Novel Optical Sensing Systems for Primary Level Science Education

by

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I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Master of Science is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: .... ID no.: 96382449

Candidate

Date: 20th Sep. '04

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Orla, thanks for helping me out in the stress department, I know it was pretty often, especially towards the end!!

Abstract:

In the last three years, a number of Irish primary schools have been using LEGO Mindstorms technology in order to investigate the use of project-based learning as an alternative teaching tool. This has involved the use of LEGO bricks combined with standard electronic motors and some commercial sensors (e.g. temperature). In order to develop this project into the area of science education, we have developed a range of miniaturized optical sensors, which are compatible with the LEGO platform.

In particular a working oxygen sensor has been designed and fabricated. The principal design features were compatibility with the programmable LEGO platforms and robustness for classroom use. This sensor uses the method of intensity quenching to determine oxygen concentration. This sensor has been demonstrated in a learning environment. Similarly a carbon dioxide sensor has been developed.

In addition, simple colour sensors have been produced. The aim of developing such sensors is to familiarise students with the concept of colour detection and to introduce them to the basic principles of spectroscopy. A specific use for the colour sensor has been identified, in the role of a pH sensor. A simple method of detecting nickel sulphate using colorimetric diffuse measurements has been demonstrated. The performance of both sensor types has been evaluated.

Contents

Chapter 1

Introduction

1.1 Introduction

The work presented in this thesis has been undertaken in order to develop sensors for use in a science education environment. The recent decline in the numbers studying science subjects in school has led to a severe decrease in third level science graduates. In order to address this issue, the introduction of science to children at primary school level must occur in such a way as to maintain attention and stimulate interest. In particular, the hands-on approach, where children conduct their own experiments is the goal of this work. One of the drawbacks to this approach is equipment cost. The cost and robustness of the sensors, and the ease with which they can be incorporated into scientific experiments, which effectively demonstrate basic concepts must be considered.

As science has recently been incorporated into the Irish primary school curriculum, this work was undertaken in tandem with several primary schools in order to demonstrate the effectiveness of these sensors as a learning aid. Two areas of interest were focused on: gas sensing, colour identification and their applications. The incorporation of the sensors developed into the relevant data-logging platforms is described.

1.2 Beyond Black Boxes overview

The project 'Beyond Black Boxes' [1] was developed by researchers at Massachusetts Institute of Technology (MIT) in order to bring science alive and to motivate children in the area of science. It involves the development of sensing platforms with data logging capability and a range of sensors, motors and gears, with which children can observe and measure quantities and also design and engineer systems which will act according to a set of instructions and the stimuli being measured.

The main tool in the project developed by MIT is the 'Cricket' [2]. This is essentially a micro-computer which has sensor inputs and programmable outputs. There are several different models of the Cricket platform, each new evolution with better capabilities than its predecessor. The project (Beyond Black Boxes) is ongoing and its purpose is to develop children's knowledge in science and also to develop an understanding of the relationship between science and technology [3].

1.3 Lego Mindstorms overview

In 1998, LEGO released a robotic construction kit, known as LEGO Mindstorms. This package is the result of technology and ideas developed by Seymour Papert [4] through research at MIT. The Logo brick was the result of early research in this field. Sensors and motors could be attached to it in order to allow it to monitor its immediate surroundings and to react to certain stimuli.

The programming language 'Logo', was specially designed for the purpose of communicating with and programming the Logo brick. Children could now control the movement of various mechanical projects by connecting the "programmable bricks" to an interface box and using Logo to programme them. The first "programmable bricks" needed to be hardwired to a desktop to facilitate programming and data retrieval. This greatly limited the potential for truly autonomous machines.

Eventually the LEGO RCX brick was developed. This had the advantage that it did not need to be physically connected to a desktop computer. Programming is carried out remotely using an infra-red communication link. Furthermore, information gathered by the brick through the use of sensors can be relayed to the desktop via an IR link.

The Lego Mindstorms kit is based around the RCX, and includes parts with which small robotic sensing and data logging systems may be created. LEGO have now produced many Mindstorms kits, which are readily available on the retail market. Although these kits differ in size, content and project capabilities, they all consist of the following components:

- RCX brick
- Motors and various sensors
- LEGO bricks, including axles, gear wheels and other mechanical components

The RCX brick is at the centre of any project built from these kits. The RCX brick is essentially a miniature computer with an LCD screen, and contains the circuitry required to drive motors and collect data using a collection of miniaturized sensors. The brick converses with the desktop by means of an IR "tower". However, this is directional and the IR transceivers of both the brick and the tower must be lined up to allow communication.

1.4 Sensor Technology

Researchers at Massachusetts Institute of Technology (MIT) have already developed a range of sensors and actuators, for use with both the Cricket and LEGO Mindstorms platforms. The sensors developed for use with the LEGO RCX brick are of the resistive type. This means that the sensors' resistance changes with changing stimulus. An example of this would be a light dependent resistor (LDR), whose resistance changes with changing light levels. The RCX determines the reading by applying a fixed voltage to the sensor, measuring the potential drop, and thereby determining the resistance of the sensor. The sensor output is then recorded as an 8 bit number between 0 and 1023. Some of the sensors detailed later output a voltage, which is proportional to the parameter being measured. The method by which these sensors are interfaced to the particular sensing platforms is explained later in this work.

Most of the sensors constructed for use with the Cricket platform are of the resistive type also. However the Cricket platform lends itself to the development of more complex and accurate sensors. This is because of the single-line bus communication feature of the device. This enables communication between the embedded micro-processor on the Cricket and a micro-processor on the sensor itself. A/D capability on the microprocessor greatly enhances the functionality of the sensor, and therefore does not limit the sensor to a resistive based-sensing system.

The merits and drawbacks of both the Cricket and Lego RCX sensing platforms are discussed in greater detail in Chapter 2, the applications in which one is more suited than the other, and the educational value of both from a scientific viewpoint.

1.5 Objectives

The primary aim of this project was to develop miniaturised optical sensors for use with the Cricket platform as educational tools in a learning environment. With some modification, the developed sensors could also be used with the LEGO Mindstorms (RCX) educational kit. The sensors to be developed were chosen so that they could be employed in simple classroom experiments without the need for expensive laboratory equipment. The analytes were chosen to demonstrate everyday phenomena such as respiration, acidity and colour recognition.

The sensors were developed for the following analytes:

- Gas sensors
    - Oxygen
    - Carbon Dioxide
- Colour sensing
    - pH
    - Nickel Sulphate

The main driver in the development of educational sensors was cost effectiveness, but the reliable performance of the sensors was a crucial requirement.

1.6 Thesis Outline

In Chapter 2, both sensing platforms (Cricket and RCX) are discussed in greater detail, focusing on the attributes and the capabilities of each system and how they were integrated into the educational environment. Chapter 3 focuses on the development of both oxygen and carbon dioxide sensing films and also of the various methods through which the respective gas concentrations may be determined. The incorporation of this gas sensing chemistry into employable sensors is described. The circuits required in order to operate the sensors, the method by which they were connected to the RCX and Cricket platforms and results obtained from the detection of the individual gases are also presented. Chapter 4 outlines the construction of a colour sensor and its implementation in conjunction with the RCX system.

Chapter 5 details the extension of colour sensing into the determination of pH and the detection of nickel sulphate. The optical measurement of pH solutions is presented. Determination of nickel sulphate concentrations in a water solution by diffuse reflectance measurement and the transmission intensity of incident light at a particular wavelength with respect to a reference light source is discussed. Chapter 6 concludes with how this new technology was demonstrated using both sensing systems, and how these sensors could be integrated into primary schools.

References

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Chapter 2

MLE Cricket and LEGO RCX Platforms

2.1 Introduction

The incorporation of sensors into an educational programme where science is the main focus requires suitable technology in order to relate scientific ideas to children and develop an interest on their part. This chapter discusses the two main platforms used in this project, their merits and the way in which they were employed in an educational capacity with currently available sensors as well as developed optical sensors.

Two sensor platforms, Cricket and LEGO RCX, that operate on the same principles were investigated. Each platform has a standard set of sensors and a specific programming language interface that allows data transfer between the PC and sensing platform. The methods by which additional developed sensors can be interfaced to the Cricket and the RCX are discussed and the communication protocol that allows communication between more complex sensors and the Cricket is explained.

2.2 Cricket Overview

The Cricket is a miniature programmable computer which can directly control motors and receive information about its immediate surroundings using a collection of specialized sensors. It was developed as part of the Beyond Black Boxes project by

Brian Silverman and Bakhtiar Mikhak (Massachusetts Institute of Technology) [1]. As shown in Figure 2.1, it is a very compact system and is based around a PIC microcontroller (PIC16C715), which is programmed to enable the cricket to collect, store and send the data gathered by means of attached sensors.

Figure 2.1 Cricket with 9V battery

The following features are integrated into the Cricket micro-computer:

- PIC16C715 with 2K Programme memory and 128 bytes Data memory
- 2 Bus Ports
- 2 Resistive Based Sensor ports
- 2 Independent Bi-directional Motor Ports with Directional LEDs
- Bi-directional IR link

The Cricket may be programmed, and can communicate with a desktop computer by means of a bi-directional infra-red link. It is also suitable for remote applications since it does not need to be hardwired to the desktop. This is especially useful when using the Cricket for remote sensing and data collection.

The software environment, Cricket Logo, is used to programme the Cricket, and is shown in Figure 2.2. Procedures may be written in the right hand window and downloaded onto the microcontroller situated on the Cricket. Commands may be downloaded to the Cricket via this window, so that an immediate response from the Cricket may be initiated. This window may also be used in order to gain real time sensor readings from the sensors plugged into the cricket.

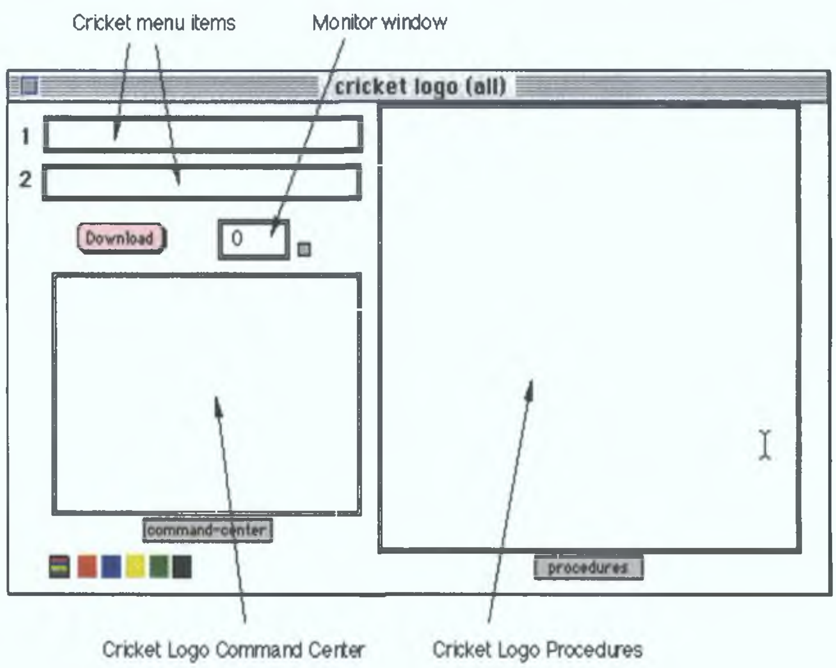

Figure 2.2 Cricket Logo programming environment

For remote applications, when the Cricket is to be used away from the desktop, procedures may be downloaded to the Cricket. To initiate the programme, a button on the Cricket may be pressed. Therefore the programming environment is not essential in order to initiate procedures at a distance from the desktop computer.

More recently, a programming environment, called Logo Blocks, has been developed for use with the Cricket platform by researchers at MIT [2]. It is an iconic system, which is more appealing to children, since it is not necessary to remember commands. Moreover, the blocks will only fit into each other in a logical order, much like a jigsaw puzzle. This programming environment is shown in Figure 2.3.

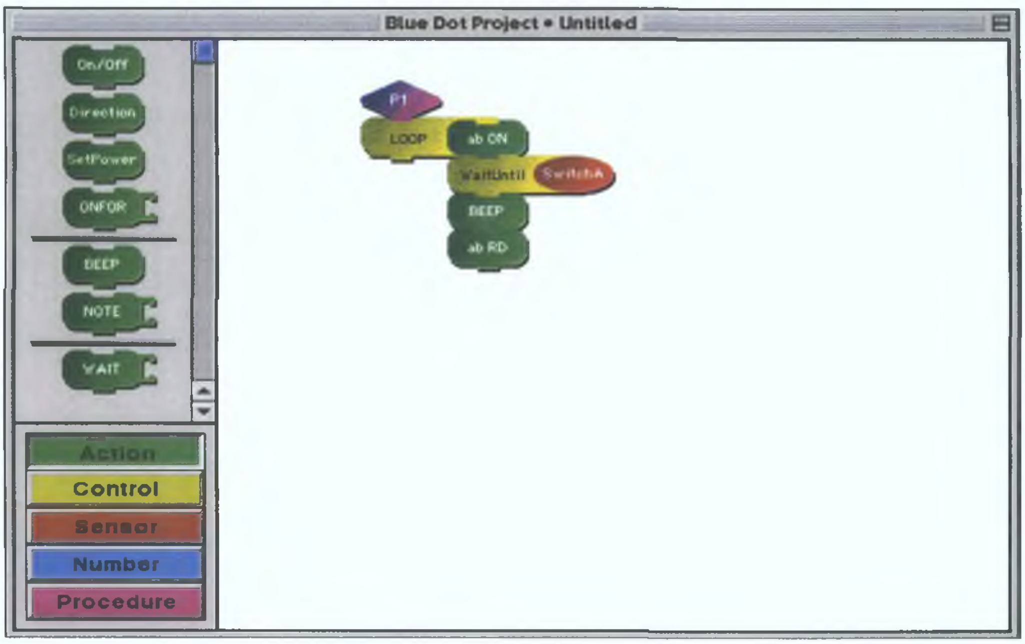

Figure 2.3 Cricket 'Logoblocks' programming environment

The method by which this programme operates nullifies the need to type code in order to compose programmes. This saves time and avoids the incorporation of punctuation, which can lead to mistakes and frustration, an inherent feature of many programming languages.

2.3 Cricket Sensors, Communication and Bus Protocol

A wide range of sensors has been developed or adapted by MIT researchers in order to expand the projects and experiments in which the cricket system may be used. Many of these sensors are relatively simple in their construction and operation, and in most cases do not require to be incorporated into electronic circuits. Examples of such sensors are devices that measure:

- Light
- Temperature
- Touch

All the above are resistive sensors: their resistance changes as a function of the changing stimulus associated with the particular sensor. These are interfaced with the cricket using one of two ports, each of which is capable of measuring the resistance output of the sensor and recording it as a number whose value is between 0 and 1023.

As well as sensors, simple actuators are also available. The cricket is capable of powering two motors simultaneously. These motors can be driven independently and in either direction, depending on the programme format.

Sometimes a desired measurement parameter cannot easily be changed into a resistance. Voltage and current may also be used in order to measure a changing signal. In order to utilise these signal indicators a different approach is needed to determine the magnitude of the quantity being investigated.

An expansion port, or bus port, is included on the Cricket platform. This allows complex sensors and actuators to be integrated into the Cricket system. The addition of bus devices greatly enhances the use of the Crickets as a learning and development tool. Examples of such sensors, produced by MIT researchers, in order to measure stimuli for which there are no simpler sensors available include:

- Heart rate monitor
- Optical distance sensor
- Clap sensor
- Reflectance sensor

A microcontroller is embedded onto these sensors in order to measure their responses and to communicate this information to the Cricket. These sensors are also known as bus devices, signalling the need for a communication bus in order to transfer measurements and information back and forth. Other devices that have been developed for use under this system include:

- Hex display
- LCD display
- RF communication board

The bus devices are interfaced to the cricket through a three-core wire, from the Cricket's bus port to the devices. One wire is held at +5 volts, another at ground (0 volts) and the third is connected directly from the pin RB0 on the Cricket's microcontroller to the corresponding pin on the bus device's microcontroller.

Each bus device has its own identification, since many bus devices can be daisy-chained to the Cricket. A master-slave method is implemented when using such bus devices. The Cricket acts as the master, and the sensors as slaves, waiting until a command is sent from the Cricket before implementing an instruction [2].

Figure 2.4 shows a graphic representation of the bus protocol. The bus line is held in the high state, with the pins dedicated to communication from each device connected together. A transmission consists of a 100 microsecond pre-start pulse, where the bus line is driven low, followed by a start bit, 8 data bits and a 9th bit to indicate whether the bitstream was data or a command. A 'one' signifies a command, while a 'zero' indicates data. A low 10th bit follows to signify the end of the transmission.

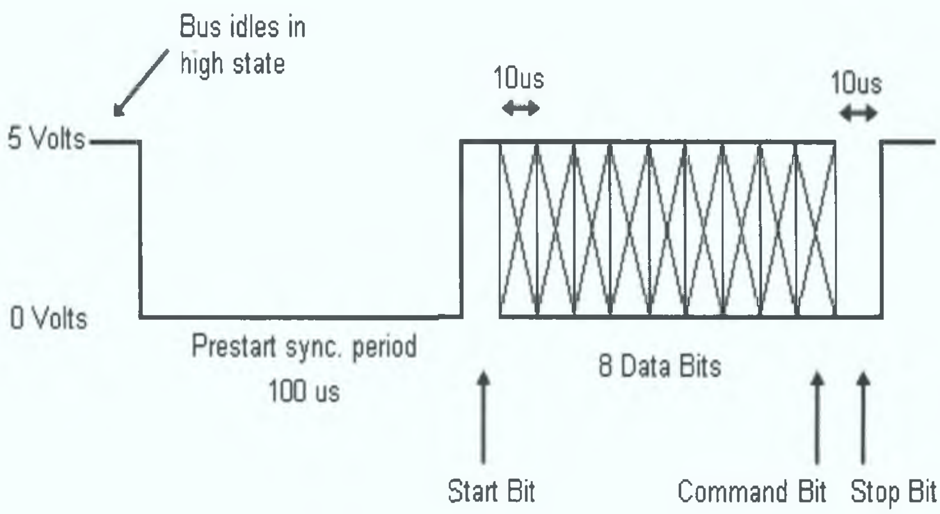

Figure 2.4 Bus protocol signal

The pre-start synchronization pulse allows all connected bus devices to prepare to capture and process the proceeding bus data. Every device connected to the communication bus should be ready to receive data before the synchronization pulse ends. Since every bus device has its own identification address, only the device with which the Cricket is selected to communicate, will dedicate its time to the Cricket after processing the bus data. The rest of the bus devices connected will return to their previous state, either collecting data, or waiting for their address to be called.

