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DEVELOPMENT OF AN OPTICAL SENSOR FOR
BTEX AND CHLORINATED SOLVENTS

Final report of two NOBIS/NOVEM projects

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Samenvatting

Het doel van dit project was de haalbaarheid te onderzoeken van sensoren gebaseerd op optische fibers voor het (in situ) meten van BTEX en gechlorideerde oplosmiddelen. Dit project is uitgevoerd door een consortium van sensorontwikkelaars, technologische instituten, adviesbureaus en locatie-eigenaren. Het project heeft geresulteerd in een vernieuwde versie van het reeds bestaande PetroSense instrument van FCI Environmental Inc. Deze nieuwe versie heeft een detectielimiet voor p-xyleen in de orde van grootte van 50 µg/L, hetgeen 10 keer lager ligt dan die van het oorspronkelijke instrument. Dit instrument is gevoelig voor omgevingsfactoren, zoals zoutgehalte en temperatuur. Daarnaast is dit instrument gevoelig voor een aantal componenten, zoals BTEX en naftaleen. Hierdoor moet een meting worden gezien als een waarneming van een som-parameter en blijft de interpretatie soms een probleem.

Gedurende het project zijn een aantal nieuwe ideeën ten aanzien van het meetprincipe, de implementatie van de elektronica in de sensor en de toepassing van gevoelige *coatings* uitgewerkt. Dit heeft geresulteerd in een compleet nieuwe sensor waarvan het meetconcept is aangetoond in een demonstratie-instrument. Dit demonstratie-instrument bestaat uit een sensor met een referentiefiber en gepulste elektronica om meetruis te verminderen. Het nieuwe meetconcept toont aan dat een aantal omgevingseffecten zijn weggenomen (zoals zouteffecten). Haalbaarheidstudies laten zien dat als de elektronica en het sensorontwerp is geoptimaliseerd, detectielimieten in de orde van grootte van 20 µg/L voor p-xyleen en trichlooretheen haalbaar kunnen zijn. Prototypes moeten echter nog wel worden ontwikkeld.

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Abstract

The goal of this project was to test the feasibility of improved fibre optical sensors for the (in situ) measurement of BTEX and chlorinated solvents. This project was carried out by a consortium in which sensor developers, consultants, technological institutes and site owners collaborated. The project resulted in a new version of the commercially available PetroSense instrument by FCI Environmental Inc. This new instrument has a detection level for p-xylene in the order of 50 µg/L which is approximately a tenfold improvement over the older version. However, this instrument is very sensitive to environmental effects such as salt content and temperature. In addition the instrument is sensitive to a number of compounds including all BTEX and naphthalene. The measurement is therefore some kind of total analysis and the interpretation of the results can sometimes be difficult.

During the project, new ideas concerning the measurement principle, the implementation of the electronics and the application of sensitive coatings were developed. These ideas resulted in a totally new sensor of which the measurement concept was demonstrated in a demonstrator instrument. This concept consisted of the use of a reference fibre and of using pulsed electronics in order to reduce measurement noise. The new measurement concept proves that a number of environmental influences have been removed from the measurement (such as salt effects). Feasibility tests show that using optimised electronics, detection limits in the order of 20 µg/L p-xylene and trichloroethylene are possible. Prototype instruments, however, still need to be developed.

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SAMENVATTING

Development of an optical sensor for BTEX and chlorinated solvents

Een snelle, eenvoudige in situ bepaling van de concentratie aan BTEX en gechloreerde koolwaterstoffen is een droom die de komende jaren verwezenlijkt kan worden. In het kader van een gecombineerd NOBIS/NOVEM-project zijn een aantal optische sensorconfiguraties ontwikkeld die het mogelijk maken om het gehalte aan BTEX en CKW te bepalen. Deze sensoren zijn gebaseerd op optische technologie (ze meten de concentratie met licht dat door een stukje glas-fiber gaat) en vertegenwoordigen een grote vooruitgang op het meetprincipe dat is ontwikkeld en toegepast in de 'PetroSense' instrumenten die op dit moment worden vermarkt door FCI Environmental Inc. voor lekdetectie.

Het doel van dit NOBIS/NOVEM-project was een haalbaarheidsonderzoek te doen naar de realiseerbaarheid van optische sensoren die een hoge gevoeligheid hebben voor BTEX en gechloreerde koolwaterstoffen met daarbij een lage detectiegrens die in de orde van grootte ligt van 50 µg/L.

Het meetprincipe van de gebruikte optische sensoren is gebaseerd op het aanbrengen van een chemische stof op een optische fiber (de 'coating'). De te meten stoffen gaan uit het water in deze coating zitten en veranderen daarmee de licht-geleidende eigenschappen van de optische fiber. Door het verschil in hoeveelheid licht dat in de fiber en uit de fiber gaat te meten, kan de concentratie van de te meten stof worden bepaald.

De resultaten van het onderzoek laten zien dat de stabiliteit en de ruisniveaus van de meetsignalen van sensoren de belangrijkste parameters zijn waarlangs de bestaande sensoren zijn te verbeteren. Daarnaast zijn er een aantal nieuwe coatings ontwikkeld, waarmee het mogelijk is om naast BTEX ook CKW te meten met vergelijkbare gevoeligheid en detectiegrenzen. Ook zijn er coatings gevonden die totaal niet gevoelig zijn voor deze stoffen.

Op basis van de resultaten uit de haalbaarheidsstudie is het bestaande PetroSense instrument van FCI verbeterd en de eerste prototypes van dit verbeterde instrument zijn ingezet in een kolomexperiment in het laboratorium. De resultaten, die zijn verkregen met dit experiment, tonen aan dat detectielimieten in de orde van grootte van 20 µg/L p-xyleen te realiseren zijn. De resultaten laten echter ook zien dat de metingen met de verbeterde PetroSense een sterke gevoeligheid hebben voor temperatuurveranderingen.

Naast de verbeterde PetroSense zijn een aantal demonstratie-instrumenten gebouwd waarmee een nieuw meetconcept is gedemonstreerd. Dit nieuwe meetconcept is gebaseerd op het combineren van twee optische fibers, eentje met een BTEX- of CKW-gevoelige coating, de andere met een niet-gevoelige coating. Het idee achter dit nieuwe ontwerp is dat de niet-gevoelige (referentie)fiber wel gevoelig is voor andere factoren, zoals het zoutgehalte. Door deze referentiefiber in de meting te betrekken zou de langetermijnstabiliteit van de sensor moeten verbeteren. Gebleken is dat effecten zoals wisselende zoutconcentraties volledig verdwijnen. De demonstratie-instrumenten tonen duidelijk aan dat het meetprincipe goed werkt. Het is echter belangrijk om te realiseren dat de demonstratie-instrumenten nog tamelijk veraf staan van prototype sensoren. Zo is bijvoorbeeld het elektronisch ontwerp nog niet geoptimaliseerd voor een zo laag mogelijk ruisniveau. Hierdoor zijn optimale prestaties niet mogelijk. De huidige demonstratie-instrumenten bijvoorbeeld hebben een detectielimiet rond de 50 mg/L.

Door het meetsignaal elektronisch te middelen is het ruisniveau sterk gereduceerd, waarbij tegelijkertijd het energieverbruik is afgenomen. De eerste tests met elektronische middeling van het signaal laten zien dat detectielimieten in de orde van grootte van 20 µg/L p-xyleen haalbaar zijn.

Naast de technische resultaten zijn er minder concrete resultaten die het gevolg zijn van discussies tussen de eindgebruikers en ontwikkelaars tijdens het project. Eén van de belangrijkste conclusies is dat er ten aanzien van de toepassing van dit soort sensoren een grote hoeveelheid kennis ontwikkeld en gecommuniceerd moet worden. Eén van de belangrijke aspecten is dat optische sensoren, zoals ontwikkeld in dit project, niet selectief één component, zoals benzeen, meten. Deze sensoren zijn gevoelig voor alle BTEX-componenten en ook andere, zoals bijvoorbeeld naftaleen. Daarnaast is het ook zo dat de gevoeligheid voor benzeen een factor 3 lager ligt dan de gevoeligheid voor xyleen. Laboratoriumanalyses, om de precieze samenstelling van de verontreiniging vast te stellen, blijven noodzakelijk. De sensoren zijn bij uitstek geschikt om trends in de tijd, die optreden tussen laboratoriummetingen, te volgen.

SUMMARY

Development of an optical sensor for BTEX and chlorinated solvents

The goal of this project was to test the feasibility of improved fibre optical sensors for the (in situ) measurement of BTEX and chlorinated solvents. This project was carried out by a consortium in which sensor developers, consultants, technological institutes and site owners collaborated. The project resulted in a new version of the commercially available PetroSense instrument by FCI Environmental Inc. This new instrument has a detection level for p-xylene in the order of 50 µg/L which is approximately a tenfold improvement over the older version. However, this instrument is very sensitive to environmental effects such as salt content and temperature. In addition the instrument is sensitive to a number of compounds including all BTEX and naphthalene. The measurement is therefore some kind of total analysis and the interpretation of the results can sometimes be difficult.

During the project, new ideas concerning the measurement principle, the implementation of the electronics and the application of sensitive coatings were developed. These ideas resulted in a totally new sensor of which the measurement concept was demonstrated in a demonstrator instrument. This concept consisted of the use of a reference fibre and of using pulsed electronics in order to reduce measurement noise. The new measurement concept proves that a number of environmental influences have been removed from the measurement (such as salt effects). Feasibility tests show that using optimised electronics, detection limits in the order of 20 µg/L p-xylene and trichloroethylene are possible. Prototype instruments, however, still need to be developed.

CHAPTER 1

INTRODUCTION

Why determine the concentration of soil pollution by sampling in the field and analysis in the laboratory? Why not measure directly in the soil where the pollution is found? The reason is a lack of generally available in situ measurement techniques. But times are changing!

A consortium of site owners, consultants, instrument builders and sensor technology developers, developed sensors that measure aromatic hydrocarbons (primarily benzene, toluene, ethylbenzene, xylenes (BTEX) and naphthalene) and chlorinated solvents in the soil environment. The project was co-financed by NOBIS and NOVEM.

This report gives an overview of the project and presents the most important technical results obtained during the project. Chapter 2 describes the setting and the goal of the project. Chapter 3 gives a short description of the project approach. Chapter 4 gives a relatively detailed description of the developed sensor technology and the results of the feasibility studies. Chapter 5 gives the results of a column experiment carried out by TNO-NITG. Finally Chapter 6 presents some of the tacit knowledge that is the result of discussions held during the several consortium meetings that took place during the project. The appendix A of this report is a report by TNO-NITG on the application of the sensor technology in column breakthrough experiments in the laboratory.

CHAPTER 2

PROBLEM DEFINITION AND GOAL

2.1 Background and bottlenecks

In the last 20 years we have become to realize that soil pollution is extremely widespread. Although soil pollution can be caused by a wide diversity of different contaminants, a very large number of polluted sites is caused by contamination with aromatic hydrocarbons such as BTEX and naphthalene and chlorinated solvents such a perchloroethylene and trichloroethylene.

Initially the idea was that these polluted sites could be cleaned by intensive soil sanitation. The vastness of the problem, the difficulties associated with the sanitation and the lack of funding lead to the development of less intensive clean-up procedures such as biological in situ methods or natural attenuation. Although these approaches are cheaper and perhaps more effective on the long run, it is clear that the pollution will remain in the soil for a longer period of time. Often (local) authorities will demand that behaviour of the remaining soil pollution must be monitored.

The shift to more extensive clean-up procedures has also led to a different approach to soil pollution. Initially we were primarily interested in total concentrations of the contaminants in the soil; nowadays we are also very much interested in how the contaminants are present (dissolved, reversibly sorbed or precipitated) and what the chemical and physical processes are that have an effect on these contaminants. As a result, we require a different type of information. For example in addition to the concentration we also want to know how the concentration changes with time.

These shifts in approach to soil pollution have resulted in a number of bottlenecks:

- Measurements for quantifying processes can best be done in situ where these processes occur. However, there is a severe lack of good and validated in situ measurement techniques.
- Direct measurement of the (bio)degradation of pollution in situ is not possible. Proof for bio-degradation is most often based on indirect evidence such as changes in redox situation, the occurrence of degradation products etc.
- There is a lack of cheap reliable in situ measurement techniques that could be used for characterization and monitoring.
- No techniques are available for the direct measurement of soil pollution in the soil.
- The techniques that are available and that are widely used for determining contaminant concentrations and the composition of the soil depend on sampling in the field and analysis in the laboratory. During all handling phases errors occur which are very difficult to quantify.

2.2 Availability of sensor techniques

Recently there have been major developments in optical sensor design. Concentrations of a large number of compounds can be measured with optical sensors. The principle of an optical sensor is that optical properties (i.e. light transmission or fluorescence) of a sensor changes as a function of the concentration of the compound to be measured. This type of sensors appear to have a very large potential for application in the field of soil pollution and soil clean-up. For example the American company FCI is currently selling probes (PetroSense®) based on fibre optic technology for application in the field of leak detection below underground storage tanks. Further development and enhancement of the application of this type of sensors may provide a means for solving some of the bottlenecks mentioned in section 2.1.

2.3 Problem definition

At the start of this project, the optical sensors and the instruments in which these sensors are applied had a number of limitations and drawbacks that severely limited the application:

- The sensor technology was not sensitive enough (in the mg/L range instead of the µg/L soil range).
- The sensor technology was not selective enough. Only total hydrocarbons were measured. In addition the sensor was more sensitive to the larger hydrocarbons. Therefore, only indicative (qualitative) results were obtained.
- The instruments were designed to be used in shallow aquifers only.
- The range of instruments based on fibre optic technology was limited to application in access conduits or tubes. As a result they suffered the drawbacks associated with access tubes. In addition application of this type of sensors in profiling instruments would make characterization studies much easier.
- In the Netherlands we did not have much experience with this type of technology.

