National Development Plan 2007 - 2013

Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

STRIVE
Report Series No.36

Analytical Devices for Autonomous Monitoring of the Environment

STRIVE
Environmental Protection Agency Programme
2007-2013

SSTI

Comhshaol, Oidhreacht agus Rialtas Áitiúil
Environment, Heritage and Local Government

Environmental Protection Agency

The Environmental Protection Agency (EPA) is a statutory body responsible for protecting the environment in Ireland. We regulate and police activities that might otherwise cause pollution. We ensure there is solid information on environmental trends so that necessary actions are taken. Our priorities are protecting the Irish environment and ensuring that development is sustainable.

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EPA STRIVE Programme 2007-2013

Analytical Devices for Autonomous Monitoring of the Environment

(2004-RS-AIC-M4)

STRIVE Report

Prepared for the Environmental Protection Agency

by

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ACKNOWLEDGEMENTS

This report is published as part of the Science, Technology, Research and Innovation for the Environment (STRIVE) Programme 2007-2013. The programme is financed by the Irish Government under the National Development Plan 2007-2013. It is administered on behalf of the Department of the Environment, Heritage and Local Government by the Environmental Protection Agency which has the statutory function of co-ordinating and promoting environmental research.

We gratefully acknowledge the role played by associated researchers throughout the course of the project: Dr King Tong Lau, Dr Benjamin Schazmann, Conor Slater, Nameer Alhashimy, Dr Daniel Kim, Dr Sarah Brady, Silvia Scarmagnani (Dublin City University); Dr Christina McGraw (University of Otago, New Zealand); Dr Roderick Shepherd (University of Wollongong, Australia); and Shannon Stitzel (Towson University, USA). We acknowledge too the contributions of our collaborators Dr Shane Peper (Pacific West National Laboratory, USA); Dr Eric Bakker (Curtin University of Technology, Australia); Mitsubishi Electric Research Laboratories (Boston, USA); and University College Dublin. We also acknowledge Dr John Hurley from NITON UK for technical guidance with the XRF instrument.

Finally, we thank the Science Foundation Ireland, Marine Institute, Enterprise Ireland and the CLARITY CSET for the additional funding, which has enabled the research activity to continue, and for research outputs to be commercialised in Ireland and Europe. We thank the Environmental Protection Agency for providing the resources to enable us to make this important contribution to the realisation of next-generation monitoring technologies.

The EPA STRIVE Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

EPA STRIVE PROGRAMME 2007–2013

Published by the Environmental Protection Agency

PRINTED ON RECYCLED PAPER

ISBN 978-1-84095-321-3 10/09/150
Price: Free

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Executive Summary

The project 'Analytical Devices for Autonomous Monitoring of the Environment' was organised into three sub-projects:

1 Development of an autonomous phosphate analyser for measuring nutrient levels in rivers, lakes and coastal regions.

2 Development of a light-emitting diode (LED)-based instrument for colorimetric measurement of light-modulated photoswitchable polymeric films.

3 Development of methods for qualifying the elemental (mainly heavy metal) content of soils and dust samples.

A portable system for the long-term monitoring of phosphate was developed. This completely autonomous device incorporates sampling, reagent and waste storage, colorimetric detection, wireless communication, and a power supply into a complete, miniaturised system. The integration of a wireless communication device allows acquisition parameters to be controlled remotely and adjusted according to individual needs. In addition, wireless communication capabilities allow the results to be downloaded remotely and displayed in real time. The autonomous capabilities of the system – combined with the portability and wireless communication – provide the flexibility needed for on-site phosphate monitoring. This system demonstrates the potential of truly autonomous microfluidic platforms for use in long-term environmental monitoring. The current limit of detection (LOD) of the system is approximately 0.3 mg/L P-PO_4, which limits the application of the system to water bodies with elevated phosphate levels, and the monitoring of point sources. Improvements to the sensitivity of the system through optimisation of the microfluidic manifold and detection system is ongoing, with the aim of decreasing the LOD towards the lower limits specified in the relevant European Union directives.

The results of the light emitting diode (LED) research show that it is possible to use low-power LED light sources to detect colour changes arising at different regions of the visible spectrum, and to control the state of surfaces functionalised with photoswitchable molecules. In the future, such capabilities could be vital for the realisation of surfaces whose binding characteristics can be controlled using light, which could greatly extend the useable lifetime of sensing surfaces exposed to hostile samples i.e. switch between active (measuring) and passive states.

Attempts to deploy ion-selective electrodes (ISEs) for Pb^{2+} sensing show that solid-contact ISEs can be utilised successfully for soil analysis. The introduction of a conductive polymer as an inner contact between the ion selective membrane and the solid support improved the performance of ISEs. It was shown that the detection limit of the electrodes is comparable with the detection limit of atomic atomic absorption spectrophotometry (AAS), a routinely used instrumental technique in environmental analysis. Sample digestion with diluted nitric acid by simple ultrasonication resulted in concentrations of Pb^{2+} that were measurable with both ISEs and AAS, with good correlation between the two methods. This digestion can then be applied for *in situ* soil digestion, significantly simplifying sample preparation. Furthermore, a good correlation between results obtained with ISEs and AAS implies there is a possibility of applying the former technique in soil analysis. Inexpensive construction, good detection limits and a simple experimental set-up make ISEs an excellent prospect for *in situ* environmental analysis.

The results demonstrate that portable X-ray fluorescence (XRF) instruments could be employed to provide rapid *in situ* detection of the presence of toxic metals such as lead (Pb), arsenic (As), copper (Cu) and zinc (Zn) in soil, or in episodes of dust blow-offs. Even though AAS technology is used widely and very precise, it is very expensive, laborious

and slow. Since the area tested is under a constant risk (the Silvermines area in Co. Tipperary), there is a need for a reliable analytical methodology that can be fast, low cost and performed under field conditions. The XRF instruments provide simultaneous analysis of up to 25 elements, which significantly cuts the time required for sample characterisation. In addition, the technique allows the detection of heavy metals in soil as samples can be analysed in the solid state, and therefore no digestion (wet chemistry) is required. This represents a *critical advantage* of the proposed technique, when compared with the conventional methods of analysis.

1 General Introduction

This document summarises research activities and outcomes funded under the EPA grant (2004-RS-AIC-M4). The research was organised into three sub-projects focused on the:

1 Development of an autonomous phosphate analyser for measuring nutrient levels in rivers, lakes and coastal regions.

2 Development of a light-emitting diode (LED)-based instrument for colorimetric measurement of light-modulated photoswitchable polymeric films.

3 Development of methods for qualifying the elemental (mainly heavy metal) content of soils and dust samples.

Each of these sub-areas will be described and the progress made summarised. At the end of the document, pointers to sources of additional information are given for readers who wish to see how the work continues beyond the lifetime of the project.

2 Background to the Development of the Microfluidic Phosphate Analyser

Eutrophication is a process in which the elevated nutrient levels in a water system stimulates excessive plant growth (algae, weeds, etc.). This process, which causes deterioration in the health of an aquatic ecosystem (Mainstone, 2000; Smith, 1999) by decreasing the amount of dissolved oxygen available for other organisms, is one of the most common water quality issues for many regions (Carpenter, 1998; Smith, 1999). Phosphorus, in the form of phosphate, is a key component in the eutrophication process as it is typically the limiting nutrient in freshwater bodies. The monitoring of phosphate levels is therefore a crucial step in the protection of vulnerable areas. Phosphate measurements are typically made by manual collection and filtering of samples. This approach to monitoring is labour intensive and costly, and provides only limited information about the spatial and temporal distribution of phosphate throughout a water system. The need for high-frequency phosphate measurements was highlighted by Donohue et al. (2005) who, through sampling every two weeks and every month, monitored distributions of nitrogen and phosphorus in 11 rivers over a two-year period. River flow rates were obtained for each sample and the relationship between river flow and nutrient concentration was studied. Their results indicated that the transfer of nutrients to rivers can occur in the order of hours. In addition, significant seasonal differences in phosphate concentrations were found, highlighting the need for an autonomous sensor capable of making high-frequency measurements over an extended period of time.

The objective of this research was to develop the previous bench-top system into a deployable prototype for a portable, autonomous analyser for phosphate in natural waters. The requirements for this system can be summarised under the headings of:

- Sensitivity – sufficient for use in freshwater.
- Power consumption – minimal, to maximise deployable lifetime.
- Cost – ownership and operation must be affordable for target users.
- Size/portability – size and weight of system must suit easy portability and deployment.
- Measurement frequency – high-frequency measurements should be integral (a key advantage of *in situ* monitoring systems).
- Robustness – the system must be robust enough to withstand transport between sites and prolonged deployment in typical outdoor conditions.

In this work, a compact and portable system for the detection of phosphate in natural waters was developed. This completely autonomous device incorporates sampling, reagent handling, mixing of reaction products, colorimetric detection, waste containment, wireless communication, and a power supply. The system employs a low-power detection and communication system, so the entire instrument can operate autonomously for seven days on a 12 V battery. The deployable lifetime can be extended significantly through incorporation of a solar panel. The integration of a wireless communication device (global system for mobile communication [GSM] modem) allows acquisition parameters to be controlled remotely and adjusted according to individual needs, in addition to enabling data transfer. In recent work at Dublin City University (DCU), the power budget allows for more than three months operation with a single 12 V battery, using a measurement frequency of 1 measurement/30 min (Cleary, 2009).

Typically, phosphate detection is based on the yellow vanadomolybdophosphoric acid method. The 'yellow method' is a simple colorimetric technique that involves the formation of vanadomolybdophosphoric acid when a phosphate containing sample is mixed in a 1:1 ratio with an acidic reagent containing ammonium molybdate and ammonium metavanadate. The resulting yellow-coloured solution absorbs light strongly below 400 nm. The measured absorbance of this solution is used to determine the concentration of phosphate in the original sample. Previous studies have shown that this method can be adapted to a microfluidic manifold (Bowden, 2002) which greatly reduces the volume and amount of reagent required per sample. In addition, the long-term stability of the reagent makes the technique well suited for autonomous, field deployment (Bowden, 2003). Using a microfluidic manifold in combination with a bench-top pump and spectrophotometer, the yellow method was used for analysis of phosphate in river water (Bowden, 2002). Although phosphate concentrations as low as 0.1 mg/L can be detected with the microfluidic system, the samples required on-site collection and filtration before being brought back to the laboratory for analysis. The current system extends this previous work by packaging the entire analysis system into a portable and autonomous device.

2.1 Microfluidic Chip Design

In the initial prototype phosphate sensor, colorimetric detection in the microfluidic chip was based on a microcuvette with a 400 μm path length (Bowden, 2002). The sample and reagent were introduced into the chip through separate inlets and mixed in a 1:1 ratio at a T-junction. The resulting yellow solution passed into the microchip's optical cuvette where detection of phosphate was made possible by aligning an LED and photodiode detector on opposite sides of the microcuvette. However, when a bubble entered or formed in the microcuvette, the miniature pump did not provide enough energy to deform the bubble and push it into the waste channel. Hence, the bubble would remain in the optical cuvette, preventing accurate absorbance measurements, until the chip was flushed by hand. This bubble trapping limited the lifetime of the sensor to about 12 h of autonomous operation. To improve this, a new microfluidic chip was designed, which eliminated the microcuvette and replaced it with a serpentine channel (Fig. 2.1a). The smooth dimensions of the serpentine channel allow bubbles which enter the microfluidic chip to pass through without becoming trapped. The chip is fabricated in a 2mm×16mm×32mm piece of clear polymethyl methacrylate (PMMA) using micromilling techniques. Before milling, the top surface of the PMMA is coated with black ink in order to minimise the amount of background light reaching the detector. After milling, the chip is sealed with a second layer of PMMA using pressure sensitive adhesive. The sample and reagent are introduced into the chip through separate inlets and mixed at a T-junction. The solution flows through the 22-mm long serpentine channel, designed to cover the entire active area of a photodiode detector, before exiting the chip through a waste outlet. Channels of 200 μm width and 200 μm depth ensure that mixing of the reagent and sample occurs through diffusion in the timescale of the experiment (Fig. 2.1b).

The development of a field-deployable device requires that the system be protected from the environment, while still allowing sampling and communication. To achieve this, the entire system is packaged into two waterproof polycarbonate boxes (Fig. 2.2). A 28.0 cm×18.5 cm×13 cm base station box contains the power supply, hardware, and communication components; a 16.5 cm×13.5 cm×9.5 cm sensor box houses the peristaltic pump, microfluidic chip, thermistor, light source, detector, and reagent and waste containment bags. These boxes are connected by an 8-m communication cable, although radio communication between the two boxes has been demonstrated in a similar system (Crowley, 2005).

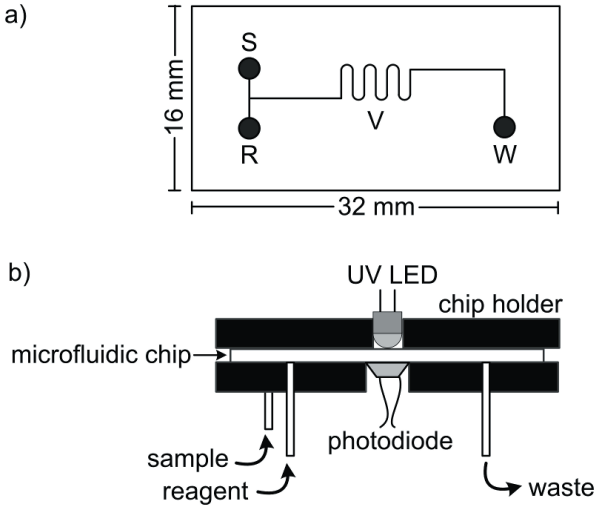


Figure 2.1. (a): Microfluidic chip layout with sample (S) and reagent (R) inlets, a serpentine reaction channel and viewing area (V), and waste outlet (W); (b) cross-sectional view of the microfluidic chip holder and detection components (from McGraw et al., Talanta [McGraw, 2007], p. 1181, Fig. 1).

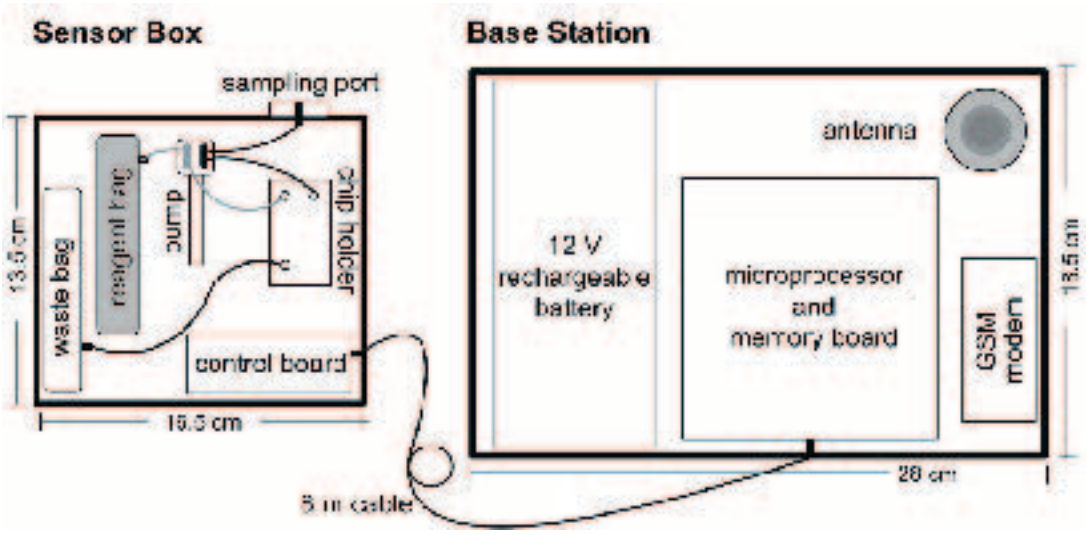


Figure 2.2. Diagram of the phosphate sensor and base station (from McGraw et al., Talanta [McGraw, 2007], p. 1182, Fig. 2).