It is possible to communicate directly with a bus device using the Command Centre window present in the Cricket Logo software (Figure 2.2). If, for example, one wished to find the value being recorded at an instant by a bus device, typing 'send bsr $150' would tell the bus device with address '50' to relay its current reading back to the Cricket, where the '1' signifies this is a command and not data. The Cricket in turn would send the value back to the PC, and this would appear in the monitor window of the software.

An RF transceiver (Radiometrix RF TRX v1.2, Lemos Int., USA) has already been developed as a bus device for the Cricket platform. This can be used to relay information from one Cricket to another, or to and from the PC via the interface used to communicate with the Crickets. This enables remote sensing where line of sight is restricted, and the infra-red communication abilities of the platform are compromised.

2.4 RCX Brick Overview

LEGO have produced many Mindstorms construction kits that are readily available on the retail market. Although these kits differ in size, content and project capabilities, they all consist of the following core components:

- RCX brick
- Motors and various sensors
- LEGO bricks, including axles, gear wheels and other mechanical components

The RCX brick (Figure 2.5) is at the centre of any project built from these kits. It is based upon the same principles of operation as the Cricket, although it is housed in a more robust package. However, it does lack the feature of a bus line, and therefore the developmental attributes of the RCX are not as wide-ranging as those of the Cricket. Essentially, the RCX is a miniature computer with an LCD screen, and contains the circuitry required to drive motors and collect and store data using a collection of miniaturized sensors.

There are three input sockets allowing the RCX to collect data from up to three resistive sensors simultaneously. Three output sockets allow the RCX to drive miniature motors in both directions for any stated length of time. There is also the option of driving the motors at any one of seven operational speeds.

Figure 2.5 RCX Brick

Any project built around the RCX brick can be almost completely autonomous. Like the Cricket, the RCX converses with the desktop by infra-red means, through an IR 'tower'. This is directional, however, and the IR transceivers of both the brick and the tower must be lined up to allow communication.

2.5 RCX Programming Environment

The programming environment, RCX Code, is used with the RCX brick. It is essentially the same as the Logo Blocks software that has already been discussed for use with the Cricket. Programmes are "written" by piecing together the various shaped icons, each of which has a specific command assigned to it. This simplifies the task of writing programmes and also makes it more appealing to children, since the software is graphic-based and programmes do not have to be manually typed.

Other programming software, that has been developed by LEGO Mindstorms enthusiasts, is also available. These programming environments are more suitable for people who want to develop new sensors and transducers for use with the RCX platform. One of these software packages (NQC) [3] has been used in the development of the colour sensor outlined in chapter 4, and is discussed in more detail in section 4.3.

2.6 Conclusion

Two different sensor platforms have been introduced and their application to primary level education discussed. A simple and accessible method of programming the RCX and Cricket that allows children to control the respective platforms has been described. The method of communication with basic resistive sensors has been introduced along with the incorporation of such sensors into the Cricket platform. The way in which more complex sensors can be created and the communication protocol that allows data exchange between the sensor and Cricket has also been discussed.

The method by which simple sensors are linked to the RCX has been addressed, and the capabilities of the system discussed. The incorporation of a more complex sensor, (colour) and the programming of the RCX in order to interface the developed sensor is discussed in chapter 4.

The differences in capability between the two platforms are evident and the considerations when developing sensors for use with either have been addressed. It is also apparent that the Cricket is of more benefit to the researcher because of the presence of a bus line to allow more complex sensors be attached. The LEGO RCX is more suitable for use with children, as it was developed to be. The programming language, although sufficient to programme the RCX, is not very beneficial to the researcher, therefore prompting some to develop their own programming environments in order to use the RCX at its full potential.

References

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2. Martin, F., Mikhak, B. and Silverman, B., **'MetaCricket: A designers kit for making computational devices'**, IBM systems journal, 39: 7 - 30, 2000.

3. NQC download website: http://www.cs.uu.nl/people/markov/lego/

Chapter 3

Oxygen and Carbon Dioxide Sensors

3.1 Introduction

Oxygen sensors have been developed for a wide range of applications. Such uses include the measurement of dissolved oxygen in water [1], monitoring of exhaust gases in cars [2] and the measurement of oxygen concentration in enclosed environments such as in food packaging applications [3]. Likewise, carbon dioxide sensors are used in many industrial applications [3] and for the monitoring of indoor air quality [4].

The development of sensors for both analytes for educational purposes is outlined in this chapter. The detection methods employed, their performance and data logged in the case of both sensors are discussed.

The primary objective here was to develop simple sensors to be used in experiments designed to demonstrate physical facts. In experiments where only one gas was being sensed, e.g. 'candle in a jar' which demonstrates that oxygen is required for combustion, only the oxygen sensor was used. Other experiments demanded the use of both sensors simultaneously, e.g. photosynthesis, where the concentration of one gas increased as the concentration of the other decreased.

It was not imperative for the developed sensors to be extremely accurate. The ability to detect changes in oxygen concentration of around two percent was deemed acceptable for the purposes required. The emphasis was placed on making a robust sensor that would perform repeatably. It was also necessary for the sensors to have a fast response to the changing analytes so that any changes could be measured in close to real-time. The method by which these attributes were obtained is discussed in this chapter.

3.2 Oxygen Sensing

The operation of the oxygen sensor described in this chapter is based on the quenching of fluorescence in the presence of oxygen. Luminescent transition metal complexes such as ruthenium polypridyl complexes are quenched by oxygen. There are many ruthenium complexes suitable for oxygen sensing. The particular fluorescent ruthenium complex, $[Ru(Ph_2phen)_3]Cl_2$ is used in this application to quantify the concentration of oxygen, where (Ph_2phen = 4, 7-diphenyl-1, 1—phenanthroline) [5]. This compound has a high absorption in the blue-green region of the spectrum and is excited using a blue LED. A large Stokes-shift is associated with the compound and it emits in the red spectral region.

The oxygen quenching process is described by the Stern – Volmer equation [6],

$$I_0/I = 1 + K_{SV}p[O_2]$$

$$K_{SV} = k\tau_0$$

where I and I_0 are respectively the fluorescence intensity in the presence and absence of oxygen. K_{SV} is the Stern-Volmer constant, and $p[O_2]$ is the oxygen gas partial pressure. τ_0 is the excited-state lifetime of the fluorophore in the absence of oxygen, and k is the bimolecular quenching constant. These equations lead to a calibration plot associated with oxygen sensors of I_0/I verses the oxygen partial pressure.

3.3 Oxygen Sensor

The oxygen sensor developed employed the method of quenching of fluorescence intensity. The reasons for doing this were:

1. It is a relatively easy detection method to realise
2. The required circuitry is minimal

The disadvantages of using this method are:

1. Each sensor must be individually calibrated
2. The LED intensity, and therefore the output signal, may fluctuate
3. The position of the LED and photodiode relative to the sensing film must remain constant

The sensing film was prepared by incorporating the ruthenium complex in a sol-gel silica film. In particular 17mg of the oxygen-sensitive complex, $[Ru(Ph_2phen)_3]Cl_2$, was dissolved in 5.248ml of ethanol and mixed with 1.313ml of pH1 HCl whilst stirring. The required amount, 2.870ml, of methyltriethoxysilane (MTEOS), the sol-gel precursor, was then added drop-wise whilst stirring and the mixture was stirred for a further 4 hours at room temperature. The film was then deposited onto PMMA slides by stamp-printing and then cured at 70°C for 18 hours.

The sensor configuration was based on a patent for efficient fluorescence capture [7]. A sensing film was deposited on top of a waveguide. This was illuminated directly using a blue excitation LED (I_{max} = 470nm, NSPB 500 Nichia, Germany). The fluorescence from the sensing film was coupled into the waveguide and guided through its length to be detected at the end-face by the photodiode. The fluorescence from the sensor film is not coupled isotropically into the waveguide. At a certain angle the fluorescence intensity is a maximum. The photodiode is positioned at this angle with respect to the end-face for efficient detection [8]. It was observed that for this sensing configuration, the angle at which the intensity was greatest was 30°.

Figure 3.1a shows an outline diagram of the flow-cell used to house the slide and also to retain the electronic components at the correct distances and angles with respect to the coated slide.

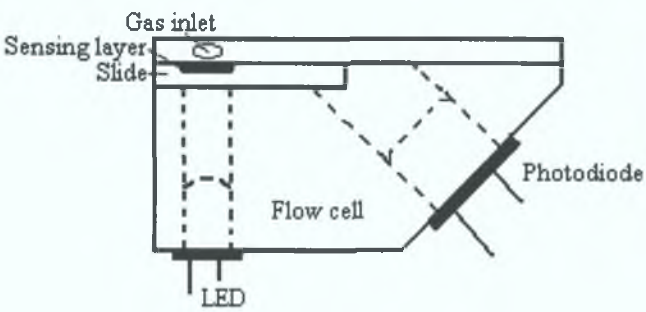

Figure 3.1a Sensor Flow Cell

Figure 3.1b Cell on PCB

The cell was machined from aluminium, and was mounted directly onto the printed circuit board (Figure 3.1b) that also incorporated the necessary circuitry. It was only 15mm high and did not add significantly to the size of the sensor. The top of the cell was made detachable so that the slide could be easily replaced. The gas inlet port was positioned directly above the sensing layers position so that the gas mixture could flow freely across the sensing film's surface.

3.4 Sensor Outline

Figure 3.2 shows a block diagram of the electronic components used in the fabrication of the oxygen sensor. Since the sensor works on the basis of measuring light intensity, it could be adversely affected by ambient light. The flow cell eliminates most of the ambient light falling directly onto the photodiode. However, to overcome this problem fully, the excitation light source must be modulated and lock-in detection used. A reference signal of the same frequency as the modulation signal (666Hz) is required so that the detection circuitry, which includes a lock-in chip (AD630), can effectively extract the emitted signal from the sensing film.

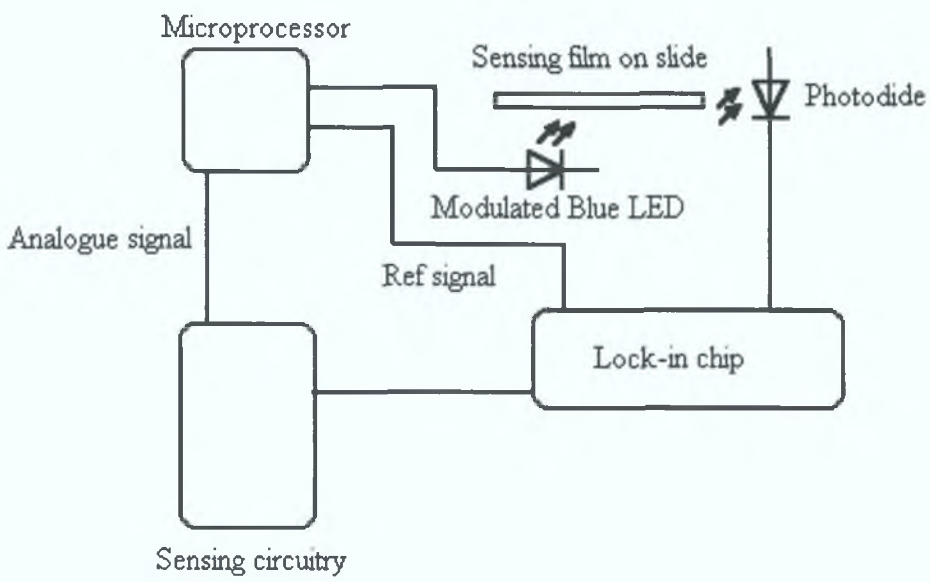

Figure 3.2 Sensor Block Diagram

A microprocessor controller (PIC16f872) was used in order to control the circuit. This microprocessor was chosen because of its analogue to digital capability. This allowed the raw sensor reading to be fed directly into one of the input pins on the microprocessor, where it was changed to a digital format that could be communicated to the sensor platform to which the sensor was connected. Another feature of this microprocessor is that it has a large onboard programme memory (2K), making it suitable for storing the necessary programme code and also the required look-up tables.

Figure 3.3 is a circuit diagram of the sensing circuitry used in order to determine the oxygen concentration using the flow cell and coated PMMA slide outlined in the previous section. The circuit is based around the lock-in chip, AD630, which receives a modulated signal, from the photodiode, which is proportional to the intensity of the emitted light from the sensing film.

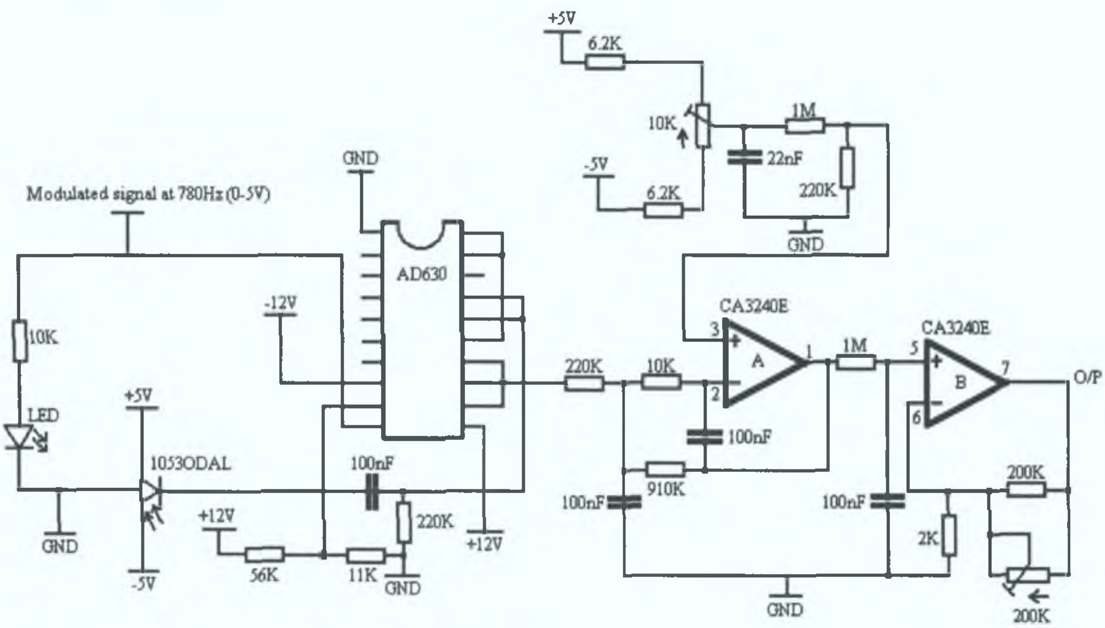

Figure 3.3 Oxygen sensor circuit diagram

An integrated photodiode amplifier (IPL 10530 DAL, IPL Inc, Dorset, UK) was used to detect the emitted light. This photodiode was chosen because it has a fast response and is therefore capable of detecting the signal from the film at the frequency at which the LED is modulated. The integral amplifier cancels the need for a preamplification stage before the signal is received by the AD630. This has the effect of minimizing the number of components needed, and therefore reducing the overall size of the sensor.

To reduce the size of the sensor circuit further, the microprocessor was used to modulate the excitation light source, instead of using a dedicated frequency generating circuit. This resulted in stable square-wave frequency modulation (< 5 Hz distortion) of the LED used to illuminate the ruthenium complex, due to the fact that a crystal oscillator was used for the timing of the microprocessor. The modulated signal ranged from 0 to 5 volts. The modulated signal was driven from two of the output pins of the microprocessor. One of these pins was channeled directly to the reference port on the lock-in amplifier chip, while the other was connected to the LED through a current-limiting resistor in order to provide the excitation light for the sensing film. This results in a very clean and stable excitation light output.

Since the sensor was designed for remote applications, it was necessary to use a battery as the power source. This required a reduction in the power consumption of the circuit. Because the AD630 and the op-amp used (CA3240E) needed a positive and negative supply to function properly, two nine-volt batteries were used to provide the required power. After the modulated signal is extracted from the noise by the AD630, it is demodulated and turned into a dc signal. This is then amplified once more before being fed into one of the analog ports on the microprocessor.

The final gain stage of the sensor is variable, so that changes in the quantity of the oxygen sensitive film from sensor to sensor i.e. variations in sensitivity, can be accommodated. There is also an internal offset, which can be adjusted so that the sensing range of the film can be centered on the oxygen concentrations being measured.

The circuit used with the RCX needed miniaturization so that it could be incorporated into a wide range of applications where size was a limiting factor. Figure 3.4 shows a circuit diagram of the miniaturized circuit based on the circuit in Figure 3.3. This circuit was produced by Whistonbrook Technologies Limited, (Luton, UK). The circuit is powered by two AAA batteries. The flow cell and the size of the LED and photodiode are the limiting factors in the size of this sensor. However, even with these limitations, the sensor still has a footprint of only 55 by 25mm.