Due to the above limitations associated with the commercially available fibre optic sensor, application in other fields than leak detection is limited. Many parties that have to cope with soil pollution would like to have similar instruments that can measure contaminants selectively and with a sensitivity in the ppb range (µg/L). In addition, the possibility of applying the instrument directly in the soil would be welcomed. Based on technology and developments at FCI (chip based optical technology) the consortium was convinced that an optical sensor could be made that is considerably improved in comparison with the available sensors at the start of the project.

2.4 General approach to solve the problem

The general approach adopted in this project was to use the sensor principle developed by FCI and improve this principle with respect to sensitivity, selectivity and stability. The sensor developed by FCI has been optimized to the detection of para-xylene. The instrument is called a total petroleum hydrocarbon (TPH) sensor and senses a wide range of different hydrocarbons (mostly aromatic) with different sensitivities. The lower detection limit for p-xylene lies in the order of 0.1 mg/L to 1 mg/L.

When we compare the detection limits to the Dutch intervention levels (see table 1) it becomes very clear that the lower detection limits of this type of instrument should be improved by at least a factor 10 or more. If the detection limit reaches the level of 10 µg/L it can be expected that application of the sensor is fruitful in many situations.

Table 1. Overview of several Dutch intervention levels for groundwater.

compound	intervention level (µg/L)
benzene	30
toluene	1000
ethylbenzene	150
xylenes	70
trichloroethylene	500
tetrachloromethane	10
vinylchloride	5
chlorobenzene	180

The current FCI instrument is primarily meant to detect aromatic hydrocarbons. A problem, however, is that the instrument is sensitive to most volatile aromatic hydrocarbons. Therefore an uncertainty remains about what specific compound is being detected. Improving the selectivity of the sensor and widening the range of compounds to chlorinated solvents would improve the applicability.

It was felt that the development of sensors for other compounds along the same lines as the FCI sensor would fulfill a need. A logical group of compounds to focus on were the chlorinated hydrocarbons.

2.5 **Goal of this project**

The goal of this project is to improve the current sensors of FCI with respect to stability, sensitivity and selectivity for BTEX compounds. Based on this experience the sensor design may be modified in order to enable chlorinated solvent measurements.

The developed sensors should be applied in instruments allowing for testing the performance of the sensors in a soil environment.

CHAPTER 3

PROJECT APPROACH

3.1 Project activities

At the start of the project four separate activities were foreseen:

- activity 1: Evaluation of the FCI sensor, definition of goals;
- activity 2: Feasibility study for the development of an improved BTEX sensor (a) and a feasibility study for the development of a chlorinated solvent sensor (b);
- activity 3: Development of an instrument in which the applicability of the sensor can be demonstrated (preferably in a field application);
- activity 4: Development of a cone mounted instrument for application in penetration tests.

Figure 1 gives a schematic overview of the planning realized in the project. Activity 2b (the feasibility study for the chlorinated sensor) was carried out in parallel with activity 3. This was possible because the improved principle for the BTEX sensor formed the starting point for the feasibility study for the chlorinated solvent sensor.

	dec-97	dec-98	dec-99	may-00
Activity 1	■			
Activity 2a		■		
Activity 2b			■	
Activity 3			■	■

Fig. 1. Outline of the chronology of the project.

Due to a number of circumstances that had to do with the results obtained in this project (for example pressure sensitivity of the sensors) and others outside this project that had to do with combining efforts from several other projects that were carried out within NOBIS and NOVEM, activity 4 was not carried out within this project.

3.1.1 Activity 1

Activity 1 consisted of an evaluation of the FCI instrument. This activity had two goals:

- obtaining hands-on experience with the FCI instrument and a more detailed understanding of the measurement principle;
- specification of the approach to be followed in activity 2a and 2b.

3.1.2 Activity 2a

Activity 2a consisted of the feasibility study for the improvement of the current FCI instrument (i.e. the BTEX sensor). The feasibility was primarily focussed on the improvement of the detection limit and the selectivity. Several approaches defined in activity 1 were followed. A number of these approaches proved to be successful others less so. In general the feasibility study showed that it is very well possible to reach detection limits in the order of 50 µg/L but that the improvement of the selectivity is less feasible. In chapter 6 the problem of the selectivity is discussed and reasons are given why selectivity may be less of a problem than initially thought.

3.1.3 *Activity 2b*

Using the results from activity 2a and activity 3 several approaches were investigated to develop a sensor that is sensitive for chlorinated solvents. The results showed that the development of a sensor for chlorinated solvents with the required detection limit should be feasible, however, as was the case for the BTEX sensor, the selectivity is limited. In fact the proposed sensor for chlorinated solvents has more or less the same sensitivity for TEX as for chlorinated solvents. The xylene sensitivity is similar to the BTEX sensor. However, this sensor is much less sensitive for benzene than the BTEX sensor.

3.1.4 *Activity 3*

In activity 3, the results from the feasibility study are used to develop an instrument with which the feasibility can be proved. Initially it was thought that relatively minor changes to the sensor design were necessary so that the development of a field prototype instrument was foreseen. However, set-backs in the project and the results from the feasibility studies proved that the development of field prototypes was a step too far. The changes in sensor design and the required changes in the electronics in the instruments were so major that given the short time and limited budget so-called demonstrator instruments were most feasible. A drawback is that these demonstrators are not suitable for field application and further development is required.

The results from the feasibility study did lead to an improved version of the FCI instrument which did have a much lower detection limit. This instrument was used by TNO-NITG in a laboratory column experiment to prove the applicability of the sensor to accurately measure concentration changes in the soil solution.

TECHNICAL RESULTS

4.1 Evaluation of the sensing principle

This project is focussed on the evaluation, improvement and further development of an existing measurement concept applied by FCI Environmental Inc., in their PetroSense® instrument. The PetroSense is claimed to be sensitive to aromatics in the C₆ to C₁₀ range, both in the vapour as well as the liquid phase. The sensor is calibrated with respect to p-xylene and consequently the output of the instrument is expressed as p-xylene, regardless of the actual compound detected. Temperature correction is included within the instrument. The main applications for this instrument is leak detection at storage tanks. The instrument is used in access conduits in the soil such as drain pipes or monitoring wells and monitors changes in total petroleum hydrocarbons (TPH) in situ. At the moment detection limits in the field are in the ppm range (i.e. > 1 ppm p-xylene). Careful laboratory tests have shown that detection limits in the range of 0.1 ppm p-xylene are possible.

The first activity in this project is an evaluation of the FCI probe. The operating principle of the instrument is based on the application of optical sensor techniques. The basic set-up of the FCI sensor is displayed in the figures 2 (side view) and 3 (top view).

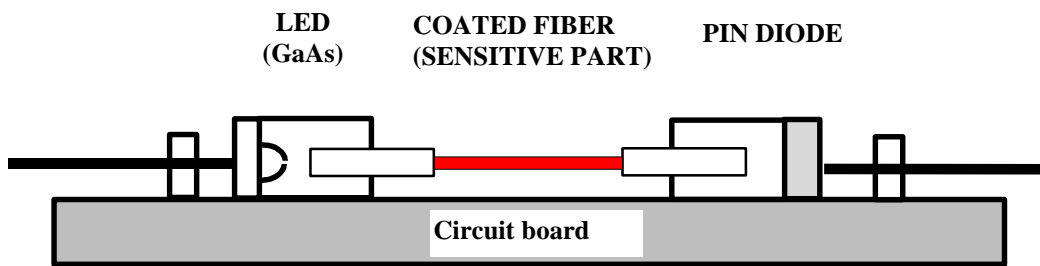


Fig. 2. Basic set-up of the FCI sensor, side view of the circuit board.

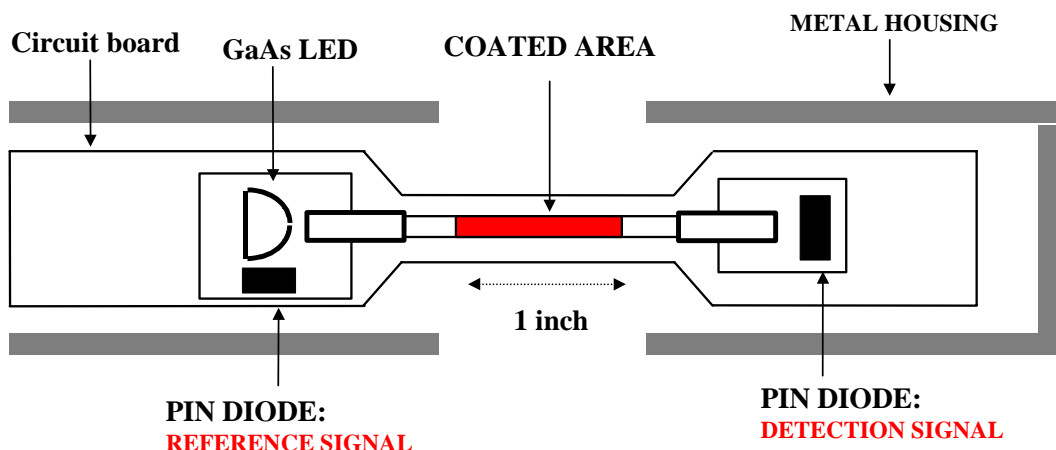


Fig. 3. Basic set-up of the FCI sensor, top view of the circuit board.

The detection assembly consists of a LED (light emitting diode) with reference photodiode, an optical fibre and a detection photodiode with daylight filter. This detection assembly is mounted onto a circuit board containing the basic electronics.

The detection principle of this fibre optic sensor is based on the enrichment of aromatic components (mainly BTEX) in a special polymer coating developed by FCI. This enrichment leads to a change in the optical properties of the fibre (the refractive index changes). The approach adopted by FCI results in a relatively high sensitivity with relatively short fibres. Moreover, the instrumentation can be used in situ, is robust and relatively cheap.

The measurement principle is based on transmitting light from the LED through the fibre and quantifying the light losses by measuring the ratio of the amount of light entering the fibre (reference photodiode) and leaving the fibre at the end (detection photodiode). If the measured signals of the detection and the reference photodiode is taken as the sensor signal; the ratio R is:

$$R = \frac{mV_{det}}{mV_{ref}}$$

The higher the concentration of analyte (in this case BTEX), the higher the light losses will be and as a result the measured ratio will be lower. The amount of light leaking from the fibre is correlated with the concentration of the analyte in the fibre coating which is related to the concentration surrounding the fibre through a partitioning coefficient.

The experiments carried out within this project showed that so-called 'lossy modes' within the fibre are of primary importance in the sensing principle. Refractive index changes enhance these lossy modes which result in a higher response of the sensor.

4.2 Calculation of concentration from measured ratios

The interpretation of the measurements is facilitated by translating the measured ratio values to values that can be interpreted as some kind of concentration. Figure 4 gives a graphical interpretation of the calibration curve. The equation used for the calibration curve is given by:

$$B = B_0 + \left((R - R_0) \frac{(B_1 - B_0)}{(R_1 - R_0)} \right)$$

in which:

- B is the calculated concentration of the BTEX (in mg/L);
- B₀ is the lowest concentration used for the calibration (generally 0 mg/L);
- B₁ is the concentration of the highest calibration point;
- R is the measured ratio for which concentration B is to be calculated;
- R₀ is the ratio corresponding to concentration B₀;
- R₁ is the ratio corresponding to concentration B₁.

Assuming that B₀ = 0 mg/L, this equation can be rewritten as:

$$[B] = R \cdot f_1 + f_2 \text{ or } R = (1/f_1) \cdot B - (f_2/f_1)$$

in which f₁, f₂ are the constants:

$$f_1 = B_1 / (R_1 - R_0)$$

$$f_2 = -f_1 \cdot R_0$$

As can be seen in figure 4, the slope of the curve is given by $1/f_1$ which relates to the sensitivity of the sensor. Very sensitive sensors show a large response in ratio to small changes in concentration (i.e. f_1 is small).

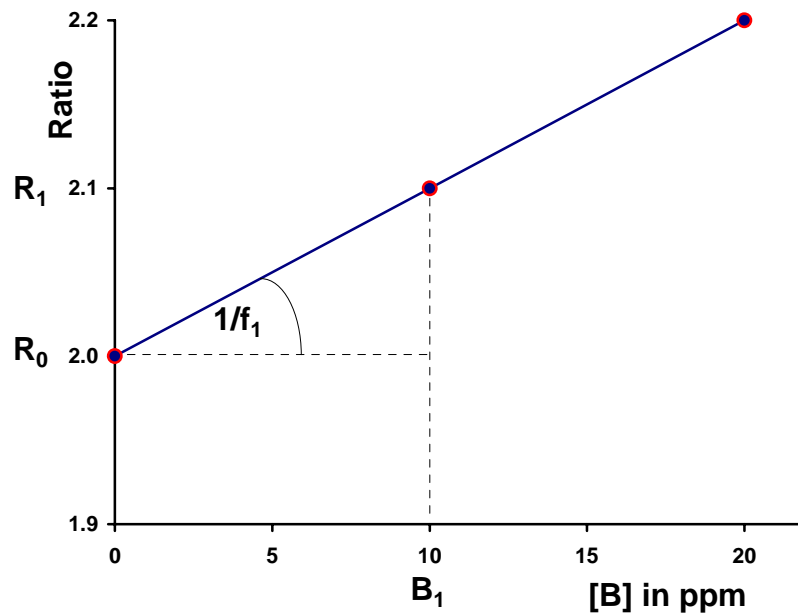


Fig. 4. Explanation of the equation used for the calibration curve.

It was known that the sensor is sensitive to a number of compounds. FCI chooses to express the measured concentration in units p-xylene. A measure to indicate the differences in sensitivity for the other compounds for which the sensor is sensitive and therefore quantify the selectivity of the sensor is the relative response factor (RRF) defined by:

$$RRF = \frac{R_{p\text{-xylene}}}{R_{\text{analyte}}}$$

Table 2 summarizes a number of measured RRF values for different compounds. The RRF value of p-xylene is by definition 1, values below unity mean that the sensitivity is better than for p-xylene, values above unity mean that the sensitivity is less than that for p-xylene.