The base station (Whistonbrook Technologies Ltd, Luton, UK) contains the electronic control, data acquisition, and communication components, powered by a 12 V, 7 Ah lead acid battery and sealed in the larger waterproof box. The measurement parameters can be changed via a laptop computer, which communicates with the base station through either a GSM modem or a serial port. Customised software allows the user to set the pumping time, define a measurement delay to ensure completion of the reaction, choose the number of measurements to be made, and decide whether communication with the system is done through the serial port or the GSM modem. Individual measurements can be performed manually or a series of measurements can be made automatically at user-defined intervals. The system is capable of storing up to 40 measurements before it is necessary to download the data to the computer. In the following experiments, all communications with the sensor base station were performed wirelessly from a laptop computer using the GSM modem.

2.2 Measurements

The sensitivity of the system was determined using the 0.0, 0.5, 1.0, 5.0, 10, and 20 mg/L $P–PO_4^{3-}$ standards. The minimum time needed for each measurement is 15 min: 10 min for sample and reagent pumping (to ensure that a new water sample is filtered and introduced to the sampling chamber) and 5 min for the completion of the reaction of the phosphate and reagent. At the end of the reaction time, the LED is pulsed for 1 ms while the photodiode measures the intensity. In order to obtain an estimate of the variation of the measurement, each measurement was repeated four times. Intensity values were converted to absorbance using the 0 mg/L $P–PO_4^{3-}$ standard as the reference sample. The ability of the system to operate autonomously was evaluated in the laboratory over a five-day period. Using the acquisition parameters given above, measurements of the phosphate standards were made every 30 min for 117 h. For each concentration, a series of 10–136 intensity measurements was made.

A field trial of the phosphate sensor was carried out in the Towns river, Co. Offaly, Ireland during a 36-h period between 27 and 29 March, 2006. Due to a decrease in the reaction time caused by the cold environment, it was necessary to increase the time between measurements to 45 min. The final concentration was calculated from the average of two consecutive measurements. On-site calibration was possible by alternating measurements of phosphate in the river with 0 and 5 mg/L $P–PO_4^{3-}$ standards brought to the field. During the river measurements, the sensor was submerged in the water and the base station left on the nearby bank. Data were downloaded remotely to a laptop computer using the base station's GSM modem. During the field trial, three water samples were collected for analysis back in the laboratory. After collection, each sample was immediately filtered with the polyethersulfone membrane filter, stored in an acid-washed sample bottle, and frozen within 30 min of collection. In the laboratory, aliquots of each thawed sample were mixed with the yellow reagent and the absorbance of the solution was measured in a bench-top spectrophotometer (Cary 50, Varian, Inc., Palo Alto, CA).

2.3 Sensor's Performance

Calibration results show a linear relationship between absorbance and $P–PO_4^{3-}$ concentration. The linear fit of the calibration data is described by $A = 1.98\times10^{-3} \times C + 1.01\times10^{-3}$ where A is the absorbance of the solution and C is the concentration of phosphate in the original sample (mg/L). The R^2 value is 0.998 and the standard errors of the slope and intercept estimates are 2.0×10^{-5} and 2.0×10^{-4}, respectively. The limit of detection (LOD) of the system, defined as the concentration equal to three times the standard deviation of the measurement above the background absorbance, is 0.3 mg/L.

The ability of the sensor to operate autonomously over five days is shown in Figure 2.3. During the test period, 241 measurements were collected and analysed. Although this experiment was performed in the laboratory, the system was not disturbed during this time period and the device was controlled and data collected remotely using the GSM modem. In more recent trials, continuous operation has now been demonstrated for periods of up to seven weeks (Cleary, 2009).

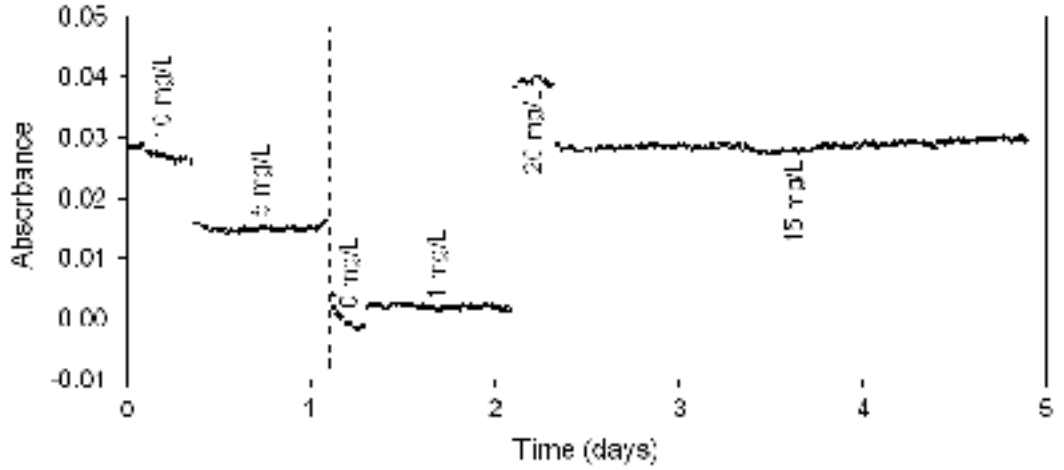


Figure 2.3. System response to varying P–PO_4^{3-} concentrations during a five-day lab trial.

The laboratory results (see Fig. 2.3) indicate that the system is capable of operating autonomously on a single, rechargeable, 12 V battery for extended periods of time. As expected, the absorbance changes linearly with P–PO_4^{3-} concentration. However, the system shows a drift in intensity of approximately 0.01%/h over the time course of the experiment, which is likely caused by staining of the viewing window by the vanadomolybdophosphoric acid. The effect of the observed drift is minimised by applying a constant correction factor to the intensity measurements. A linear fit of the concentration versus absorbance data for the long-term run is described by $A = 2.08\times10^{-3} \times C + 1.88\times10^{-3}$. $R^2 = 0.985$ and the standard errors of the slope and intercept estimates are 2.4×10^{-5} and 2.0×10^{-4}, respectively. These values agree with the calibration results and show that the sensor response remains linear over the longer time period.

The system LOD over the five-day laboratory trial was 1.5 mg/L P–PO_4^{3-}, five times higher than the LOD of the initial calibration experiment. The significant increase in LOD during this five-day laboratory trial is caused partly by changes in temperature, as the brightness of the LED varies with temperature and leads to small changes in measured intensity. The temperature-induced intensity changes are most clearly observable in the 0 mg/L series of data in Figure 2.3. A 5 ºC change in temperature inside the sensor box at time = 1.1 days led to the spike in absorbance seen in the 0 mg/L data. This resulted in a relatively large standard deviation for the 0 mg/L data and increased the LOD of the sensor during the five-day laboratory trial.

The system's intensity drift of approximately 0.01%/h also led to a higher LOD for the five-day laboratory trial. The calibration experiment was done over a 7-h time period, while the laboratory-based long-term run lasted for 117 h. The expected changes in intensity due to drift for these experiments are 0.1% and 2%, respectively. While the drift correction minimises the long-term increase in absorbance, Figure 2.3 shows it does not fully correct the upward trend. This drift increases the measurement error, leading to a further increase in the LOD.

The drift-corrected results from the Towns river measurements are shown in Figure 2.4. During the 36-h field trial, the water temperature varied between 7 and 9 ºC. Using the 0 and 5 mg/L data for on-site calibration, the measured concentrations of P–PO_4^{3-} in the river were 0.9±0.5 mg/L (n = 7) and 0.7±0.5 mg/L (n = 5) for the two series of measurements. The LOD of the sensor in the field was 1.0 mg/L P–PO_4^{3-}. River samples taken during the trial were analysed in the laboratory and gave phosphate levels of 0.4±0.1 mg/L (n = 3). These laboratory results are lower than the average field test results, but fall well within the 95% confidence intervals of the Towns river measurements given above and reflect the fact that phosphate levels vary with time. In addition, the field

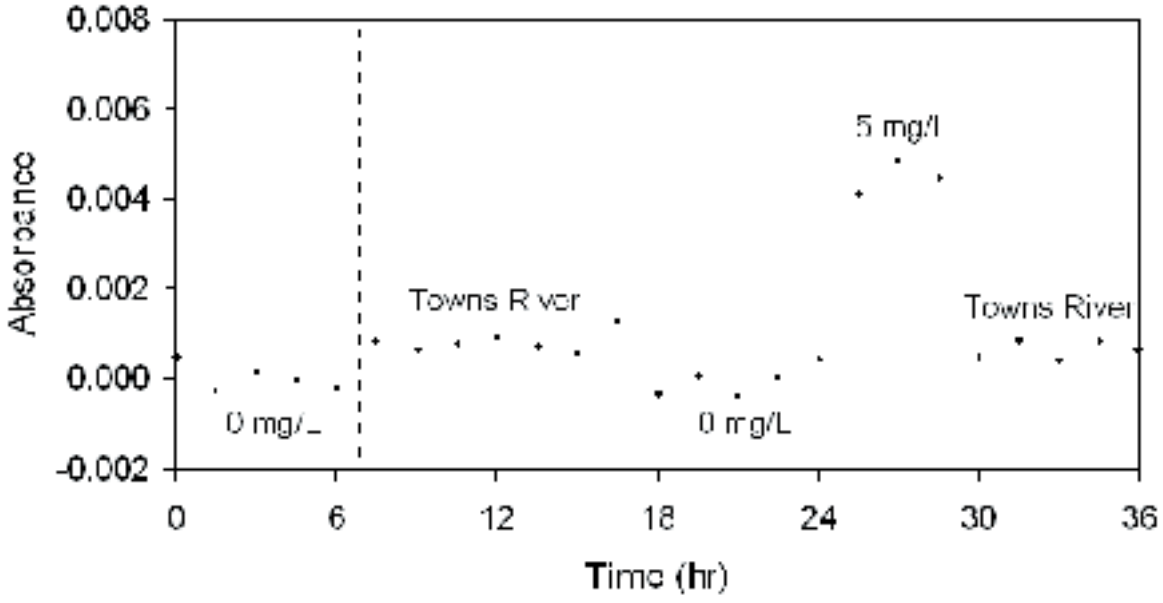


Figure 2.4. Field measurements of P–PO_4^{3-} in the Towns river, Co. Offaly, Ireland.

results in Figure 2.4 show clearly that the instrument is sufficiently sensitive to distinguish between the blank standard (i.e. 0 mg/L P–PO_4^{3-}) and the measured river concentrations of phosphate.

The LOD of the phosphate sensor over long time periods is clearly affected by the effects of temperature and drift, and would be significantly improved if these effects could be reduced. The latest prototype phosphate sensor uses a blank solution and a standard phosphate solution to perform a regular calibration procedure. This allows the effects of short-term temperature variations and long-term signal drift to be compensated for.

Long-term deployment of the sensor using this design is limited by the lifetime of the sensor's battery and the reagent and waste storage capabilities. At current sampling rates, it is possible to make 32 measurements a day, with a reagent consumption of less than 1 mL per day. Reagent consumption, and waste containment, could be reduced further if the sampling rate was decreased. For example, six samples per day would still allow daily events to be monitored, but would also lead to an eight-fold reduction in reagent consumption. At this reduced sampling rate, less than 50 mL of reagent would be consumed annually, a volume easily contained in the waste storage bags. Further reduction in reagent consumption could be achieved by minimising the dead volume of the system through more efficient use of the system's tubing.

In addition to minimising the amount of reagent consumed, reducing the sampling frequency would extend the lifetime of the sensor. At current sampling rates of 48 measurements and 2–6 GSM downloads per day, the sensor can operate for seven days off a single, rechargeable 12 V battery. Since operation of the pump is the most significant drain on the battery, the sensor's lifetime would increase significantly if the sampling rate were decreased. Minimisation of the system's dead volume would allow shorter pumping times and a subsequent decrease in power consumption. Alternatively, incorporation of a solar-powered device could be used to extend the battery life significantly.

A second limitation to long-term deployment of the sensor is fouling of the filtration membrane. The fouling may be due to colloidal clogging of the membrane pores or the formation of a biofilm on the membrane surface itself. Biofouling is caused by the growth of biological organisms on submerged surfaces and limits deployment

periods of environmental sensors (Kerr, 2003). In eutrophic water systems (where this sensor is designed to be deployed), the effects of biofouling are especially significant. In response, the sampling port is designed for fast and easy on-site replacement of the filtering membrane. More work, including longer-term testing under environmental conditions, is needed to determine how often the membranes should be replaced for long-standing deployment of the sensor in natural waters.

The LOD for laboratory-based experiments performed on a short time scale was 0.3 mg/L $P–PO_4^{3-}$. For longer trials and field measurements, the LOD increased to 1.0–1.5 mg/L $P–PO_4^{3-}$. While this is greater than the 0.1 mg/L $P–PO_4^{3-}$ level defined by the EU's environmental directives as an indicator for excessive algal growth (Morais, 2005), higher concentrations of phosphate have been measured in agricultural, industrial, and densely populated areas. For example, a study of phosphate in Dublin's Broad Meadow river used the yellow method to detect an average concentration of 1.5 mg/L $P–PO_4^{3-}$ (Bowden, 2002). The autonomous sensor results indicate that the device is sufficiently sensitive for *in situ* measurements of phosphate in these regions.

The majority of the objectives for this project have been achieved or exceeded. A compact, and easily portable, self-contained unit has been developed incorporating all necessary functionality. The sensor system is contained within a break-proof, water- and air-tight enclosure. The power budget allows for greater than three-months operation using a single 12 V battery and a solar panel can be added to enable longer periods of operation. The fabrication cost is approximately €2500 per unit; while reasonable for an early stage prototype, further reductions are highly desirable so as to allow commercialisation of the system as a competitive product. A number of significant cost reductions have been identified and are currently being implemented. A frequency of 1 measurement/30 min can be implemented.