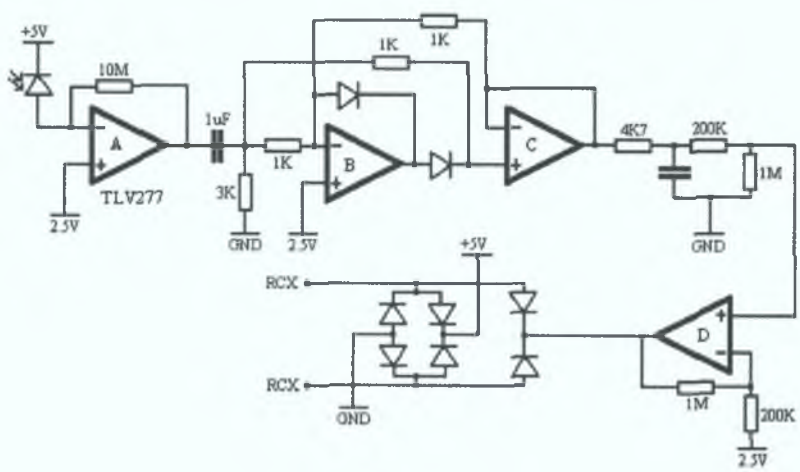

Figure 3.4 Miniaturized Oxygen Sensor Circuit

3.5 Interfacing Oxygen Sensor with RCX and Cricket Platforms

The circuit diagram, which is shown in Figure 3.3, is common to both sensors designed for the particular sensing platforms. In both cases, a PIC microprocessor is used to modulate the excitation LED, and also provide the reference signal that is used in the AD630 in order to extract the sensor signal from noise.

As explained in chapter 2, Figure 2.4, the Cricket platform uses a bus protocol in order to extract data from sensors whose output is in a form other than a changing resistance. In order for the Cricket to communicate with the oxygen sensor, a microcontroller was embedded in the sensor in order to convert the analog output signal of the sensor into a digital signal, which then could be relayed to the Cricket using the bus line.

A PIC16F872 was used in order to control the sensor and to communicate with the microprocessor on the Cricket. It was chosen because of the fact that it has onboard analogue to digital capability, and also a large memory bank (2K). This allows calibration information of the sensor to be stored in the memory and therefore an actual concentration reading can be sent to the Cricket, as opposed to an arbitrary number between 0 and 256.

The configuration of the additional circuitry needed in order to interface the sensor with the Cricket is shown in Figure 3.5. Two separate I/O pins were used to modulate the LED and provide a reference signal for the AD630. As a power saving consideration, the sensor could also be programmed so that it was continuously in stand-by mode. Upon receiving the appropriate signal from the Cricket, the microprocessor would turn on the detection circuitry needed to determine the oxygen concentration, turn on the LED, take in the analogue signal and return the oxygen concentration to the Cricket in digital form. After the information was sent, the microprocessor then shuts off the power to the rest of the circuit while it continuously tests for a new command from the Cricket.

The I/O pin, RB0, was used as the communications channel between the oxygen sensor and the Cricket platform. This is because previous sensors designed for use with the Cricket use this pin as the communication channel. This simplifies the programming, so that the part of the code used for taking readings from the respective sensors need not be changed in any way.

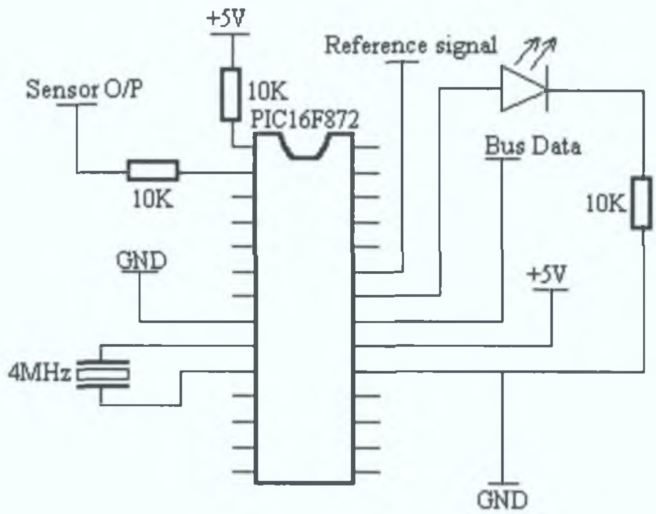

Figure 3.5 Microcontroller circuit on oxygen sensor

When interfacing the sensor with the RCX Brick, a different approach was needed. The Brick had no facilities to allow a bus protocol communications line to be implemented in order to communicate directly with an external sensor. Instead, the RCX determines the sensor value by measuring the resistance of the sensor output. Because the oxygen sensor uses a photodiode in order to measure the fluorescence of the oxygen sensitive dye, the output of the sensor is nominally a changing voltage. In order to connect the sensor to the RCX, the output voltage of the sensor needed to be changed to a resistance. Figure 3.6 shows the circuit used to accomplish this.

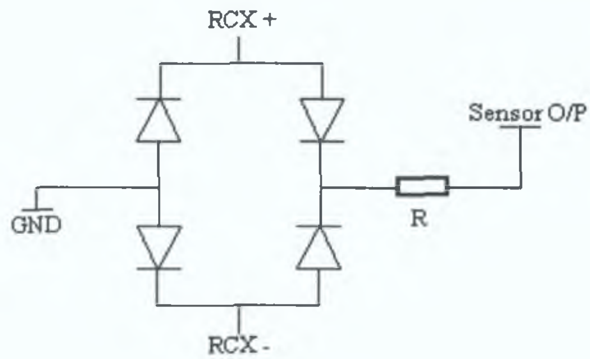

Figure 3.6 Oxygen sensor/RCX interface circuit

All diodes used in the circuit were 1N4148 diodes. The sensor output was connected to the diode bridge through the resistor R. The value of this resistor determined the linearity of the output resistance with respect to the output voltage of the sensor. Figure 3.7 shows the effect of using different resistors in the position of resistor R. It is evident from this graph that as the resistance value R is increased, the linearity of the sensor output also increases over the sensing range. However, this also led to a reduction in the sensitivity of the sensor. This can be seen from the slope of the individual resistance plots in Figure 3.7. Without a series resistance, the R value was 0.99849, using a resistance of 1kΩ gave an R value of 0.99827 and a resistance value of 10kΩ gave an R value of 0.99939. The output from the RCX is a 10 bit A/D conversion of the voltage across the sensor.

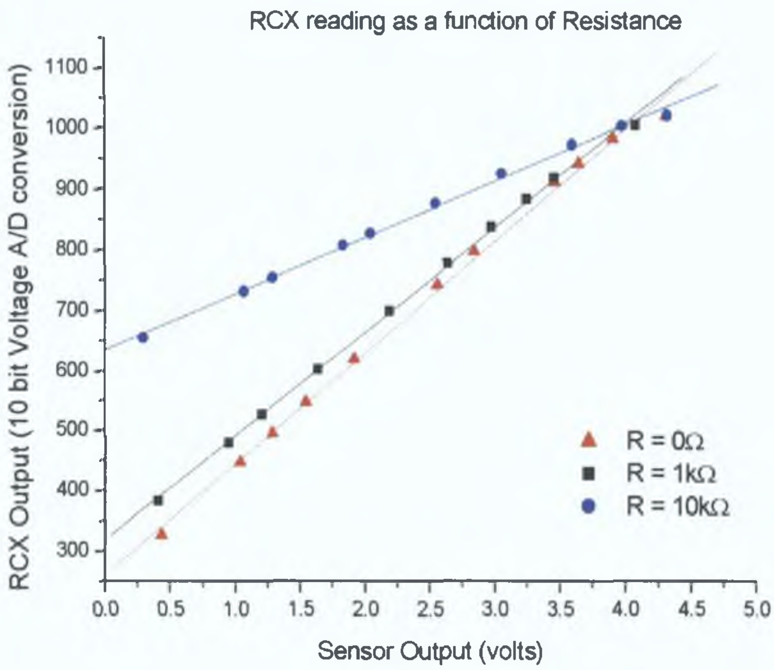

Figure 3.7 Effect of changing Resistance value

A value of 1kohm was used in the circuit developed for use with the RCX platform. This gave a linear response over a wide range and also allowed for a good resolution of the sensor output. The oxygen sensor was continuously on when used with the RCX platform.

The software used in order to display the oxygen concentrations measured by the sensor connected to the Cricket is the graphing function of the Cricket Logo software. Figure 3.8 shows the real time graph of the changing oxygen concentrations using this software. The oxygen concentration was stepped from 25% to 5% in steps of 5%.

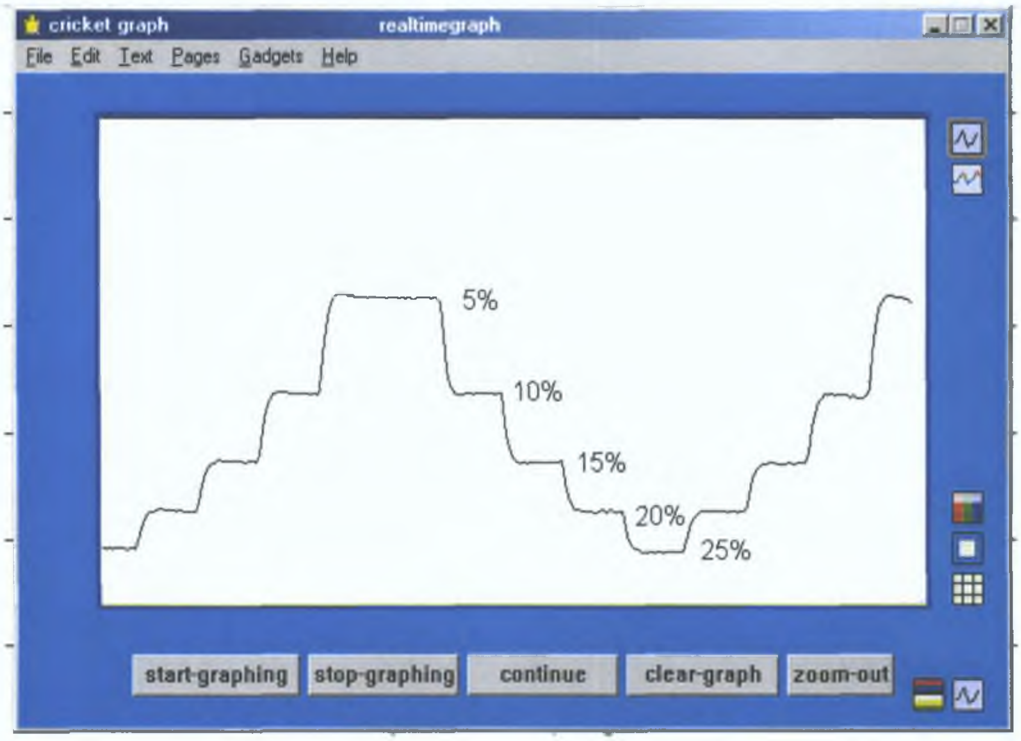

Figure 3.8 Cricket Software interface

3.6 Sensor Calibration

To calibrate the oxygen sensors, different concentrations of oxygen were flowed over the sensing film while the sensor output was being recorded by the platform for which the sensor was designed. The method by which the oxygen concentration was regulated is as follows. A Labview programme was used in order to control two mass flow controllers (MFCs). One MFC controlled the flow of oxygen, while the other controlled the flow of nitrogen gas. Figure 3.9 is a schematic representation of the calibration set-up.

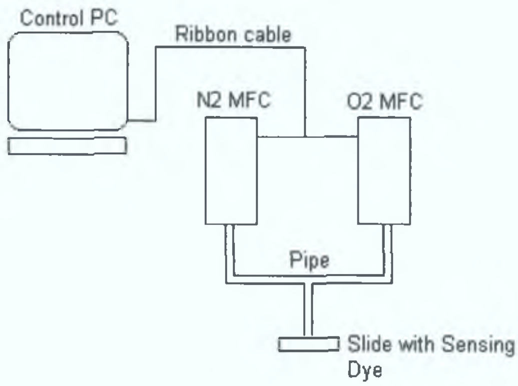

Figure 3.9 Gas Calibration System

The outputs from the two MFC's were then mixed together and the resultant gas mixture flowed over the oxygen sensitive film. The sensor output in volts can be recorded by various means.

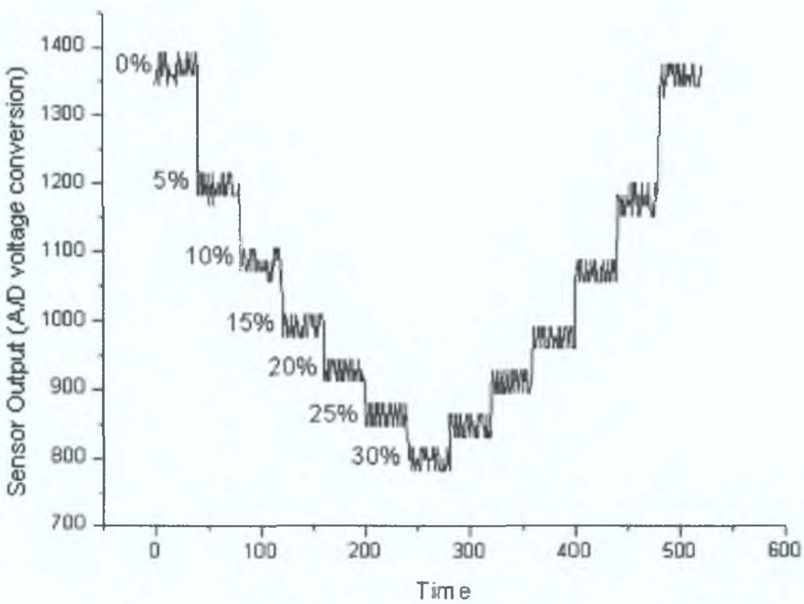

Figure 3.10 Sensor output for different oxygen concentrations

One method is to digitise the signal and load it into a PC. This is carried out by using a Bytronics card (MPIBM multifunction I/O), which takes the analogue voltage signal from the sensor and transforms it into a digital signal that the PC may store. A plot of these data from an MTEOS R=4 oxygen sensitive film is shown in Figure 3.10. Using the Stern-Volmer equations outlined in section 3.2, a Stern-Volmer plot of the data for this slide was plotted. This is shown in Figure 3.11. This graph can then be used as a calibration plot for the particular film.

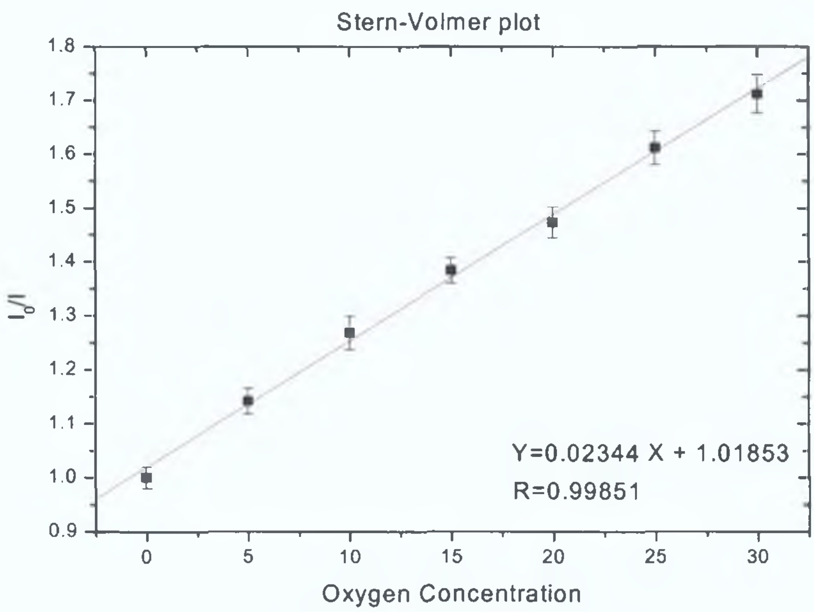

Figure 3.11 Stern-Volmer plot

The software interface in Figure 3.8 was used in order to display the oxygen concentration. Each individual sensor had to be calibrated independently, since the method of intensity measurement was employed in the sensors.

The same process of obtaining calibration data was employed for both the RCX and Cricket platforms. A typical graph of the raw data reading displayed on the RCX brick while calibrating a sensor is shown in Figure 3.12. The equation of the graphed line was calculated and was then used in the visual basic code so that the oxygen concentration could be plotted in real time from that particular sensor.

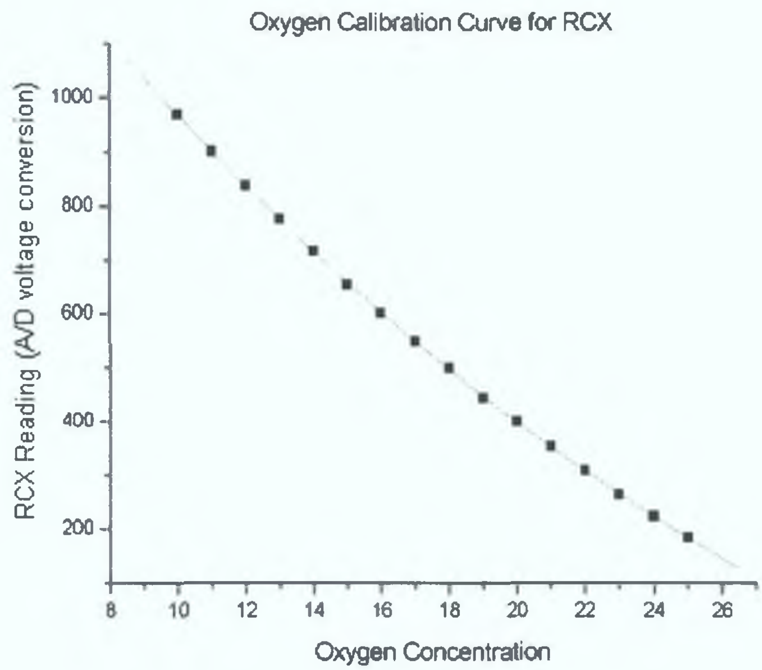

Figure 3.12 Calibration curve of RCX oxygen sensor

The above method was used both for the initial intensity measurement circuit shown in Figure 3.3, using lock-in detection, and the miniaturized circuit, which is outlined in Figure 3.4.

