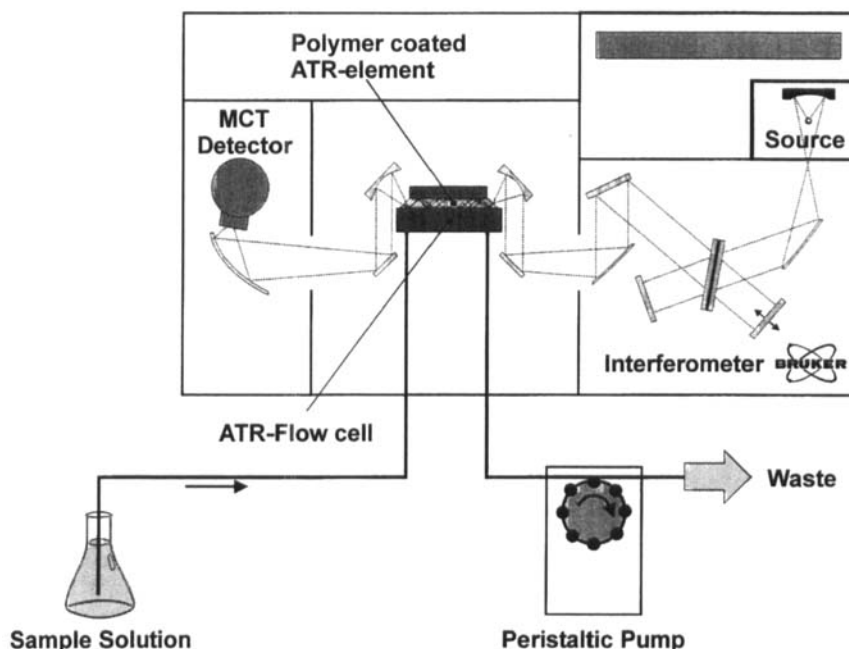


FIGURE 3 Experimental set-up. A peristaltic pump located behind the ATR cell pumps the sample through stainless steel capillaries. This set-up prevents losses due to the volatile and hydrophobic nature of the analytes

vent evaporate. Subsequently, the polymer coating was subjected to a hot air treatment (150 °C, 5 min) to remove remaining solvent traces. Following this procedure, it was possible to produce homogenous polymer layers in a sufficiently reproducible way. The average layer thickness was determined by differential weighing and found to be approximately 10 μm .

CHC sample solutions in artificial seawater

Severe problems of preparing aqueous sample solutions are caused by (i) the low solubility and (ii) the high volatility of the analytes. The international regulations for CHC analysis standards define aqueous solutions of CHC's as non-diluteable and non-storable and, therefore, require each calibration sample to be freshly made from a nonaqueous stock solution ^[16, 17]. In a first experimental stage, the sensor response was tested with CHC-solutions containing different amounts of methanol in the concentration range 0.1 % to 10 % (v/v) ^[18]. These experiments showed, that while the means remained unaffected in the range 0 – 2,5 % methanol, the standard deviations were considerably higher at methanol concentrations