Table 2. RRF values measured with standard FCI coating in the PetroSense.

compound	RRF standard FCI coating
p-xylene	1
benzene	2.9
toluene	1.7
ethylbenzene	1.1
naphthalene	2.2
n-hexane	1.0
trichloroethylene	2.6
tetra	2.6

4.3 Results from the feasibility research for improving of the sensor

4.3.1 *General*

Based on the results obtained in activity 1a number of issues were selected for further study. It was thought that investigating these issues would be the fastest way to obtain the required improvements of the sensor.

Issues investigated were:

- fibre dimensions;
- spectral properties of the sensor components;
- noise level;
- other coatings of the optical fibre; this issue is important for improving the sensitivity and the development of a sensor sensitive for chlorinated solvents;
- long-term stability of the measurement signal;
- temperature effects;
- salt effects;
- pressure effects.

Most items in this list are focussed to improve the detection limit. The detection limit is determined by the sensitivity of the sensor and the noise level. A high sensitivity means that a small change in concentration will result in a large change in the measured signal. For any change in concentration to be detected, the change in signal must be significant when being compared to the noise level on the signal.

Sensors with a low detection limit (i.e. high sensitivity and low noise levels) should also be very stable over a long period of time. Unstable sensors that show a drift in the baseline for example, may lead to false conclusions. Lowering the detection limit simultaneously requires an improvement in the stability.

4.3.2 *Test assembly*

In order to facilitate the feasibility tests, a test assembly was designed in which several fibres could be characterized under similar circumstances. This test assembly allowed for easy changes of fibres and other relevant variables. Signals were measured with advanced electronics available at the laboratories of TNO Food and Nutrition. Raw data were collected electronically and stored on a PC for subsequent processing.

4.3.3. *Optimization of fibre dimensions*

Important parameters that define the dimensions of the fibre are the length of the coated section, the thickness of the coating and the diameter of the fibre. The most obvious parameter to optimize when considering the dimensions of the fibre is the length of the coated area, which can be considered as the interaction length of the sensor. Because FCI had already optimized the thickness of the coating, this was not studied in this project. Therefore, most attention was focussed on optimization of the interaction length.

From tests with different lengths of the coated area it became clear that the optimum sensitivity is obtained for fibres with an interaction length of about 1 inch. The results of the tests also showed that the performance of the sensor remains the same if the interaction length decreases from 1 to 0.75 inch. This is of importance for miniaturizing the sensor.

Reducing the diameter of the fibre was thought to increase the lossy modes. Experiments carried out did not show a significant improvement while the fibres were extremely fragile.

4.3.4 *Spectral optimization*

Although it was obvious that the main part of the signal in the original sensor could be attributed to changes in refractive index changes, it was investigated whether or not absorption of light by the analyte could possibly enhance the signals obtained. In the current sensor an infrared GaAs LED is applied as the light source. The emission maximum of this LED lies at 935 nm +/- 30 nm. The emission region of this LED only partially overlaps the absorption spectra of the xylenes, ethylbenzene, and toluene and no overlap is found for the absorption spectra of benzene.

Another LED, the GaAlAs LED, has an emission maximum at 880 nm which overlaps the absorption spectra of all the BTEX including benzene. It was thought that using this LED might include an absorptive effect in the measurement which could increase the sensitivity to especially benzene.

Measured improvements for benzene were insignificant using the GaAlAs LED, but the tests also showed that the launching angle of light from the LED was important for the sensitivity. Increasing the launching angle of the LED from 8 degrees to 20 improved the sensitivity with 30 %.

4.3.5 *Decreasing the noise level*

The results from the evaluation study showed that a reduction in noise level would be the most promising approach to reduce the detection limit of the current probes in relatively short time. Therefore a number of experiments were carried out in order to measure the noise level and find ways to reduce this noise.

The noise level is quantified by taking a measurement series in pure water. The standard deviation of this measurement series is the noise level. The value is expressed as a percentage of the standard deviation of the ratio (% STDEV-R). An estimate of the detection level can be calculated by multiplying this value by 3 (98 % confidence level) and then multiplying it with the sensitivity f_1 .

In the instruments produced by FCI the sensor signals are taken in a continuous mode without averaging. In this measurement mode, the LED is always on. An electronic form of averaging can be obtained by applying the LED in a pulsed mode which reduces the noise level and consequently lowers the detection limits. In order to simulate the process of electronic averaging, the noise in the ratio was monitored for different sampling rates and different rise times of the amplifiers. The data collected at different sampling rates were averaged off-line (on the PC) over a varying number of data points. These experiments showed that the noise levels were at least a factor 10 lower than the noise levels of the original sensor.

4.3.6 *Other coatings for higher sensitivity and chlorinated solvents*

To improve the sensitivity of the sensor and seek coatings that are sensitive for chlorinated solvents, 9 different types of coatings were tested. Coatings were applied to stripped fibres. After the cladding was removed, the stripped surface was coated with a suitable polymer.

The application of the polymer coatings is different for each polymer and has been optimized for each polymer or blend of polymers. Different techniques for coating the stripped surface were used: airbrushing, dip-coating and polymerization of the polymer with UV light coupled into the fibre. The first two methods were most successful.

A suitable coating for detecting chlorinated solvents consists of a mixture of PDMS (polydimethylsiloxane) and PTMSP (polytrimethylsilylpropyne). Unfortunately this coating is also sensitive to the BTEX compounds, but the sensitivity for both compounds is similar to the BTEX coating of FCI. A comparison of the results of tests with the FCI coating and a pure PDMS coating for the

BTEX compounds are shown in table 3. Table 4 shows the results obtained for different coatings in different chlorinated solvents. For comparative reasons all results are expressed as RRF values with respect to p-xylene.

Table 3. Mean RRF values for the FCI coating and PDMS for BTEX.

	FCI coating	PDMS
p-xylene	1	1
ethylbenzene	1	1.2
toluene	1.7	3.2
benzene	3.7	> 500

Table 4. Mean RRF values for some of the coatings for chlorinated solvents.

	FCI coating	pol7 (2:1)	PDMS	pol9	PS
p-xylene	1	1	1	1	1
TCE	3.5	0.93	0.66	1.78	0.22
tetra	3	0.78	0.55	-	0.95
chloroform	50	23	-	-	3.43
Cl-benzene	-	2.0	-	1.39	-

A sensor with a PDMS coating should be able to have a similar sensitivity as the FCI coating which is a detection limit in the order of 50 µg/L or less. The coatings, however, remain sensitive to a relatively wide range of compounds. Applying different sensors that have different selectivity may be a solution for this problem.

As can be seen in table 4, the PS coating is most sensitive for chlorinated solvents, but a serious drawback is that the coating is irreversibly changed by the measurement

4.3.7 *Improvement of stability*

In the original instrument the ratio is determined from the measurement of the light intensity from the LED directly and the light intensity at the other end of the optical fibre. An approach to improve the (long-term) stability of the measurement is based on the application of a reference fibre in the sensor. Light passing through the reference fibre is then measured by a reference photodiode. The ratio between the reference diode and the detection diode is used as the sensor signal.

Before an optical fibre can be used as a reference it must meet certain demands such as that it must:

- be insensitive for BTEX and chlorinated solvent;
- be stable in time;
- have the same or almost the same sensitivity for environmental parameters, such as temperature, turbidity, salts, pH, etc. as the detector fibre.

Different coatings were tested and finally two polymers were found that were applicable as a coating for a reference fibre; PMMA and a cross-linked fluorinated siloxane. Both reference materials proved to be insensitive to p-xylene and trichloroethylene (see fig. 5). Both polymers proved to be sensitive (but less pronounced) to salt effects and to variations of the refractive index of the sample solution. This was tested with solutions of both NaCl and ethanol. A potential problem with the PMMA coating is that this type of coatings is known to degrade gradually when exposed to water. Long-term stability experiments are required to test which polymers are best suited for application on a reference fibre.

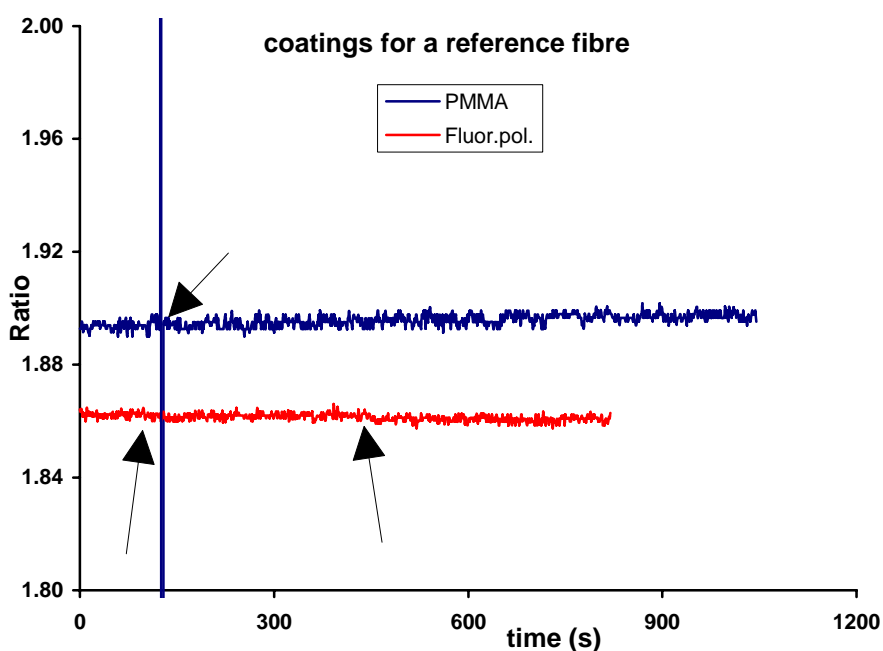


Fig. 5. Response of PMMA coating to p-xylene. Arrows indicate the moments where 20 ppm of p-xylene was added.

4.3.8 *Effects of temperature and salt concentration*

The stability of the sensor depends a lot on the temperature. This is the reason why a temperature correction is carried out in the current FCI probes. Due to limitations in the memory capacity of the electronics applied in the instrument, this temperature correction is very crude. Experiments show that the stability of the measurement could be improved significantly by applying a more advanced calibration procedure (i.e. a more detailed temperature correction based on calibration over a much smaller temperature range). Results also showed that the temperature primarily effects the baseline stability, the sensitivity remains the same.

Salt concentration is another effect that influences the sensor signal and consequently a varying salt concentration introduces an error. This effect is caused by the fact that the fibre also senses to some extent refractive index changes of the solution. This salt effect proved to be linear with salt concentration over a large range. The response of the old sensors to salts such as KCl and NaCl is in the order of 1 $\mu\text{g/L}$ as p-xylene/% (wt/vol) salt. Application of a reference fibre can be a method to remove the sensitivity to salt concentration.

4.3.9 *Effect of water pressure*

The effects of pressure on the measurements were also studied. It became clear that when pressure increases (for example by pushing the instrument into the ground), the baseline shows a shift. For the old sensors a dramatic decrease of the output signal of 18 mg/L was observed for an overpressure of 3 bar.

4.4 Development of demonstrators

4.4.1 General

The third activity of the project consisted of implementing the results obtained in the feasibility study so that developed concepts can be proved using commercially available electronics.

The feasibility study showed that averaging the measurement signal would result in lower noise levels and as a result in lower detection levels. In addition to the averaging, the concept of including a reference fibre in the sensor was thought worthwhile to test. In addition an attempt would be made to implement some of the new coatings.

Contrary to what was thought at the beginning of the project, the feasibility study showed the required changes to the sensor and instruments were large. As the budget and time was limited the consortium chose to proceed along two lines:

- FCI would modify the software in their acquisition instrumentation in order to allow for an off-line averaging of the measurements. Two prototypes would be provided so that TNO-NITG could carry out some column experiments.
- A completely new electronic averaging approach was implemented by TNO Food and Nutrition in a series of so-called demonstrator instruments. The demonstrator instruments consist of two parts, the probe with the sensor (with only the minimal amount of front-end electronics) and a special test box with all the other back-end electronics. The advantage of this approach is that this test box can be used with a number of different probes.

4.4.2 FCI probes with numerical averaging

As the signal averaging alone would result in a significant lower detection limit, FCI developed new software for their instruments. This resulted in two prototype probes that were applied by TNO-NITG in a column experiment (see chapter 5).

The averaging was done over 100 points. It turned out that a single averaged measurement required 20 minutes, during which the probe had to be switched on.

4.4.3 Test box

The averaging approach chosen is based on the use of a pulsed LED. Applying 0.5 millisecond pulses and summing the values of the output signals over a number of pulses, provides a means for averaging the signals in an electronic way. In addition, energy consumption is reduced significantly when compared with the continuous measurement because a single measurement is completed within 1 second. The heart of the test box consists of an electronic circuit board with software which was developed in order to demonstrate the principle of operation and its advantages. Figure 6 gives an impression of the user interface to the software.

The noise level in the reference and the detection channel is a function of the number of pulses applied. Experiments showed that 255 pulses resulted in similar noise levels as previously obtained by averaging 100 data points off-line afterwards in a PC; 0.05 % STDEV-R. The decrease in energy consumption in the pulsed mode is more than a factor 700. If an additional averaging by software is applied of 10 data points for instance, the noise level is further reduced to a value below 0.02 % STDEV-R, resulting in a possible detection limit for p-xylene less than 20 ppb. Table 5 gives some results obtained with the test box in combination with the test assembly used for the feasibility testing.