To calibrate the sensor for use with the Cricket, a similar approach was employed. However, during the calibration, the Cricket Logo software interface was used in order to determine the sensor output value, which was an arbitrary number between 0 and 255. The values corresponding to a set of oxygen concentrations were recorded, and a table drawn up such as that in Figure 3.13.

A look-up table was then built corresponding to that particular sensing film and this was then stored in the memory of the on-board microprocessor. This enabled the sensor to send out the real oxygen concentration to the Cricket software, or to calculate and store the concentrations over a period of time..

Oxygen	Sensor O/P	Oxygen conc.	Sensor O/P
0	175	15	48
5	128	16	44
6	120	17	40
7	111	18	35
8	102	19	32
9	92	20	27
10	85	21	23
11	77	22	19
12	71	23	15
13	65	24	12
14	59	25	9

Figure 3.13 Look-up table for Cricket oxygen sensor

The calibration curve relevant to this sensing film is shown in Figure 3.14.

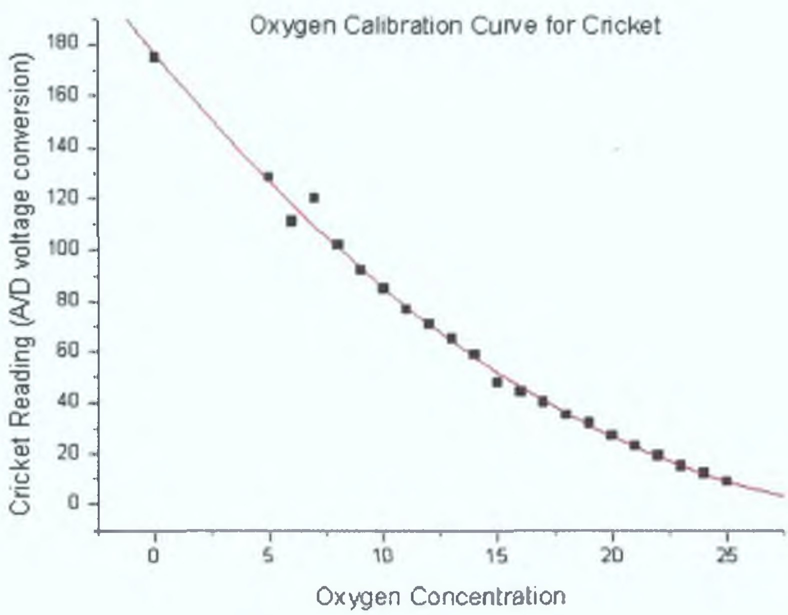

Figure 3.14 Calibration curve of Cricket oxygen sensor

The non-linearity of the sensor response to changing oxygen concentration is intrinsically linked to the fundamental non-linearity suggested by the Stern-Volmer equation (page 21).

3.7 Oxygen Sensor Conclusion

The underlying theory of sol-gel based oxygen sensors has been outlined. An oxygen sensitive film has been constructed and the Stern-Volmer equation introduced to characterise the film. Oxygen sensors fabricated for use with both the Cricket and RCX platforms have been explained in detail, as have the methods by which they are interfaced with either platform. The calibration method used has been outlined and graphs of the calibrations plotted and analysed. The detection range of the sensors has been optimised for oxygen concentrations relevant to their applications in educational experiments i.e. from 0% to 25%.

3.8 Carbon Dioxide Sensing

The development of an intensity based carbon dioxide sensor was undertaken to complement the oxygen sensor. The gas-sensing component was again sol-gel based. This section outlines the construction of the carbon dioxide sensitive material. The pH sensitive fluorescent dye, 1-hydroxypyrene-3,6,8-tri-sulfonate (HPTS) was used as the indicator for carbon dioxide concentration determination. This dye has an absorption band in the blue spectral region (440nm) and an emission band in the green (515nm). When gaseous carbon dioxide is dissolved in water, carbonic acid is formed. This acid reacts with the deprotonated dye and causes a reduction in the green fluorescence [9].

3.9 Carbon Dioxide Sensor

The electronic circuit used to determine the carbon dioxide concentration data using the pH sensitive film was the same as that used for the oxygen sensor shown in Figure 3.3, the only difference being that the LED used to excite the dye has a spectral peak at 450nm, (Roithner LaserTechnix, LED450-01U, Austria). The pH sensitive fluorescent dye discussed in the previous section was stamp-coated onto a PMMA slide. The same flow cell that was used in the oxygen sensor, Figure 3.1, was again employed in this role.

3.10 Sensor Calibration

The calibration of the carbon dioxide sensor was carried out in the same manner as for the oxygen sensor. Using two MFCs, one for carbon dioxide and another for nitrogen, controlled by a Labview programme, different concentrations of carbon dioxide gas were flowed through the cell containing the sensing film. Again, the output of the sensor was monitored and recorded using a Bytronics card (MPIBM3 multifunction I/O) to digitise the analogue signal from the sensor circuit, and a PC was used to store and display the data.

The main difference in the calibration procedure was that the gases needed to be humidified. This was necessary so that water was present with which carbon dioxide could form carbonic acid. This leads to a change in the pH and causes a change in fluorescence intensity. To achieve this, the gases were flowed through glass wash bottles filled with de-ionised water, whereupon a humidity of 100% was maintained. Concentrations in carbon dioxide of between 0% and 100% were used and a graph of the sensor output obtained and is shown in Figure 3.15.

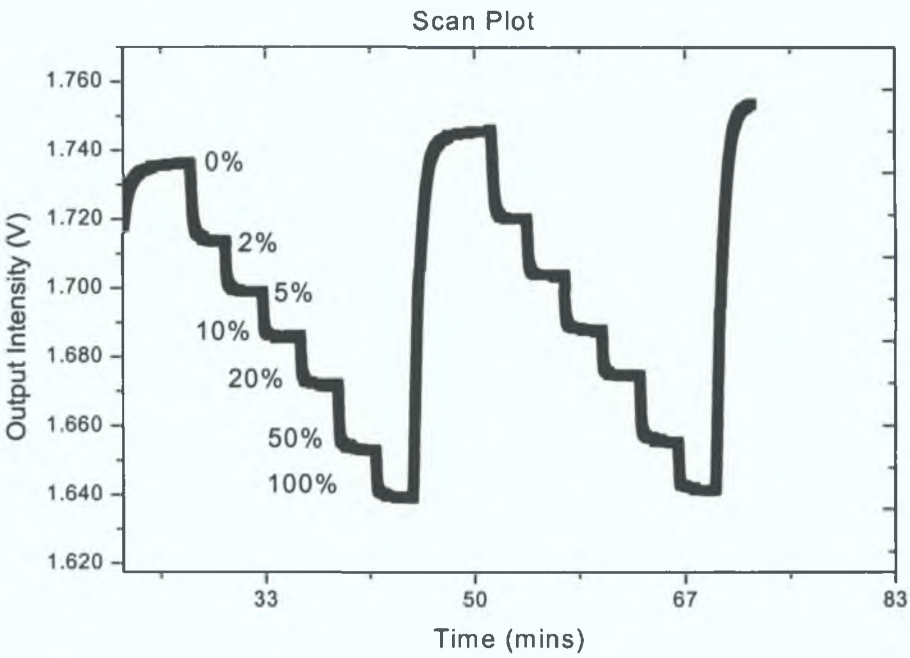

Figure 3.15 Sensor output for various concentrations in CO_2

In a classroom experiment, this sensor could be used to detect CO_2 concentrations in exhaled air. The sensing film is sensitive enough to distinguish the small CO_2 difference between inhaled and exhaled breath. These data were used to create a calibration curve for the particular film used. The calibration curve employed in carbon dioxide sensing plots $(I_0 - I)/I$, where I_0 is the intensity of the fluorescence when the carbon dioxide concentration is zero, and I is the fluorescence intensity at a particular concentration, against the carbon dioxide concentration [10]. The calibration plot obtained using the data in Figure 3.15 is shown in Figure 3.16.

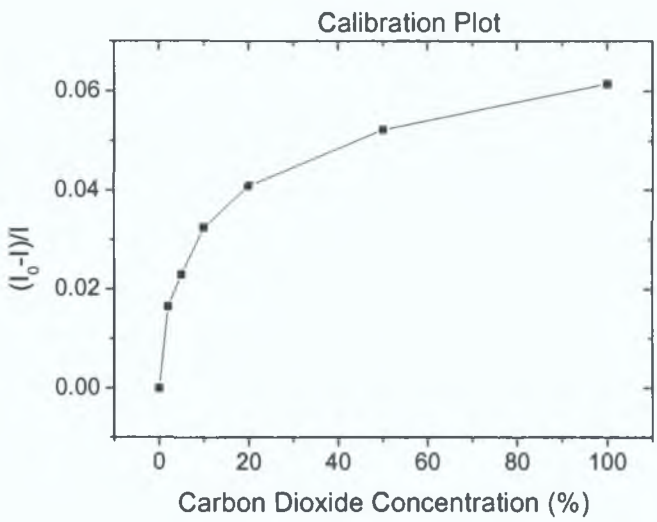

Figure 3.16 Calibration plot for Carbon Dioxide sensor

3.11 Carbon Dioxide Sensor Conclusion

A carbon dioxide sensor has been developed based on fluorescence intensity measurements using a pH sensitive indicator dye. The electronic configuration used in this sensor is identical to that of the oxygen sensor. The same excitation light source can be used, but would lead to a smaller spectral separation between the excitation and emitted light. This sensor has been shown capable of detecting the full range of carbon dioxide concentrations (0 to 100%).

3.12 Sensor Demonstration

The oxygen sensor developed in this work has undergone pilot tests in a classroom environment. Figure 3.17 shows primary school children using this sensor to determine the effect of exercise on the amount of oxygen consumed by the body. Further work will be required to fully validate the robustness of the sensors.

Figure 3.17 Children using Oxygen Sensor with RCX in Realtime

3.13 Conclusion

Compact, portable and robust sensing circuitry for fluorescence based sensors using intensity measurements has been developed. This technology has been applied to both oxygen and carbon dioxide sensing applications. The oxygen sensor has been interfaced with both the RCX Brick and Cricket sensor platforms. The performance of the oxygen sensor as an educational resource has been demonstrated in a classroom environment. The oxygen sensor has been used to quantify the difference in the amount of oxygen consumed when carrying out different levels of exercise. Future work could involve the incorporation of the CO_2 sensor into these platforms in a similar way

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Chapter 4

Colour sensor

4.1 Introduction

The sense of vision plays a great role in human life, especially the recognition of different colours. Colour is used in everyday life to indicate warnings, signals or as a process control measurement, for example [1]. The eye can easily distinguish not only between different colours, but also between colours of the same hue and different shade. To duplicate this sensory adaptation accurately using an electronic system is difficult to achieve. In order to develop such a system for use as an educational tool, a simple system using basic optoelectronic components was created.

4.2 Colour Sensor

A colour sensor was developed for use with the RCX brick platform in this project. This allows children to "teach" the RCX to recognise a set of colours. The sensor consisted of a light generation system to illuminate the object to be sensed, and a light receiving system to read the diffuse light reflected from the object. The illumination system consists of a multicolour LED (RS DN7559787) that has three different spectral components. Each component, red, green and blue, can be turned on individually by biasing the pin specific to the required colour.

A PIC microcontroller (PIC16F84) is used to produce various colours in sequence upon receiving a string of pulses from the RCX. The sensing element consists of a light dependent resistor (RS DN4442286) in a voltage divider configuration, the resistance of which changes in accordance with the intensity of the light reflected onto it. This resistive reading is then recorded and processed by the RCX.

4.3 Colour Sensor Circuit and Calibration

The circuit used to enable the RCX to identify a range of pre-determined colours is shown in Figure 4.1. This enables the colour sensor to be linked to the RCX using only one of the sensor inputs present on the RCX. To operate this circuit, the RCX sends out an initial pulse. This makes the PIC microcontroller turn on the first output, thereby enabling the multicolour-LED to emit in the red region.

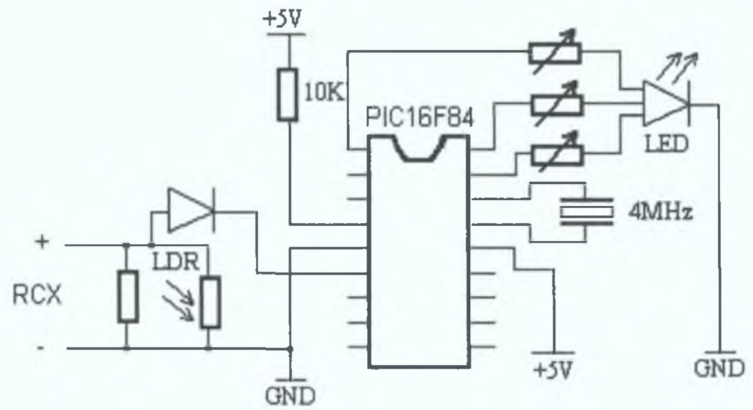

Figure 4.1 Colour Sensor Circuit

The RCX then switches to passive sensor mode and reads the value of the LDR. A second pulse is sent out to the microcontroller by the RCX, thus prompting the emission of the green component of the multicolour-LED. This value is recorded and the blue component is then illuminated and the LDR's resistive value recorded in the RCX.

The process of colour identification takes place by loading each of the three values into an array. This array of numbers is accessed by an algorithm, that is pre-recorded in the RCXs memory. The output result of the RCX is compared to a predetermined set of values for a range of colours that were investigated during the calibration of the sensor.

Each LED component is connected in series with a 10K potentiometer, the value of which determines the intensity of each spectral component. The relative reflected light intensity could then be varied so that the sensor could be calibrated. To do so, the sensor was placed on the white square of a colour rendition chart (T37-756, Edmund Optics Ltd.) and the potentiometers adjusted until the voltage reading across the LDR was the same irrespective of the spectral component being illuminated.

The light reflected from a surface is given by:

$$R = \frac{I_r}{I_0}$$

where, R is the fraction of incident light that is reflected from the surface under illumination, I_r is the reflected light intensity and I_0 is the intensity of the incident light [2]. The resistance of the LDR increases as the intensity of the incident light decreases. Therefore the reflectance can also be described as:

$$R = \frac{r_r}{r_0}$$

where, r_r is the resistance of the LDR while the coloured surface is illuminated and r_0 is the resistance measured using the reference white surface.

Since the voltage across the LDR is the same for each LED component after calibration using a white surface, the r_0 value is the same for each. Therefore the reflectance, R, is dependent only on the r_r term. The ratios of the reflected components could then be used to recognise a set of colours.

The limitations of this approach are such that any colour to be identified must first be "taught" to the RCX by placing the sensor head on the coloured surface and recording the values of the LDR under illumination of each spectral component in turn. Using the above method, only very similar colours to those predetermined could be recognised, so an error margin is written into the programme.

The LED and LDR are placed together at an angle of forty-five degrees in a black LEGO brick. Care is taken so that no light from the LED is shone directly onto the LDR, but is reflected diffusely from the surface under investigation. Figure 4.2 shows how the LED and LDR are placed with respect to each other.

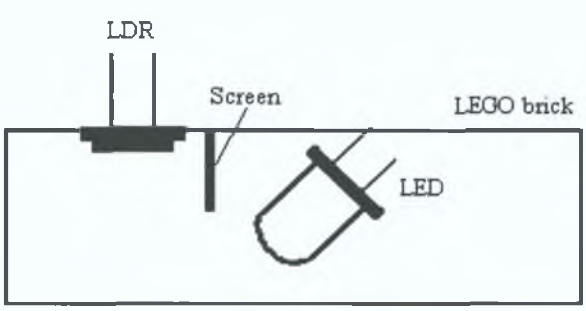

Figure 4.2 LED and LDR positioned in LEGO brick

Figure 4.3 shows the relative intensities of the three components of the multicolour LED using an 'Ocean Optics' spectrometer. In each case, a current-limiting resistor of 200Ω is used. It is clear from this figure that the blue part of the LED gives the greatest emission intesity.

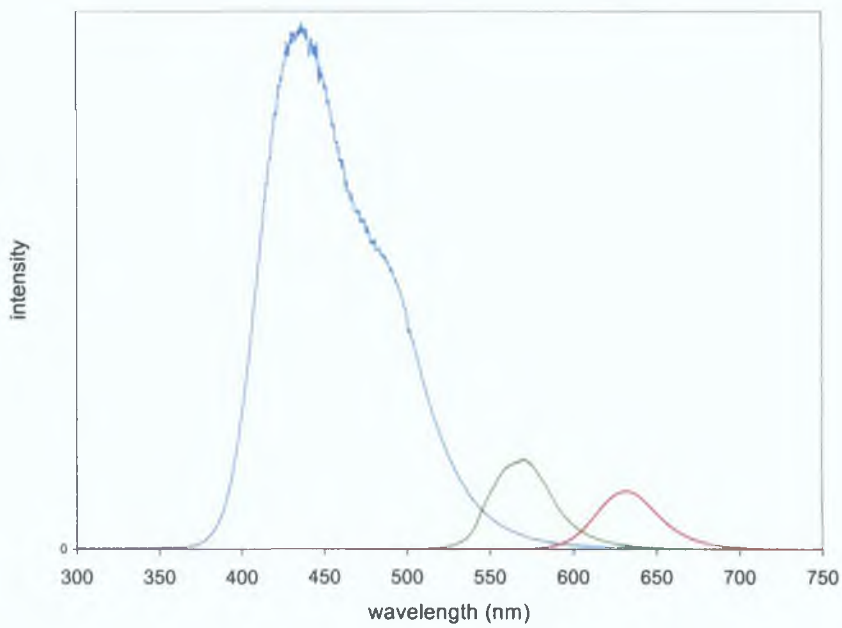

Figure 4.3 Spectral Emission of Multicolour LED

The above method of adjusting the current through each LED component enables the user to ensure that the individual components emit light at the same intensity. It also reduces the need to use the software on the RCX to compensate for the intensity differences and cancels the necessity for scaling factors to be written into the programme.