One aspect which requires further attention is the sensitivity of the system. The current LOD of 0.3 mg/L $P\text{-}PO_4$ allows the system to be applied to monitoring water bodies where phosphate pollution is a significant issue. The current system is therefore suited to the operational and investigative modes of monitoring described in the Water Framework Directive,[1] as well as to the analysis of outputs from wastewater treatment plants. It is also worth noting that even in water bodies with typically low phosphorus levels, high inputs over short periods (for example, following heavy rainfall events) can lead to significantly elevated phosphorus levels over short time periods (Jordan, 2005; Kronvang, 2002). Such events are unlikely to be captured using manual sampling but a high-frequency monitoring device of even limited sensitivity could provide valuable data on these transient inputs.

Nevertheless, further improvement in the LOD is desirable in order to maximise the applicability of the developed system and, with this in mind, optimisation of the microfluidic chip design, detection system and colorimetric chemistry is ongoing. Continued funding for (a) continued optimisation and commercialisation of the phosphate system, and (b) for further development of the platform technology provided by this system, has been gained from Enterprise Ireland under the Innovation Partnership Scheme 2008 (Grant code IP/2008/544) and the Commercialisation Fund – Technology Development Fund 2008 (Grant code CFTD/08/111) respectively.

2.4 Conclusions

A portable system for long-term monitoring of phosphate has been developed. This completely autonomous device incorporates sampling, reagent and waste storage, colorimetric detection, wireless communication, and a power supply into a complete, miniaturised system. Integration of a wireless communication device allows acquisition parameters to be controlled remotely and adjusted according to individual needs. In addition, wireless communication capabilities allow the results to be downloaded remotely and displayed in real time.

[1] The Water Framework Directive defines three types of monitoring. *Surveillance monitoring* must enable the classification of water bodies and assessment of their ecological status. It must also assess any long-term changes in the water environment, whether natural or due to changes in human activity. *Operational monitoring* is targeted at water bodies which are at risk of not meeting the requirements of the directive. Operational monitoring will be used to confirm the risk and monitor improvements that result from the measures taken. *Investigative monitoring* will be used to identify and/or quantify the impact of a human pressure on a water body.

The autonomous capabilities of the system, combined with the portability and wireless communication, provide the flexibility needed for on-site phosphate monitoring. This system demonstrates the potential of truly autonomous microfluidic platforms for use in long-term environmental monitoring.

3 Light Emitting Diodes as Light Detectors

The concept of using a light emitting diode (LED) as a light detector was first proposed by Mims III (1990, 1992). Using a simple circuit that contained an operational amplifier to measure the photocurrent obtained by a reversed biased LED, the LED sensor was first applied to the detection of sunlight. Berry et al. (1997) applied the use of LED detectors for pH determination and heavy metal analysis. The system employed comprised a tungsten halogen lamp as the light source coupled with an array of various coloured LEDs as the light detectors (Berry, 1997). Each LED was assembled with a separate amplifier; however, Berry et al. determined that the blue LED required a two-stage gain to compensate for its significantly lower sensitivity. Few have adopted the use of LEDs operating as photodiodes because of the lack of sensitivity with regard to the photocurrent generated (Kerr, 2003).

The novel use of an LED as both light source and detector for analytical applications was first reported by Lau et al. (2004; O'Toole, 2005). The emitter LED is forward biased while the detector LED is reverse biased. As an alternative to measuring the photocurrent directly as reported by Mims III (1992) and Berry (1997), a simple timer circuit is used to measure the time taken for the photocurrent generated by the emitter LED to discharge the detector LED from 5 V (logic 1) to 1.7 V (logic 0) to give digital output directly without using an A/D converter or operation amplifier. Operating the system in this way achieves excellent sensitivity in comparison to the method of employing an LED to measure the photocurrent directly (i.e. similar to a photodiode) (O'Toole, 2007). A typical discharge profile of a detector LED with an emission λ_{max} of 610 nm was obtained using a Fluke Scopmeter® (Fluke Corporation, WA, USA). As shown in Figure 3.1, the detector LED was charged up to 5 V for 500 µs before being switched to discharge mode. In this example, the time taken for the capacitor voltage to decay from 5 V (logic 1) to a preset voltage of 1.7 V (logic 0) was ca. 132 µs. The circuitry used in combination with the paired emitter-detector diode (PEDD) incorporates a voltage comparator to check whether the actual capacitive

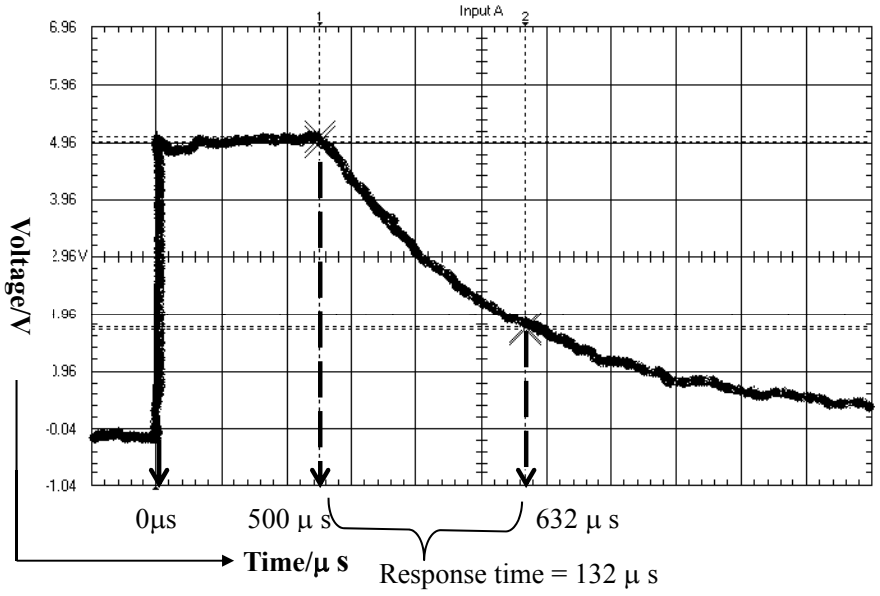


Figure 3.1. Typical discharge curve for an LED charged up to 5 V and then discharged to a threshold of 1.7 V under artificial lighting (fluorescent tube).

voltage is greater than or less than a preset threshold. Comparisons are made at rapid intervals and the number of values for which the voltage is greater than the set value is integrated over a fixed time interval (e.g. 100 μs). The time taken to discharge the capacitance voltage is indirectly proportional to the emitter light intensity, i.e. the discharge time will decrease if the light density (and hence the photo-discharge current) increases, and vice-versa.

Lau et al. (2004) constructed a pair of fused LEDs at a 90^0 angle with respect to each other to form an optical probe used for colour and colour-based pH measurements as shown in Figure 3.2. The PEDD device was used in reflectance mode and placed directly into the sample of interest. Sensor function is based on the level of light received by the detector diode, which varies with the reflectance of the interface between the device and its environment, or the chemochromic membrane that covers the LEDs (Lau, 2006; Lau et al., 2004). The sensor was successfully applied for colour-based pH measurements and also colour detection of dyes.

Lau et al. also developed a multi-LED photometer as an alternative reflectance-based optical sensor configuration (Lau, 2006). The sensor employs an array of LEDs as the light sources, which surround the centre detector LED. This approach allowed the analysis of multiple dyes separately and as dye mixtures. O'Toole et al. developed a PEDD flow cell (2005; 2007; Riley, 2004) and applied the device as a detector in liquid chromatography (Barron, 2006; O'Toole, 2006). Under optimised conditions the PEDD detector achieved a linear range of 0.9–100 μM and an LOD of 90 nM for Mn–PAR complex. A linear range of 0.2–100 μM and an LOD of 90 nM for Co–PAR complex were achieved. All optical measurements were taken by using both the HPLC variable wavelength detector and the PEDD optical detector for data comparison. The PEDD flow cell could detect lower concentration levels of Co–PAR than that of an expensive, commercially available bench-top instrument. A distinct advantage of using the PEDD optical sensor in comparison with the widely used LED photodiode system is that the LED–LED combination is less expensive in both the cost of components and the cost of the signal transduction circuitry (Lau, 2004). The measuring technique employed by the PEDD device does not require a relatively expensive A/D converter as the output seen by the microprocessor is a direct pulse-duration-modulated signal. Other advantages to the PEDD device include the variability in size, low power consumption (it can operate in microwatts range), ability to detect low absolute light levels, response to a broad spectral range (247 to >900 nm) and a good signal-to-noise (S/N) ratio.

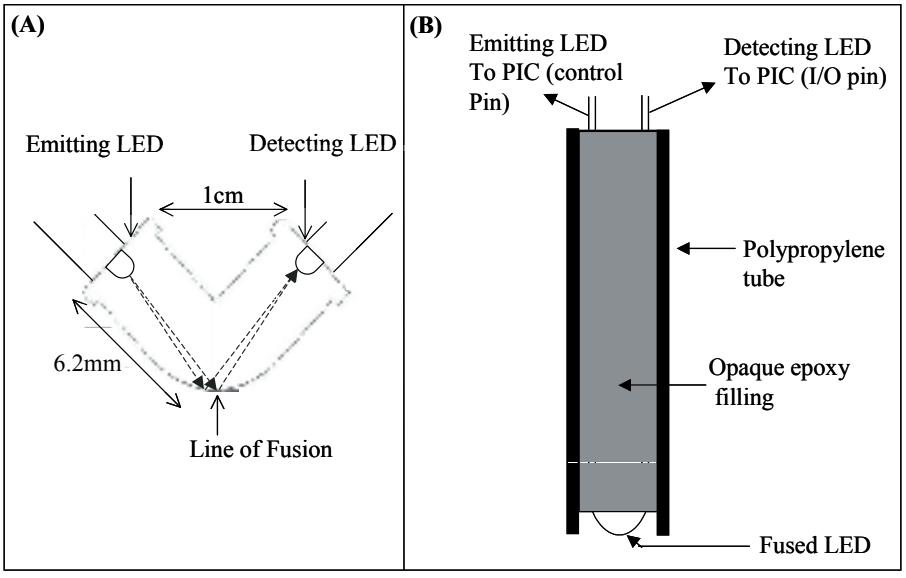


Figure 3.2. Schematic of (A) fused-LEDs and (B) cross-section of the optical probe. (From O'Toole et al., Sensors and Actuators A [O'Toole, 2008], p. 2463, Fig. 9.)

3.1 Research Objective

In most microanalytical systems neither the light source nor the photodetector is integrated into the same substrate as the fluidic channel network. This is because the integration of all components necessary for performing a total chemical analysis is very complex (Geschke, 2004). The work presented herein focused on a novel integrated optical sensor, the PEDD. The aim of this work was to design and develop an optical sensing device for colorimetric flow analysis that employed an LED as both the light source and and as a light detector. The LEDs were configured in transmittance mode at 180^0 with respect to each other. An optical flow cell was constructed using the two LEDs, which allowed sample to flow through the co-joined LEDs. This work demonstrated that the integrated PEDD flow analysis system was extremely useful for colorimetric analysis. The PEDD has the advantages that it is small, inexpensive, highly sensitive, low power and requires small sample volumes. These are desirable characteristics for miniaturised field-deployable devices used in autonomous monitoring systems (Zukauskas, 2002). This optical sensor has shown the ability of detecting low concentrations levels (nanomolar).

3.2 Data Processing and Selectivity

The photometer was configured to measure reflectance from a surface. Here, light emitted from the LEDs passed through the substrate before being reflected back from a white surface on the bottom of the cell to the detector. This approach is similar to a method that used an LED light source and a light dependence resistor (LDR) as the light detector for the detection of a metal ion (Matias, 2003). In this case, this optical device measures the time the reflected light discharges the detector LED. As Equation 3.1 shows, taking the white reflected surface with the blank solution as reference to give the theoretical ideal reflectance, the discharge time measured is related to reflectance *R* by:

$$R = \frac{t_o}{t} \tag{3.1}$$

where t_0 is the discharge time measured for blank solution and t is the discharge measured for samples. In order to simplify the data interpretation, the absorbance (inverse of the reflectance) of the light passing through sample was used. Hence, the raw data were processed according to Eq. (3.2) to obtain the percentage relative absorbance values:

$$Relative\ absorbance\ (\%) = \frac{t_{sample} - t_{blank}}{t_{blank}} x100 \tag{3.2}$$

where t_{sample} and t_{blank} are the discharge times measured for the sample and for the blank solution, respectively. Therefore, the final data output was the percentage relative absorbance with reference to the blank. Since weaker light intensity results in greater discharge time, the values (t_{sample}–t_{blank}) are ≥0. In this context, the expression shows that a higher dye concentration results in more light being absorbed and leads to greater discharge time. When t_{sample} >> t_{blank} it may result in values > 100%.

3.3 Disco Photometer

Super bright infrared, red, orange, yellow, green, blue and ultraviolet (UV) LEDs were purchased from Kingbright, USA. The characteristics of the LEDs are shown in Figure 3.3. The electronic circuitry used in this disco photometer has been described elsewhere (Lau, 2004). The LEDs were arranged such that the detector LED protected by a black heat shrink to exclude the light coming in from the side as shown in Figure 3.4(a) is surrounded by emitter LEDs. The emitter LEDs were inclined towards the centre so that all light beams merged at a spot approximately 1 cm in diameter and 2 cm from edge of the detector LED (Fig. 3.4(b)).

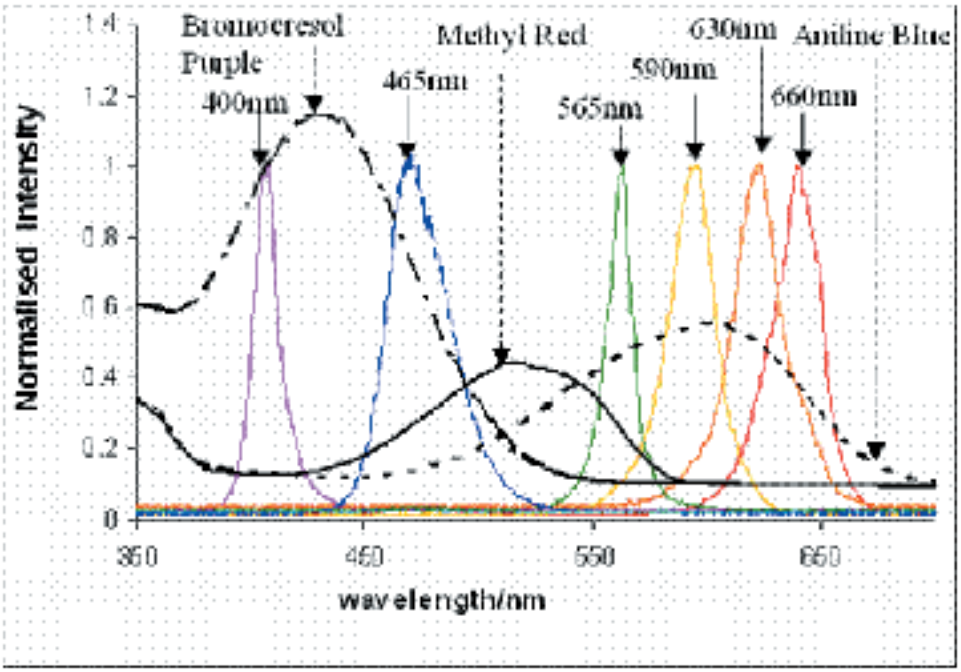


Figure 3.3. Emission spectra of the LED light sources used in the photometer and the UV–vis absorption spectra of bromocresol purple (BCP), aniline blue (AB) and methyl red (MR) obtained from the original dye stock solutions made up with 0.1M HCl (from Lau et al., Sensors and Actuators B [Lau, 2006], p. 822, Fig. 2).

