1. **Project Champion:** **Geoffrey Wilcox**

2. ***Project Title***

SENSING OF BENZENE AND RELATED COMPOUNDS IN WATER WITH POTENTIAL FOR APPLICATIONS IN AIR

3. ***Principal Investigator(s)***

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4. Description

4.1 Problem

Benzene is an aromatic hydrocarbon found in petrol and is used for a range of industrial purposes. Benzene is classified as a human carcinogen. It is a volatile compound that is toxic to the hematopoietic system and has caused acute myelogenous leukaemia in populations with high occupational exposures [1] [2]. Although there is doubt concerning the leukemogenic effect of benzene at lower concentrations, the suspicion that long-term exposure to even small amounts of benzene may be harmful, together with the widespread exposure of the general population has caused concern. Environmental levels of benzene are in the sub ppb range and thus the significant research challenge is in developing a sensing device that can measure below that level to be of value to industry and the agencies monitoring the environment.

In recent years the standard procedures for determination of hydrocarbons (chlorinated solvents, pesticides and petroleum hydrocarbons) includes extraction from water using in some cases perhalogenated solvents and subsequent infrared spectrometry or GC-MS. The **solvent extraction** technique must be replaced due to the environmental need to reduce the solvents which are being used. In the determination of chlorinated pesticide concentrations, large volumes of samples are required to enable pre-column enrichment, and this can be tedious and prone to error. **Solid-phase extraction** followed by thermal desorption or liquid-liquid extraction using hexane or pentane, with gas chromatography for single substance determination does not provide results which are satisfactory. The GC traces are complex, particularly in the case of wastewater analysis and the technique is expensive.

4.2 BTEX compounds

There are large quantities of organic compounds, which are manufactured and used by industry, the federal government and municipalities, which have created the greatest potential for ground water pollution. The soluble aromatic hydrocarbons associated with petroleum fuels or lubricants are one such group. The group includes benzene, toluene, ethylbenzene, and various xylene isomers (BTEX) often associated with petroleum spills. The BTEX compounds are part of the list of major organic contaminants according to the Environmental Protection Agency as in table 1.

Volatiles	
Acrolein	1,1-Dichloroethylene
Acrylonitrile	trans-1,2-Dichloroethylene
Benzene	1,2-Dichloropropene
Bis (chloro methyl) ether	cis-1,3-Dichloropropene
Bromodichloromethane	Trans-1,3-Dichloropropene
Bromoform	Ethylbenzene
Bromomethane	Methylene chloride
Carbon tetrachloride	Styrene
Chlorobenzene	1,1,2,2-Tetrachloroethane
Chloroethane	1,1,2,2-Tetrachloroethene
2-Chloroethyl vinyl ether	Toluene
Chloroform	1,1,1,-Trichloroethane
Chloromethane	1,1,2-Trichloroethane
Dibromochloromethane	Trichloroethylene
Dichlorodifluoromethane	Trichlorofluoromethane
1,1-Dichloroethane	Vinyl chloride
1,2-Dichloroethane	Xylene

[1] Infante, P.F., Lancet 2 (8028): 76-78 (1977)
[2] Wong, O., Occup Environ Med 52:380-384 (1995)

Table 1 Environmental Protection Agency List of priority pollutants

The BTEX compounds are aromatic hydrocarbons with a molecular structure based on that of the benzene ring, C_6H_6. Table 2 shows the structures of the BTEX compounds together with important physico-chemical parameters. The benzene molecule molecule consists of 6 carbon and 6 hydrogen atoms in a cyclical form. The ring in the centre represents a delocalised cloud of electrons. The carbon atoms in benzene are also capable of bonding to functional groups, and isomerisim is possible.

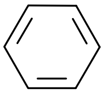
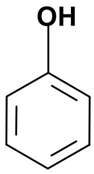
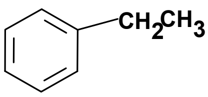
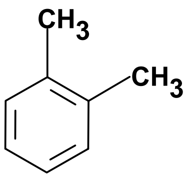
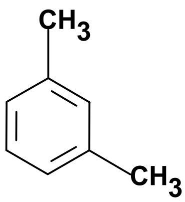
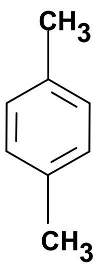
Name	Structure	Molecular weight in g	Solubility in water (mg/L)	Soil-Water partition coefficient
Benzene		78.11	1780	97
TOLUENE		92.1	500	242
Ethylbenzene		106.17	150	622
Xylene, ortho		106.17	170	182
Xylene, meta		106.17	173	331
Xylene, para		106.17	200	622