Figure 4.4 shows the LDR output when the sensor is placed on different colours of the rendition chart under illumination of each of the three spectral components of the tricolour LED. Initially the sensor head was placed on the white square of the rendition chart and the current flowing through each of the LED's components adjusted accordingly so that the light intensity from each one falling on the LDR was equal.

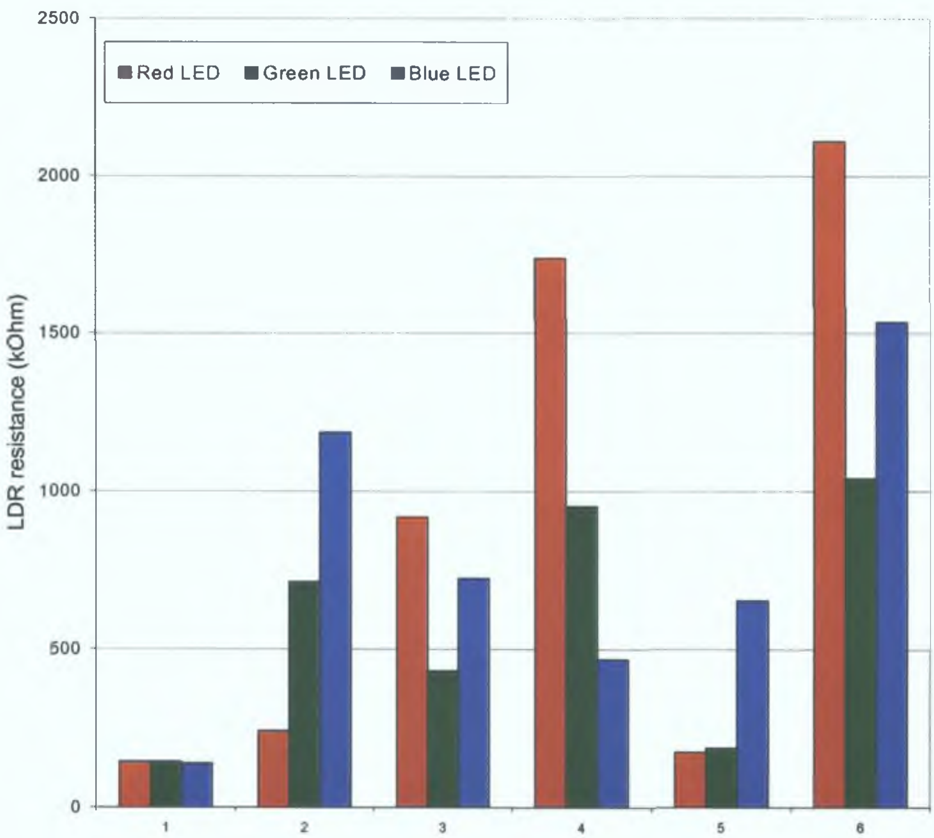

Figure 4.4 LDR readings for White (1), Red (2), Green (3), Blue (4), Yellow (5) and Black (6) cards

The readings shown in Figure 4.4 show that as the spectrum under investigation is traversed from higher to lower wavelengths, the relative intensity of reflected red light decreases, while the intensity of reflected blue light increases.

4.4 Programming

Although the commercially available programming software can be used when prototyping any new sensor developed for the RCX brick, there is also a freeware programme called “Bricx” which is available for download [3]. Figure 4.5 is a screen capture of this particular programming environment.

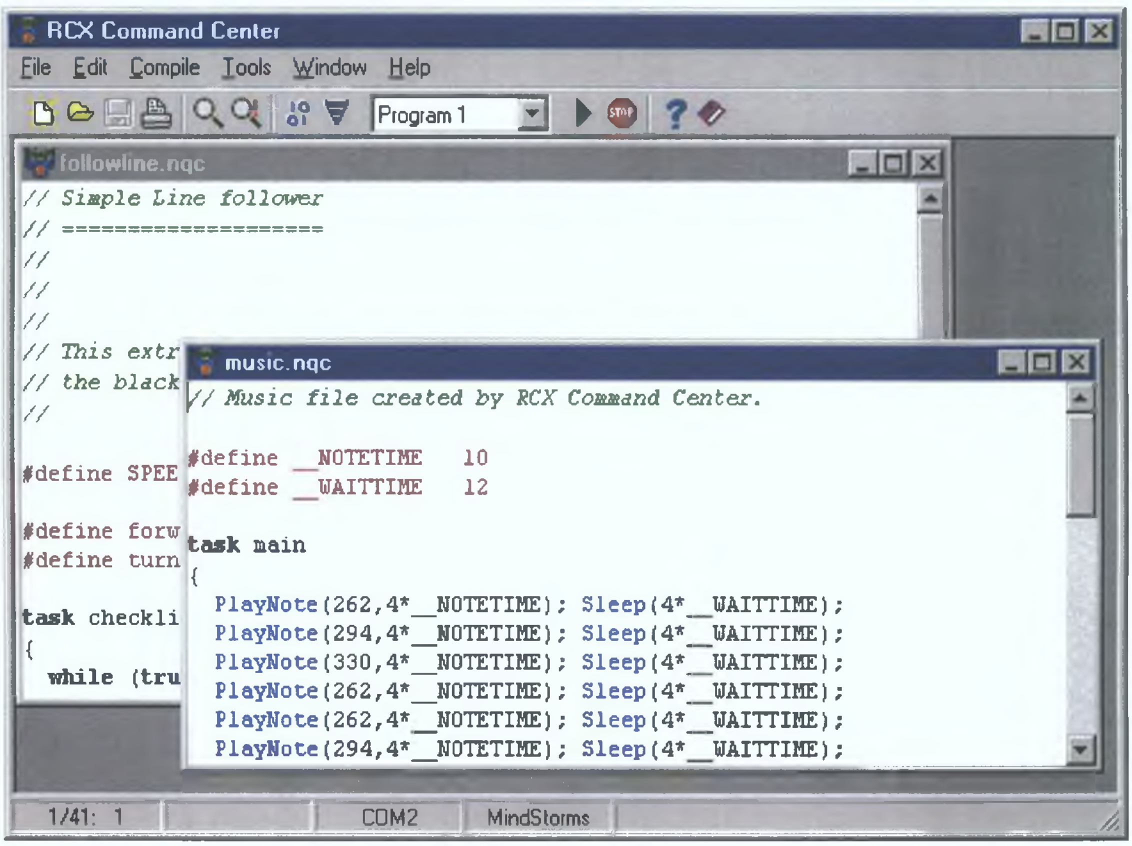

Figure 4.5 Bricx Programming Environment

This software allows a higher level of programming to be used when developing new sensors. The code used in order to write programmes using the Bricx command centre is known as NQC (Not Quite C). It is similar to C in most respects, but has additional commands relevant to common tasks performed by the RCX. It is not especially suitable for children to use but is very effective when used in a developmental capacity.

The finished programme is downloaded to the RCX in the usual manner by way of the IR tower. The code written in order to integrate the colour sensor with the RCX is given in Appendix C. In this example the colour sensor has been 'taught' to recognise five different colours.

4.5 Colour Sensor for the Cricket

A colour sensor for use with the Cricket was also developed. Because the Cricket is very limited in its data processing abilities, this particular sensor was very basic. A microprocessor (PIC16F872) was incorporated into the sensor to enable communication with the Cricket and also to control the sensor. The multicolour LED described in the section 4.2 was also employed in this sensor. Figure 4.6 is a circuit diagram of this sensor.

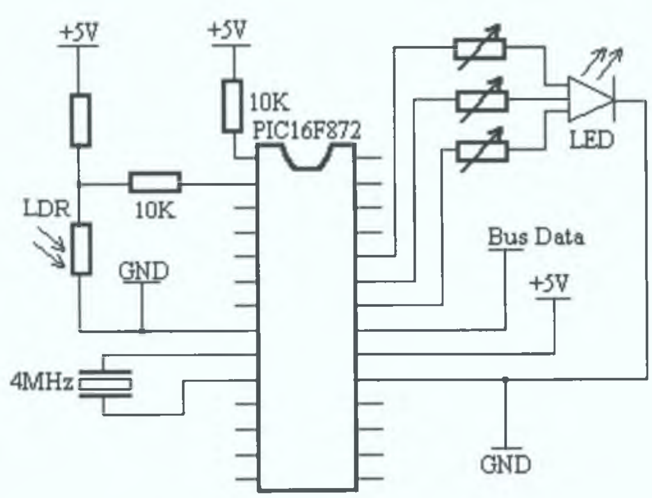

Figure 4.6 Colour Sensor for use with Cricket

The sensor is able to recognise the three primary colours. In order to determine others, more programming capability is required. The sensor operates by reading the voltage difference across the LDR while the target surface is illuminated with each component of the LED in turn as in the sensor for the RCX. The LED and LDR were both housed in a black LEGO block as in Figure 4.2.

The microprocessor can then evaluate the colour being sensed by using the recorded voltages. This was simply done by determining which spectral component produced the largest reflected light intensity. The sensor was calibrated using the red, green and blue segments of the colour rendition chart and adjusting the variable resistors so that the red spectral component gave the greatest reading on the red segment and so forth. A predetermined value is then relayed back to the Cricket depending on the determined colour.

4.6 White LED

Initially the possibility of using a white LED (Farnell 352-6860) in order to make the detector smaller was examined. It was decided to use a white LED in conjunction with a tri-colour photodiode (Hamamatsu S7505). This photodiode consisted of three separate detector sections coated respectively with different optical filters (red, green and blue). Hence the three different colour components of the reflected light from the surface of the item being interrogated could be measured simultaneously.

The spectral output of the LED investigated (shown in Figure 4.7) was determined using an Ocean Optics spectrometer. Although the output of the LED appears white, it is clear from the graph that there is a high peak in the blue region of the spectrum.

This led to a very large reading from the blue filtered photodiode component regardless of the colour being investigated.

If the above components were to be used in a colour sensor, the three components of the photodiode would need to be amplified individually before the voltages being processed by the microprocessor. This would involve the integration of a series of amplification stages therefore enlarging the overall circuit. By using a single photodiode and a tri-colour LED, the same effect is achieved by employing three variable resistors.

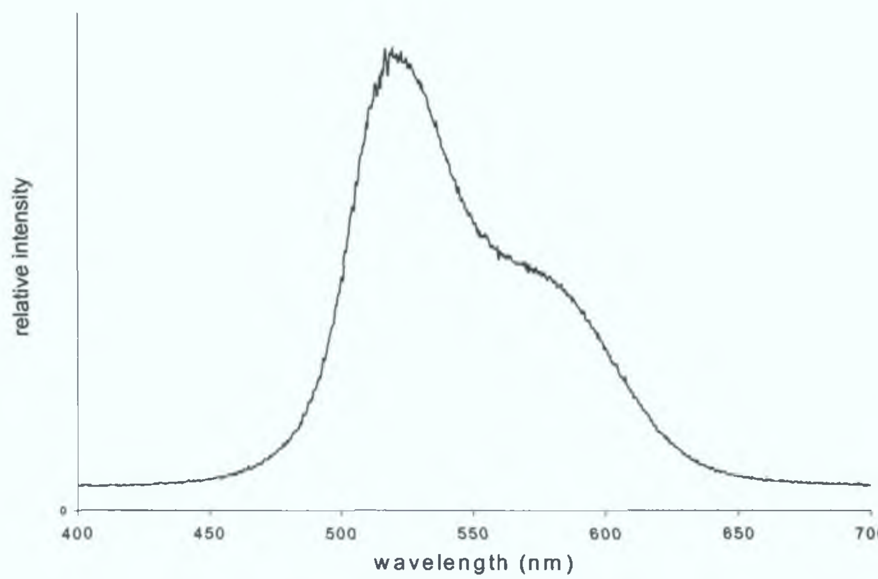

Figure 4.7 Spectral output of White LED

The need for a more complex circuit and the large intensity difference across the spectrum of the white LED determined that a tri-colour LED be used in conjunction with a single photodiode in this role. This approach is applicable only if the complexity of the of the detection circuit can be justified i.e. in detecting smaller colour changes as in the case of chemical reactions.

4.7 Conclusion

This chapter has detailed the construction of a simple colour sensor. This sensor was used with the RCX to recognise a pre-determined set of colours. The method of programming the sensor has been outlined. This sensor could be used with the LEGO Mindstorms kit to follow coloured lines on differently coloured backgrounds, or to use different colours to initiate a response from the RCX. The sensor was developed further to detect analytes, such as pH and nickel sulphate, using colour based measurements. These processes are detailed in chapter 5.

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Chapter 5

Colour Sensing Applications

5.1 Introduction

The colour sensing technique discussed in chapter 4 was applied to the development of a pH sensor. The development of a novel pH sensor for educational purposes as an introduction to the concept of pH and its performance is described. The applications of such a sensor in a learning environment could include pH determination of different beverages and of household products such as cleaning agents etc. The pH measurement of condiments, such as vinegar, baking soda, salt and sugar solutions, could also be safely carried out by children using this sensor.

As a proof of principle in an environmental application, a nickel sulphate sensor based on colour measurement was also developed. The presence of nickel sulphate in water poses a health risk to aquatic life and, in the case of drinking water, a hazard to humans. Nickel sulphate is a known carcinogen [1][2]. The detection of nickel sulphate in water solutions using the colour sensor was investigated. The detection and measurement of nickel sulphate concentrations involves the use of an analytical reagent, dimethylglyoxime (DMG) [3]. It is obvious that the chemicals employed in the detection of nickel sulphate make this an unsuitable demonstration in a primary level educational environment, but it could be used in a controlled laboratory setting.

5.2 pH Sensor

The construction of a simple sol-gel based pH sensor was undertaken as an application of the colour sensor. This sensor could be used in a classroom environment to demonstrate pH measurements using such simple household materials as vinegar and baking soda. Two LED's were used to illuminate the sensing film in turn, and a photodiode was employed to measure the reflected light intensity from the film. This section discusses the fabrication of a pH sensor for use in an educational context.

5.3 pH Sensitive Sol-gel Preparation

A pH sensing film was prepared in the following manner. 29.4mg of bromocresol purple (BCP) was weighed into a glass vial and 4g of ethanol (C_2H_5OH) added. This was stirred for 10 minutes. 2g of pH1 HCl was added drop-wise whilst stirring and the contents left for a further 10 minutes. 5.4g of tetraethoxysilane (TEOS) and 0.54g of methyltriethoxysilane (MTEOS) were also added drop-wise. The contents of the vial were left mixing for 1 hour. The resultant solution was left to age at room temperature overnight [4].

Glass slides were prepared by immersion in a sodium hydroxide (NaOH) solution for 1 hour. They were then washed with de-ionised water and dried using compressed dry air. The slides were dip coated in the pH sensitive solution by withdrawal at a rate of 1.5 mm/s. They were then dried at $70^{O}C$ for 17 hours. The coated slides were then immersed in a $2x10^{-5}$ molar solution of NaOH for 48 hours. This process reduces the reaction time of the films to changing pH by reducing the population of silanol groups within the sensor matrix, therefore allowing them to react rapidly with protons in the analyte solution [5]. Figure 5.1 is a graph representing the absorbance of the pH sensitive film after immersion in different pH solutions for a period of 10 minutes at a time. The spectra were obtained using a UV-vis spectrometer.

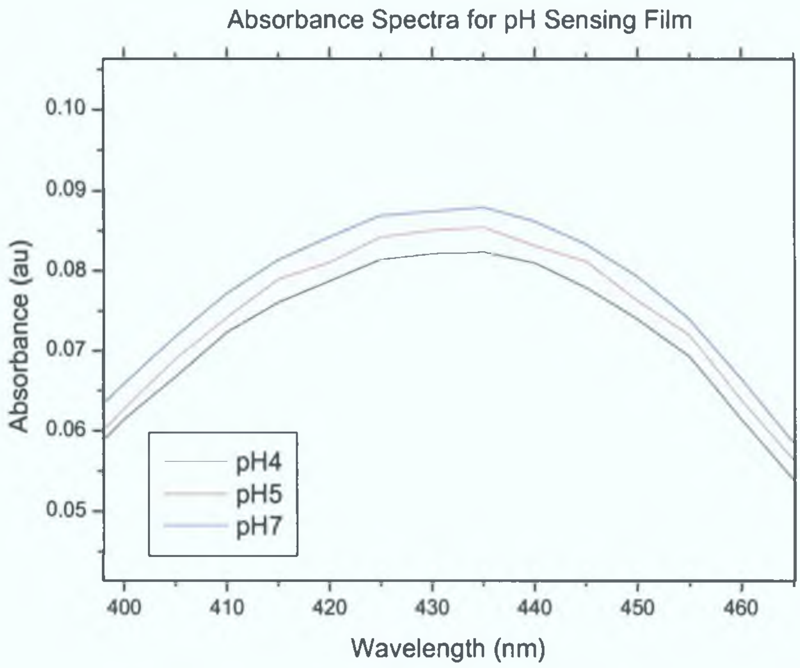

Figure 5.1 Absorbance spectra for pH sensing film

The absorbance of the film for pH solutions from pH4 to pH7 was approximately constant in the near infra-red region of the spectrum. This is shown in Figure 5.2.