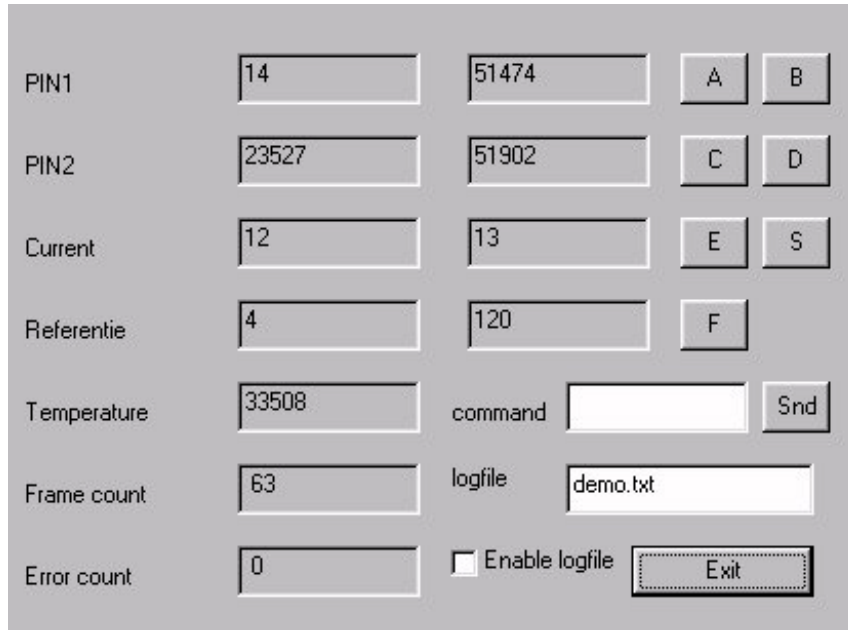


Fig. 6. An overview of the user interface of the software.

Table 5. Improvement of noise level and energy consumption applying summing the signals of 255 pulses in the processor on the test assembly, with an additional averaging in the PC as compared to the continuous mode (15 mA) applying 100 data points for averaging.

number of points used for additional averaging in a PC	% STDEV-R (255 pulses)	decrease factor energy consumption
0	0.050	784
2 *	0.035	392
5	0.022	157
10	0.016	78

* running average

4.4.4 Demonstrator probe with a reference fibre

The demonstrator probe including an optical design in which both a detection and a reference fibre are applied, requires a way to divide the light coming from a single LED over two fibres. This can be achieved with a beam-splitter. In this way there will also be a compensation for variation in the intensity of the LED, just as in the original design without a reference fibre.

A search on commercial available splitters did not result in a splitter that could be used for this purpose. They were either too big (the splitter has to fit into the metal housing of the sensor probe) or they were extremely expensive. Typically, commercially available splitters are designed for telecommunication purposes and they are designed to split the light into two or more branches with equal intensities. This is, however, not a criteria for the splitter in this research as the amplification factors in the electronics for both fibres could be different.

Therefore, a special splitter device was to be developed to which a LED module could be coupled on one end and the detection and the reference fibres on the other end. The use of commercially available micro-optical components would still lead to dimensions that are too large. Therefore the idea was to use optical fibre parts only and a metal container to fixate the fibre parts.

Two different designs have been realized; a rectangular device and a device with curved fibres (see fig. 7). Both devices have been functionally tested.

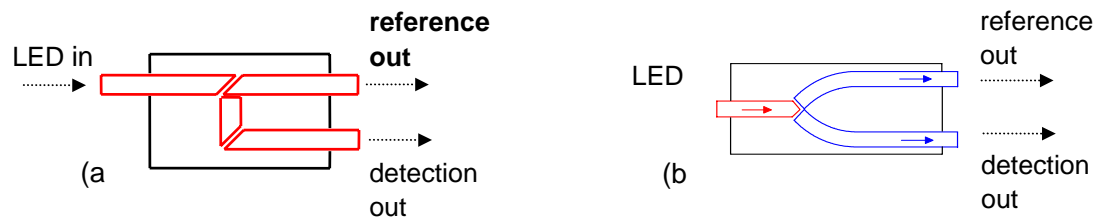


Fig. 7. Rectangular (a) and curved (b) splitter design.

The rectangular device is the easiest to produce but after testing it became clear that the amount of light going through the fibres was insufficient. Therefore the splitter with curved fibres was used, although it was difficult to produce (much handwork).

In order to build a probe, an electronic circuit board was developed to fit into the metal housing of FCI. This circuit board contains the basic electronic for the optical sensor: an optical splitter, a reference and a detection fibre, a LED and three photodiodes. This is schematically depicted in figure 8. The sensor part is glued on top of this print and the finished print was sent to FCI to put it into a metal housing.

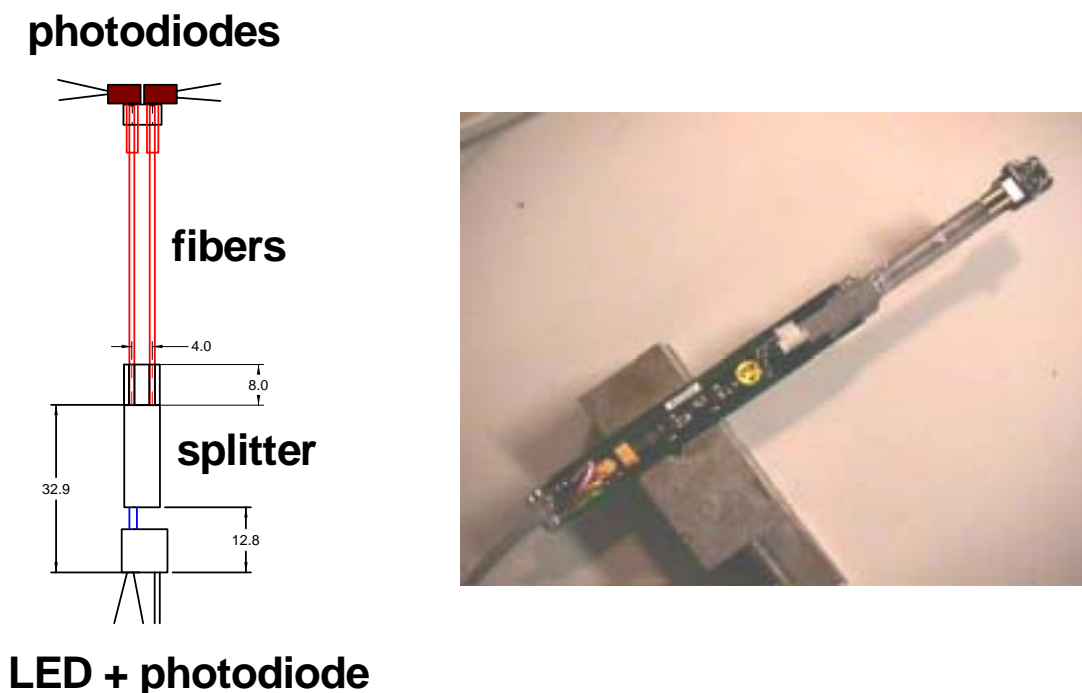


Fig. 8. Sensor part (global design) and photograph of finished demonstrator print.

Three demonstrator probes have been realised on basis of this design:

- BTEX sensitive fibre with a PMMA polymer reference fibre;
- BTEX sensitive fibre with a fluorinated polymer reference fibre;
- chlorinated solvent sensitive fibre with a fluorinated polymer reference fibre.

All demonstrators are functionally operating as expected. Unfortunately, the splitter in the first demonstrator had a poor transmission, in particular for the detection fibre. Therefore the first demonstrator could not be used for testing purposes.

It is also important to note that the demonstrators are primarily meant to demonstrate the detection principle. Therefore, the specifications of the demonstrators are not very good (i.e. the noise levels in the electronics are high resulting in detection limits in the order of 50 ppm). In addition to demonstrating the measurement principle, the demonstrators can be used to define the best approach towards the development of a prototype that meets the specifications that are required for the final instrument. Aspects that need to be improved upon are the use of optimal low noise electronic components, further improvements in the design of the splitter, etc.

Temperature

The demonstrator probes show a similar temperature dependency as the original FCI probes. The temperature effect is probably related to physical stress factors in the instrument. The temperature effects are repeatable and can therefore be compensated by using a calibration table or equation.

Salt effect

A test with the demonstrator equipped with the BTEX sensitive detection fibre and the fluorinated polymer reference fibre proved that the salt effect decreased to such an extent that it even could not be observed for salt concentrations up to 1 % (wt/vol).

Pressure

For one of the demonstrators the pressure tests were carried out similar to the experiments carried out in the sensor evaluation. The results were similar; 17 mg/L decrease of the output signal for an overpressure of 3 bar. After removing the pressure, the baseline did not drop to the same zero value. Apparently some kind of very slow relaxation process plays a role.

Chlorinated solvents

The sensitivity of the chlorinated solvent fibre to trichlorethylene (TCE) proved to be at least a factor 10 lower than the sensitivity to p-xylene. As this response to TCE is smaller than expected (the results from the feasibility showed similar sensitivities), it is assumed that the composition of the polymer applied in the demonstrator is different from the optimal composition determined in the feasibility study. Future experiments are required to fully understand this aspect.

4.5 Summary of the technical results

- The basic design and electronics of the chlorinated solvent sensor are similar to the design of the BTEX sensor.
- The main improvement is reached by averaging the measurements. This can be achieved electronically by using pulsed electronics or using software averaging. Averaging of the data resulted in less noise (% STDV-R). At this moment the noise levels are in the order of 0.02 % STDV-R. A combination of electronic and software averaging improves the noise level still further.
- With averaging the detection limits are improved by a factor 10 (compared to the detection limits of the old sensor). The detection limit of the new sensors applying electronic averaging has been shown to be in the order of 50 µg/L for BTEX and 100 µg/L for chlorinated solvent. Combining this with software averaging (10 points average) results in a detection limit of less than 20 µg/L for BTEX and less than 40 µg/L for chlorinated solvent. Compared to the old sensors, the energy consumption in the new sensor design is in that case still a factor 80 times lower.

- The sensing principle does not depend on the absorption of individual BTEX or chlorinated solvent compounds but is based on refractive index changes as a result of the BTEX or chlorinated solvent compounds. The sensor measures the total BTEX or chlorinated solvents.
- The BTEX sensor is primarily sensitive for BTEX and naphthalene but also for other compounds such as perchloroethylene. The sensitivity for the other compounds is, however, much less (at least a factor 3). The same counts for the chlorinated solvent sensor.
- The stability of the sensors can be improved by using a reference fibre. Application of a reference fibre (exactly the same fibre as the detection fibre, but coated with a non-BTEX or chlorinated solvent sensitive coating) improved the stability of the measurement.
- The optimum length of the fibre lies between 0.75 and 1 inch.
- The built in temperature correction needs to be improved (software).
- The new sensor design in the demonstrator is insensitive to variations of the salt content, but still sensitive to pressure variations.
- Two prototype instruments based on the FCI PetroSense technology with software averaging included have been built.
- Three demonstrator type instruments have been built in order to demonstrate the feasibility of the instruments that include a reference fibre and the new pulsed LED technology for electronic averaging.

LABORATORY COLUMN EXPERIMENTS

5.1 General

The new prototype instruments built by FCI with the new software averaging were applied in a column experiment to test the specifications under conditions that are more similar to field application than the laboratory batch tests that have been carried out before.

A breakthrough experiment is an experiment in which the transport of solutes through a soil can be studied in detail. Such an experiment can be used to test the ability of the sensors to detect the first arrival of a pollution front and to measure concentration changes in time.

The development of the new type of sensors with the pulsed electronics and the reference fibre has taken more time than expected. As a result no column experiments have been carried out with the demonstrator instruments.

5.2 Experimental set-up for the column experiments

The improved version of the FCI PetroSense is tested in the laboratory. Column experiments were developed to test the performance of the improved PetroSense. Specific aims were:

- a. to obtain the limit of detection for p-xylene;
- b. to test the stability of the baseline signal.

The limit of detection for p-xylene was obtained from breakthrough experiments: the response of the sensor on increasing concentrations of p-xylene was measured, while pore water samples were taken for separate analysis of p-xylene by gas chromatography. The stability of the baseline signal was investigated on the basis of the data collected sensor over a 2-month period. A photograph of the experimental set-up for the column experiments is given in figure 9 and a schematic representation in figure 10.

Openings for sensors were made in the side wall of the column. Opposite from the sensor openings, openings were made to enable the sampling of groundwater. The column was used in vertical configuration. Four sensors were placed in the column, the sensitive fibres directed downward. Two prototype PetroSense sensors and two CTD sensors (Conductivity-Temperature-Depth) were placed in the holes. The CTD sensors were meant to monitor the breakthrough of a conservative tracer, which was injected together with the p-xylene. Unfortunately, the CTD sensors did not function properly as no signal for conductivity was obtained.

The breakthrough experiment was started by forcing a constant flow of artificial groundwater through the column. The flow direction was from the bottom upwards. When constant flow conditions were achieved, a solution of p-xylene and NaBr was injected in the groundwater flowing in the column. Groundwater samples were taken at the moment the p-xylene reached probe 1 (see fig. 10). Sampling was continued for every 30 - 60 minutes, until the signal of the prototype sensor stabilized. The next day, after the system reached steady state, one final sample was taken from probe 1. The sampling procedure was optimized to minimize contact between pore water and air. The concentration of p-xylene in these samples was determined by gas chromatography (GC).



Fig. 9. Photograph of the column experiment.