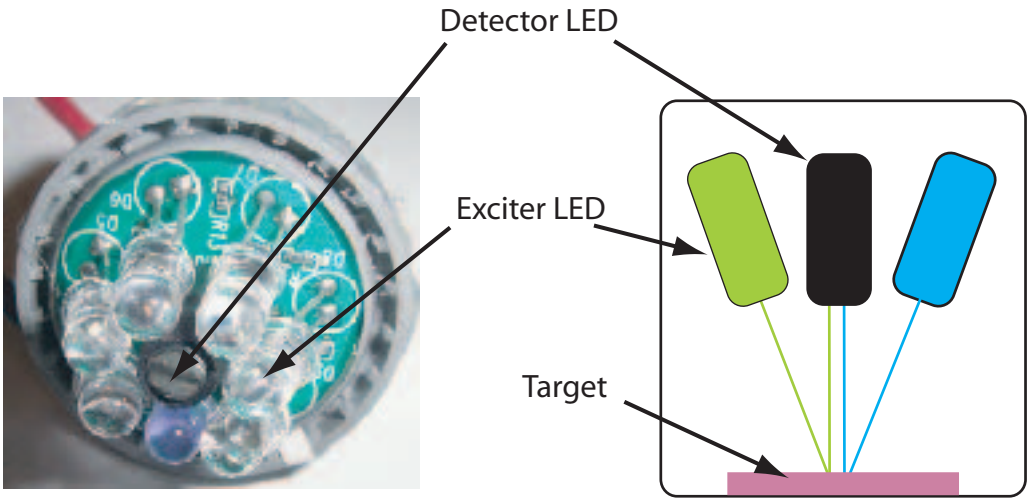


Figure 3.4. Picture of the disco photometer (a) and a sketch of the disco photometer to illustrate the light detection pathway (b).

3.4 Example 1: Paired Emitter-Detector Diode for Solution Samples

This disco photometer used reverse biased infrared light-emitting diode (ILR) LED as a universal light detector. The selectivity of this optical device is based on the degree of overlapping between the emission band of the LED light sources and the absorption band of the analyte species (i.e. the dyes). A selection of three dyes – namely methyl red (MR), bromocresol purple (BCP) and aniline blue (AB) – with an overlapping absorption area between MR and BCP and between MR and AB as shown in Figure 3.3 were used to characterise the photometer. The anticipated selectivity of the system under study therefore depends on the emission spectra of the LEDs used in the photometer together with the absorption spectra of the dyes, which are also shown in Figure 3.3.

3.4.1 Single Component Samples

The initial investigation was to calibrate three sets of solutions, each containing various concentrations of a specific dye. To simplify the analysis these dyes were made up in 0.1M HCl to ensure only the acid form existed. Figure 3.5, calibration plots a–c were obtained from plotting the relative absorbance of the dye solutions obtained with Eq. 3.2 against their corresponding concentrations.

The linear calibration plots shown in Figure 3.5 also inferred that quantitative information could be obtained by using data from individual LEDs. For example, a linear range between ca. 0 and 50 μM with R^2 = 0.999 and an LOD of 3.3 μM calculated using 3×standard deviation of the baseline for MR dye based on LED #7 (Figure 3.5(a)) were observed. Similarly, a linear range of ca. 0–30 μM with a calculated LOD value of 0.70 μM for BCP based on LED #8 (Fig. 3.5(b)); and a linear range between 0 and 10 μM with an LOD of 0.10 μM for AB based on LED #3 (Fig. 3.5(c)), respectively, were observed. The differences between the LOD values reflected the different molar absorptivity of the analytes, which is in the order of AB> BCP> MR. Very low relative standard deviation (RSD) values, typically <1 % for n = 3, were obtained for all analyses, which suggested the data obtained from this optical photometer were highly reproducible.

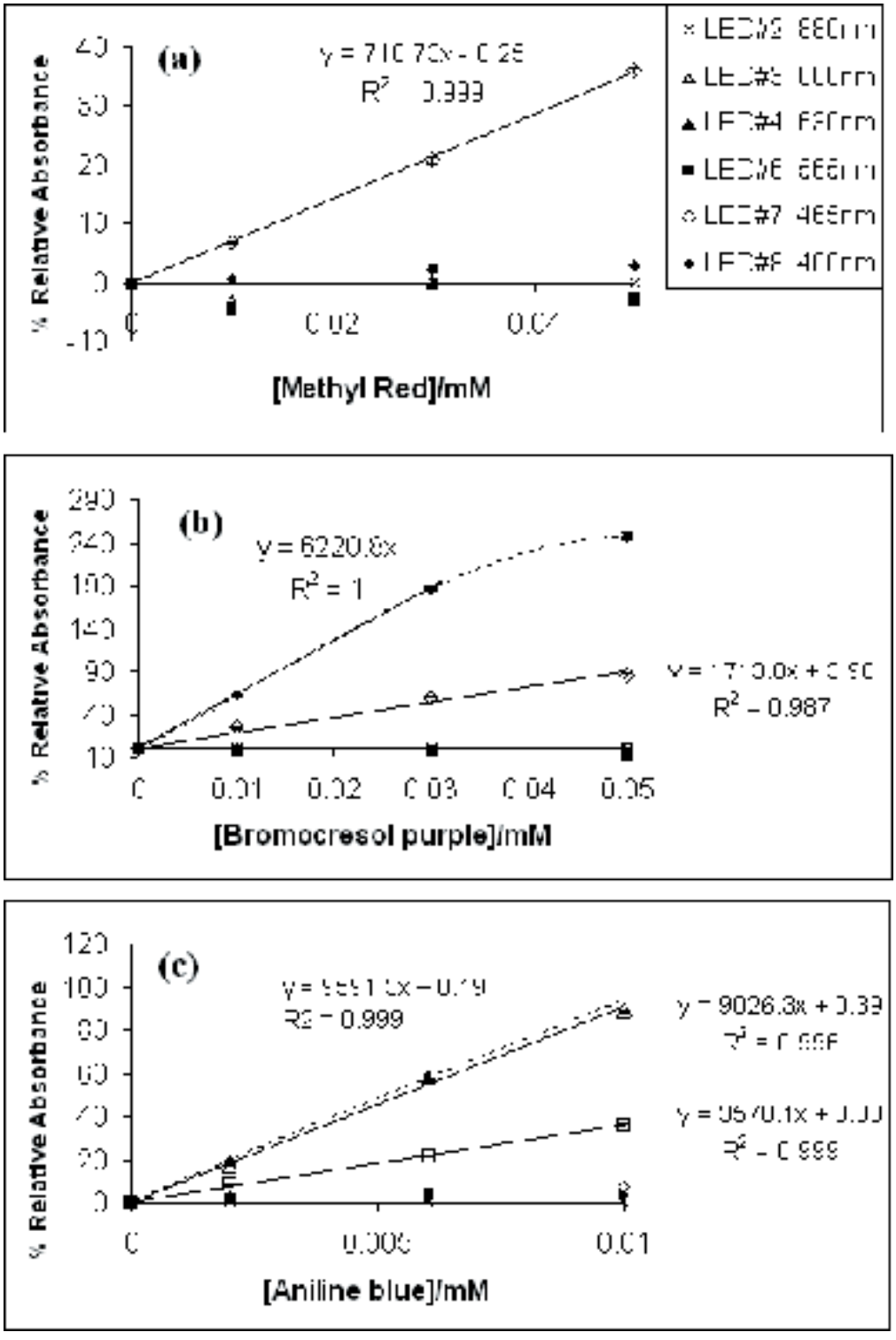


Figure 3.5. Calibration plots obtained for (a) methyl red, (b) bromocresol purple and (c) aniline blue using the disco photometer. The data were processed according to Eq. (3.2) to obtain the relative absorbance value. (From Lau et al., Sensors and Actuators B [Lau, 2006], p. 822, Fig. 3.)

3.5 Example 2: Paired Emitter-Detector Diode and Stimuli-Responsive (Switchable) Surfaces

In addition to liquid systems, PEDD was used in solid (switchable polymer) systems too. Here, an exciter LED illuminates the target and the resulting diffuse reflectance from the surface is measured by the detector LED. For the spiropyran-merocyanine (SP-MC) system[2], UV, blue (425 nm), green (560 nm) and red (660 nm) LEDs are used to illuminate the surface. The UV and green LEDs are used to initiate switching between the SP and MC forms whereas the blue and green LEDs are used to monitor complex formation (λ_{max} ~ 430 nm) and MC formation (λ_{max} ~ 560 nm), while the red LED provides a means for reference measurements since no significant spectral changes occur in this region. For switching between the SP and MC forms, illumination for 60 s with UV and green LEDs is used, while the colour measurements are performed using a sequence of 10 pulses of 0.5 s duration with the blue, green and red LEDs in sequence, and calculating the mean signal. The short-pulsed illumination is particularly important at 560 nm since light of the same wavelength is used for measurement and for transformation of MC to SP form. A protocol that uses short pulses is a reasonable compromise that allows reproducible colorimetric measurements with minimal disruption of the SP–MC equilibrium.

Figure 3.6 demonstrates the use of the LED array for switching between SP and MC and measuring the intensity of the colour at potentially important wavelengths over multiple cycles. A piece of approximately 1×1 cm of SP-modified PMMA film was cut, placed approximately 3 cm

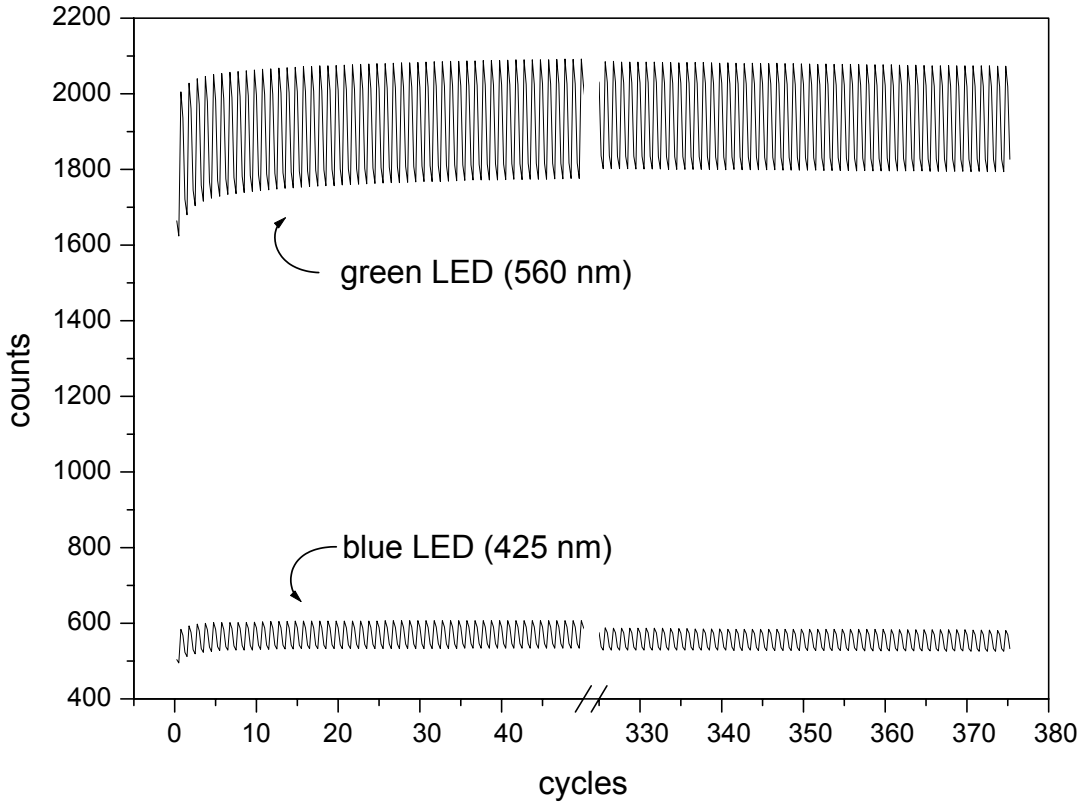


Figure 3.6. Multiple optical switching and monitoring of a single location on a spiropyran-modified polymethyl methacrylate film using LED cluster. Despite an overall reduction of ~25% (431 nm) and ~14% (560 nm) in the signal, a remarkable number of cycles can be achieved.

[2] These are two forms of the same molecule: SP is when the molecule is in 'closed' form, and the MC when it is 'open'. Open and closed formations are switched depending on the wavelength of light used for irradiation of the molecule.

below the LEDs, and the measuring protocol described above engaged. Figure 3.6 shows the response of the detector LED when the surface is illuminated with the blue LED (425 nm) or green LED (560 nm) over a large number of repeat-switching cycles. It is very interesting that even after more than 370 cycles no substantial photodegradation is observed. Therefore, switching to low power sources (approximate irradiance of LEDs is 1 mW/cm^2 [Stitzel, 2006]) can clearly help with the realisation of surfaces that can be repeatedly switched between active (sensing) and passive (non-sensing) states.

3.6 Application of Paired Emitter-Detector Diode and Future Work

This novel integrated optical flow analysis device has the potential for very broad analytical applications, given that it offers high sensitivity and precision with excellent S/N characteristics. The optical sensor cannot replace the UV-VIS spectrophotometer; however, it offers many advantages such as its low cost, versatility, simplicity, ease of use, low power consumption, size, and easy integration into field-deployable autonomous systems. The PEDD has been demonstrated as a sensitive detector in flow analysis systems and for the detection of multiple analytes when operated in conjunction with a separation technique in liquid chromatography. Due to the broad possibilities of analytical applications of the PEDD, a number of areas can be targeted for future works in this project. To develop the PEDD as a photometric detector for HPLC or any flow analysis system, further improvement of sensitivity and selectivity will be investigated with the use of multi-LED systems. Multi-wavelength LEDs are already commercially available in a variety of shapes and sizes. With the use of surface mount LEDs, a photometric detector covering almost the entire UV-VIS range would allow the detection of multiple components as part of a mixture or separately.

3.7 Conclusions

The results in this section show that it is possible to use low power LED light sources to detect colour changes arising at different regions of the visible spectrum, and to control the state of surfaces functionalised with photoswitchable molecules. In the future, such capabilities could be vital for the realisation of surfaces whose binding characteristics can be controlled using light, which could greatly extend the useable lifetime of sensing surfaces exposed to hostile samples i.e. switch between active (measuring) and passive states.