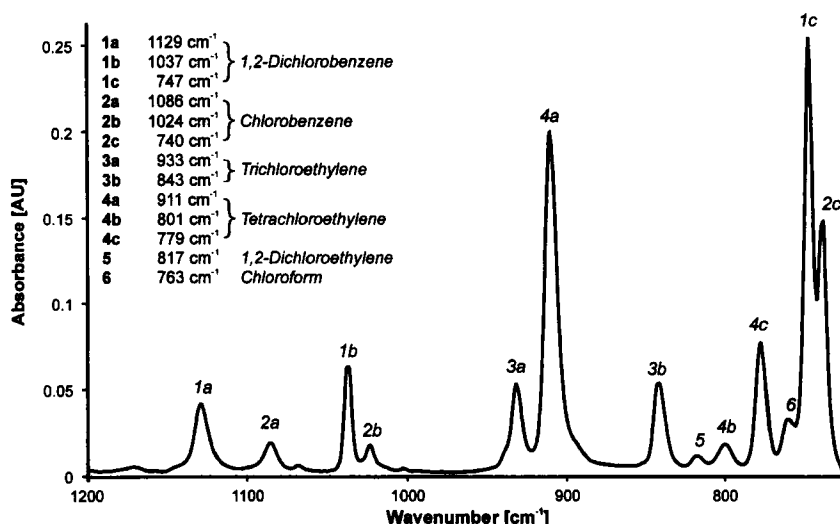


FIGURE 4 Example spectrum for simultaneous detection of six environmentally relevant chlorinated hydrocarbons in artificial seawater at a concentration of 20 $\mu\text{l/l}$ each. With the exception of chloroform, each analyte shows at least one absorption peak that is clearly separated from those of other analytes, allowing direct quantitative analysis by peak-area evaluation

below 0,5 %. At high concentrations, the means decreased, probably due to the changed partition coefficients. Based on these results, methanol at a level of 1 % (v/v) was used as solubility mediator throughout the experiments, except for the turbidity measurements, where the methanol might have interfered with the formazine polymer. The stability of measuring solutions of CHC's in ASW was determined by repetitive measurements at different concentrations to be $\pm 3\%$ on the average. All sample solutions were prepared from stock solutions containing 1g / l of each analyte in pure methanol. The required amount was introduced into the ASW already containing the amount of methanol to result in a total methanol concentration of 1 % (v/v) in the respective sample solution. The sample solutions were prepared freshly directly before each measurement.

RESULTS AND DISCUSSION

Multi-component analysis

One advantage of spectroscopic methods is the ability to perform multi-analyte detection. As can be seen from Figure 4, the simultaneous qualitative determina-

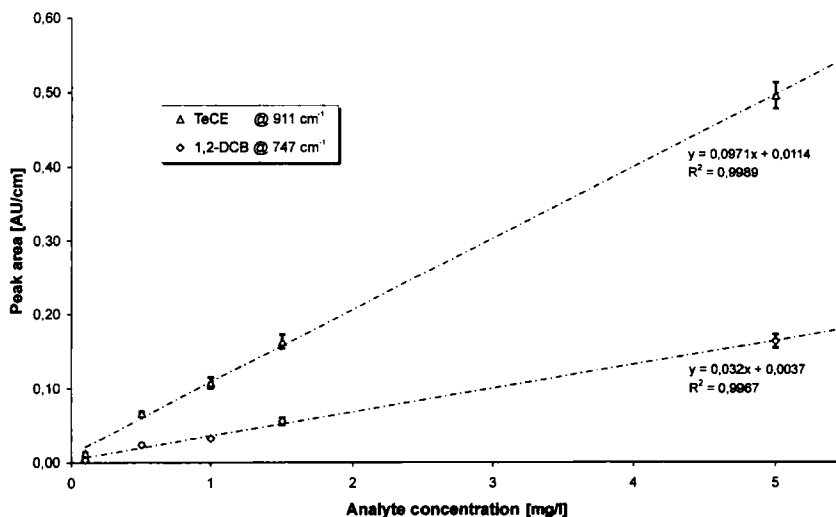


FIGURE 5 Calibration curves for tetrachloroethylene (TeCE) and 1,2-dichlorobenzene (1,2-DCB), derived from the peak area evaluation. The peak-area evaluation of the strongest non-overlapping band of each analyte is shown

tion of chemically similar compounds is possible due to their distinctive, molecule-specific absorption patterns in the fingerprint region of the mid-IR.

All analytes were present in the sample at a concentration of 20 $\mu\text{l/l}$ each. The differences in the relative peak intensities can be attributed firstly to the different absorbance intensities of the analytes and secondly to the different enrichment properties of the chlorinated hydrocarbons in the E/P_{Co} coating. Chloroform, for example, is known to show comparatively poor enrichment factors in E/P_{Co}. Consequently, only a weak absorption band can be observed.