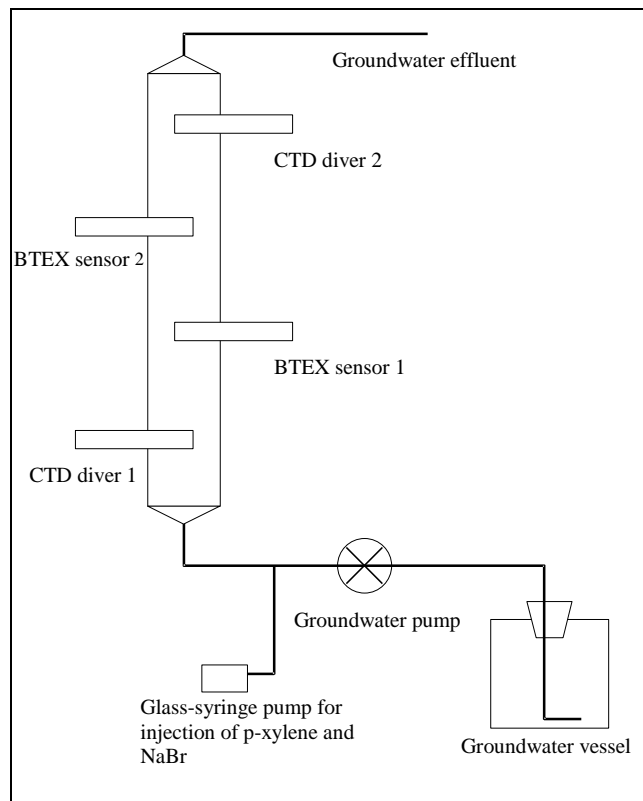


Fig. 10. Schematic representation of the column experiment.

5.3 Results

The results of a breakthrough experiment are shown in figure 11. Since the results of earlier breakthrough experiments were influenced by temperature variations in the laboratory, a number of measures were taken to control the temperature in the column was improved: the column was wrapped with tubing through which water with a constant temperature was flowing, the variation in temperature was less than 1 °C.

Figure 11a gives a comparison between the concentration measured by the prototype and the concentration determined with GC analysis. The scales used in figure 11a are chosen for optimal comparison. The results show that the sensor is capable of detecting the breakthrough of p-xylene. The limit of detection for p-xylene was calculated on the basis of the results from figure 11b. The (short-term) variation in the baseline signal is quantified statistically by calculating the average (μ) and standard deviation (s) of the base-line signal over the 5-day period before p-xylene was injected. Subsequently, the 99.7 % confidence interval (CI) was calculated as $\mu - 3s$. If the sensor signal drops below the 99.7 % CI, p-xylene is detected with a probability of 99.7 %. The p-xylene measurements carried out separately with the GC showed that the first detection of breakthrough was coupled to 22 $\mu\text{g/L}$ p-xylene. The GC analyses were carried out on samples that were taken over the same time interval as the particular sensor measurement (i.e. once every 20 minutes).

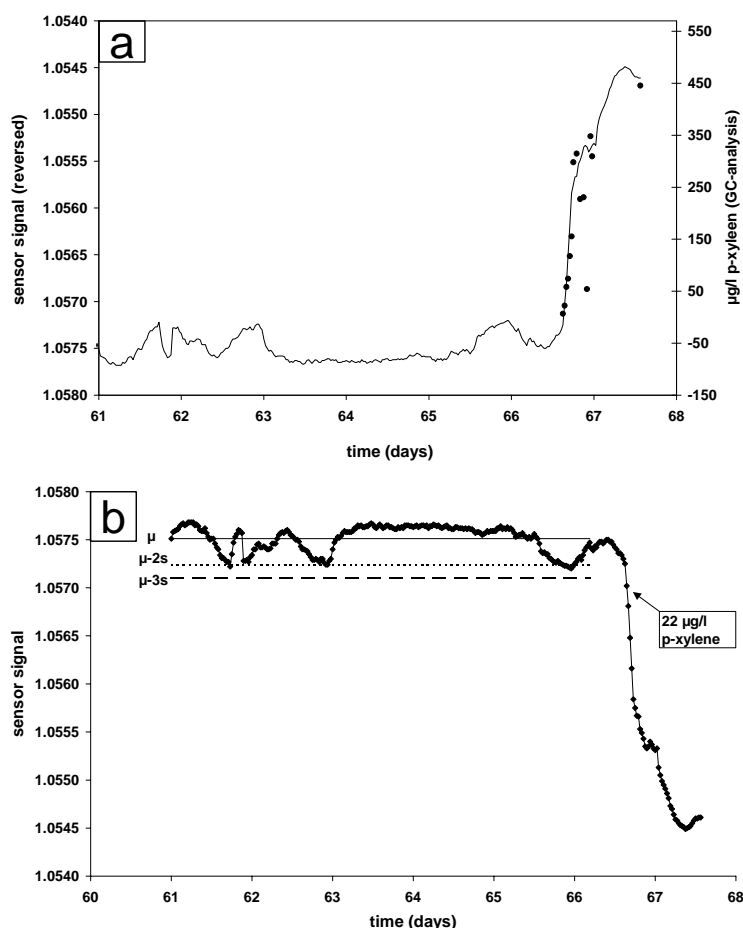


Fig. 11. Results of breakthrough experiment at $t = 66$ days. (a) Sensor signal (left axis) and GC analysis results (right axis) as a function of time. (b) Statistical analysis of baseline data: μ = average baseline signal, s = standard deviation, $\mu - 2s$ = 95 % CI, $\mu - 3s$ = 99.7 % CI. Statistics were calculated over a 5-day interval.

5.4 Conclusions drawn from the column experiments

Sensor properties

- These column experiments have demonstrated that it is possible to obtain a limit of detection for p-xylene with the PetroSense in the order of 50 µg/L. This limit of detection was obtained from a (linear) regression analysis of all the GC analysis results and corresponding sensor signals shown in figure 11. The actual limit of detection, however, is strongly dependent on the stability of the baseline, which is strongly effected, for example, by variations in temperature.
- The sensor signal is extremely sensitive to variations in temperature: a temperature variation of 1 °C already has a significant effect on the sensor signal.
- A drift in sensor signal was observed during the first month of testing. The sensors were new and never used before. Apparently, it takes time for (new) sensors to equilibrate.

Data processing

- A statistical analysis of the sensor baseline data is to be recommended. On the basis of a 99.7 % CI, the noise in the sensor signal can effectively be distinguished from the detection of p-xylene: if a sensor measurement falls below the 99.7 % CI, it is for 99.7 % sure that p-xylene is detected.

Sensor application

- The PetroSense seems to be especially suited to detect changes in BTEX concentrations.
- In the column experiments the concentration of p-xylene was increased from zero to approximately 500 µg/L. This means that the PetroSense was applied as a 'watch dog'. The good results obtained are promising for the application of the PetroSense as a watch dog in the field.

5.5 Recommendations

General

- Improve the software for the temperature correction of the sensor signal.
- Allow new sensors to equilibrate in 'clean' water for at least one month.
- Allow for sufficient time to let (new) sensors equilibrate with the groundwater.

Additional laboratory testing

- The application of the PetroSense in a BTEX plume. The response of the sensor on relatively high concentrations of BTEX, for example, is not known. Limits of detection for the prolonged application of the sensor in BTEX plumes should be determined.
- The recovery of the sensor signal after detection of p-xylene. There are indications that this period of recovery may last for several days, the current idea is that this may be due to the occurrence of multiple flow regimes in the soil column.
- The long-term effect of high concentrations of salt on the sensor response.

GENERAL INSIGHTS CONCERNING THE APPLICATION OF THE BTEX AND CHLORINATED SOLVENT SENSORS

6.1 Introduction

In the project many discussions were held within the consortium. These discussions were sparked by the results obtained during the project and resulted in a number of insights and ideas related to the application of the sensors. However, many of these ideas still have to be tested on real instruments and as a result the content of this chapter should be seen as an outlook to the future.

6.2 General

As was shown in the earlier chapters, the sensors developed in this project produce a signal in response to concentrations of certain compounds dissolved in the solution (or air) surrounding the sensor. Properties of the coating of the optical fibres in the sensor change as a function of the concentration of these compounds. The electronics in the sensor quantify these changes and produce a number related to these changes.

When applying these sensors it is important to realize that the measurement is an indirect measurement of the concentration we are interested in. This has several consequences for the application.

6.3 Response time of the sensor

When concentrations in the environment change the sensors require a certain period of time (typically in the order of 10 minutes) before a measurement can be made that is representative of the environment of the sensor. If concentrations in the environment change very fast, the sensor will lag behind. The effect of this on the measurement is that an averaged result is obtained, with lower peaks and higher valleys.

For monitoring purposes in the subsoil, the response time in the order of minutes is not a very large problem. Changes are generally very slow and the sensor has more than enough time to react to changes in the environment.

For application in column experiments it is important to realize that the response time of the sensor results in measurements that average changes that occur in a time shorter than 10 minutes. For example a step change in a concentration will appear to be a smooth rise over a period of 10 minutes.

The response time of the sensor also limits the application as a fast screening tool. Each measurement will require at least 10 minutes. If calibrations are required in between measurements this may take even longer. This reduces the attractiveness of these sensors for application in a cone mounted instrument, the slow response time will reduce the number of meters that can be screened per day significantly. However, there may be ways to circumvent this problem. The results show that the way the signal responds is very similar for different situations. Perhaps it is possible to describe the signal response with a function and extrapolate the function based on the first number of measurements. However, this requires much more testing than has been done at the moment. The accuracy of the measurements will be lower.

6.4 Selectivity of the sensor

The feasibility study clearly showed that the sensors are not very selective for specific compounds. The sensor gives a response to a number of compounds. The BTEX sensor for example, is most sensitive to p-xylene, but also reacts to the other xylenes, ethylbenzene, toluene and benzene but for each compound, the sensor shows a different sensitivity. In this project we quantify the sensitivity for a specific compound with the so-called relative response factor (RRF) which gives the sensitivity of the probe to a certain compound relative the sensitivity of p-xylene.

All sensors, except the reference sensors were sensitive to BTEX, chlorinated solvents, naphthalene etc. Tables 3 and 4 show examples of measured RRFs for the sensors tested in this project. It is clear that each sensor reacts to a number of compounds. This means that whenever we apply the sensor in the field we never know exactly which compounds are being detected unless we carry out a separate analysis in the laboratory. The sensors are calibrated with a p-xylene solution. The results of the measurements are then given as a concentration in p-xylene units, which is of course an arbitrary choice. It could just as well been toluene for that matter.

This has some large consequences for the application of the instruments. It means that laboratory measurements are always required because otherwise you never know exactly what you are dealing with. The reason to apply a sensor is to accurately monitor relative changes in the mixture of compounds being detected by the sensor between laboratory measurements. This enables the study of in situ process rates etc.

A complicating factor is that the RRF of the sensor for each compound may differ and if the mixture of compounds in the in coming groundwater changes in time (i.e. as a result of degradation) a very complicated picture may arise. This is especially the case for the chlorinated solvents, where the degradation of for example perchloroethylene results in the production of trichloroethylene which each have a different RRF. In simple situations, however, degradation results in a decrease in the total amount of compounds so a decrease in the sensor signal is expected.

In many situations we want to apply the sensor as a 'watch dog' because we are interested in the front of a pollution plume. In this application the sensor is positioned so that it can detect the arrival of a pollution front as early as possible. This application is very similar to the detection of a breakthrough curve presented in chapter 5. These sensors are perfectly suited for this application as they react to number of compounds, especially if they initially are installed in clean groundwater because then the detection limit can be optimized by statistically enhancing the signal.

6.5 Stability of the sensor

Long-term monitoring requires a very stable measurement signal. We want to be certain that a change in the signal is a result of a change in the concentration of one of the compounds we want to detect and not an artefact of changes in the sensor properties or changes in the environment of the probe that have nothing to do with the analyte.

The results from the feasibility tests and the column experiments with the improved PetroSense showed that the sensors are very sensitive to temperature changes. In addition it was also shown that pressure changes and background salt concentrations also have an effect on the sensor response. In a single fibre sensor, the temperature sensitivity is corrected for using a temperature correction procedure. However, for the new types of sensor this temperature correction procedure is too crude and needs to be refined.

Another approach that is the result of this project is to use reference fibres in the sensors. These reference fibres have the same response to some of the environmental changes as the BTEX or chlorinated solvent fibres. Using the signal from the reference fibre would result in a superior long-term stability. The tests carried out with the reference fibre show that salt effects are removed from the signal. The temperature sensitivity remains but can be corrected with a detailed calibration. The pressure sensitivity is still measured but the response is different with respect to the single fibre sensor. More experiments are required in order to understand these effects fully.

6.6 Laboratory reference measurements

Calibration of these instruments in field applications will be a challenge! As the instruments measure a number of different compounds, it will be very difficult to calibrate the sensors against a specific compound in the groundwater. An approach may be to calibrate the instruments against reference samples with predefined compositions.

Another issue will be the comparison of the sensor measurements with analyses carried out in the laboratory. If groundwater samples are taken according to protocol, monitoring wells should be flushed at least 3 times before taking a sample. Sensors hanging in such a well would be in equilibrium with the standing water. This equilibrium would be disturbed as a result of the flushing. It is important that when comparing the measurements carried out with sensors with laboratory measurements, multiple groundwater samples from a single well should be taken. The first sample should be of the standing water, the second sample according to protocol.

It is well-known that organic contaminants behave in complex ways in porous media. When large differences in pore sizes are encountered (a monitoring well is a huge pore!) it will be difficult to predict the behaviour. We often see that the organic contaminants collect in the well resulting in higher concentrations than in the surrounding groundwater. This complex behaviour has important impacts on the application of instruments that continuously measure groundwater quality in monitoring wells.

The fact that the standing water has a different concentration than the water after flushing is a potential problem for the application of sensors that measure groundwater quality. Perhaps certain measures should be undertaken in order to prevent the standing water in the monitoring well to disturb the quality of the groundwater in the filter. In the so-called Discrete Multi-Layer Samplers (DMLS) rubber discs are used to separate each dialysis cell from the others. This enables the detailed sampling of a concentration profile over a very long filter (i.e. up to 20 metres!).