4 Development of an Autonomous Portable Device for Remote Detection of Metals in Airborne Dust

The objectives of this research were to:

1 Develop solid-contact ion-selective electrodes (ISEs).

2 Apply ISEs for the determination of heavy metals (e.g. lead) in soil.

3 Evaluate the results obtained with ISEs by comparison with a standard laboratory technique (e.g. atomic absorption spectrophotometry [AAS]).

Contamination of soil by heavy metals is an important environmental problem. Heavy metal hotspots often occur around mining facilities in rural areas. For many years, the Silvermines area in Co. Tipperary, Ireland, was a centre for mining silver and barium, and when mining operations ceased in 1993, the area was left with heavily polluted soils. Several reported incidents of cattle deaths in the area (linked to soil contamination of herbage), episodes of toxic dust blow during dry periods (posing a constant threat to the local community) and the possibility of contamination of the surrounding areas through surface water pose a significant concern for the quality of life in this area. In 2000, the Environmental Protection Agency (EPA) of Ireland published a report on the problem of pollution in the Silvermines area, where relevant metals discussed included lead, cadmium, arsenic, zinc, copper and mercury. The report stated that the area is a safe place to live and to work, provided that certain precautions are taken and an active monitoring programme exists in the area (Office of Environmental Enforcement, 2004). Consequently, this opened up the need for a low-cost, sensitive analytical method that can be applied to the analysis of one or more of these target species, with potential for use in multiple locations to map the extent of pollution in the area in real time.

Lead can be detected by several conventional analytical techniques such as electrochemical methods, chromatographic separation and spectroscopic techniques. Analysis by atomic absorption spectrophotometry (AAS) is a well-known method for the detection of lead in aqueous samples. However, lengthy and often complicated extraction procedures for heavy metals from soil samples mean they can be used only in laboratory conditions. Moreover, these procedures necessitate using harsh conditions – for example, the *aqua regia* method requires boiling of samples and the use of concentrated HCl and HNO_3 for pseudototal extraction of trace metals (International Organization for Standardization, 1995). The need to monitor pollution in areas such as Silvermines at multiple locations and at relatively short intervals raises the need for a simplified extraction method that can be more easily employed in the field. Enabling real-time measurement of pollutants in the field, especially where the sample is in the form of dust, must couple a simple extraction method with an appropriate analytical method.

4.1 Deployment of Ion Selective Electrodes

The detection limit of ion selective electrodes (ISEs) has recently been improved from the classical ppm to ppb levels, opening the way for new applications in environmental analysis (Bakker, 2005). Their sensitivity, low manufacturing cost and simple instrumentation make them an excellent detector platform for field deployable sensing devices for routine *in situ* analysis. Moreover, there is a large selection of commercially available ionophores selective for common pollutants such as Pb, Cd, Zn, Cu which have been identified in the EPA report as the main pollutants in the Silvermines area (Buehlmann, 1998).

In this section, the possibility of using solid contact ISEs in environmental analysis combined with a simplified extraction method based on dilute HNO_3 that can be carried out in the field is examined. AAS was used as a reference method. Measured concentrations of lead

using AAS and ISEs were compared and conclusions about the applicability of ISEs with improved operating characteristics as a field deployable analytical technique are discussed.

4.1.1 Soil Samples Collection and Treatment

Soil samples were collected in the vicinity of Silvermines, Co. Tipperary, Ireland, and the surrounding area. Sampling locations of sediments and soil included abandoned mining sites, tailings, dried ponds, farm and urban areas within the village locality. A total of 16 samples were collected. Each sample was stored in a polyethylene bag and kept on ice until reaching the laboratory. In the laboratory, soil samples were spread on plastic trays and dried under ambient conditions. Once each sample was dry, the soil was ground with a mortar and pestle and passed through a 1-mm mesh. The samples were dried in an oven at 48 °C for an additional two days. The soil samples were placed in polyethylene bags for storage and rehomogenised before samples were taken out for analysis.

For the nitric acid digestion, a relatively rapid digestion was possible through the use of an ultrasonic bath: 1 g of sample was placed in a vial with 40 mL of 2.5×10^{-3} M nitric acid. The solution was sonicated for 3 hours in a small bench-top ultrasonic bath before filtration with a Whatman 42 filter. The residue was rinsed twice with 5 mL of water and the solution was made up to the 100 mL mark. A blank solution was also prepared using the same reagents and techniques described above. All samples were analysed using AAS (Varian SpectrAA50) with a wavelength of 283 nm and standards in the range of 0.5–50 ppm.

4.1.2 Construction of Ion Selective Electrodes

A copper rod (1 cm in length and 3 mm in diameter) was polished, soldered to a conducting wire and coated with gold in a sputter coater. A 3-mm diameter hole was drilled in a teflon tube (*ca.* 5 cm in length) and the coated rod was inserted in it. This serves as a platform for the deposition of conductive polymer having the role of intermediate layer between the electrode and ion-selective membrane. Conductive polymer used in this case was polypyrrole (PPy). It was deposited on the gold surface galvanostatically, using a PG580 Electrochemical Analyser (Uniscan Instruments) with a current density of 0.1 $mAcm^{-2}$, for 10 hours. Polypyrrole solution was prepared as a mixture of 0.06 M pyrrole, 0.05 $C_2F_6LiNO_4S_2$ and 0.5% water in 1,2- propylencarbonate (PC, as described elsewhere [Wu, 2006]). After PPy deposition, a sleeve of polyvinylchloride (PVC) tubing was attached to the end of the teflon tube which enclosed the PPy-covered gold surface. The ion selective membrane was prepared by mixing the Pb IV ionophore (9.0 mmol/kg), NaTFPB (2.8 mmol/kg) PVC (33.8 wt%) and dioctylsebacate (DOS) (65.0 wt%) in 1 ml of tetrahydrofurane (THF). The ion-selective membrane was applied to the tip of the electrode and cast into the PVC sleeve. After the membrane dried in air, the electrode was submerged in 10^{-3} M $Pb(NO_3)_2$ solution and left overnight for preconditioning. Recent advances in the theory of ISEs instruct us that before using the electrodes for analytical measurements, a second conditioning step is necessary in order to minimise the occurrence of zero-current ion fluxes within the membrane (Ceresa, 2001). In the second conditioning step, the electrodes were transferred into a conditioning solution that contained 10^{-9} M $Pb(NO_3)_2$, 10^{-4} M HNO_3 and 10^{-3} M $Ca(NO_3)_2$. The scheme for constructing the electrodes is shown in Figure 4.1.

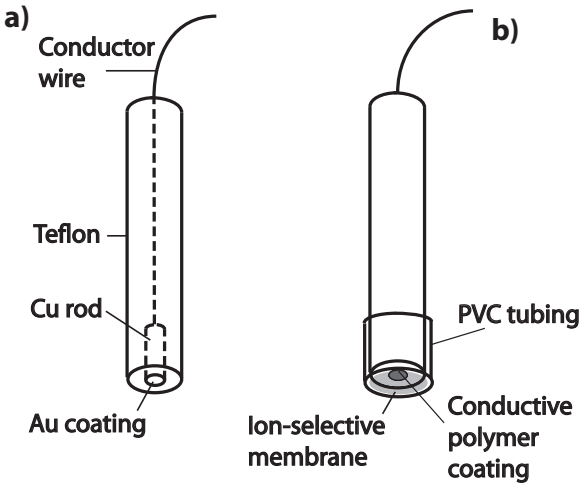


Figure 4.1. Schematic of construction of solid-contact ion selective electrode: (a) body of an electrode before deposition of ion-selective membrane, (b) end product – ISE.

Calibrations were performed in a blank of the nitric acid digestion medium, by addition of known aliquots of 10^{-3} M and 10^{-1} M $Pb(NO_3)_2$ and monitoring the potential. The concentration of Pb^{2+} was measured by AAS directly from supernatant (diluted 10 times where needed). In the case of the ISE measurements, 30 mL of supernatant was transferred into a beaker, stirred with stirring bar and the potential was determined. An aliquot of standard solution ($\Delta\ c_i$) of $Pb(NO_3)_2$ was added and new potential reading recorded. The results were evaluated using Microsoft Excel by estimating the parameters E^o (all constant potential contributions), s (Nernst slope) and c_x (unknown concentration) of the function (Eq. 4.1):

$$E = E^0 + s\log(c_x + \Delta c_i) \quad (4.1)$$

4.1.3 Experimental Results and Discussion

Figure 4.2 depicts the calibration curve obtained in the range of 10^{-7} M to 10^{-3} M Pb^{2+}obtained in the background of 10^{-3}M HNO_3. The detection limit is estimated as 1.2×10^{-6} M (0.25 ppm) at the intersection of the extrapolated linear Nernstian segment (segment in which ISEs responds to the increase of the concentration of lead with a so-called Nernstian slope for divalent ions of 29.6 mV/decade) and the linear extrapolated segment of the calibration plot at low concentrations of Pb^{2+}.

The experimentally observed detection limit of the ISEs was slightly better than that of AAS (2.4×10^{-6} M or 0.5 ppm). This observation supports the possibility of using ISEs for this application. It should be noted that a slightly better detection limit of 0.1 ppm using AAS can be achieved by using the spectral line at 217 nm but with a more restricted dynamic range of 0.1-30 ppm. Since a large concentration distribution within the samples was anticipated, it was decided to compromise on detection limit in favour of a longer dynamic range. It should be noted that ISEs have a wide response range. The linear Nernstian response was observed from 1.2×10^{-6} M to 1×10^{-3} M (0.25–200 ppm), indicating that no sample dilution was necessary in contrast to AAS. Soil samples were processed by digestion with dilute nitric acid (10^{-3} M) as an alternative to the *aqua regia* method for obtaining pseudototal metal content. Soil digestion with *aqua regia* requires boiling with conc. HCl and HNO_3 (3:1 ratio) – conditions that are not desirable for *in situ* sample preparation and analysis. Using less aggressive conditions and ultrasonication of the samples rather than boiling, only a fraction of total metal is extracted. The concentration of HNO_3 employed was a good compromise between the need for a high concentration of acid necessary for the extraction of lead

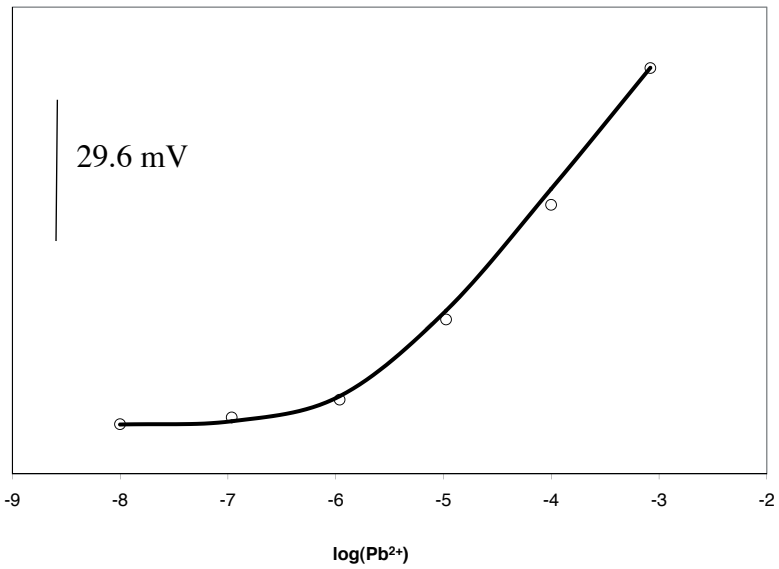


Figure 4.2. Characterisation of ISEs – calibration curve.

from the soil and the need for a low concentration of H^+ ion representing the interference to lead-selective electrode, reducing its optimal detection limit. Nevertheless, the simplicity of this approach and the fact that it generates the easily mobilised fraction of heavy metal pollutants (which is most important in studying their bioavailability) should not be underestimated.

Table 4.1 shows the results of measurements of Pb concentration in nitric acid digests of 16 soil samples. The AAS results indicate uneven distribution of Pb in soil samples, with very wide range of Pb concentrations. The highest Pb concentrations correspond with sampling locations of abandoned mining facilities and a dried tailings pond (Samples 4 and 9, respectively).

The results obtained with ISEs are represented as the average value of four used electrodes with an average percent of relative standard deviation (%RSD) of 14%. The %RSD was always <20% for all samples except in the case of samples 1 and 3 (35% and 45% respectively). Interestingly, % recovery (determined as $\frac{[Pb]_{ISE}}{[Pb]_{ASS}} \times 100$)

Table 4.1. Pb concentrations of soil samples treated by HNO_3 digestion-comparison of ISE and AAS results. Samples 1–5 are sediments, 6–14 soil and 15–16 are tailings.

Sample ID	ISEs (mg Pb^{2+}/kg (soil)	AAS (mg Pb^{2+}/kg (soil)	% recovery
1	93	190	49
2	109	280	39
3	124	230	54
4	853	1270	67
5	411	710	58
6	33	50	67
7	72	140	51
8	63	50	127
9	4754	11800	40
10	56	80	69
11	49	60	82
12	36	40	91
13	33	50	66
14	43	80	54
15	76	140	54
16	299	360	83

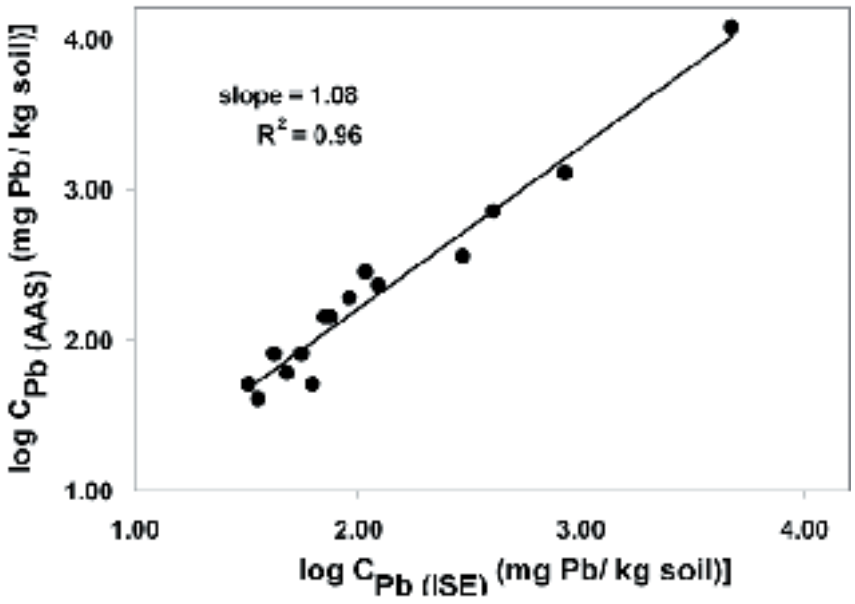


Figure 4.3. Comparison of the Pb^{2+} measurements in NHO_3 digestion samples; AAS vs ISEs.

ranged from 39% to 127% with 65% as an average value. These differences may be attributed to the ability of ISEs to measure the activity of analyte as opposed to total concentration. Soil samples are known to be very complex and their digestion may have resulted in species able to complex metal ions, thereby masking that fraction. It is important to note that ISEs could determine only the freely available (i.e. not complexed) metal ions; values obtained with AAS would include even the fraction of ions that is complexed. This is an important fact that emphasises the complementary nature of the two methods. The determination of only freely available species in a sample is very important in the determination of speciation and bioavailability (Chakraborti, 2003).