As shown in Figure 4, with the exception of chloroform, all components have at least one absorption peak that is clearly separated from those of the other analytes. These peaks allow direct peak-area evaluation. Figure 5 shows the calibration curves for two analytes (tetrachloroethylene and 1,2-dichlorobenzene) in ASW. The equilibrium readings 60 minutes after start of the enrichment were evaluated, to provide maximum sensitivity and reliability for this study. By selecting sufficiently separated absorption bands for evaluation, linear calibration curves down to the lower $\mu\text{l/l}$ range (LOD's: TeCE: 100 $\mu\text{l/l}$ 1,2-DCB: 115 $\mu\text{l/l}$) can be achieved even without application of chemometric methods. The development of new sensor head designs with higher sensitivity and optimisation of the coating should lower the limits of detection even further.

Figure 6 shows the characteristic enrichment curves for two exemplary analytes (TeCE and 1,2-DCB) into a 10 μm E/PCo layer on a ZnSe ATR crystal. As can be seen from the curve, in addition to evaluating the *equilibrium reading*, as employed here, an alternative *kinetic evaluation method* could be applied for quantitative analysis. While the first method evaluates a signal corresponding to the equilibrium concentration of the analyte in the polymer layer, kinetic methods evaluate e.g. the slope of the tangent to the enrichment curve. The kinetic methods are less accurate and more susceptible to interferences influencing the speed of diffusion, like temperature variations, but could give much faster results. Hence, they would be well suited for rapid screening applications at higher analyte concentrations, e.g. in an industrial effluent stream.

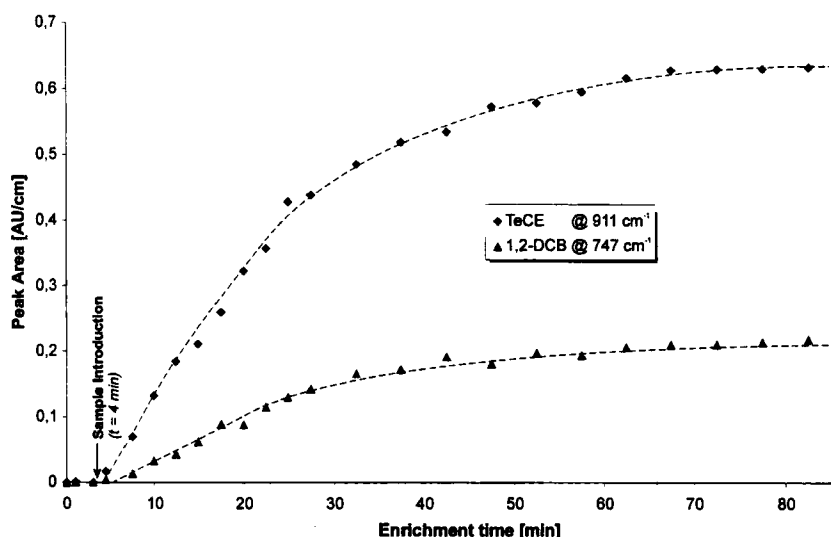


FIGURE 6 Typical enrichment curves for tetrachloroethylene (TeCE) and 1,2-dichlorobenzene (1,2-DCB) into a $\sim 10 \mu\text{m}$ E/PCo coating on a ZnSe ATR crystal

Interferences by natural seawater components

Three natural seawater constituents have been defined as key factors, either due to the amounts present in seawater or because they are known to cause problems with optical systems in the marine environment.

- Salinity
- Turbidity
- Humic acids

The first two potential interferents have been investigated in this study. The investigation of humic acids is not yet complete. Up to now there are no indications that humic acids, which are large, hydrophilic molecules, show any tendency to diffuse into the used polymer layers. Consequently, they do not directly influence the sensor response. However, it is known to be a general problem in seawater analysis that CHC's, as well as other analytes, adsorb to large molecules and particulate matter, which causes reduced finding rates.