Table 2 BTEX related compounds

Benzene is reported to be a carcinogenic and inhalated benzene is readily absorbed by blood and is strongly taken up by fatty tissues. Benzene can be converted to phenol by an oxidation reaction in the liver that is responsible for the unique toxicity of benzene, which involves damage to marrowbone, and is known to cause leukemia. Benzene is also a skin irritant and can affect the central nervous system. Toluene is classified as moderately toxic and is much less toxic than benzene because it is readily excreted from the body.

4.2 Previous work in the area

We have already investigated the potential for certain materials to enrich benzene and related compounds. This work was completed as part of a PhD thesis. [3] The study highlighted some key principles in diffusion characteristics of each of the aromatic analytes. Table 1 illustrates structures of each of the analytes under investigation.

It was found that analyte shape has an impact on its enrichment for example ortho- meta- and para- xylene each had different diffusion coefficients. [4] By incorporating materials that can enrich aromatic species with a fibre-optic it was possible to effect continuous measurements using infrared spectroscopy.[5] Research by Lima and co-workers [6] has shown the use of silicone as a sensing material for BTEX determination in conjunction with near infrared spectroscopy. Sensitivities in the region of 1.1-1.8 ppm and limit of detection of 0.7 ppm were obtained. More recently ZnO nanoparticles have been used to enhance sensitivity of measurements for determination of gaseous benzene. [7] While there is a significant volume of work reported in sensors for environmental organic pollutants, there is still much scope for work in the area of BTEX monitoring – that can be applied to on-line continuous monitoring for the stakeholders.

4.3 Hypothesis / anticipated solution.

This project aims to develop sensors based on smart materials capable of extraction of benzene and related compounds of industrial importance. The general requirements for an analytical measurement technique include sensitivity, short response time and reversibility. These requirements are met by choosing an appropriate polymer film for the sensor element. The organic and mostly hydrophobic, molecules diffuse out of the aqueous phase into the polymer, where they can be detected by the absorption of IR radiation (Figure 1).

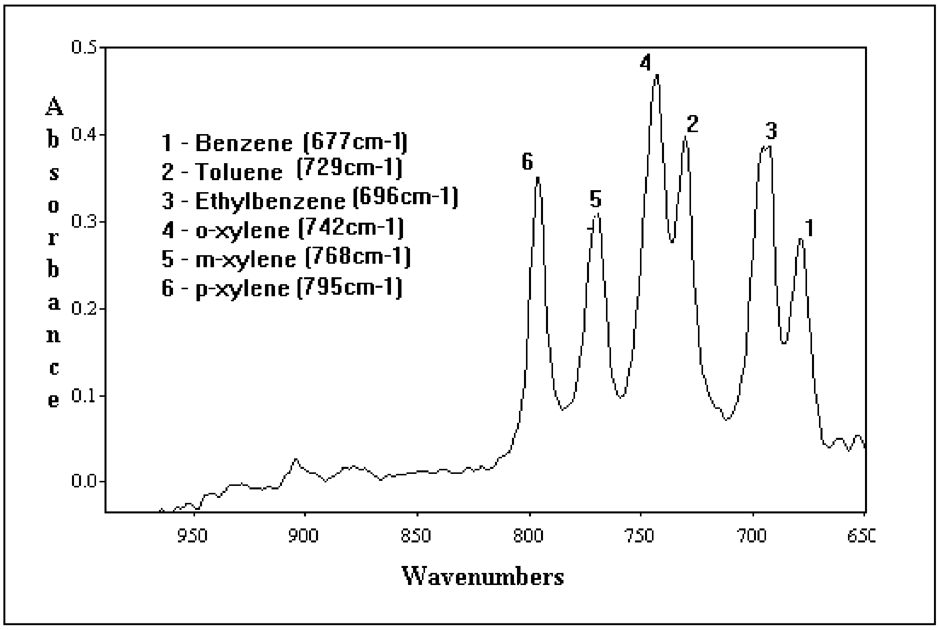


Figure 1: Spectrum of mixture of BTEX compounds analysed with polymer coating consisting of 2% PVC with 75% diisooctyl azelate (no. Scans = 64, Resolution=2). Illustrates that specific IR bands can be used for each analyte.