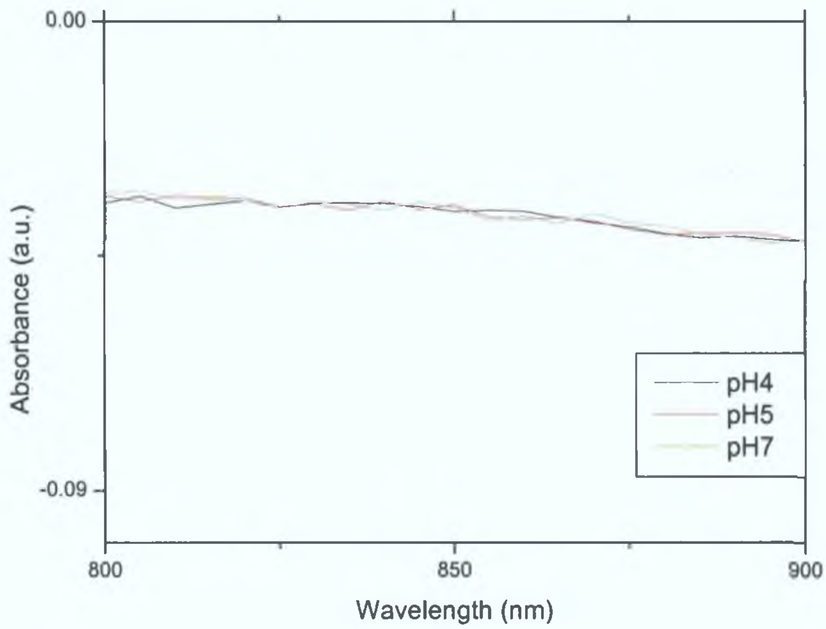

Figure 5.2 Absorbance spectra in IR range

5.4 pH Sensor Outline

Buffer solutions at pH integer values between pH4 and pH8 inclusive were prepared to test the films. The cell shown in Figure 5.3 was used to house the sensing film and the optoelectronic components. The buffer solutions were flowed in turn across the bottom of the slide and voltage readings taken corresponding to the reflected light intensity from the sensing layer in each case under illumination of the blue LED and then the IR LED.

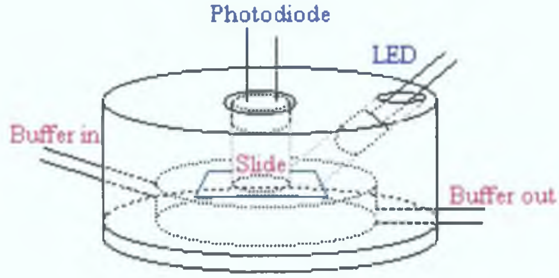

Figure 5.3 pH sensor cell

The IR LED was chosen so that its output spectrum coincided with the region in which the absorbance of the pH sensing film was approximately constant over the range of pH values for which the film was tested.

The blue LED used was the blue component of the tricolour LED that was described in section 4.3 and whose spectral peak coincided with the absorbance peak of the sensor film. This LED was used because the absorbance of the film at the wavelengths emitted by the LED was dependent on the pH of the solution.

Each buffer was left in contact with the film for 10 minutes before the voltage readings were recorded to ensure a complete colour change in the dye. Figure 5.4 is a graph showing the circuit output as a function of pH solution using both blue and IR LEDs.

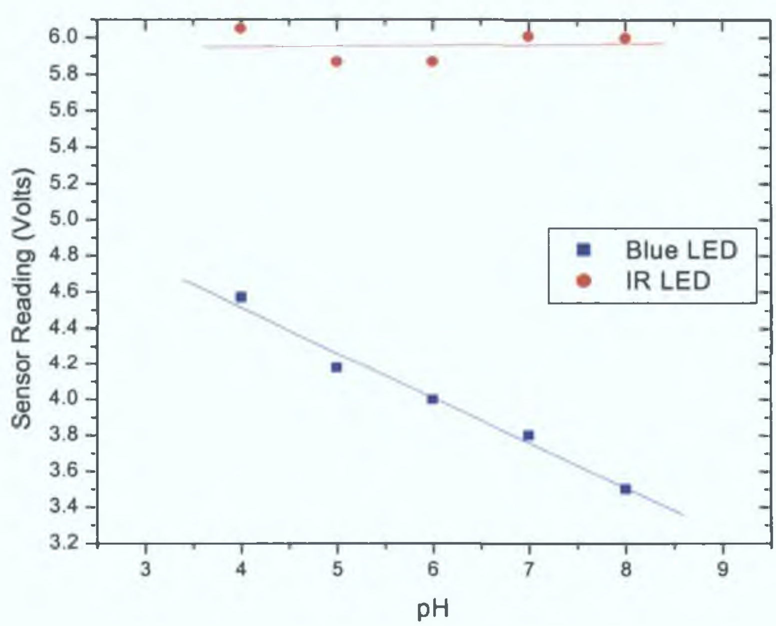

Figure 5.4 *Sensor Output (V) v pH*

Because the voltage reading over the range of pH solutions does not significantly change under illumination of the IR LED, these readings could be used as a reference. As the pH increases, the absorbance of the film increases in the blue visible wavelength range, hence the reflected blue light intensity decreases [6]. By comparing the ratio of the two signals, the pH of the solution in contact with the sensing film could be determined.

5.5 pH Conclusion

A simple optical arrangement has been implemented to illuminate a pH sensitive film and record the reflected light intensity. An NIR and blue visible LED were used, one as a reference and the other to determine film absorbance, which is dependent on pH. The reflected intensity from the film decreases as the pH increases, thereby enabling determination of pH of the solution. The response time of the sensing film was of the order of minutes. This could be controlled by changing the length of time that the films were treated in the NaOH solution, or by changing the molarity of same [5].

5.6 Kubelka-Munk Reflectance Theory

The theory of reflectance devised by P. Kubelka and F. Munk [7] was initially developed as a method of investigation of paint films. The calibration of nickel sulphate sensors described in the following section, is governed by this relation. The assumption is made that the particles making up a surface are much smaller than the thickness of the layer being investigated. It is also assumed that both scattering and absorbing particles are distributed uniformly throughout the layer. In the case of using this method in the analysis of liquid solutions, the solution being scrutinised should be homogeneous. Illumination of the solution should ideally employ diffuse monochromatic light and the reflected light should be viewed from an angle such that the specular reflections from the solution or surface should be minimal.

When a light beam passes through a liquid solution, the attenuation of the light is expressed by the Beer-Lambert law given by:

$$T = \frac{I_t}{I_0} = \exp(-\varepsilon l C)$$

where, T is the transmittance, I_0 is the intensity of the incident light, I_t is the intensity of the transmitted light, ε, the molar absorptivity, C is the concentration of the analyte and l, the thickness.

Using reflectance analysis, the reflectance of the diffuse light incident on a surface, where the distribution of the scattering and absorbing particles is uniform, can be expressed by:

$$R = \frac{I_r}{I_0}$$

where, R is the fraction of incident light that is reflected from the surface under illumination, I_r is the reflected light intensity and I_0 is the intensity of the incident light.

An LED is used in this case to illuminate the solution and a photodiode is employed to measure the reflected diffuse light. When light falls on a photodiode, configured in photovoltaic mode, a voltage, V, is produced that is proportional to the intensity of the incident light, i.e. V = kI, where k is a constant. The voltage increases with increasing light intensity. In reflectance analysis, the optical density, A, of the reflected measurement is given by

$$A = -\log R$$

and therefore

$$A = -\log\left(\frac{V_0}{V}\right)$$

where V_0 is the voltage registered from the reflected light off a reference white surface, or in this case where the concentration of the analyte is zero.

The Kubelka-Munk relation used to determine the concentration, C, of an analyte relative to the diffuse reflectance, R, is given by

$$f(R) = \left[\frac{(1-R)^2}{2R}\right] = \frac{\varepsilon C}{S}$$

where S is the scattering coefficient of the solution [8]. A plot of f(R) versus the concentration of the analyte therefore should yield a straight line graph.

5.7 Preparation and Measurement of Nickel Sulphate Solutions

The preparation of the various nickel sulphate solutions whose concentrations were to be measured using a diffuse reflectance method is outlined as follows. A quantity of $NiSO_4$ was dried in an oven at 150°C for 6 hours. This was then ground to a fine powder and dried at the same temperature for a further 12 hours. This ensured that any water present in the $NiSO_4$ had been evaporated. A 1% alcoholic solution (w/v) of Dimethylglyoxime (DMG) was arranged by dissolving 1g of DMG in Ethanol.

Concentrations of $NiSO_4$ between 100ppm and 800ppm were prepared by adding the respective masses of $NiSO_4$ to a number of 10ml vials. 2ml of Nitric Acid (HNO_3), was added to each vial and the mixture heated to 70°C whilst stirring for approximately 12 hours until dissolution. The contents of each vial were then transferred to 100ml volumetric flasks and the volume in each completed with distilled water [3].

To investigate the prepared samples, a quantity of 2ml was taken from the prepared solution and transferred to the cell, B, shown in Figure 5.5. To this was added 0.15ml of ammonium hydroxide (28%) and then 0.1ml of DMG in ethanol. On addition of the DMG the solution turned a pink colour. The cell containing this solution was covered with the LED and photodiode housing, A, as shown in Figure 5.5, and the voltage reading recorded while the solution was being illuminated by a red LED and then by a green LED. This was repeated for all the prepared nickel sulphate solutions. The cell, A, was fabricated from white nylon, whilst the housing, B, was made from black plastic to exclude as much ambient light as possible.

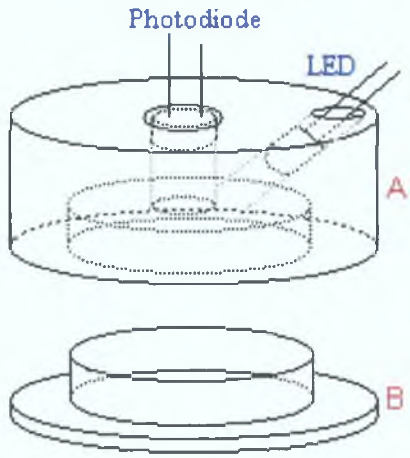

Figure 5.5 Cell used for diffuse reflectance measurements

The circuit used to detect the signal is based on an amplified and filtered current to voltage converter as shown in Figure 5.6.

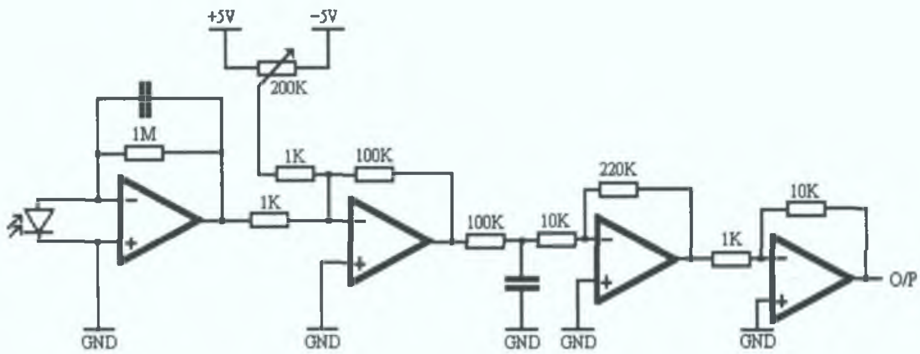

Figure 5.6 Light intensity detection circuit

The LED used to illuminate the various samples was the tricolour LED introduced in the previous chapter. Figure 5.7 shows the voltage readings for the samples investigated under illumination of both the green and red spectral components of the LED. The voltage decreases with increasing nickel sulphate concentration, indicating that the reflected light intensity is inversely proportional to the analyte concentration.

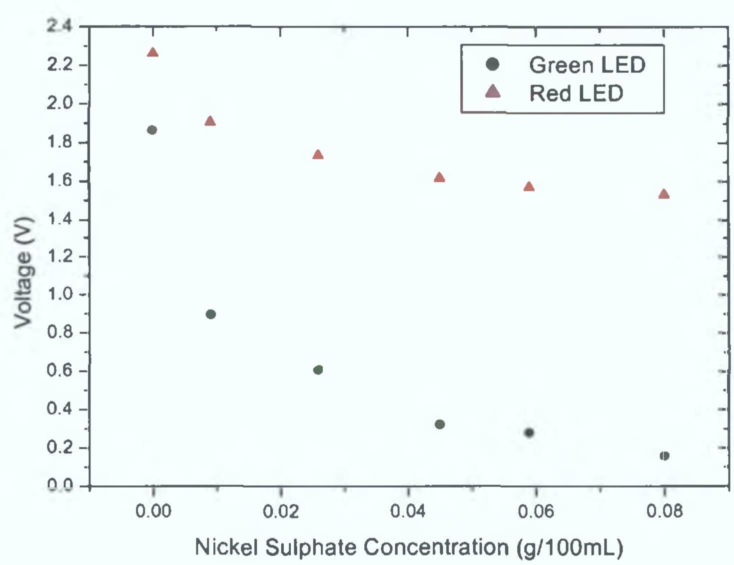

Figure 5.7 Relationship between sensor output and $NiSO_4$ concentration

Using the voltage readings taken while illuminating the samples with the red spectral component of the LED, a graph of the Kubelka-Munk relation, f(R), was plotted against the nickel sulphate concentration [3]. A straight line graph was observed for low concentrations of between 0 and 0.08g/100ml, as shown in Figure 5.8. An R value of 0.99256, from a linear fit of the data, confirms that there exists a linear relationship between the reflectance and $NiSO_4$ concentration. This indicates that the procedure discussed can be used as a reliable method in the measurement of $NiSO_4$ concentrations in a water solution, using the relation:

$$R = \frac{I_r}{I_0} = R_W \exp(-kC)$$

where, R_W is the reflectance from a reference white surface and k is a proportionality constant .

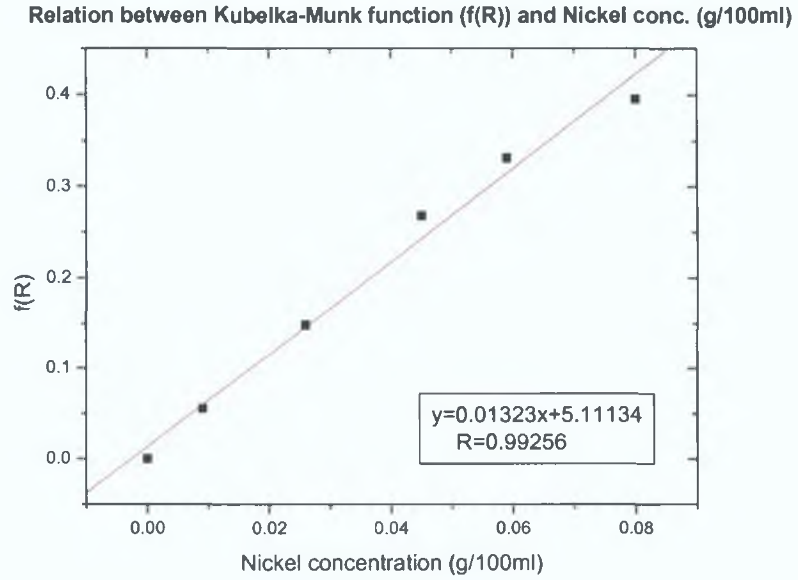

Figure 5.8 Relation between Kubelka-Munk function and $NiSO_4$ concentration

5.8 Summary of Nickel Sulphate Work

A simple method of measuring $NiSO_4$ concentrations has been established using diffuse reflectance measurements and low cost electronic components and circuitry. A suitable reaction cell has been made. Initially, the determination of nickel sulphate concentration was to be undertaken using the same principles as those employed in the pH sensor. This involved determining a region in the absorbance spectrum where the absorbance was constant for changing analyte concentration. Figure 5.9 shows the transmission spectra for different concentrations of nickel sulphate in solution.

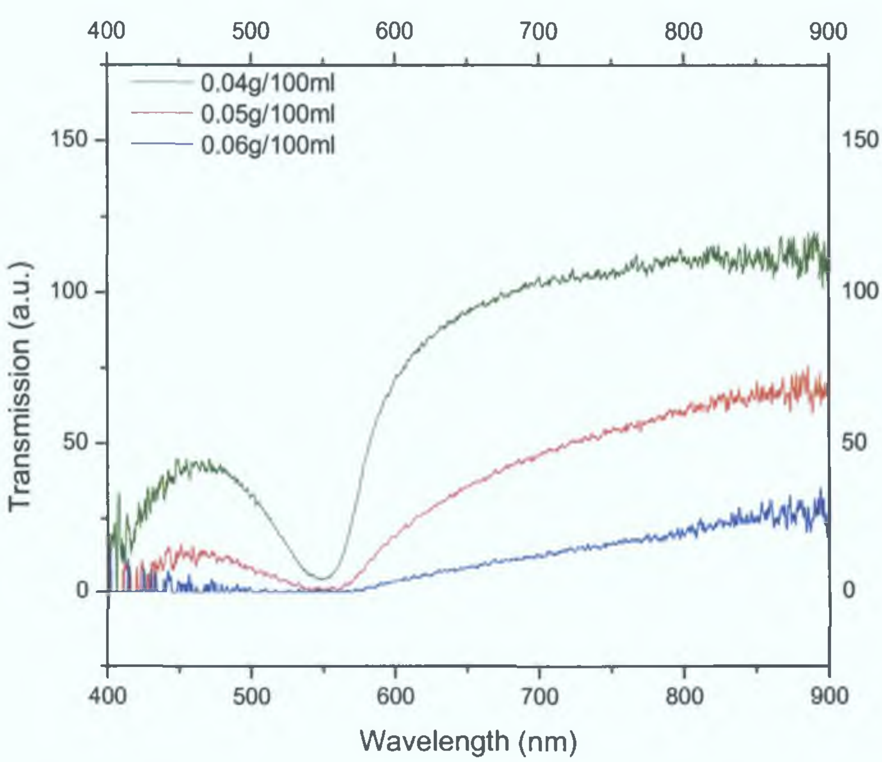

Figure 5.9 Transmission Spectra for $NiSO_4$ solutions

The results observed show that there is no region where the transmission, and therefore the absorbance, is the same for different concentrations. This proves that the method of referencing employed in pH sensing cannot be applied in this case. Hence, only simple, non-referenced colorimetric analysis methods can be used to determine the concentration of $NiSO_4$ in this example.