The evaluation of all interference studies was performed by doing a linear regression analysis and calculating the confidence interval of the slope at a confidence level of 95% [19]. A slope significantly different from zero indicates interference, while a confidence interval of the slope including zero proves the absence of interferences.

Salinity

In the oceans, salinity ranges typically up to 2 % (w/v). A variation of the salinity values from zero (sweet water) to 3,25 % (w/v) revealed no significant influence on the sensor reading. Table I shows the results for three analytes at one exemplary analyte concentration. The statistical evaluation shows clearly that the slope is not significantly different from zero. Consequently, variations in salinity do not significantly affect the measurements.

Turbidity

The range of turbidity in the oceans varies strongly, depending on the location. Typically, values up to 250 NTU will be encountered in the open sea, but in coastal areas these readings can be considerably higher. In this study, turbidity up to 300 NTU proved to be without effect on the sensor readings, as demonstrated in Table II.

These results were obtained under laboratory conditions, using a formazine polymer as turbidity. In real-world applications, other effects, including biofilm formation on the sensor heads, are to be expected. These effects, together with the aforementioned adsorption of the analytes to particulate matter, will be the topics of the next development steps.

Interferences by seawater pollutants of anthropogenic origin

The second group of potential interferents are other organic pollutants. While inorganic substances are expected to behave like salinity and consequently should not influence the measurements, the wide range of organic substances might cause disturbances. Many of these substances are small, lipophilic and dif-

fuse easily into a polymer layer. The interference scenarios are spectral interferences, and changes in the partition coefficients and hence the sensor response due to (irreversible) enrichment of interfering compounds in the sensitive layer. To assay these possibilities, the main pollutants have been divided into two chemical classes; two model analytes were chosen for each class and used for the experiments.

- Non-chlorinated lipophilic hydrocarbons and derivatives. n-Hexane was chosen as the model analyte for aliphatic and toluene for aromatic substances.
- Chlorinated hydrocarbons. Chloroform was chosen as a lipophilic species and pentachlorophenol as a hydrophilic analyte.

TABLE I Characterisation of the sensitivity of sensor response to salinity, shown for four exemplary analytes (1,2-DCB: 1,2-dichlorobenzene, 0,5 µl/l; TCE: trichloroethylene, 0,5 µl/l; TeCE: tetrachloroethylene, 0,1 µl/l; CB: chlorobenzene, 0,5 µl/l). As proven by the statistical evaluation, varying salinity does not significantly influence the sensor response

<i>Sensor Response to Varying Salinity</i>				
Analyte	1,2-DCB	TCE	TeCE	CB
Peak	747 cm ⁻¹	859 cm ⁻¹	911 cm ⁻¹	1086 cm ⁻¹
Salinity [%]				
3,20	0,009463	0,002929	0,039710	0,001794
3,20	0,009848	0,003634	0,041357	0,001468
3,20	0,010307	0,003412	0,041332	0,001475
1,07	0,008937	0,002538	0,040960	0,001027
1,07	0,008977	0,001994	0,039487	0,000973
1,07	0,008298	0,002689	0,039543	0,000763
0,43	0,010219	0,003068	0,043541	0,001400
0,43	0,010848	0,003425	0,038312	0,001382
0,43	0,009986	0,003502	0,041261	0,001604
0,00	0,010929	0,002822	0,042388	0,001039
0,00	0,009498	0,002075	0,042241	0,001389
0,00	0,010344	0,002287	0,042242	0,001289
<i>Intersect</i>	0,009937	0,002635	0,041388	0,001192
<i>Slope</i>	-0,000114	0,000196	-0,000305	0,000092
<i>Confidence Interval of the Slope</i>	± 0,000431	± 0,000278	± 0,000801	± 0,000148