It should be noted that there is a significant body of research examining the use of invertebrates (e.g. earthworms) as bio-monitors of heavy metals in soils (Lukkari, 2004; Nahmani, 2007). However, the topic of this work was the examination of an analytical technique that has not so far been used in soil analysis (ISEs) and its comparison with a standard technique (AAS), so no earthworms were analysed.

Additional correlation tests were carried out to assess whether two methods performed equivalently. Figure 4.3 shows the comparison of the results obtained by ISEs and AAS. Pb^{2+} concentrations ranged over several orders of magnitude, so both scales were log-transformed, in order to reduce the influence of high-concentration data points in the model fit. The estimated slope was 1.08 (standard error = 0.06; 95% confidence interval = 0.96 – 1.20), the estimated intercept was 0.04 (standard error = 0.12; 95% confidence interval = -0.21 – 0.29), and R^2 = 0.96. It was also examined whether the response varied by soil type, but there was no evidence (p = 0.11) to suggest that although there were limited data to investigate this. The good correlation (0.98) between the methods over a large concentration range suggests that ISEs have excellent potential as detectors of heavy metal pollution in soils. However, it is important to note that AAS tends to generate higher values than the ISE, which is due to the former method responding to total concentration, whereas the ISE only detects the activity of the free lead fraction.

Although the log-log plot shows very good correlation, it should be noted that the absolute values differ sometimes quite significantly, although it could be seen that the biggest difference occurs in the most polluted samples. This indicates that ISEs can indeed be used as an early warning system. Only if the pollution is detected by ISEs, additional analysis will have to be performed using more traditional analytical techniques (e.g. AAS) to provide a definitive assessment.

4.1.4 Conclusions

The results demonstrated in this work show that solid-contact ISEs can be successfully utilised for soil analysis. Solid-contact ISEs were prepared according to protocols recently reported in the literature, leading to improved detection limit and better stability of the signal. The introduction of conductive polymer as an inner contact between the ion selective membrane and solid support improved the performance of ISEs. It was shown that the detection limit of ISEs is comparable with the detection limit of AAS, a routinely used instrumental technique in environmental analysis. Sample digestion with diluted nitric acid by simple ultrasonication resulted in concentrations of Pb^{2+} that were measurable with both ISEs and AAS, with good correlation between the two methods. This significantly simplified sample preparation can then be easily applied for *in situ* soil digestion. Furthermore, a good correlation between results obtained with ISEs and AAS implies the possibility of application of the former technique in soil analysis. Inexpensive construction, good detection limits and a simple experimental setup make ISEs an excellent prospect for *in situ* environmental analysis. A prototype field-deployable instrument for automated soil sampling, digestion, and analysis with wireless communications capabilities is currently being developed.

In addition, a focus in being placed on the miniaturisation of ISEs and their integration into microfluidic devices. Moreover, electronic circuitry with capabilities for data acquisition and wireless data transmission are being developed. This will allow significant lowering of the cost of the final design of the measuring device.

4.2 Deployment of Portable X-ray Fluorescence

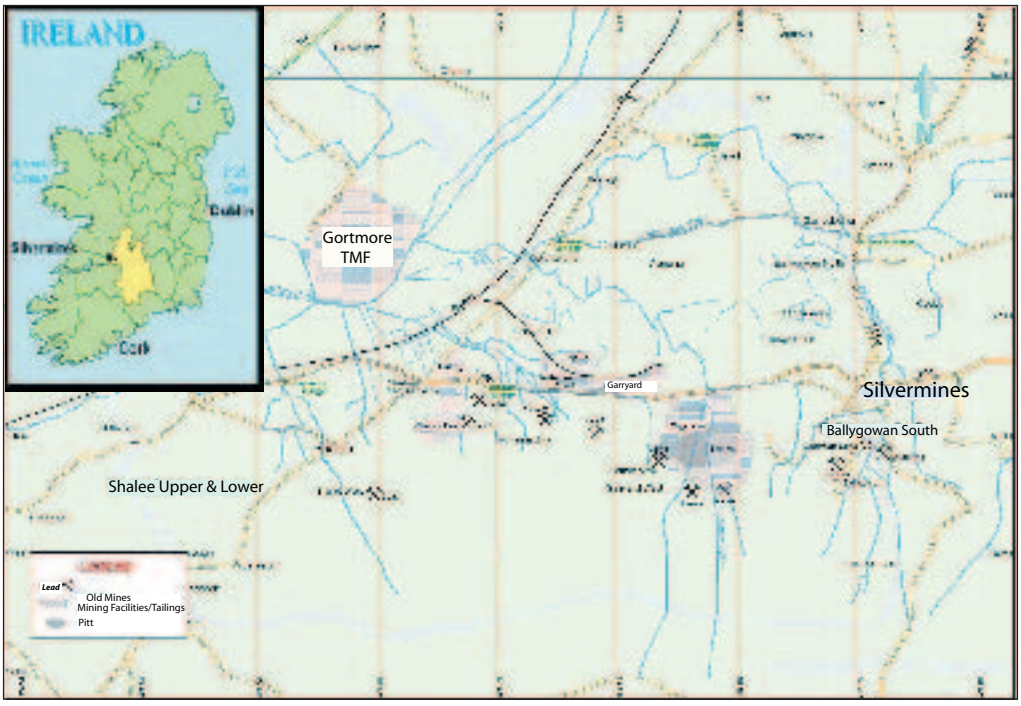
Extraction procedures for heavy metals from soil samples typically involve lengthy processes that require the use of harsh conditions. For example, pseudo total extraction of trace metals using the *aqua regia* method requires boiling of samples and the use of concentrated HCl and HNO_3 (International Organization for Standardization, 1995). Analysis of soil samples in solid state using portable XRF instruments significantly simplifies in-field analysis with the possibility of real time in-field monitoring. Rapid pollution monitoring is especially important in instances of toxic dust blow. This is when a timely on-site analysis and fast decision-making are of the highest importance, in order to protect the health of local communities.

Handheld Thermo Scientific NITON energy-dispersive x-ray fluorescence (EDXRF) analysers ('portable XRF analysers') are able to perform fast and non-destructive analyses of environmental samples, including soils, dust collected on air monitoring filters or wipe samples, rocks, and metal samples. Providing simultaneous analysis of up to 25 elements, this technique significantly cuts the time required for sample characterisation. The instrument is pre-calibrated to operate in several testing modes, including bulk sample, thin sample and lead in paint testing. The portable XRF technique was identified as a suitable analytical tool for detection of heavy metals in soil as samples can be analysed in solid state, and therefore no digestion (wet chemistry) is required. This represents a *critical advantage* of the proposed technique, when compared with the conventional methods of analysis.

The portable XRF technology is now part of several official methods, such as the Environmental Protection Agency (EPA) Method 6200 (EPA) and the National Institute for Occupational Safety and Health (NIOSH) Method 7702 (NIOSH). So far, portable XRF has been tested by numerous researchers for the determination of metals in soil (Bernick, 1995; Carr, 2008; Clark, 1999; Mäkinen, 2005; Markey, 2008; Shefsky, 1997) and air filters (Bernick, 1995; Morley, 1999). A very good agreement between the portable XRF technology and conventional method of laboratory-based analysis is usually found. The possibility of real-time sample analysis with little or no sample preparation makes this technique very attractive in ever-expanding fields of application.

4.2.1 Soil Samples Collection and Treatment

Seventeen soil samples were collected in the area of North Tipperary, Ireland, including the village of Silvermines and abandoned mining sites. Sampling locations were



(taken from Office of Environmental Enforcement, 2004, p. 2)

Figure 4.4. Soil sampling locations: Area of the village Silvermines, Co. Tipperary, Ireland.

chosen based on the pollution maps published by the Expert Group (Office of Environmental Enforcement, 2004). A detailed map of sampling locations is given at Figure 4.4. Sampling locations included the Gortmore Tailing and Mining Facilities (TMF) Silvermines village and the surrounding area. The areas of Gortmore TMF and Ballygowan (south of village Silvermines, see Fig. 4.4) were identified as pollution hotspots in the *Final Report of the Expert Group for Silvermines County, Tipperary* (Office of Environmental Enforcement, 2004). Soil samples were collected, stored in polyethylene bags and kept on ice until brought to the laboratory. In the laboratory, samples were spread on trays and air-dried at ambient conditions. After this, soil was ground by mortar and pestle, passed through a 1-mm mesh sieve and oven-dried at ~50 ^{o}C for 48 hours. The samples were then stored in polyethylene bags. Before being used for analysis, the samples were re-homogenised.

The soil samples were digested using the *aqua regia* digestion method (the 11466 ISO standard method) (ISO, 1995); 3 g of soil was placed in a 100-mL round-bottom flask with 21 mL 35% HCl and 7 mL 65% HNO_3. The solution was kept at room temperature overnight before a water condenser was attached and the solution heated to boiling for 2 hours; 25 mL of water was added down the condenser before filtration of the mixture through a Whatman No. 42 filter. The filtered residue was rinsed twice with 5 mL of water and the solution was made up to 100 mL. All solutions were prepared with Milli-Q deionised water. The above procedure was also used to obtain a blank control sample.

Concentrations of Pb, As, Cu, and Zn of the digested samples were determined using AAS (Varian SpectrAA50). Calibration was carried out using standard solutions, and the instrument was adjusted to 283 nm, 193.7 nm, 324.7 nm, and 213.9 nm, for Pb, As, Cu, and Zn, respectively. For samples with very high levels of contamination, the digested soil solutions were diluted by a factor of ten to bring them within the calibration range.

Two portable XRF instruments used in this work were obtained from Thermo Scientific NITON UK (shown in Fig. 4.5). Two types of instruments were used: the XLp 703 Cd-109 source analyser and the XLt 793 miniaturised X-ray tube for thin sample and bulk (soil) sample analyser.

Figure 4.5. NITON handheld portable XRF analyser.

The major difference between the two is the excitation source, with traditional radioisotope source versus the miniaturised X-ray tube. Operating the instrument is achieved using simple 'point and shoot' operation. The analysing mode used was bulk mode option for the soil samples. Soil was analysed for 45 s per sample. During the XRF trial, soil samples were analysed through a freezer bag, and several samples were prepared for analysis by placing soil in special cups used for XRF analysis.

Statistical analysis of data was performed using Origin 6.0 and Microsoft Excel Analysis ToolPak. Linear regression was used to correlate AAS and XRF data and each data set checked for potential outliers. Any measurement where the ratio of the calculated residual of the regression model and the standard error was larger than 2 was considered to be an outlier.

4.2.2 Results and Discussion

As described above, soil samples were initially digested by the *aqua regia* acid digestion method and the concentration of heavy metals was determined by AAS. The data obtained from the AAS analysis indicated very high levels of pollution with the metals of interest. The median concentrations of Pb, As, Cu, and Zn in soils around the world are 29.2, 11.3, 25.8, and 59.8 mg/kg, respectively (Office of Environmental Enforcement, 2004). Note that when comparing mean values to the median, if the distribution is scattered the mean will always be higher. In numerous instances, these concentrations were surpassed in the Silvermines soils, as shown in Table 4.2. Many lead concentrations in particular were much higher than 1000 mg/kg. The value of 1000 mg/kg was the recommended guideline by the Expert Group (Office of Environmental Enforcement, 2004), above which an 'active management' of soil would be required to minimise the risk of exposure.

Seventeen soil samples were analysed using the portable XRF NITON instrument(s). To compare the performance of the isotope source instrument to that of the miniature tube-powered instrument, both instruments were initially tested using soil samples. Results of the sample analysis were expressed in units of ppm. Also, for each sample analysis, spectra and the major analytical peaks were generated, stored, and transferred to a PC. Even though this methodology provides simultaneous analysis of 25 elements, focus was directed towards Pb, As, Cu, and Zn, as these metals were previously identified as the major contaminants in the area. The instrument's limit of detection for the above metals in soil samples is 13 ppm, 11 ppm, 35 ppm, and 25 ppm, respectively.

Table 4.2. Summary of the results obtained from AAS and XRF analysis of Pb (tube and isotope instrument), As (tube), Cu (tube), and Zn (tube) for 17 samples collected from the Silvermines area. Concentrations are expressed in units of ppm. ± represent standard deviation.

	Pb (ppm)			As (ppm)		Cu (ppm)		Zn (ppm)	
	AAS	XRF tube	XRF isotope	AAS	XRF tube	AAS	XRF tube	AAS	XRF tube
max	30000 ±3000	32000 ±3000	37000 ±3000	1230 ±90	1400 ±90	910 ±60	1250 ±90	9000 ±600	13000 ±1000
min	80±6	24±2	40±3	*	*	10±1	*	260 ±20	37±3
average	8000 ±600	7100 ±500	7900 ±600	350 ±30	440 ±30	230 ±20	220 ±20	2900 ±200	3000 ±300

*concentration below limit of detection

Statistical tests were conducted to determine if the examined methods performed equivalently. Figure 4.6 shows the correlation between the XRF and AAS measurements, using isotope- and miniature tube-powered instruments, operating in the bulk mode. For both instruments, an excellent agreement of the two techniques was achieved. R^2 values of 0.995 and 0.996 were obtained for the tube and isotope instrument, respectively. This agreement was further improved by selecting the soil samples with <1% Pb (<10 000 ppm) (data not shown). This confirmed an excellent performance at lower concentrations. Note that lower concentrations of metals in soils are more likely to occur in common environmental samples, as the soils used in this research contain unusually high concentrations of pollutants. The soil detection mode used primarily for this work is a unique method of combination of Fundamental Parameters (FP) mode with Compton Normalisation (for background matrix automatic correction). This method is excellent for typical soil samples with concentration < 1% and certainly no greater than 3%. Other detection modes available on the instrument would be more suitable for those samples containing unusually high concentrations of analytes, for instance the mining mode (full FP capability up to high concentrations) or even empirical calibration options. Similarly, a very good correlation between the flame AAS and the portable XRF techniques was reported by Clark et al. (1999).

Finally, performance of the isotope and tube instruments was compared directly. Directly plotting the soil results for the two instruments shows an excellent correlation, with the R^2 values of 0.998. The slope was slightly greater than 1 (1.129), indicating a slightly positive bias for the isotope instrument, when compared to the tube instrument. Additionally, the instruments showed very good data repeatability. This indicated that both instruments appear to be technically suitable for the targeted elements analysis. Due to the very close correlation between the two instruments, further results will be shown only for the miniature tube-powered instrument.