5.9 Conclusion

The colour sensor outlined in the previous chapter has been applied in the role of pH sensing and the colour monitoring of solutions (as a surrogate for environmental monitoring). It has been shown that the method employed in the determination of the pH of different solutions was not suitable in the sensing of nickel sulphate. These sensors could be used as a demonstration of curriculum related phenomena in the classroom or as tools in educational projects.

As in any optical sensor, parameters such as temperature and ambient light may have an adverse effect on accurate measurement. When using an LED, the intensity and spectral distribution may vary with temperature. To overcome these effects, a circuit employing a temperature compensation module could be developed. Ambient light effects on the sensor output could be negated by using lock-in techniques.

References

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2. Kasprzak, K. S., Sunderman, J., William, F. et al. "**Nickel carcinogenesis.**" Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis **533**(1-2): 67-97, 2003.

3. Matias, F., Vila, M. et al. **"A simple device for quantitative colorimetric diffuse reflectance measurements."** Sensors and Actuators B: Chemical **88**(1): 60-66, 2003.

4. Burke, C.S., Polerecky, L. and MacCraith B.D. **"Design and fabrication of enhanced polymer waveguide platforms for absorption-based optical chemical sensors."** Measurement Science and Technology **15:**1-6, 2004.

5. Ismail, F., Malins, C. et al. **"Alkali treatment of dye-doped sol-gel glass films for rapid optical pH sensing."** Analyst **127**(2): 253-257, 2002.

6. Makote, R. and Collinson, M. **"Organically modified silicate films for stable pH sensors."** Analytica Chimica Acta **394**(2-3): 195-200, 1999

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8. Lau, K. T., Baldwin, S. et al. **"Novel fused-LEDs devices as optical sensors for colorimetric analysis."** Talanta **In Press, Corrected Proof**

Chapter 6

Conclusions

The work presented in this thesis described the development of various optical sensors and their incorporation into sensing systems that could be used in an educational role. The hardware and software issues of the two sensing platforms have been discussed and their attributes outlined.

The oxygen sensor has been demonstrated in a classroom environment. At the time of writing, the carbon dioxide sensor had not been interfaced with either sensing platform, although there is no reason why this cannot be achieved in the future. A colour sensor was also fabricated for use with the RCX. This was achieved using basic low cost optoelectronic components and circuitry.

An absorption based pH sensor capable of detecting pH in the range from pH4 to pH8 has been demonstrated. By using two spectrally different LED's, i.e. one visible and one NIR, the sensor has an in-built reference. To make the pH sensor suitable as an educational tool, the sensing layer must be housed in a light proof casing that is permeable to liquid, so that the solution whose pH is being determined may contact the sensing layer. This configuration would allow the ingress of the solution whose pH was being investigated, whilst excluding ambient light. Again, lock-in circuitry could be employed to nullify the need for the above arrangement.

The process by which the concentration of an analyte in solution could be determined by diffuse reflectance was also investigated. In particular, nickel sulphate was used as a proof of principle. It was found that this process was an unsuitable application for the colour sensor because there was no suitable region in the absorbance spectrum where a reference measurement could be obtained. The chemistry involved in preparing the solution for interrogation makes this sensor inappropriate as a classroom based experiment, although this could be demonstrated in a controlled laboratory setting.

Future work could involve the incorporation of the carbon dioxide sensor into classroom experiments. The employment of this sensor in conjunction with the oxygen sensor has uses in experiments that demonstrate photosynthesis and respiration. To take this project further, the integration of the developed colour based sensors into classrooms could be undertaken.

Appendix A

Code used for Cricket to communicate with Oxygen Sensor:

```
[const @ 0]
[const timer 1]
[const pcl 2]
[const status 3][const c 0][const z 2][const bank2 5]
[const status1 83]
[const @@ 4]
[const porta 5][const porta-ddr $85]
[const portb 6][const portb-ddr $86]

[const option 1]
[const counter $20]
[const bus-data $21]
[const bus-port portb][const bus 0]
[const bus-port-ddr portb-ddr]
[const temp $22]
[const adcon $1f]
[const adresh $1e]
[const percent $23]
[const adcon1 $9f]
[const adresl $9e]

start
        [bsr io-init]

loop
        [bset 1 portb]
        [bset 2 portb]
        [ldan 5][bsr big-delay]

        [btss bus bus-port]
```

```
        [bsr main]
        [bset z adcon]
loop1

        [btsc z adcon][bra loop1]
        [bclr 1 portb]
        [bclr 2 portb]
[ldan 5][bsr big-delay]
        [btss bus bus-port]
        [bsr main]
        [bset z adcon]

loop2
        [btsc z adcon][bra loop2]
        [bra loop]

main
        [bsr btyi20]
        [btss c status][bra loop]
        [lda bus-data]
        [xorn $94]
        [btss z status][bra loop]
        [clra]
        ;[bset bank2 status]

        [clra]
        [lda adresh]
        ;[bclr bank2 status]

        ;BRANCH TO SUBROUTINE 'TABLE' TO GET %AGE O2
        [bsr table]
        [sta percent]
        [sta bus-data]
        [bsr bus-tyo]
```

```
        [bra loop]                    ; and loop!

; the form of a byte is
; 100 usec low time (to allow for interrupt latency)
; start bit(1) + 8 data bits + stop bit (0 for cmnd 1 for data)
; each bit is exactly 10 usec long. The bits should be sampled in the
; middle (this code samples between 4 and 7 usec in)
;
; return a byte in bus data
; also return the inverse of the stop bit in the carry
; commands have a 0 stop bit -> carry set
; data has a 1 stop bit -> carry clear

bus-tyi [btsc bus bus-port]
        [bra bus-tyi]
btyi20  [btss bus bus-port][bra btyi20]        ; wait for sync edge
        [ldan 8][sta counter]
        [bsr an-rts]
btyi30  [nop][nop][nop]
        [ror bus-data]
        [bclr 7 bus-data]
        [btsc bus bus-port]
        [bset 7 bus-data]
        [decsz counter]
        [bra btyi30]
        [bsr an-rts][nop]
        [bset c status]
        [btsc bus bus-port][bclr c status]     ; no stop bit -> carry clear
an-rts
        [rts]

; send a byte down the bus. the "stop" bit is always 0
; of a data byte
; input in bus-data
```

```
bus-tyo [ldan bus-port-ddr][sta @@]
        [bclr bus bus-port][bclr bus @]
        [ldan 24][bsr delay-loop]       ; give receiver a chance to sync
        [bset bus bus-port]             ; start bit
        [ldan 8][sta counter]
        [bsr an-rts][nop][nop]
btyo50          [ror bus-data]
        ; bit -> carry
        [bclr bus bus-port]
        [btsc c status]
        [bset bus bus-port]
        [nop][nop][nop]
        [decsz counter]
        [bra btyo50]
        [nop][nop]
        [bset bus @]
        [rts]
big-delay
        [btss bus bus-port][bsr main]
        [sta temp]
        [ldan 33][bsr delay-loop]
        [btss bus bus-port]
        [bsr main]
        [lda temp]
        [addn -1][btss z status][bra big-delay]
        [rts]

delay-loop
        [addn -1][btss z status][bra delay-loop]
        [rts]
io-init
        [bset bank2 status]
        [bset 0 porta]
```

```
        [bclr 1 portb]
        [bclr 2 portb]
        [ldan $81]
        [sta adcon1]                    ;set adcon1 as 10000001
        [clra]

        [bclr bank2 status]
        [ldan $1]
        [sta adcon]                     ;set up adcon0 as 10000001
        [clra]

        [ldan 60][sta counter]

ioin20
        [clra]
        [bsr delay-loop]
        [decsz counter][bra ioin20]
        [rts]

        ;SUBROUTINE TO FIND CORRESPONDING O2 %AGE
        ;load working register into program counter
        ;using the command   addwf PCL,F

table
        [ldan 0]
        [andn $0f]
        [lda adresh]
        [addm pcl]
        [rtv 255]       ;0
        [rtv 254] [rtv 253] [rtv 252] [rtv 251]
        [rtv 250]
        [rtv 249]
        [rtv 248]
        [rtv 247]
```

```
[rtv 246]
[rtv 245]        ;10
[rtv 244]
[rtv 243]
[rtv 242]
[rtv 241]
[rtv 240]
[rtv 239]
[rtv 238]
[rtv 237]
[rtv 236]
[rtv 235]        ;20
.
.
.
.
.
[rtv 9]
[rtv 8]
[rtv 7]
[rtv 6]
[rtv 5]          ;250
[rtv 4]
[rtv 3]
[rtv 2]
[rtv 1]
[rtv 0]          ;255
```

Code used in RCX Oxygen Sensor

;Modulate pin 1 and 2 of port b in 16f872 for

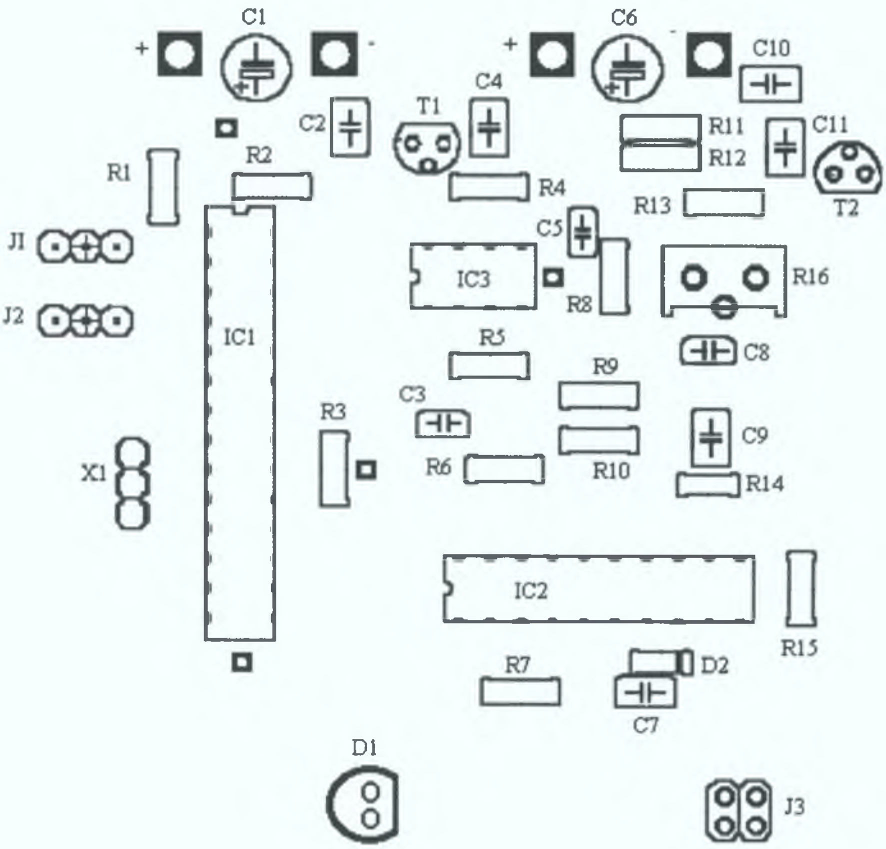
```
;O2 sensor for use with RCX. Freq is 769Hz


          [const @ 0]
          [const timer 1]
          [const pcl 2]
          [const status 3][const c 0][const z 2][const bank2 5]
          [const @@ 4]
          [const porta 5]
          [const portb 6]
[const option 1]
          [const temp $0c]

start     [bset bank2 status]
          [bclr 0 portb]
          [bclr 1 portb]
          [bclr 2 portb]
          [bclr bank2 status]

loop
          [bset 1 portb]
          [bset 2 portb]
          [ldan 1][bsr small-delay]
          [bclr 1 portb]
          [bclr 2 portb]
          [ldan 1][bsr small-delay]

          [bra loop]

small-delay

          [sta temp]
          [ldan 160][bsr delay-loop]              ;26
          [lda temp]
```

```
        [addn -1][btss z status][bra small-delay]
        [rts]

big-delay

        [sta temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [addn -1][btss z status][bra big-delay]
        [rts]

delay-loop

        [addn -1][btss z status][bra delay-loop]
        [rts]

delay-loop2

        [addn -1][btss z status][bra delay-loop]
        [rts]
```

Appendix B

Oxygen Sensor Board Layout

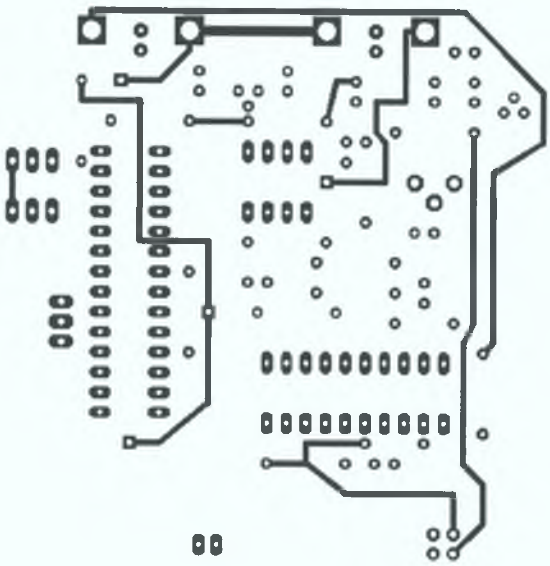
Component Layout:



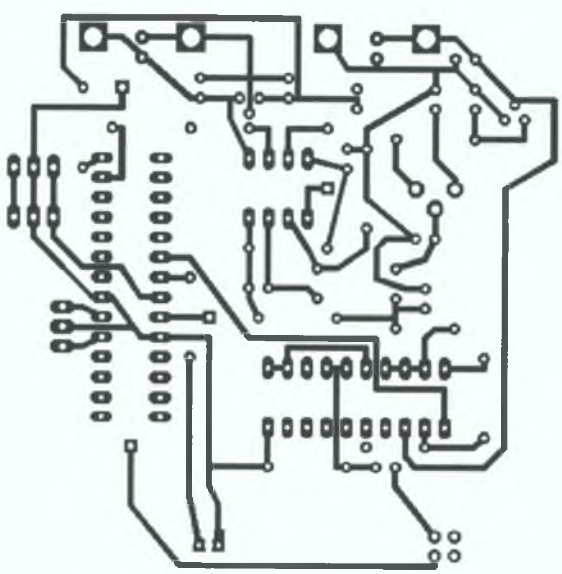
Component Values:

Component	Value	Component	Value
IC1	PIC16F872	C2-5,7,9-11	100nF
IC2	AD630	C8	22nF
IC3	CA3240E	R1,3,10	10K
X1	4MHz crystal	R2	1K
J1/J2	3 pin connector	R4,7,8,14	220K
J3	1053odal	R5,9	1M
D1	NSPB500s LED	R6	910K
D2	2.1V zener	R11	2K
T1	78105	R12,13	6.2K
T2	79105	R15	50K
C1/C6	47uF	R16	10K pot

Top layer tracks and pads:



Bottom layer tracks and pads:



Appendix C

Programme code to recognise 5 colours

```
#define Color SENSOR_2
#define ScaleFactor 38
#define Offset 1023
#define Threshold 1015

int Red, Green, Blue;
int RGB, RGB1;
int R1, B1;
task main ()
{

   SetSensor (Color, SENSOR_LIGHT);
   SetSensorMode (Color, SENSOR_MODE_RAW);

   InitColSensor();
   //OnFwd(OUT_A);
   //OnFwd(OUT_C);
    SetPower(OUT_A+OUT_C,0);
    OnFwd(OUT_A+OUT_C);
   for (;;)
     {
       //SetOutput(OUT_A + OUT_C, OUT_On);
       //OnFwd(OUT_A+OUT_C);
       //OnFor(OUT_A+OUT_C, 10);  ****
       //OnFor(OUT_C, 10);
        Wait (10);
        //SetOutput(OUT_A + OUT_C, OUT_Off);
        ReadColor();
        R1=Red*10;
        B1=Blue/10;
```

```
        RGB=R1/B1;
    if(RGB > 90 && RGB < 110)    //red
    {
      PlayTone(440, 50); // Play 'A' for one half second
    }

     if(RGB > 110 && RGB < 119)   //green
     {
      PlayTone(470, 50); //
     }

      if(RGB > 135 && RGB < 150)    //blue
     {
      PlayTone(490, 50); //
     }

     if(RGB > 125 && RGB < 135)    //purple
    {
      PlayTone(520, 50); //
    }

     if(RGB > 119 && RGB < 125)   //pink
     {
      PlayTone(550, 50); //
     }



       // Motorise();


   }
  }

   void InitColSensor ()
  {
```

```
  while (Color < Threshold)
 {
  NextColor ();
 }

}

// Reads all three color components and place them in Red, Green and Blue
variables
sub ReadColor ()
{
  NextColor ();
  Wait (10);
  Red=Color;
  Wait (10);
  NextColor ();
  Wait (10);
  Green=Color;
  Wait (10);
  NextColor ();
  Wait (10);
  Blue=Color;
  Wait (10);
  //Skip Dummy
  NextColor ();
  //if (Color > Threshold)  InitColSensor();
}


void NextColor ()
{
  SetSensor (Color, SENSOR_LIGHT);
  SetSensorType (Color, SENSOR_TYPE_TOUCH);
  SetSensor (Color, SENSOR_LIGHT);
```

```
   SetSensorMode (Color, SENSOR_MODE_RAW);
}

sub Motorise()
{

 }
```

List of Publications and Conference Presentations:

Oral Presentations:

"Optical Sensing Systems for Primary Level Science Education" **A. Markey**, B. Tyers, R. Shepherd, A. K. McEvoy, B. D. MacCraith, B. Mikhak, C. Strohecker, *Opto-Ireland Conference*, Galway, September 2002.