6.7 Automated in situ measurement

The largest benefit of the application of sensors in the subsoil to measure groundwater quality in situ is that the measurement becomes more accurate. Losses that occur along the route from sampling to analysis in the laboratory do not occur. In addition, instruments that contain sensors are often fitted with data logging facilities. This makes a more or less continuous measurement feasible.

The fact that continuous measurements are possible also reduces the calibration difficulties. Often we are more interested in relative changes. For example when studying microbiological degradation we often are primarily interested in a decrease in concentration in time. Relative changes are more important than knowledge of absolute values.

Continuous measurements allow for statistics which increases the possibilities in the data analysis. An example is the interpretation of the column breakthrough experiments carried out in this project. In addition the combination of automatic sensor measurements with traditional sampling and laboratory analyses gives new opportunities for detailed quantitative studies in the kinetics of ongoing in situ processes.

6.8 Application of the sensors in cone penetration instruments

At the start of the project, it was thought that the sensors could be applied in cone mounted instruments for profiling applications. During the project we saw that the sensors have a response time of approximately 10 minutes which is too slow for application in a cone penetration instrument. Adding the pressure effects on the signal to this makes the application of this type of sensors in a profiling instrument not feasible.

Another question is the installation of the sensor in the soil. At the moment, the only way to carry out an in situ measurement is by hanging the sensor in a monitoring well which as was mentioned previously has a number of problems. Ideally the sensor would be installed directly in the soil. A way to do this would be to push the sensor in the soil to the required depth and leave it there. Many problems have to be overcome before this application becomes a reality. For example one of the most important ones concerns the retrievability of the instrument.

6.9 Aspects for future research

The results of this project show that the measurement of BTEX and chlorinated solvents is feasible with optical fibres. As a result three demonstrators have been developed with which the application of the sensors can be tested. Before continuing to develop instruments for field application it is important to obtain experience with the demonstrators.

Issues that require further study are:

- What conditions influence the measurements. Aspects to be studied in detail are temperature, pressure, salt, different contaminant mixtures etc.
- How should the sensors be applied in order to obtain a correct and interpretable measurement. What demands should be met for application in monitoring wells or for direct application in the soil.
- Protocols should be developed to compare the results obtained with these sensors with the traditional laboratory measurements.
- Guidelines should be developed for the interpretation of the results. Perhaps new units should be developed in order to present the measurement results.

The importance of these questions should not be underestimated. It is very well possible that these instruments provide superior results in comparison with the currently available measurements. The problem is that the standard we apply is based on the traditional measurements and strange results will be attributed to errors in the sensors. Often these strange results are not errors but true effects that were not picked up by the traditional measurement techniques. This could cause field practitioners to be suspicious of the results obtained with the new technology.

6.10 Additional research questions

Some questions have not been addressed in this project and some new questions have arisen. In addition to the questions from the previous paragraph these are:

- In what way can we describe the averaging process due to the response time? Knowing the type of averaging may allow us to develop a method to use the slope of the signal to determine the final concentration which may make the waiting time for a good measurement shorter.
- The concentrations of the samples used for comparisons were given in ppm. The sensor probably reacts to the amount of molecules it senses, what would the effect be of expressing the concentration as moles per litre be on the RRF?
- Detailed study of long-term stability! Development of improved algorithms to correct for temperature, pressure and salt effects. These algorithms could be based on filters based on transfer function approaches etc.
- The application of sensors that measure concentrations of certain compounds should be based on sound understanding of the chemical and physical processes in the subsoil. An issue that certainly should be addressed are the processes associated with the distribution of organic compounds in the subsoil.

APPENDIX A

**PHASE 2, ACTIVITY 3: LABORATORY COLUMN EXPERIMENTS WITH THE
IMPROVED PETROSENSE**

TNO-NITG report 00-155-B

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SUMMARY

Phase 2, activity 3: Laboratory column experiments with the improved PetroSense

This report describes the experimental results of laboratory column experiments with a prototype of the improved version of the FCI PetroSense [Veen, 2000a en b]. The PetroSense is a fiber optic sensor for aromatic compounds, which is in particular sensitive for BTEX compounds.

Column experiments were developed to test the performance of the sensor. Specific aims were:

- a. to obtain the limit of detection for p-xylene;
- b. to test the stability of the baseline signal.

The limit of detection for p-xylene was obtained from breakthrough experiments: the response of the sensor on increasing concentrations of p-xylene was measured, while pore water samples were taken for separate analysis of p-xylene by gas chromatography. The stability of the baseline signal was investigated on the basis of the collected sensor signals over a 2-month period.

On the basis of a statistic evaluation of the data, it has been demonstrated that it is possible to obtain a limit of detection for p-xylene with the PetroSense in the order of 50 ppb in column experiments. This limit of detection was obtained from a (linear) regression analysis of all the gas chromatographic analysis results and corresponding sensor signals. It also includes the standard deviation in the p-xylene concentration obtained by sampling and subsequent gas chromatographic analysis. The actual limit of detection, however, is strongly dependent on the stability of the baseline.

An important factor that determines the stability of the baseline appears to be the temperature: even a temperature variation of 1 °C was enough to affect the sensor signal. This means that the temperature correction that was included in the software of the data acquisition system has to be improved. Apart from the temperature effect, a drift in sensor signal was observed during the first month of testing. The reason for this drift is not known. It is recommended to take sufficient time for (new) sensors to equilibrate when applied to a (different) groundwater environment.

Recommendations for sensor data interpretation and future use of the PetroSense are given. The PetroSense seems to be especially suited to detect changes in BTEX concentrations. The results obtained in this project are promising for the application of the PetroSense as a guard in the field.

CHAPTER 1

INTRODUCTION

This report describes the experimental results of laboratory column experiments with a prototype of the improved version of the FCI PetroSense [Veen, 2000a en b]. The PetroSense is a fiber optic sensor for aromatic compounds developed by FCI Environmental Inc. It is claimed to be sensitive to aromatics in the C₆ to C₁₀ range both in the liquid phase and in the vapour phase. The improvements were made by TNO and FCI in an earlier phase of this project and mainly concern software improvements. The sensor was used with the data acquisition and data storage system CMS5000.

The PetroSense is the most sensitive for BTEX compounds, which are benzene, toluene, ethylbenzene and xylene. Basic specifications are given in table 1. The sensitive part of the sensor is a polymer coating applied on a 1 mm silica fiber. The principle of detection is based on the enrichment of aromatic components in this coating, resulting in a change in the coating's light guiding properties (refractive index). The detection assembly consists of a GaAs LED with reference photodiode, a fiber and a detection photodiode with daylight filter. The ratio of the detection photodiode and reference photodiode is taken as the sensor signal.

Table 1. Reported basic specifications; data obtained from FCI [Veen, 2000a].

parameter	properties for water
lower detection limit	0.1 ppm (as p-xylene)
sensitivity towards C _x H _y compounds	C ₆ and higher
relative response factors	7.14/2.82/1 (benzene/toluene/p-xylene)
accuracy	± 10 %
response time (95 %)	< 5 min

Column experiments were developed to test the performance of this improved PetroSense. Specific aims were:

- a. to obtain the limit of detection for p-xylene;
- b. to test the stability of the baseline signal.

The limit of detection for p-xylene was obtained from breakthrough experiments: the response of the sensor on increasing concentrations of p-xylene was measured, while pore water samples were taken for separate analysis of p-xylene by gas chromatography. The stability of the baseline signal was investigated on the basis of the collected sensor responses over a 2-month period.

CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 Introduction

A set of two prototype PetroSense sensors and a single CMS5000 unit arrived at TNO by the end of October 1999. Both prototype sensors were never used before. After arrival at TNO, the sensors were first conditioned for 1 hour in a 25 ppm solution of p-xylene. The sensors were then rinsed in streaming water for 1 hour and subsequently stored in a water vessel for several days, before they were placed in the column.

The experimental set-up for the column experiments is described in section 2.2, the experimental procedure for the breakthrough experiments is described in section 2.3.

After finishing the experimental set-up, BTEX-free groundwater was pumped slowly into the bottom of the column. The breakthrough experiments were started five weeks later. This initial 5-week period was used to monitor the baseline signal and to test the response of the sensor on the injection of p-xylene.

It became clear that the response of the PetroSense was very sensitive to small (2 - 3 °C) variations in temperature. These temperature variations arised from a difference between day and night temperature in the laboratory. Although a temperature correction was included in the software of the data acquisition system, this temperature correction was apparently not accurate enough. In the course of the experiments, measurements were taken to isolate column, probes and groundwater vessel in order to minimize the effect of temperature variations during the experiments (see section 2.2).

2.2 Column equipment

Column

A photograph of the experimental set-up is given in figure 1 and a schematic representation in figure 2. The column was made from glass. The length of the column was 80 cm and the diameter was 10 cm. In the side walls of the column, openings were made for sensors at 10 cm/0°, 30 cm/90°, 50 cm/180° and 70 cm/270°. On opposite sides of the sensor openings, openings were made for sampling purposes. A few centimetres of viton tubing (diameter 1.6 mm) was connected to each sampling opening. The column was used in vertical configuration.

Sensors

Four sensors (length 25 - 26 cm, diameter 1.9 - 2.2 cm) were placed in the column, the sensitive fibers directed downward. The two prototype PetroSense sensors were placed in the holes at 30 cm/90° and 50 cm/180°. Two CTD sensors (CTD means Conductivity-Temperature-Depth) were placed in the upper and lower holes. The CTD sensors were meant to monitor the breakthrough of a conservative tracer, which was injected together with the p-xylene. Unfortunately, the CTD sensors did not function properly as no signal for conductivity was obtained.

Sediment

The column was filled with sterilized quartz sand with grain sizes of 1.6 - 2 mm and a porosity of approximately 0.6.



Fig. 1. Photograph of the experimental set-up.

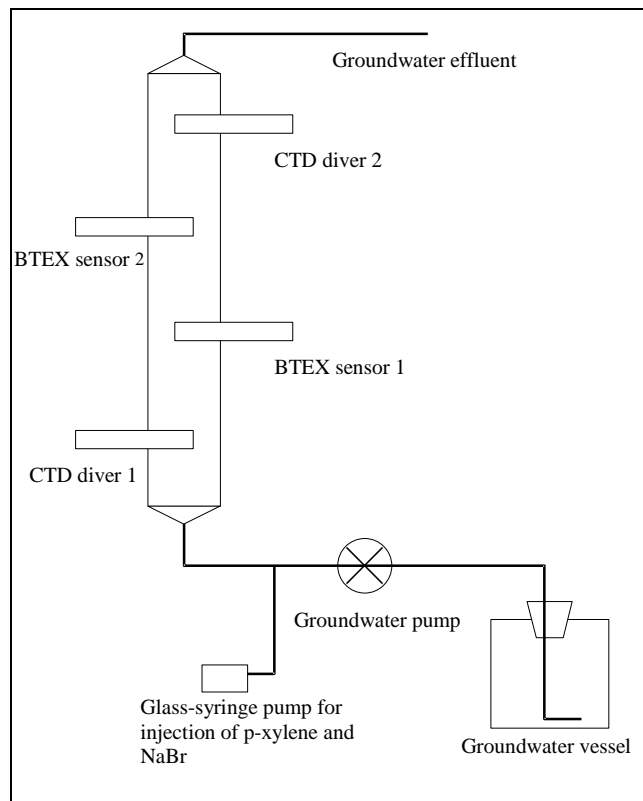


Fig. 2. Schematic representation of the experimental set-up.

Groundwater

The groundwater was artificially made and consisted of 33 mg/L Ca, 80 mg/L HCO₃, 30 mg/L Na, 57 mg/L Cl and 0.01 % azide (NaN₃). Azide was added as a poison to prevent the biodegradation of p-xylene during the experiment. The groundwater was pumped via tygon tubing into the bottom of the column at a speed of 1.2 ml/min. or 40 cm/day. The sodiumazide was added to the groundwater only during breakthrough experiments, to minimize the production of waste water.

Temperature control

During the first breakthrough experiment at t = 34 days, column, probes and groundwater vessel were isolated with several layers of plastic with air bubbles surrounded by aluminium foil. This method of isolation, however, appeared not to be successful enough: the temperature variation in the sensor signal was still 2 - 3 °C. Therefore, an improved method for temperature control was applied to the second breakthrough experiment at t = 61 days. During this second experiment, tubing was wrapped around the column that was filled with water that was temperature-controlled by a thermostat cooler. The temperature was set to 17 °C. The probes were isolated with several layers of plastic with air bubbles surrounded by aluminium foil. With this improved method, the temperature variation in the sensor signal was reduced to less than 1 °C.

Injection of p-xylene

p-Xylene and NaBr were added to the groundwater just before entering the column using a separate 50 ml Hamilton gas-tight syringe pump. The NaBr was added as a conservative tracer. The concentration of p-xylene in the syringe pump was measured by gas chromatography: the concentration was approximately 25 mg/L. Equilibrium concentrations of p-xylene and NaBr in the column were calculated to be 1.4 µg/L and 50 mg/L, respectively.

2.3 Breakthrough experiments

General procedure

Before the start of the breakthrough experiments, groundwater with 0.01 % azide was pumped through the column for a period of 5 days at a steady flow. Then, without changing any of the experimental conditions, the breakthrough experiment was started by the injection of a solution of p-xylene and NaBr to the groundwater entering the column. In order to smoothen the breakthrough curve of p-xylene, the rate of injection was slowly increased from zero to the desired rate in 40 minutes. The injection of p-xylene and NaBr was subsequently kept at a constant rate for at least 40 hours. Final concentrations of p-xylene and NaBr in the column were calculated to be 1.4 µg/L and 50 mg/L, respectively.

Sampling and analysis

From the moment that the p-xylene had reached probe 1 (see fig. 2), samples were taken for GC analysis every 30 - 60 minutes as described below, until the signal of probe 1 stabilized. The next day, with the system in steady state, one final sample was taken for GC analysis from probe 1. The time schedule for the experiments is given in table 2.