Comparison of the data obtained from As, Cu, and Zn analysis is given in Figures 4.7–4.9. In all three instances satisfactory correlations were achieved, where R^2 values for As, Cu, and Zn were 0.991, 0.959, and 0.997, respectively. Where necessary, outliers were calculated and removed when performing linear regression. The instances where the reported XRF values were positively biased when compared to that of the AAS analysis may be explained by the following: the XRF technique measures all forms of lead (metals), even the one incorporated in an undissolvable silica matrix (Drake, 2003; Shefsky, 1997). The digestion methods cannot extract metal that is bound to silica, unless digestion with hydrofluoric acid is performed.

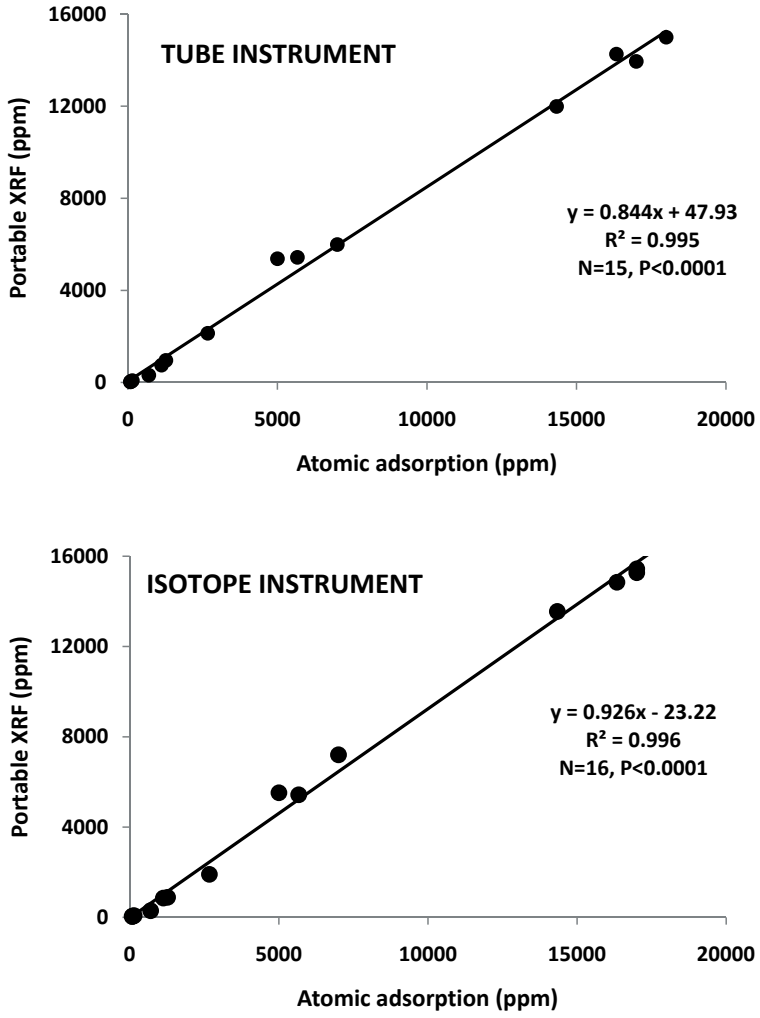


Figure 4.6. Correlation between Pb measurements obtained by isotope and tube powered XRF instruments and the AAS.

4.2.3 Conclusions

The long history of mining activities in the Silvermines area of Co. Tipperary, Ireland, has left behind highly polluted soil. This soil poses a constant threat to local communities, due to the possibility of pollution spreading to the surrounding areas. Results of the AAS analysis presented in this research confirm high soil pollution in the area. Even though the AAS technology is widely recognised and very precise, it is very expensive, laborious and slow. Since the Silvermines area is under a constant risk, there is a need for a fast and reliable analytical methodology that can be fast, low cost and performed in field conditions.

The results demonstrate that portable XRF instruments such as the NITON model tested in this research could be employed to provide rapid *in situ* detection of the presence of toxic metals such as Pb, As, Cu, and Zn in dust blow-offs, when coupled with an automated sampling unit.

Episodes of dust blow in the area of Silvermines can severely endanger human and animal health. There are reported incidents of cattle deaths in the area due to the poisoning by metals (Office of Environmental Enforcement, 2004). During the dust-blow episodes, fast detection of heavy metals in dust and consequent warning of the local communities would be of utmost importance. Since the portable XRF technology provides real-time analysis, pairing it with high-flow air sampling pumps would provide timely in-field sample collection and pollution detection. This would significantly help in estimating the threat

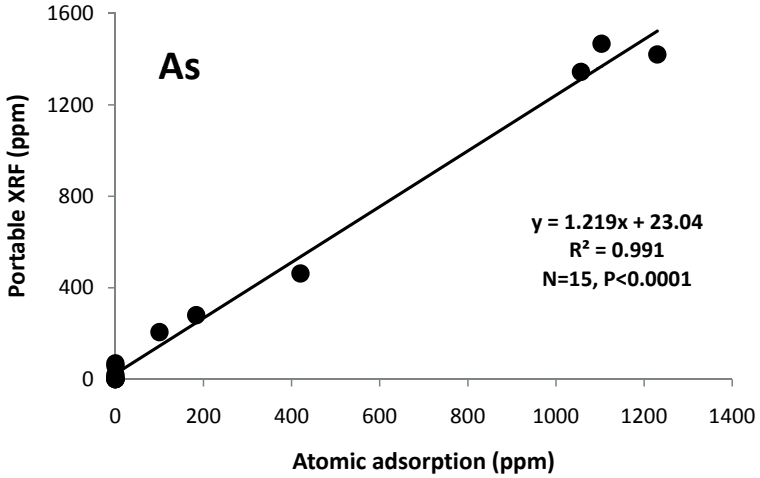


Figure 4.7. Correlation between As measurements obtained by the XRF and the AAS.

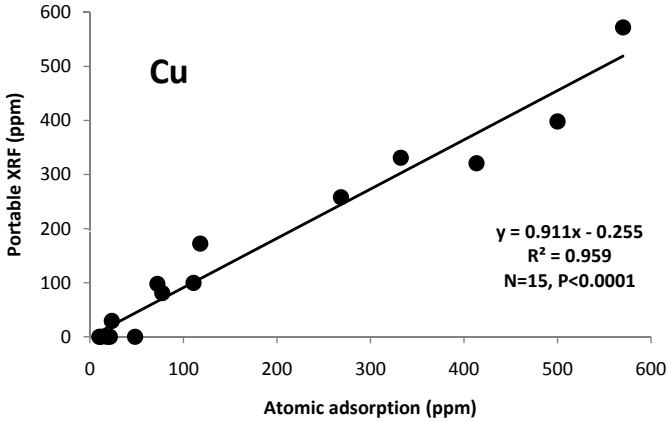


Figure 4.8. Correlation between Cu measurements obtained by the XRF and the AAS.

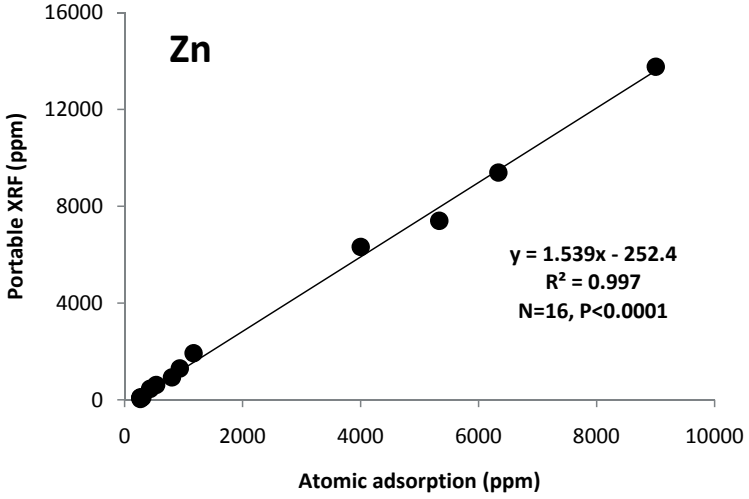


Figure 4.9. Correlation between Zn measurements obtained by the XRF and the AAS.

for the local communities. The threat should be based on the principles of risk, which will include factors such as: concentrations in the soils (their forms and toxicity); proximity to local populations; exposure rates; and prevalent climate conditions.

Since this work was completed, the Environmental Protection Agency has funded the purchase of one of these instruments, and it is now in active use in the group, and in collaboration with other environmental researchers in DCU, and across Ireland.

5 Summary and Recommendations

The research described in this report covers the development and application of a wide range of environmental sensing techniques and their adaptation to in-field analysis for a variety of environmental samples.

The portable phosphate analyser developed in the laboratories (Section 2) demonstrates the potential of automated and fully autonomous long-term analysis of phosphate in environmental samples based on a microfluidic platform. This device incorporates sampling, colorimetric phosphate detection, and wireless data transmission. The analyser is fully equipped for long-term monitoring, as it contains battery power supply, and storage containers for reagents and the waste, which is held for storage after analysis. Wireless communication and the possibility of remote control of the analyser were vital. The current LOD of the system is approximately 0.3 mg/L P-PO_4, which limits the application of the system to (a) water bodies with elevated phosphate levels, and (b) monitoring of point sources such as wastewater discharges, industrial discharges and agricultural discharges. Improvements to the sensitivity of the system through optimisation of the microfluidic manifold and detection system is ongoing, with the aim of decreasing the LOD towards the lower limits specified in the relevant EU directives.

Full control of these functions provides a tailor-made instrument which can be adjusted for specific requirements of sampling and analysis regime. For example, a user can control the instrument from a remote location and specify the sampling duration and frequency. The data can also be downloaded remotely and be displayed in real-time. All of the above characteristics provide a much needed flexibility for on-site phosphate monitoring.

The phosphate analyser research is now funded by Enterprise Ireland through an Innovation Partnership award with Episensor Ltd., a business based in Limerick, Ireland. The technology is currently being transferred from the Adaptive Sensors Group (ASG) into Episensor, and will appear in its product portfolio during 2009.

The LED/switchable surface work (Section 3) continues through the project team's participation in the Science Foundation Ireland (SFI) funded CLARITY CSET, and it is a key focus for the development of futuristic sensor/actuator technologies under that initiative. This work is also attracting considerable international interest through publications in high-quality peer-reviewed journals and presentations at conferences. It is anticipated that this research will leverage addition research funding via EU-FP7 and industry sources in the near future.

The light emitting diode (LED) work presented in this report focused on development of a novel integrated optical sensor, the so-called 'paired emitter detector diode' or PEDD configuration (Section 3). This was achieved by the incorporation of LEDs as both light source and light detector in an optical sensing device for colorimetric flow analysis. The results of this research shows that it is possible to use low power LED light sources to detect colour changes arising at different regions of the visible spectrum with tremendous sensitivity, and to control the state of surfaces functionalised with photoswitchable molecules. The PEDD has numerous desirable characteristics for miniaturised field-deployable devices used in autonomous monitoring systems: small in size, inexpensive, highly sensitive, uses low power and requires small sample volumes, it can also detect low concentrations levels (nanomolar). This sensing approach therefore has numerous potential for analytical applications, given that it has the advantages of very low cost, low power consumption and offers high sensitivity with excellent signal-to-noise characteristics. This concept was initially developed in cooperation with Mitsubishi Electric Research Laboratories, Cambridge, Mass, USA, with whom the project team holds a joint patent.

The team's research into the use of ion-selective electrodes or ISEs for Pb^{2+} sensing (Section 4) shows that solid-contact ISEs can be successfully utilised for soil analysis, provided that appropriate acid digestion and metal extraction is performed. The introduction of a conductive polymer as an inner-contact between the ion-selective membrane and solid support improved the performance of ISEs, providing lower detection limits and better stability of the electrode signal. It was shown that the detection limit of the electrodes is comparable with the detection limit of AAS, a routinely used instrumental technique in environmental analysis. Sample digestion with dilute nitric acid by simple ultrasonication was used as a simple and more environmentally friendly alternative to the *aqua regia* digestion method, which requires the use of harsh chemicals. This simple digestion resulted in concentrations of Pb^{2+} that were measurable with both ISEs and AAS, with good correlation between the two methods. This digestion can then be applied for *in situ* soil digestion significantly simplifying sample preparation. Furthermore, a good correlation between results obtained with ISEs and AAS implies the possibility of application of the former technique in soil analysis. Inexpensive construction, good detection limits and a simple experimental setup make ISEs an excellent prospect for *in situ* environmental analysis. Because ISEs measure only free concentration of ions, the results will be always negatively biased relative to AAS.

The ion-selective electrode research is continuing through a European 'Matera' project with partners in Finland and Poland. This project is generating extremely interesting results and high-impact publications, and the indications are that important commercialisable intellectual property will be generated from this work related to the use of ISEs as remotely based sensors for environmental monitoring.

In the latter half of Section 4, the issue of soil sample digestion was addressed. Currently, almost all soil analysis involves lengthy sample preparation using acid digestion followed by the AAS analysis. Even though very precise, this technique is very slow and expensive, especially due to the labour needed for sample preparation. It has now been shown that portable XRF to AAS gives very good correlation with the gold standard approach based on AAS. The results demonstrate that portable XRF instruments such as the NITON model tested in this research could be employed to provide rapid *in situ* detection of the presence of toxic metals such as Pb, As, Cu, and Zn in soil, or in episodes of dust blow-offs. Since the Silvermines area is under a constant risk of pollution spreading to the surrounding areas, there is a need for a reliable analytical methodology that can be fast, low cost and performed under field conditions. The XRF instruments provide simultaneous analysis of up to 25 elements, which significantly cuts the time required for sample characterisation. This technique is a suitable analytical tool for the detection of heavy metals in soil as samples can be analysed in the solid state, and therefore no digestion (wet chemistry) is required. This represents a *critical advantage* of the proposed technique, when compared with the conventional methods of analysis. Due to its real-time sample analysis, the XRF technique can be used for a quick pollution screening of chosen areas. Since the instrument can be paired with GPS, it can also be used for rapid generation of two- or three-dimensional pollution maps, creating a very useful and powerful visual tool.

The XRF research received a major boost through the funding of a portable Niton instrument by the EPA. This is now being used in collaborative projects with other research teams in Dublin City University (DCU), University College Dublin (UCD), National University of Ireland Maynooth (NUIM) and the National University of Ireland Galway (NUIG). The goal is to develop rapid ways to map the elemental composition of soil and dust at particular locations, and make this information remotely available through GIS data through electronic map-based interfaces to interested parties. The system will be used extensively in the coming months for a pilot project with the National Centre for Geocomputation at NUIM to link field chemical information into digital map interfaces.

The areas covered in this report continue to be very active research topics for the ASG (www.dcu.ie/chemistry/asg). Since the completion of this research, the group has received funding from a variety of sources to continue

this research. The ASG is one of the core partners in the CLARITY CSET, funded by SFI, with partners in UCD and Tyndall, and a number of important industry partners (www.clarity-centre.org/). Developing and deploying wireless sensor networks in the environment is a key demonstrator project under CLARITY (2008), which involves close cooperation with IBM Ireland and USA. The group is also funded under the Marine Institute Beaufort sensors award (www.ncsr.ie/Beaufort/index.html), and through the NCSR, the group is involved in a strategic initiative called 'SmartBay' with the Marine Institute, NUIG, UCD and NUIM, along with IBM and INTEL to instrument Galway Bay with a distributed sensor network (www.marine.ie/home/research/ProjectsDatabase/CurrentProjects/SmartBay).