TABLE II Characterisation of the sensitivity of sensor response to turbidity, shown for four exemplary analytes (1,2-DCB: 1,2-dichlorobenzene, 5 $\mu\text{l/l}$; TCE: trichloroethylene, 5 $\mu\text{l/l}$; TeCE: tetrachloroethylene, 1 $\mu\text{l/l}$; CB: chlorobenzene, 5 $\mu\text{l/l}$). As proven by the statistical evaluation, varying turbidity does not significantly influence the sensor response

<i>Sensor Response to Varying Turbidity</i>				
Analyte	1,2-DCB	TCE	TeCE	CB
Peak	747 cm^{-1}	859 cm^{-1}	911 cm^{-1}	1086 cm^{-1}
Turbidity [NTU]				
300	0,102134	0,047572	0,136593	0,024228
300	0,101815	0,049183	0,147481	0,022227
300	0,089155	0,045399	0,138839	0,028334
100	0,093153	0,046289	0,137672	0,021459
100	0,087443	0,046528	0,136989	0,022817
100	0,108134	0,044008	0,139061	0,029449
40	0,098828	0,047011	0,144841	0,021307
40	0,101972	0,047835	0,131373	0,023983
40	0,116546	0,032934	0,143153	0,023915
0	0,098245	0,043508	0,140991	0,020899
0	0,091424	0,044748	0,134070	0,022096
0	0,103242	0,043696	0,142263	0,019603
<i>Intersect</i>	0,100466	0,043389	0,138786	0,022159
<i>Slope</i>	-0,000010	0,000014	0,000006	0,000011
<i>Confidence Interval of the Slope</i>	$\pm 0,000048$	$\pm 0,000022$	$\pm 0,000026$	$\pm 0,000015$

Aliphatic and aromatic hydrocarbons

As detailed in Table III, no interferences from aliphatic or aromatic hydrocarbons could be observed, not even at high concentrations. Toluene shows a peak at 729 cm^{-1} , which did not interfere with the evaluated bands. Hexane did not appear in the observed part of the spectrum.

As the presence of these two substances does not change the sensor performance, even at levels well beyond the levels occurring in the oceans, it can be concluded that no significant interferences are to be expected, unless other components cause interferences by overlapping absorption bands.

TABLE III Characterisation of the sensitivity of the sensor response to high concentrations of two exemplary aliphatic and aromatic hydrocarbon interferents, shown for tetrachloroethylene (TeCE) and 1,2-dichlorobenzene (1,2-DCB) at a concentration of 5 µl/l each. As proven by the statistical evaluation, toluene and n-hexane do not significantly influence the sensor response up to interferent concentrations of 100 µl/l

Sensor Response to Exemplary Aromatic and Aliphatic Hydrocarbons at Varying Concentrations									
Toluene					n-Hexane				
Analyte	TeCE	TeCE	1,2-DCB	1,2-DCB	TeCE	TeCE	1,2-DCB	1,2-DCB	
Peak	911 cm ⁻¹	779 cm ⁻¹	747 cm ⁻¹	1129 cm ⁻¹	911 cm ⁻¹	779 cm ⁻¹	747 cm ⁻¹	1129 cm ⁻¹	
Toluene Concentration µl/l									
5	0,519836	0,101596	0,164713	0,077955	5	0,504524	0,102129	0,160010	0,073169
5	0,522120	0,129100	0,156010	0,070438	5	0,509000	0,090755	0,162710	0,090222
10	0,521380	0,085614	0,159470	0,072831	10	0,496840	0,084029	0,145529	0,082582
10	0,499910	0,100860	0,162990	0,061509	10	0,511000	0,078663	0,161102	0,084504
50	0,515990	0,098971	0,166040	0,069236	50	0,503010	0,090998	0,144232	0,082850
50	0,526380	0,072626	0,148820	0,072814	50	0,493110	0,101747	0,160260	0,082837
100	0,530070	0,088617	0,152436	0,055383	100	0,488890	0,090661	0,148289	0,072343
100	0,509810	0,103729	0,159724	0,070542	100	0,523160	0,085418	0,157577	0,086198
Intercept	0,516317	0,102560	0,160933	0,072158		0,503909	0,090709	0,157257	0,083186
Slope	0,000045	-0,000119	-0,000052	-0,000080		-0,000005	-0,000004	-0,000056	-0,000033
Confidence Interval of the Slope	± 0,000138	± 0,000231	± 0,000083	± 0,000093		± 0,000161	± 0,000120	± 0,000107	± 0,000088