[3] F. Walsh, Development of an optical sensing technique for BTEX compounds in the environment, using novel enrichment films with ATR-FTIR, PhD Thesis, 2003
[4] F. Regan, F. Walsh, J. Walsh, Intern. J. Environ Anal Chem, 83 7-8 621-631 (2003)
[5] R. P. McCue, J.E. Walsh, F. Walsh and F. Regan, Sens Actuators B, 114 438-444 (2006)
[6] K. Lima, I, Raimundo and F. Pimentel, Sens and Actuators, 125 229-233 (2007)
[7] C. Ge, Materials Science and Engineering, In Press (2007) doi:10.1016/j.mseb.2007.05.008

Some polymers which have shown potential in enrichment of organic species [8] [9] include, low density polyethylene, poly (isobutylene), poly (butadiene), ethylene/propylene copolymer, poly (tetrafluorethylene) and poly (vinyl chloride). We have shown for example selective and reversible enrichment of chlorinated hydrocarbons and pesticides in PIB[4] Teflon[10] and PVC[11]. The **target species** in this research are benzene, toluene, ethylbenzene and xylene and its isomers.

4.4 Objectives:

- The selection of polymers for analyte enrichment;
- Development of improved materials based on nano-particle doped polymers or sols.
- Determination of enrichment profiles (time and concentration) of aromatic compounds
- Development and optimisation of spectroscopic detection;
- Optical design and optimisation;
- Design of a dedicated laboratory-sensing instrument.

We will aim to demonstrate the potential of the sensing approach to benzene and other aromatics in water, and show proof of concept for use in air monitoring also. Our main emphasis will be on the sensitive detection of these aromatics – thus focussing on detection and analyte enrichment.
Initially the fundamental measurement technique, which forms the basis of the proposed sensor, is optical evanescent wave sensing which is an extension of the established spectroscopic technique known as attenuated total reflection (ATR) (Figure 2).

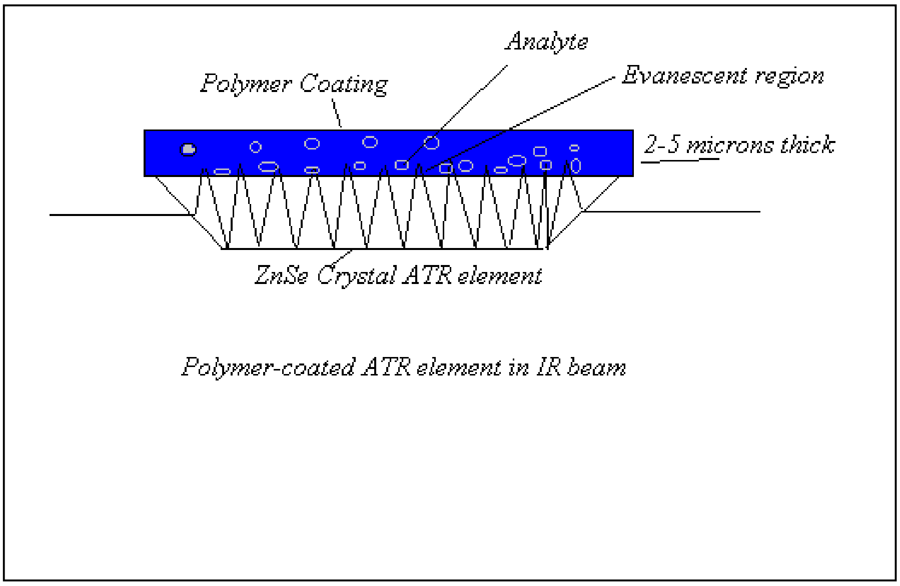


Figure 2: Diagram showing polymer-coated ATR spectroscopic set-up

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[8] Krska, R., Rosenberg, E., Tage, K. and Kellner, R., Appl. Phys. Lett., 61 (15) 1778-1780.
[9] Walsh, J. E., MacCraith, B. D., Regan, F., Vos, J. G., Meaney, M., Lancia, A. and Artjushenko, S., Proc. SPIE, 2508 (1995) 233.
[10] Regan, F., MacCraith, B. D., Walsh, O'Dwyer, K, J. E., Vos, J. G. and Meaney, M., Vibrat. Spectros., To be published in 1997.
[11] Regan, F., Meaney, M., Vos, J. G., MacCraith, D. D. and Walsh, J. E., Anal. Chim. Acta, 334 (1996) 85-92.