A sampling procedure was developed to minimize contact between pore water and air. In contact with air, p-xylene is lost rapidly by evaporation. Samples were taken from the viton tubing connected to the sampling holes using a 5-ml glass syringe. The contents of the glass syringe were then immediately transferred to the 2-ml vials used for gas chromatographic analysis. The first 3 - 4 ml of pore water obtained was not used. The 2-ml vials were stored at 4 °C until analysis. The concentration of p-xylene in these samples was determined by gas chromatography.

Table 2. Time schedule for breakthrough experiments.

activity	time
groundwater flow at 1.24 ml/min	day 1
start of p-xylene injection	day 6; 22:30 - 23:10
predicted breakthrough probe 1	day 7; 18:00
observed breakthrough probe 1	day 7; 9:00 a.m.
GC samples for probe 1	day 7; from 9:00 -18:00 every 30 - 60 minutes day 8; 10:00 a.m.
predicted breakthrough probe 2	day 8; 9:00 a.m.
observed breakthrough probe 2	day 7; 23:00
GC samples for probe 2	-

RESULTS AND DISCUSSION

3.1 Baseline stability

Figure 3 gives an overview of the sensor signal of the two PetroSense sensors during the 2-month period of testing. The presence of p-xylene in the column is marked with an asterisks. An overview of the experimental conditions as a function of time is given in appendix 1. Note that the detection of p-xylene is followed by a *decrease* in sensor signal. Figure 3c and 3d give 24-hour averages of the sensor signal, excluding the measurements made during breakthrough experiments with p-xylene. (It was assumed that the p-xylene had left the column four days after the injection was stopped).

From figure 3 it can be concluded that the sensor signal is subject to a long-term (order of several weeks) and a short-term (24 hour) variation. The smoother the baseline signal, the lower the limit of detection for BTEX compounds.

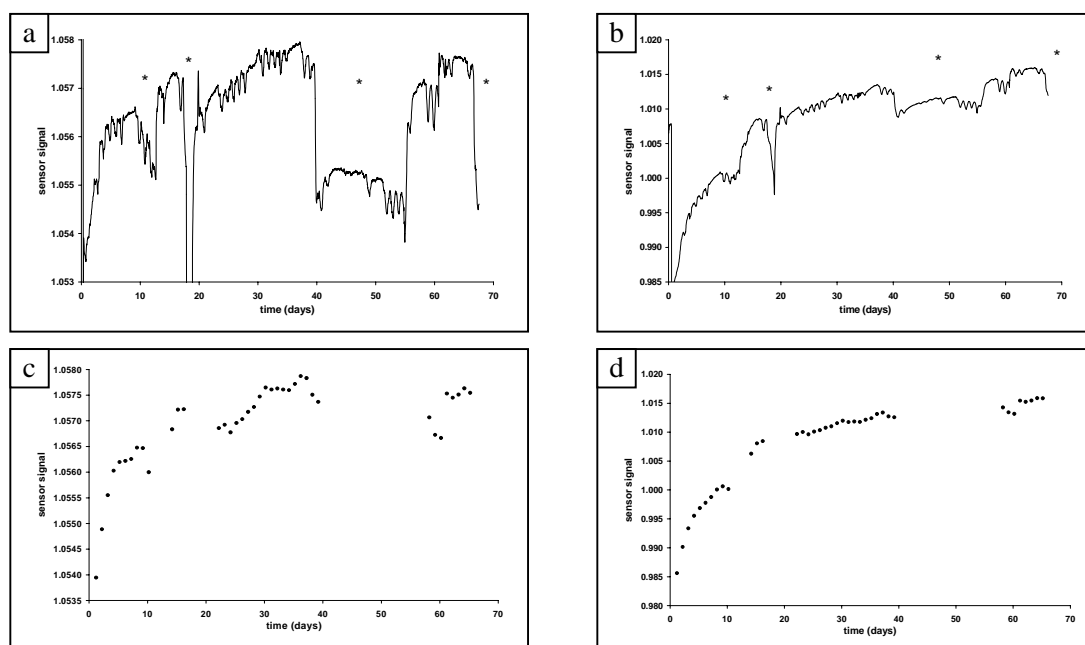


Fig. 3. Overview of sensor signal for probe 1 (a and c) and probe 2 (b and d) during the 2-month period of testing. In (a) and (b) the presence of p-xylene in the column is marked with an asterisks. Figure (c) and (d) give 24-hour averages of the sensor signal, excluding the measurements made during breakthrough experiments with p-xylene.

Short-term variation

Both sensors show a short-term (24 hour) variation in their baseline signal. This variation has been identified as a temperature effect. The temperature in the laboratory increases during the day and decreases during the night. The sensors registered a temperature variation of 2 - 3 °C. Effects on the limit of detection for p-xylene are discussed in section 3.2. Before the start of the second breakthrough experiment, we succeeded in limiting the variation in temperature to less than 1 °C (see section 3.3).

Long-term variation

Apart from the short-term variation due to temperature variations, a long-term variation in sensor signal can be observed. It is meant by 'long-term variation', a 'drift' in sensor signal over a period of days to weeks. A drift in sensor signal is clearly observed during the first month of testing. During the initial 5 days, the signal of both sensors shows a relatively sharp increase, which becomes more gradual in the next 4 weeks. After approximately one month, the sensor signal seems to be stabilized. The reason for this drift is not known. Apparently, it takes some time for new sensors to equilibrate.

Another drift in sensor signal is observed in between breakthrough experiments with p-xylene. Each time after contact with p-xylene, the sensor signal shows a gradual increase for several days. Samples for GC analysis were not taken during this period of time. Therefore, the possibility that a remnant of p-xylene was still present in the column, cannot be excluded at this time. Additional research is required to explain the reason for this observed drift.

3.2 Breakthrough experiment 1

Figure 4 shows the results of the first breakthrough experiment for probe 1, starting at $t = 34$ days.

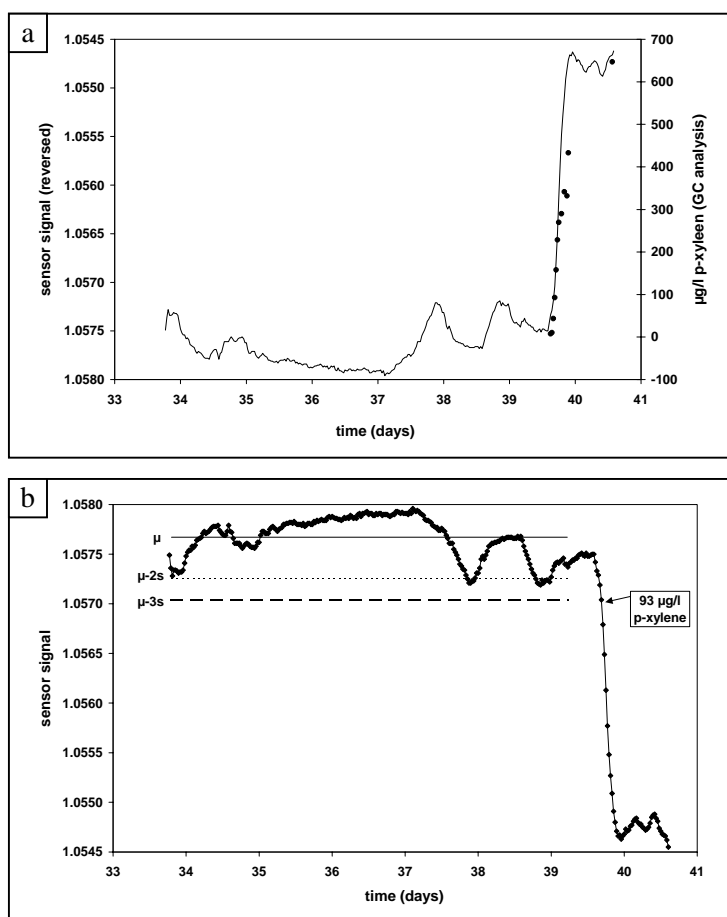


Fig. 4. Results of breakthrough experiment for probe 1 at $t = 34$ days. (a) Sensor signal (left axis) and GC analysis results (right axis) as a function of time. N.B. the left and right axes are not scaled correctly relative to each other. (b) Statistical analysis of baseline data: μ = average baseline signal, s = standard deviation, $\mu - 2s$ = 95 % CI, $\mu - 3s$ = 99.7 % CI.

In figure 4a, the response of the PetroSense and the GC analysis results are shown in one graph. At $t = 39.5$ days, p-xylene is detected by probe 1. The change in sensor signal closely corresponds to the actual change in p-xylene concentration as measured by separate GC analysis. It is not possible to obtain the limit of detection for p-xylene from figure 4a, as the sensor response signal and the GC analysis results are given on separate scales.

An indication for the limit of detection for p-xylene in this particular breakthrough experiment can be obtained from figure 4b. In figure 4b the (short-term) variation in the baseline signal is quantified statistically: average (μ) and standard deviation (s) of the baseline signal were calculated over the 5-day period before p-xylene was injected. Subsequently, the 99.7 % confidence interval (CI) was calculated as $\mu - 3s$. If the sensor signal falls below the 99.7 % CI, p-xylene is detected with a probability of 99.7 %. The first sensor signal that falls below the 99.7 % CI was found to correspond with a pore water sample with a concentration of $93 \mu\text{g/L}$ p-xylene. This concentration was determined by gas chromatography in a sample that was taken in the same time interval as the particular sensor measurement. This $93 \mu\text{g/L}$ p-xylene may be taken as a first approximation for the limit of detection for p-xylene for probe 1.

Temperature effects

Figure 5a shows the response of probe 1 and the temperature in one graph. The variation in temperature during the experiment was calculated to be $20.4 \pm 0.6 \text{ }^\circ\text{C}$. The higher the temperature, the lower the sensor signal. Note the lag between temperature changes and changes in sensor signal.

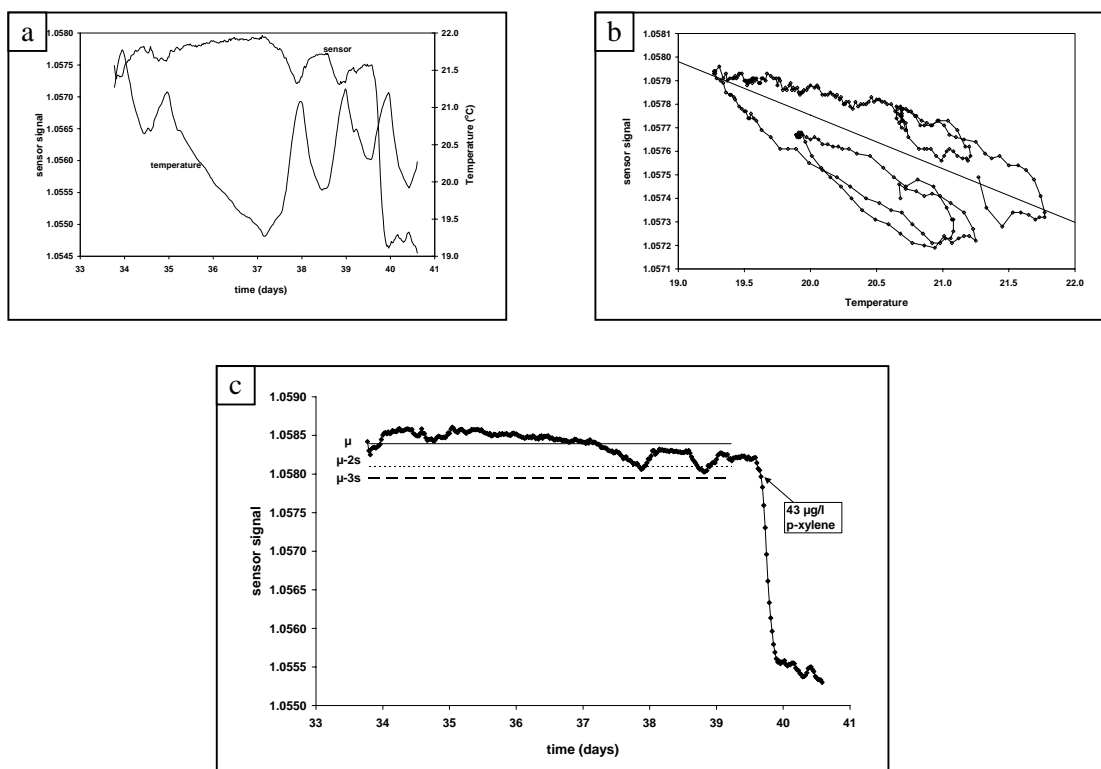


Fig. 5. Temperature dependence of the results of the breakthrough experiment at $t = 34$ days. (a) Sensor signal (left axis) and temperature signal (right axis) as a function of time. (b) Sensor signal as a function of temperature for baseline data. (c) Temperature-corrected sensor signal as a function of time and statistical analysis of baseline data (symbols are explained in fig. 4).

In figure 5b the sensor signal is shown as a function of the temperature for the 5-day period before injection of p-xylene. The sequence of data points is strongly influenced by the lag between temperature and sensor signal. Linear regression was applied to the data in figure 5b. The regression results were subsequently used to adjust the sensor signal towards a constant temperature of 17.2 °C; this is the average temperature of the second breakthrough experiment discussed in section 3.3. The temperature-corrected sensor signal is shown in figure 5c. Average, standard deviation and 99.7 % CI of the baseline data were calculated. The first sensor signal that falls below the 99.7 % CI was taken as an approximation for the limit of detection for p-xylene: 43 µg/L p-xylene.

3.3 Breakthrough experiment 2

The results of the second breakthrough experiment are shown in figure 6. Due to the improved temperature control of column and sensors, the variation in temperature is now less than 1 °C. As a result, the short-term variation of the baseline signal has strongly decreased compared to the experiment described in section 3.2.