From this summary, it is clear that this research grant has led to very significant additional funding that has enabled the research activity to continue, and for research outputs to be commercialised in Ireland, and Europe. We thank the Environmental Protection Agency for providing the resources to enable us to make this important contribution to the realisation of next generation monitoring technologies. For updated information about this, and other research ongoing within the Adaptive Sensors Group, please visit our website at www.dcu.ie/chemistry/asg/. Our work in the CLARITY CSET can be accessed via www.clarity-centre.org/.

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Acronyms

AAS	atomic absorption spectrophotometry
AB	aniline blue
ASG	Adaptive Sensor Group
BCP	bromocresol purple
CSET	Centres for Science, Engineering & Technology
DCU	Dublin City University
DOS	dioctyl sebacate
EPA	Environmental Protection Agency
GIS	geographic information system
GSM	global system for mobile communications
HPLC	high performance liquid chromatography
ISE	ion-selective electrode
LDR	light dependence resistor
LED	light emitting diode
LOD	limit of detection
MC	merocyanine
MR	methyl red
NUIG	National University Ireland Galway
NUIM	National University Ireland Maynooth
PEDD	paired emitter detector diode
PMMA	polymethyl methacrylic acid
PPy	polypirrole
PVC	polivinil chloride
SFI	Science Foundation Ireland
SME	small and medium enterprise
SP	spiropyran
STRIVE	Science, Technology, Research and Innovation for the Environment
THF	tetrahydro furane
UCD	University College Dublin
UV	ultraviolet
XRF	X-ray fluorescence

Appendix A: SPIE Poster

This poster was presented by T. Radu at the SPIE 2007 conference in Florence, Italy (September 2007).

ION –SELECTIVE ELECTRODES WITH POLYPYRROLE- AND POLY(3-OCTYLTHIOPHENE)-MEDIATED INTERNAL SOLID CONTACT IN SOIL ANALYSIS

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Adaptive Sensors Group, National Centre for Sensor Research,
School of Chemical Sciences, Dublin City University, Dublin 9, Ireland.

ABSTRACT: The integration of chemo/bio sensors in large wireless sensing networks (WSN) is currently limited, largely due to the issues related with power consumption and data handling. Also, there are very few low cost chemo/bio sensors that combine sensitive, low limit of detection capabilities with simple experimental setup. However, with recent advances, ion-selective electrodes (ISEs) may become an excellent candidate for deployment in WSNs.

In this paper, we describe a solid-contact electrode based on poly(3-octylthiophene) (POT) as an internal contact. We report its characteristics and its application to the for measurement of Pb^{2+} in 16 soil samples, with a ultimate goal of producing a small, simple and sensitive sensor that can be integrated into WSNs. The electrode had a detection in the soil digestion matrix (1×10^{-3} M HNO_3) of 1×10^{-7} M (20 ppb). The electrodes results were compared with atomic absorbtion spectrometry (AAS) as a common instrumental technique used in soil analysis. We also report on the performance of solid-contact ISEs based on polypyrrole (PPy) and POT. A superior detection limit of POT- relative to PPy-based ISEs was observed. Furthermore, a good correlation has been observed between POT-based ISEs and AAS and between the two types of ISEs.

MATERIALS AND METHODS:

- 16 soil samples were collected in the area of Silvermines, Ireland
- Soil was **digested by the dilute nitric acid method** (2.5 × 10^{-3} M), 2h ultrasonication - this **simplifies *in situ* digestion**
- All digests were analysed by the AAS for Pb, Cd, As, Zn, and Cu
- ISEs with polypyrrole or POT as a conductive polymer were constructed
- **Pb in HNO_3 digests was measured by PPy- and POT- ISEs**
- **Performance of PPy- and POT- ISEs was compared**
- **Performance of the more successful POT electrodes was compared with AAS**

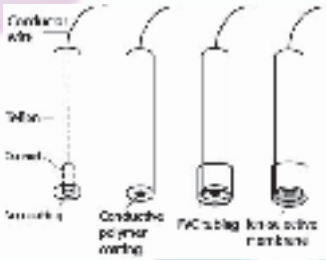


Figure 1. Schematic of the construction of a solid-contact ion selective electrode

RESULTS:

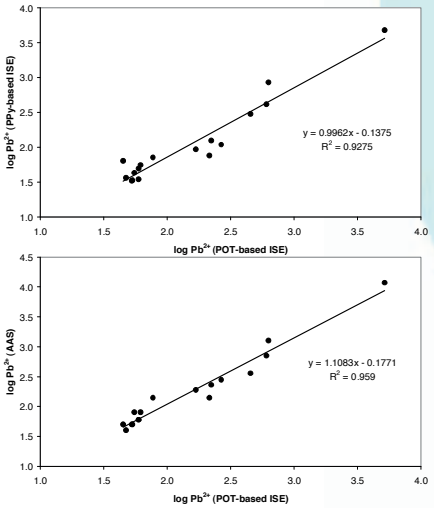


Figure 3 Top) Comparison of Pb^{2+} concentrations in soil samples digested in 1 × 10^{-3} M nitric acid. Top) comparison of PPy- and POT-based ISEs. Bottom) comparison of AAS and POT-based ISEs.

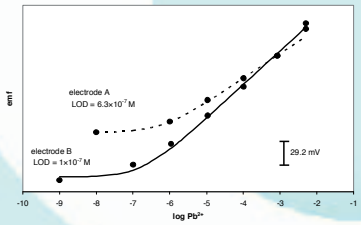


Figure 2. Calibration curves in the blank of soil digestion solution (1 × 10^{-3} M nitric acid); electrode A-PPy, electrode B- POT

CONCLUSIONS:

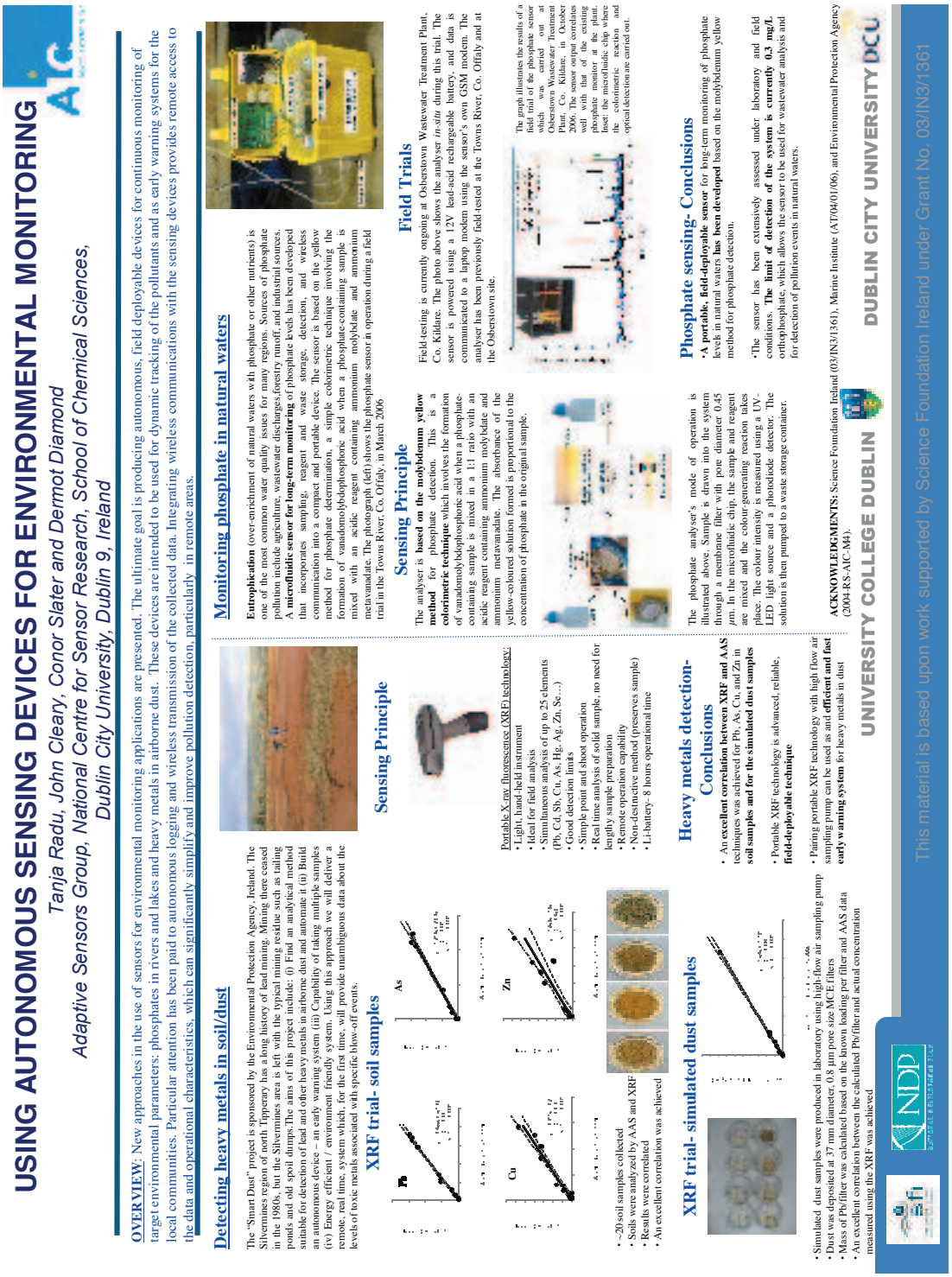
- Detection limit for POT-based ISEs obtained in used experimental conditioned was lower for almost one order of magnitude than for PPy-based ISEs
- Detection limit for POT-based ISEs was lower than the detection limit of AAS
- A good correlation between the results obtained with ISEs and AAS indicates excellent possibility of future application of ISEs in soil analysis
- A **simple construction**, **good detection limit**, very **low power demand**, and **simple experimental setup** coupled with **miniaturization opportunities** arising from solid-state format make **ISEs excellent prospect for integration in autonomous sensing devices** and ultimately their integration in large WSNs

ACKNOWLEDGMENTS: Funding sources- Enterprize Ireland 07/RFP/MASF812, EPA - 2004-RS-AIC-M4

NCSR National Centre for Sensor Research

Appendix B: ICEST Poster

This poster was presented by T. Radu at the 4th International Conference on Environmental Science and Technology in Houston, USA (July 2008). The poster won the best poster award. This was an international conference with 600 platform (oral) and poster presentations and 1,500 attendees.



Appendix C: Research Output from the Project

Peer-Reviewed Publications

T. Radu and D. Diamond. (2009). Comparison of soil pollution concentrations determined using AAS and portable XRF techniques, accepted for publication in Journal of Hazardous Materials.

N. Alhashimy, H. Muller-Bunz, B. Schazmann and D. Diamond. (2008). 5',6-Dichloro-1',3',3'-trimethylspiro [2H-1-benzopyran-2,2'-indoline]. Acta Crystalographica E64: 1430–31.

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C. McGraw, T. Radu, A. Radu and D. Diamond. (2008). Evaluation of liquid- and solid-contact, Pb^{2+}-selective polymer-membrane electrodes for soil analysis. Electroanalysis 20(3): 219–21.

C.M. McGraw, S.E. Stitzel, J. Cleary, C. Slater, D. Diamond. (2007). Autonomous microfluidic system for phosphate detection. Talanta 71: 1180–85.

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T. Radu, A. Radu, and D. Diamond. (2007). Ion-selective Electrodes with Polypyrrole- and Poly(3-octylthiophene)-Mediated Internal Solid Contact in Soil Analysis. SPIE 2007 conference proceedings. vol. 6749, 674922-(1-10).

Conference Contributions

J. Cleary, B. Kiernan, T. Radu, C. Slater, and D. Diamond. (2008). Autonomous sensors for environmental monitoring. Environmental Research Conference, poster presentation, Dublin, 2 July.

T. Radu, J. Cleary, C. Slater and D, Diamond. (2008). Using autonomous sensing devices for environmental monitoring. Environmental Science and Technology Conference, poster presentation, Huston, USA, 28–31 July.

T. Radu and D. Diamond. (2007). Heavy Metal Contamination of soil in Silvermines, Co. Tipperary, Ireland. SETAC Europe 17th Annual Meeting, poster presentation, Porto, Portugal, 20–24 May.

T. Radu, A. Radu, C. McGraw and D. Diamond. (2007). Ion-selective electrodes as simple and inexpensive detectors for soil analysis. CEST 2007, oral presentation, Kos, Greece, 05–07 September.

T. Radu, A. Radu, and D. Diamond. (2007). Ion-selective Electrodes with Polypyrrole- and Poly(3-octylthiophene)-Mediated Internal Solid Contact in Soil Analysis. SPIE 2007, poster presentation, Florence, Italy, 17–21 September.

An Ghníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomh-nithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Ghníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil agus Rialtais Áitiúil a dhéanann urraíocht uirthi.

ÁR bhFREAGRACHTAÍ

CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreail.
- Scardadh dramhuisce

FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain.
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisce agus caighdeán uisce.
- Obair le húdaráis áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí comhordú a dhéanamh ar líonra forfheidhmithe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a ngníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOL

- Monatóireacht ar chaighdeán aeir agus caighdeáin aibhneacha, locha, uiscí taoide agus uiscí talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntí a dhéanamh.

RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

TAIGHDE AGUS FORBAIRT COMHSHAOIL

- Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdéan aeir agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

MEASÚNÚ STRAITÉISEACH COMHSHAOIL

- Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le pleananna bainistíochta dramhaíola agus forbartha).

PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Ghníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstiúrthóir agus ceithre Stiúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmiúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.

NDP
National Development Plan 2007 - 2013

Science, Technology, Research and Innovation for the Environment (STRIVE) 2007-2013

The Science, Technology, Research and Innovation for the Environment (STRIVE) programme covers the period 2007 to 2013.

The programme comprises three key measures: Sustainable Development, Cleaner Production and Environmental Technologies, and A Healthy Environment; together with two supporting measures: EPA Environmental Research Centre (ERC) and Capacity & Capability Building. The seven principal thematic areas for the programme are Climate Change; Waste, Resource Management and Chemicals; Water Quality and the Aquatic Environment; Air Quality, Atmospheric Deposition and Noise; Impacts on Biodiversity; Soils and Land-use; and Socio-economic Considerations. In addition, other emerging issues will be addressed as the need arises.

The funding for the programme (approximately €100 million) comes from the Environmental Research Sub-Programme of the National Development Plan (NDP), the Inter-Departmental Committee for the Strategy for Science, Technology and Innovation (IDC-SSTI); and EPA core funding and co-funding by economic sectors.

The EPA has a statutory role to co-ordinate environmental research in Ireland and is organising and administering the STRIVE programme on behalf of the Department of the Environment, Heritage and Local Government.

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