Light coupled into an optical fibre (optical element) propagates down the fibre core due to the processes of total internal reflection between the fibre core and clad[12]. However, some of the light travelling down the fibre penetrates into the clad region. This is called the evanescent wave which propagates down the fibre and decays exponentially in amplitude with distance from the core/clad interface[7]. Any analyte in the clad region will absorb the evanescent wave at specific wavelengths and the degree of absorption is directly related to the analyte concentration [13]. Furthermore, if an analyte enriching, polymer is used as the fibre cladding greater sensitivity can be achieved.[13 14 15 16]

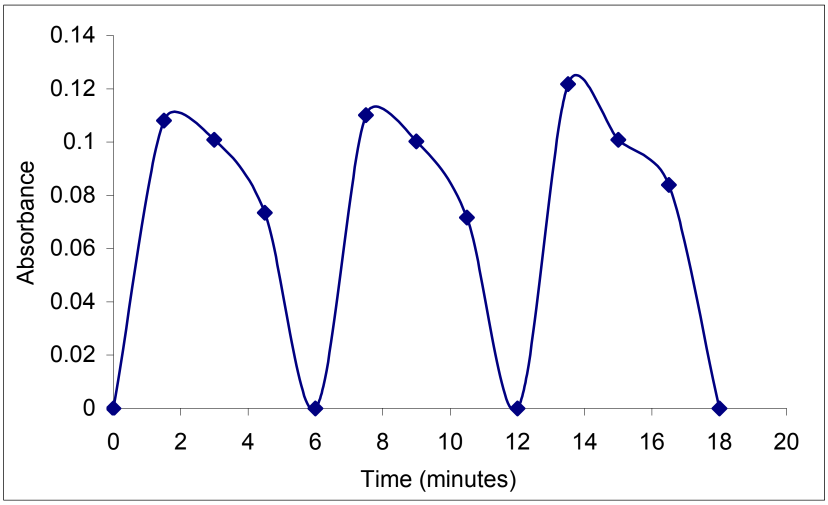

Figure 3: Reproducibility and reversibility of measurements of Toluene as part of a BTEX mixture (6% PVC with 30% diisooctyl azelate enrichment material). Measurements of Pure air containing BTEX compounds.

As part of the work in this project we aim to investigate the potential for monitoring BTEX species in AIR. Some previous studies have illustrated the potential of using the plasticised materials for determination of known concentrations of BTEX in pure air. Figure 3 shows the measurement of toluene in pure air in a mixture containing benzene. The latter shows proof of principle that the materials could be exploited for air monitoring. To achieve this aim, it will be necessary to use the materials that are studied, as passive samplers for air, and subsequently carry out IR measurement of the exposed materials.

4.5 Potential benefits

This project will deliver a proof of concept device that can measure benzene and/or related aromatics in water and potentially in air. Novel materials will be developed for enrichment of analyte species. The materials will be tested using laboratory-based infrared ATR technology and this will lead to development of a laboratory-based fibre-optic or planar waveguide approach to developing a novel sensing device i.e. a modular device.

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[12] Harrick, N.J., 1987, Internal Reflection Spectroscopy, (Harrick Scientific Corporation, New York).
[13] Schnitzer, I., Katzir, A., Schiessel, U., Riedel, W. J. and Tacke, M., Journal of Appl. Phys., 66 (1989) 5667-5670.
[14] Paiss, I., Moser, F. and Katzir, A., Fiber and Integrated optics, 10 91991) 275-290.
[15] Sanghera, J.S., Kung, F., Pureza, P. C., Nguyen, V.Q., Miklos, R.E. and Aggarwal, I.D., Appl. Optics, 33 (1994) 6315-6322.
[16] McCabe, S. P., 1994, An Investigation of Evanescent Wave Gas Sensing Using Zirconium Fluoride Optical Fibres. Ph.D. Thesis, Dublin City University.

Ultimately the benefits of such technology lie in improved monitoring of aromatic concentrations in the environment to reduce emission levels, alert alarm level increases and continuously monitor to provide valuable real-time information to the industry.