TABLE IV Influence of chloroform at high concentrations in ASW on the sensor response, shown for tetrachloroethylene (TeCE) and 1,2-dichlorobenzene (1,2-DCB) at a concentration of 5 $\mu\text{l/l}$ each. The TeCE absorption peak at 779 cm^{-1} shows a significant dependence on the chloroform concentration, while the other readings remain unaffected up to interferent concentrations of 100 $\mu\text{l/l}$. This dependence is due to a spectral overlap of the absorption peaks that could not be compensated by adaptation of the integration parameters

<i>Sensor Response to Chloroform as an Interferent at Varying Concentrations</i>				
Analyte	TeCE	TeCE	1,2-DCB	1,2-DCB
Peak	911 cm^{-1}	779 cm^{-1}	747 cm^{-1}	1129 cm^{-1}
<i>Chloroform Concentration [mg/l]</i>				
5	0,496016	0,090066	0,159534	0,064781
5	0,499739	0,112070	0,135692	0,065317
10	0,524973	0,094183	0,150461	0,071175
10	0,552034	0,081067	0,138144	0,062479
50	0,477664	0,035124	0,161160	0,064005
50	0,519001	0,023509	0,136092	0,066676
100	0,501320	-0,050527	0,110856	0,079786
100	0,508013	-0,072099	0,130159	0,070636
<i>Intercept</i>	0,515989	0,108276	0,150755	0,064250
<i>Slope</i>	-0,000149	-0,001675	-0,000254	0,000093
<i>Confidence Interval of the Slope</i>	$\pm 0,000527$	$\pm 0,000248$	$\pm 0,000317$	$\pm 0,000101$

Chlorinated hydrocarbons

Pentachlorophenol could not be detected using an E/PCo coating, even at high concentrations. Of all tested interferents, only chloroform (CF) causes a slope significantly different from zero for the evaluation of one of the weaker TeCE absorption peaks, as shown in Table IV. The readings of the other absorption peaks remain unaffected. The occurring interference between chloroform and tetrachloroethylene can be attributed to a spectral overlap of the CF absorption peak with the TeCE peak at 779 cm^{-1} . The application of a chemometric method evaluating the whole spectral range from 1400 cm^{-1} to 700 cm^{-1} would be necessary to effectively avoid such minor interferences.

CONCLUSIONS

The feasibility of an optic sensor system based on polymer coated mid-infrared waveguides for multi-component analysis of chlorinated hydrocarbons in seawater at environmentally relevant levels could be demonstrated.

The sensor system was found to be not susceptible to natural composition variations in seawater, such as salinity and turbidity, and to a set of model interfering substances for components of anthropogenic origin. The efforts to characterise the sensor system are still in progress. In addition, attempts are currently being made to evaluate the slope during the first minutes of the analyte enrichment in the polymer coating instead of the final reading, in order to increase the time resolution of the analytical system. However, this diffusion-controlled process requires close control of the temperatures and is more susceptible to external interferences.

A fibre optic sensor head will be connected to the developed underwater FT-IR spectrometer. This system will be subjected to a series of tests in a flume tank and, later on, on a mooring station, which will enable deeper insight into the system behaviour under real-world conditions.

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