It follows from figure 6a that the GC analysis results follow the change in sensor signal relatively well. The limit of detection for p-xylene was calculated on the basis of figure 6b as described in section 3.2. A temperature correction was not applied to the data. The first sensor signal that falls below the 99.7 % CI corresponds to 22 µg/L p-xylene as measured by separate GC analysis.

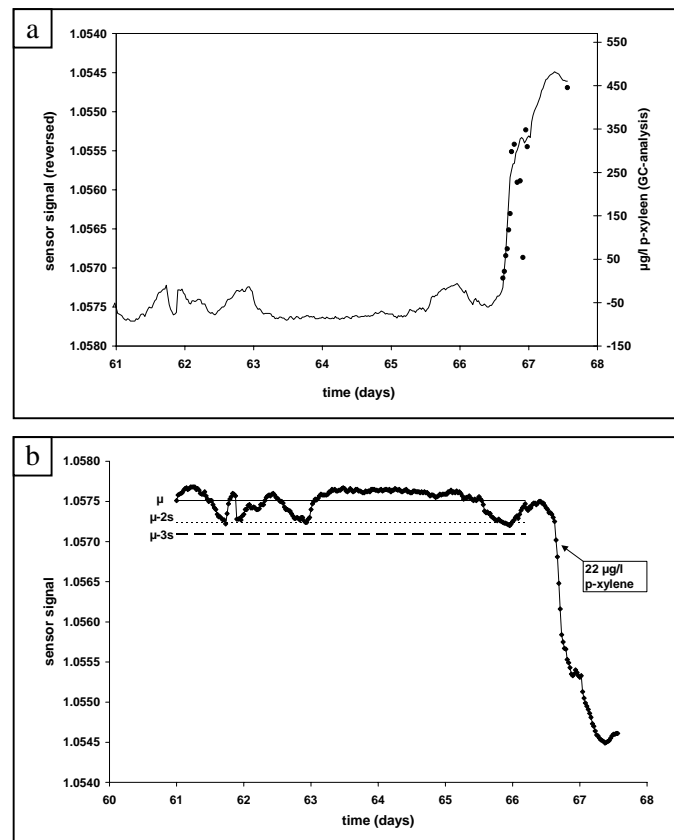


Fig. 6. Results of breakthrough experiment at $t = 66$ days. (a) Sensor signal (left axis) and GC analysis results (right axis) as a function of time. N.B. left and right axes are not correctly scaled relative to each other. (b) Statistical analysis of baseline data (symbols are explained in fig. 4).

3.4 Estimation of the limit of detection for p-xylene

This section will focus on the reliability of the detection limit of the PetroSense for p-xylene as determined from the experiments described in section 3.2 and 3.3.

The accuracy at which this limit of detection can be determined mainly depends on the reliability of the sampling procedure and the subsequent gas chromatographic analysis.

The most critical sources of errors are:

- *Loss of p-xylene during sampling*
p-Xylene is a volatile compound which evaporates in contact with air. In addition, p-xylene may be lost by adsorption on surfaces. The risk of evaporation was minimized by limiting air contact during sampling. The risk of adsorption was minimized by the use of relatively inert materials. The magnitude of the resulting error is not known.
- *The distance between the sampling hole and the sensitive part of the sensor*
Samples were taken from the sidewall of the column, while the sensitive part of the sensor was positioned near the centre of the column. Under perfectly ideal conditions, concentrations of p-xylene are equal at the side faces and the centre of the column. However, in a column that contains a number of sensors and sampling holes along its side faces, the groundwater current is probably not ideal. The magnitude of the resulting error, however, is not known.
- *The timing of the moment of sampling*
The PetroSense yields one measurement every half an hour. Each measurement is an averaged value, obtained from several individual measurements over a 15-minute period. The best moment for taking samples for GC analysis, therefore, is halfway the 15-minute period. The error introduced when the timing of the sampling is different depends on the steepness of the breakthrough curve. In the experiments described in section 3.2 and 3.3, the p-xylene concentration was observed to increase from 0 to 400 ppb in 8 hours, which corresponds to an increase of only 0.8 ppb/min. The magnitude of the error introduced by a non-ideal timing, therefore, is estimated to be small (less than 4 ppb).

The overall error in the individual p-xylene concentrations as obtained by sampling and subsequent GC analysis was obtained as follows:

First, the general variation in GC analysis results was investigated. Figure 7 shows all GC analysis results as a function of the sensor signal at the time of sampling. Figure 7a gives the data for experiment 1, the sensor signals being temperature-corrected as shown in figure 5c. Figure 7b gives the data for experiment 2.

Then, linear regression was applied to the data in figure 7a and 7b. The results of the regression calculations are included in figure 7: slope, intercept and standard error in y (p-xylene concentration). The standard error in the p-xylene concentration was calculated to be approximately 50 µg/L for both experiments.

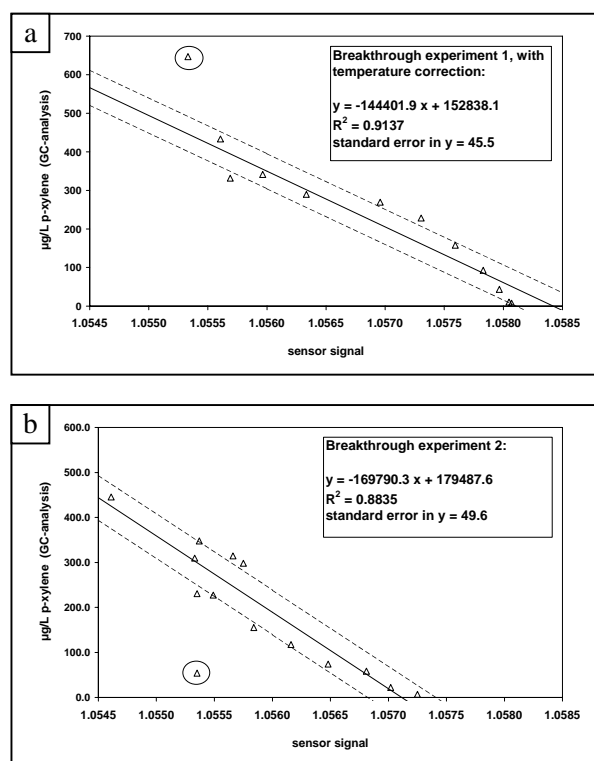


Fig. 7. Linear regression of GC analysis results and corresponding sensor signal for experiment 1 (a) and 2 (b). The data from experiment 1 are temperature-corrected as shown in figure 5c. The encircled data points were not included in the regression calculations.

Subsequently, the limit of detection for the sensor signal was taken from figure 5 (experiment 1) and figure 6 (experiment 2), which is the first sensor signal that falls below the 99.7 % CI as calculated from the baseline data. On the basis of these values and the regression equation given in figure 7, the limit of detection for p-xylene was calculated. The results are shown in table 3.

Table 3. Limit of detection of improved PetroSense for p-xylene.

experiment	limit of detection for sensor signal		limit of detection (in $\mu\text{g/L p-xylene}$)	
	CI 99.7 %	value	value	standard error
1	1.057948		68	46
2	1.057098		3	50

It follows from table 3 that the limit of detection for p-xylene in the first experiment is $68 \pm 46 \mu\text{g/L}$ and in the second experiment $3 \pm 50 \mu\text{g/L}$. These results demonstrate that it is possible to obtain a limit of detection for p-xylene of 50 $\mu\text{g/L}$ in column experiments. The actual limit of detection, however, is strongly dependent on the stability of the baseline of the sensor signal, as demonstrated with the results obtained for experiment 1 and 2.

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

Properties of the sensors

- It has been demonstrated that it is possible to obtain a limit of detection for p-xylene with the PetroSense in the order of 50 ppb in column experiments. This limit of detection was obtained from a (linear) regression analysis of all the gas chromatographic analysis results and corresponding sensor signals. It also includes the standard deviation in the p-xylene concentration obtained by sampling and subsequent gas chromatographic analysis. This limit of detection is similar to the limit of detection obtained earlier in batch experiments [Veen, 2000a en b]. The actual limit of detection, however, is strongly dependent on the stability of the baseline, which is, for example, strongly affected by variations in temperature.
- The sensor signal appears to be extremely sensitive to variations in temperature: even a temperature variation of 1 °C is enough to affect the sensor signal.
- A drift in sensor signal was observed during the first month of testing. The sensors were new and never used before. Apparently, it takes time for (new) sensors to equilibrate.

Data processing

- It has been demonstrated that it is very useful to process the sensor baseline data statistically. On the basis of a 99.7 % CI, the p-xylene signal can effectively be distinguished from the noise in the baseline signal: if the sensor signal falls below the 99.7 % CI, p-xylene is detected with a probability of 99.7 %.

Sensor applications

- The PetroSense seems to be especially suited to detect changes in BTEX concentrations. The results obtained in this project are very promising for the application of the PetroSense as a guard in the field.

4.2 Recommendations

General

- Improve the software for the temperature correction of the sensor signal.
- Allow new sensors to equilibrate in 'clean' water for at least one month.
- Take sufficient time for (new) sensors to equilibrate when applied to a different groundwater environment.

Additional laboratory testing

- The application of the PetroSense in a BTEX plume. It is not known whether the limit of detection of the sensor will change upon continuous contact with high concentrations of BTEX compounds.
- The recovery of the sensor signal after detection of p-xylene. There are indications that this period of recovery may last for several days.
- The long-term effect of high concentrations of salt on the sensor response.

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Development of an optical sensor for BTEX and chlorinated ethylenes. Activity 1. Evaluation of FCI sensors and Activity 2a. Feasibility BTEX and CKW sensors.
TNO report V 2936/01.

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TNO report V 2936/02.

APPENDIX 1

OVERVIEW OF CHANGES IN EXPERIMENTAL CONDITIONS

remarks	time (d)	date	time
groundwater pump on, groundwater without NaN ₃	0.00	99/11/12	18:30:00
new batch of groundwater added	3.02	99/11/15	18:00:00
injection of NaBr (500 mg/L) for 1.5 hours	3.70	99/11/16	10:30:00
new batch of groundwater	5.72	99/11/18	11:00:00
new batch of groundwater, 0.1 % NaN ₃ added	9.92	99/11/22	15:30:00
start injection of p-xylene, circa 1 mg/L	10.82	99/11/23	13:00:00
pump stopped (air in the system)	11.70	99/11/24	10:30:00
column emptied (of groundwater)	12.40	99/11/25	9:00:00
pump on (very slowly), groundwater without NaN ₃	13.02	99/11/25	18:00:00
new batch of groundwater, with NaN ₃	16.67	99/11/29	12:00:00
start injection of p-xylene, circa 1 mg/L	17.04	99/11/29	18:30:00
start injection of p-xylene circa 7.5 mg/L	17.82	99/11/30	13:00:00
start injection of p-xylene circa 18 mg/L	17.94	99/11/30	16:00:00
start injection of p-xylene, circa 3 mg/L	18.02	99/11/30	18:00:00
stop injection of p-xylene	18.72	99/12/01	11:00:00
column isolated, new batch of groundwater with 0.01 % azide	33.80	99/12/16	13:00:00
start injection p-xylene, circa 1 mg/L	39.22	99/12/21	23:00:00
probe 1: 7.6 ppb p-xylene	39.66	99/12/22	9:30:00
probe 1: 10.4 ppb p-xylene	39.68	99/12/22	10:00:00
probe 1: 43.4 ppb p-xylene	39.70	99/12/22	10:30:00
probe 1: 92.9 ppb p-xylene	39.72	99/12/22	11:00:00
probe 1: 158.0 ppb p-xylene	39.74	99/12/22	11:30:00
probe 1: 228.3 ppb p-xylene	39.76	99/12/22	12:00:00
probe 1: 269.8 ppb p-xylene	39.80	99/12/22	12:30:00
probe 1: 289.8 ppb p-xylene	39.84	99/12/22	13:30:00
probe 1: 341.5 ppb p-xylene	39.88	99/12/22	14:30:00
probe 1: 331.8 ppb p-xylene	39.92	99/12/22	15:30:00
probe 1: 433.2 ppb p-xylene	39.94	99/12/22	16:00:00
injection of p-xylene stopped	40.48	99/12/23	5:00:00
probe 1: 647.0 ppb p-xylene	40.60	99/12/23	8:00:00
pump stopped (holiday)	40.64	99/12/23	9:00:00
pump started	54.68	00/01/06	10:00:00
column temperature controlled by a thermostat	60.78	00/01/12	12:00:00
new batch of groundwater, with 0.01 % azide	62.85	00/01/14	15:00:00
start injection of p-xylene	66.19	00/01/17	23:00:00
probe 1: 6.8 ppb p-xylene	66.30	00/01/18	9:30:00
probe 1: 22.2 ppb p-xylene	66.65	00/01/18	10:00:00
probe 1: 58.3 ppb p-xylene	66.67	00/01/18	10:30:00
probe 1: 74.0 ppb p-xylene	66.69	00/01/18	11:00:00
probe 1: 117.4 ppb p-xylene	66.71	00/01/18	11:30:00
probe 1: 155.3 ppb p-xylene	66.73	00/01/18	12:00:00
probe 1: 298.0 ppb p-xylene	66.75	00/01/18	12:30:00
probe 1: 314.6 ppb p-xylene	66.79	00/01/18	13:30:00
probe 1: 227.3 ppb p-xylene	66.83	00/01/18	14:30:00
probe 1: 230.5 ppb p-xylene	66.88	00/01/18	15:30:00
probe 1: 54.0 ppb p-xylene	66.92	00/01/18	16:30:00
probe 1: 347.9 ppb p-xylene	66.96	00/01/18	17:30:00
probe 1: 309.6 ppb p-xylene	66.98	00/01/18	18:00:00
injection of p-xylene stopped	67.48	00/01/19	6:00:00
probe 1: 445.5 ppb p-xylene	67.56	00/01/19	8:00:00
pump stopped			

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