4.6 *Timetable*

The project is scheduled to run for 36 months. There are three main work packages divided into a series of individual tasks that will enable project progression over there three year period. The student will be part of a larger research team in the NCSR with access to expertise for a number of researchers in the Centre and the PIs research group.

WP1: Project definition: Hardware, analytes and monitoring specifications

1.1 Review relevant optical component technology
1.2 Define hardware requirements (i.e. fibre, spectrophotometers and filters)
1.3 Define range of analytes to be detected
1.4 Define design of development system
1.5 Define methodology

Description

The aim of this work package is to study the state of the art since previous work has been carried out. It will be necessary not only to study the literature, but also the technology currently available for sensing organic parameters such as those under study, and also the market for such devices should be mapped. The latter will not be done in a great depth as this would require additional financial support.

The modular components will be identified and purchased and the design of the modular system will be investigated. In the first instance it will be desirable to procure the field IR system, so that materials can be tested in-situ. This WP will run for the first 3-months, but design aspects may also take place at later stages as the work progresses.

WP 2: Design construction and testing of laboratory development system

2.1 Identify appropriate polymers for analyte enrichment
2.2 Optical evaluation of hydrocarbons and polymers
2.3 Optimise techniques for polymer coating of optical material substrates
2.4 Construct and test flow cell / sample holder for sensor head
2.5 Couple sensor head into spectrometer and detector via optics
2.6 Test set-up with calibrated samples
2.7 Optimise sensor set-up

Description

The polymers for use in the analyte enrichment are a key to the success of the work. These will be studied from the project kick-off, taking knowledge from previous work and focussing efforts on improving the detection sensitivity and also study of air sample enrichment processes in polymers.

For liquid samples it will be necessary to investigate the delivery of sample and thus flow-cell design will be studied.

Calibrated samples will be studied using GC-MS as a validation procedure and this will allow continuous validation of the material development.

WP3: Design, construction and testing of modular instrument

3.1 Development of modular instrument
3.2 Laboratory sample testing of modular prototype instrument
3.3 Recommendations & design for prototyping
3.4 Thesis and reports

Description

At the half-way stage in the project it will be necessary to start to pull the various elements of the device together. Lengthy tests in the laboratory will be carried out to establish the best working conditions and optimum measurement protocols for particular analytes. Through out this stage of work valuable knowledge will be gained as to the next steps in taking a laboratory system from bench to scale-up, to further validation and subsequent development of the sensor product in the long term. Crucial to the success of this stage will be adequate testing of the materials and device to test the performance and provide recommendations for the next stages. An important aspect at this point will also require the study of diffusion processes through the polymers and this will feed into the development of passive materials for air monitoring.

Table 2: Work plan & deliverables

Month WP	1-6	7-12	13-18	18-24	25-30	31-36
1.1						
1.2						
1.3						
1.4						
1.5						
2.1						
2.2						
2.3						
2.4						
2.5						
2.6						
2.7						
3.1						
3.2						
3.3						

4.7 Deliverables

Deliverable	Item
D1	Commencement of project and literature review
D2	Novel Material design for hydrocarbon determinations
D3	Laboratory-based sensing system
D4	Sensitivity Enhancement
D5	Publication of peer reviewed papers, PhD Thesis

The outcomes of this project will result in 4 peer-reviewed research papers, conference presentations, PhD thesis, a modular sensor system for benzene and/or related compounds and recommendations for prototype development. The student be involved in weekly research group meetings and monthly group seminars aiding in preparation for national and international conference presentations as well as Questor presentations.

4.8 Costs

COSTS €	Year One	Year Two	Year Three	Total
Salaries	15000	16000	17000	48000
Student Fees	4500	5000	5500	15000
Consumables	8000	3000	3000	14000
Travel/subsistence		2000	2000	4000
Total	25500	26000	27500	81000

It is desirable to attract a graduate qualified in analytical chemistry or materials science with an interest in optical science to carry out this work for a period of three years toward the award of PhD. The project costs are summarised in the table above. The relatively high consumables request for year 1 reflects the need for polymers, support materials for testing, gas delivery systems, ATR crystals etc. We will aim to purchase a mini IR spectrometer €14,000 that can be taken to the field to test the materials and will aim to have matching funding for this through the NCSR and Faculty.

Capital equipment items such as the FTIR spectrometer, waveguide handling instruments and optical test benches, which would normally be required as part of a proposal, already exist at the NCSR and are available for use in this project.