Conference Publications:

"Optical Sensing Systems for Primary Level Science Education" **A. Markey**, B.Tyers, R. Shepherd, A. K. McEvoy, B. D. MacCraith, B. Mikhak, C. Strohecker, *Opto-Ireland Conference,* Galway, September 2002.

"Optical Sensing Systems for Primary Level Science Education" **A. Markey**, C. Smyth, A. K. McEvoy, E. O'Brien, B. Tyers, B. D. MacCraith, B. Mikhak, C. Strohecker, *SAXII Conference*, Limerick, September 2003.

Poster Presentations:

"Optical Sensing Systems for Primary Level Science Education" **A. Markey**, C. Smyth, A. K. McEvoy, E. O'Brien, B. Tyers, B. D. MacCraith, B. Mikhak, C. Strohecker, *SAXII Conference*, Limerick, September 2003.
(Poster presentation – Awarded Best Exhibited Paper by SFI.)

"Optical Sensing Systems for Primary Level Science Education" **A. Markey**, C. Smyth, A. K. McEvoy, E. O'Brien, B. Tyers, B. D. MacCraith, B. Mikhak, C. Strohecker, *BOC Gases Poster Competition, DCU, April 2004.*

Novel Optical Sensing Systems for Primary Level Science Education

by

Joseph Adam Markey B Sc (Hons)

A thesis presented
to
Dublin City University

For the degree of Master of Science

Research Supervisor
Professor Brian MacCraith
School of Physical Sciences
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July 2004

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Master of Science is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work

Signed ______________ ID no 96382449
Candidate

Date 20th Sep '04

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Orla, thanks for helping me out in the stress department, I know it was pretty often, especially towards the end!!

Abstract:

In the last three years, a number of Insh pnmary schools have been usıng LEGO Mmdstorms technology ın order to ınvestıgate the use of project-based learnıng as an alternatıve teachıng tool Thıs has ınvolved the use of LEGO brıcks combıned wıth standard electronıc motors and some commercıal sensors (e g temperature) In order to develop thıs project ınto the area of scıence educatıon, we have developed a range of mınıaturızed optıcal sensors, whıch are compatıble wıth the LEGO platform

In partıcular a workıng oxygen sensor has been desıgned and fabrıcated The prıncıpal desıgn features were compatıbılıty wıth the programmable LEGO platforms and robustness for classroom use Thıs sensor uses the method of ıntensıty quenchıng to determıne oxygen concentratıon Thıs sensor has been demonstrated ın a learnıng envıronment Sımılarly a carbon dıoxıde sensor has been developed

In addıtıon, sımple colour sensors have been produced The aım of developıng such sensors ıs to famılıarıse students wıth the concept of colour detectıon and to ıntroduce them to the basıc prıncıples of spectroscopy A specıfic use for the colour sensor has been ıdentıfied, ın the role of a pH sensor A sımple method of detectıng nıckel sulphate usıng colorımetrıc dıffuse measurements has been demonstrated The performance of both sensor types has been evaluated

Contents

Chapter 1

Introduction

1 1 Introductıon

The work presented ın thıs thesıs has been undertaken ın order to develop sensors for use ın a scıence educatıon envıronment The recent declıne ın the numbers studyıng scıence subȷects ın school has led to a severe decrease ın thırd level scıence graduates In order to address thıs ıssue, the ıntroductıon of scıence to chıldren at prımary school level must occur ın such a way as to maıntaın attentıon and stımulate ınterest In partıcular, the hands-on approach, where chıldren conduct theır own experıments ıs the goal of thıs work One of the drawbacks to thıs approach ıs equıpment cost The cost and robustness of the sensors, and the ease wıth whıch they can be ıncorporated ınto scıentıfic experıments, whıch effectıvely demonstrate basıc concepts must be consıdered

As scıence has recently been ıncorporated ınto the Irısh prımary school currıculum, thıs work was undertaken ın tandem wıth several prımary schools ın order to demonstrate the effectıveness of these sensors as a learnıng aıd Two areas of ınterest were focused on gas sensıng, colour ıdentıficatıon and theır applıcatıons The ıncorporatıon of the sensors developed ınto the relevant data-loggıng platforms ıs descrıbed

1 2 Beyond Black Boxes overview

The project 'Beyond Black Boxes' [1] was developed by researchers at Massachusetts Institute of Technology (MIT) in order to bring science alive and to motivate children in the area of science It involves the development of sensing platforms with data logging capability and a range of sensors, motors and gears, with which children can observe and measure quantities and also design and engineer systems which will act according to a set of instructions and the stimuli being measured

The main tool in the project developed by MIT is the 'Cricket' [2] This is essentially a micro-computer which has sensor inputs and programmable outputs There are several different models of the Cricket platform, each new evolution with better capabilities than its predecessor The project (Beyond Black Boxes) is ongoing and its purpose is to develop children's knowledge in science and also to develop an understanding of the relationship between science and technology [3]

1 3 Lego Mindstorms overview

In 1998, LEGO released a robotic construction kit, known as LEGO Mindstorms This package is the result of technology and ideas developed by Seymour Papert [4] through research at MIT The Logo brick was the result of early research in this field Sensors and motors could be attached to it in order to allow it to monitor its immediate surroundings and to react to certain stimuli

The programming language 'Logo', was specially designed for the purpose of communicating with and programming the Logo brick Children could now control the movement of various mechanical projects by connecting the "programmable bricks" to an interface box and using Logo to programme them The first "programmable bricks" needed to be hardwired to a desktop to facilitate programming and data retrieval This greatly limited the potential for truly autonomous machines

Eventually the LEGO RCX brick was developed This had the advantage that it did not need to be physically connected to a desktop computer Programming is carried out remotely using an infra-red communication link Furthermore, information gathered by the brick through the use of sensors can be relayed to the desktop via an IR link

The Lego Mindstorms kit is based around the RCX, and includes parts with which small robotic sensing and data logging systems may be created LEGO have now produced many Mindstorms kits, which are readily available on the retail market Although these kits differ in size, content and project capabilities, they all consist of the following components

- RCX brick
- Motors and various sensors
- LEGO bricks, including axles, gear wheels and other mechanical components

The RCX brick is at the centre of any project built from these kits The RCX brick is essentially a miniature computer with an LCD screen, and contains the circuitry required to drive motors and collect data using a collection of miniaturized sensors The brick converses with the desktop by means of an IR "tower" However, this is dırectıonal and the IR transceıvers of both the brıck and the tower must be lıned up to allow communıcatıon

1 4 Sensor Technology

Researchers at Massachusetts Instıtute of Technology (MIT) have already developed a range of sensors and actuators, for use wıth both the Crıcket and LEGO Mındstorms platforms The sensors developed for use wıth the LEGO RCX brıck are of the resıstıve type Thıs means that the sensors' resıstance changes wıth changıng stımulus An example of thıs would be a lıght dependent resıstor (LDR), whose resıstance changes wıth changıng lıght levels The RCX determınes the readıng by applyıng a fixed voltage to the sensor, measurıng the potentıal drop, and thereby determınıng the resıstance of the sensor The sensor output ıs then recorded as an 8 bıt number between 0 and 1023 Some of the sensors detaıled later output a voltage, whıch ıs proportıonal to the parameter beıng measured The method by whıch these sensors are ınterfaced to the partıcular sensıng platforms ıs explaıned later ın thıs work

Most of the sensors constructed for use wıth the Crıcket platform are of the resıstıve type also However the Crıcket platform lends ıtself to the development of more complex and accurate sensors Thıs ıs because of the sıngle-lıne bus communıcatıon feature of the devıce Thıs enables communıcatıon between the embedded mıcro-processor on the Crıcket and a mıcro-processor on the sensor ıtself A/D capabılıty on the mıcroprocessor greatly enhances the functıonalıty of the sensor, and therefore does not lımıt the sensor to a resıstıve based-sensıng system

The merits and drawbacks of both the Cricket and Lego RCX sensing platforms are discussed in greater detail in Chapter 2, the applications in which one is more suited than the other, and the educational value of both from a scientific viewpoint

1 5 Objectives

The primary aim of this project was to develop miniaturised optical sensors for use with the Cricket platform as educational tools in a learning environment With some modification, the developed sensors could also be used with the LEGO Mindstorms (RCX) educational kit The sensors to be developed were chosen so that they could be employed in simple classroom experiments without the need for expensive laboratory equipment The analytes were chosen to demonstrate everyday phenomena such as respiration, acidity and colour recognition

The sensors were developed for the following analytes

- Gas sensors
    - Oxygen
    - Carbon Dioxide
- Colour sensing
    - pH
    - Nickel Sulphate

The main driver in the development of educational sensors was cost effectiveness, but the reliable performance of the sensors was a crucial requirement

1 6 Thesis Outline

In Chapter 2, both sensing platforms (Cricket and RCX) are discussed in greater detail, focusing on the attributes and the capabilities of each system and how they were integrated into the educational environment Chapter 3 focuses on the development of both oxygen and carbon dioxide sensing films and also of the various methods through which the respective gas concentrations may be determined The incorporation of this gas sensing chemistry into employable sensors is described The circuits required in order to operate the sensors, the method by which they were connected to the RCX and Cricket platforms and results obtained from the detection of the individual gases are also presented Chapter 4 outlines the construction of a colour sensor and its implementation in conjunction with the RCX system

Chapter 5 details the extension of colour sensing into the determination of pH and the detection of nickel sulphate The optical measurement of pH solutions is presented Determination of nickel sulphate concentrations in a water solution by diffuse reflectance measurement and the transmission intensity of incident light at a particular wavelength with respect to a reference light source is discussed Chapter 6 concludes with how this new technology was demonstrated using both sensing systems, and how these sensors could be integrated into primary schools

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3 Martin, F , Mikhak, B , Resnick, M , Silverman, B , and Berg R , **'To Mindstorms and beyond Evolution of a construction kit for magical machines'.** In Allison Druin and James Hendler, editors *Robots For Kids Exploring New Technologies for Learning*, Chapter 1 Morgan Kauffmann 2000

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Chapter 2

MLE Cricket and LEGO RCX Platforms

2 1 Introduction

The incorporation of sensors into an educational programme where science is the main focus requires suitable technology in order to relate scientific ideas to children and develop an interest on their part This chapter discusses the two main platforms used in this project, their merits and the way in which they were employed in an educational capacity with currently available sensors as well as developed optical sensors

Two sensor platforms, Cricket and LEGO RCX, that operate on the same principles were investigated Each platform has a standard set of sensors and a specific programming language interface that allows data transfer between the PC and sensing platform The methods by which additional developed sensors can be interfaced to the Cricket and the RCX are discussed and the communication protocol that allows communication between more complex sensors and the Cricket is explained

2 2 Cricket Overview

The Cricket is a miniature programmable computer which can directly control motors and receive information about its immediate surroundings using a collection of specialized sensors It was developed as part of the Beyond Black Boxes project by

Brian Silverman and Bakhtiar Mikhak (Massachusetts Institute of Technology) [1]. As shown in Figure 2.1, it is a very compact system and is based around a PIC microcontroller (PIC16C715), which is programmed to enable the cricket to collect, store and send the data gathered by means of attached sensors.

Figure 2.1 Cricket with 9V battery

The following features are integrated into the Cricket micro-computer:

- PIC16C715 with 2K Programme memory and 128 bytes Data memory
- 2 Bus Ports
- 2 Resistive Based Sensor ports
- 2 Independent Bi-directional Motor Ports with Directional LEDs
- Bi-directional IR link

The Cricket may be programmed, and can communicate with a desktop computer by means of a bi-directional infra-red link. It is also suitable for remote applications since it does not need to be hardwired to the desktop. This is especially useful when using the Cricket for remote sensing and data collection.

The software envıronment, Cncket Logo, ıs used to programme the Cncket, and ıs shown ın Fıgure 2 2 Procedures may be wrıtten ın the rıght hand wındow and downloaded onto the mıcrocontroller sıtuated on the Cncket Commands may be downloaded to the Cncket vıa thıs wındow, so that an ımmedıate response from the Cncket may be ınıtıated Thıs wındow may also be used ın order to gaın real tıme sensor readıngs from the sensors plugged ınto the cncket

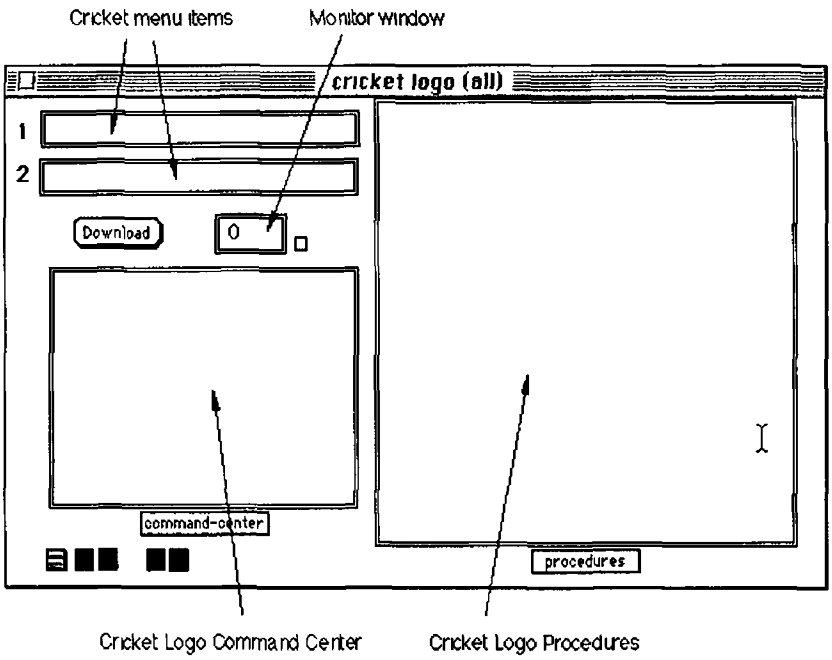

Fıgure 2 2 Cncket Logo programmıng envıronment

For remote applıcatıons, when the Cncket ıs to be used away from the desktop, procedures may be downloaded to the Cncket To ınıtıate the programme, a button on the Cncket may be pressed Therefore the programmıng envıronment ıs not essentıal ın order to ınıtıate procedures at a dıstance from the desktop computer

More recently, a programming environment, called Logo Blocks, has been developed for use with the Cricket platform by researchers at MIT [2]. It is an iconic system, which is more appealing to children, since it is not necessary to remember commands. Moreover, the blocks will only fit into each other in a logical order, much like a jigsaw puzzle. This programming environment is shown in Figure 2.3.

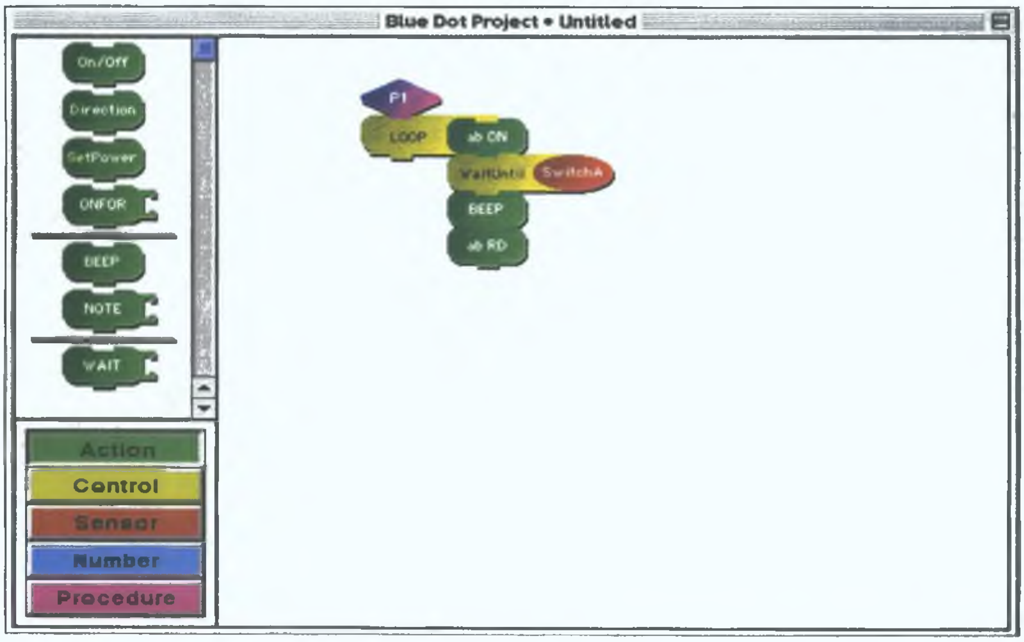

Figure 2.3 Cricket 'Logoblocks' programming environment

The method by which this programme operates nullifies the need to type code in order to compose programmes. This saves time and avoids the incorporation of punctuation, which can lead to mistakes and frustration, an inherent feature of many programming languages.

2 3 Cricket Sensors, Communication and Bus Protocol

A wide range of sensors has been developed or adapted by MIT researchers in order to expand the projects and experiments in which the cricket system may be used Many of these sensors are relatively simple in their construction and operation, and in most cases do not require to be incorporated into electronic circuits Examples of such sensors are devices that measure

- Light
- Temperature
- Touch

All the above are resistive sensors their resistance changes as a function of the changing stimulus associated with the particular sensor These are interfaced with the cricket using one of two ports, each of which is capable of measuring the resistance output of the sensor and recording it as a number whose value is between 0 and 1023

As well as sensors, simple actuators are also available The cricket is capable of powering two motors simultaneously These motors can be driven independently and in either direction, depending on the programme format

Sometimes a desired measurement parameter cannot easily be changed into a resistance Voltage and current may also be used in order to measure a changing signal In order to utilise these signal indicators a different approach is needed to determine the magnitude of the quantity being investigated

An expansion port, or bus port, is included on the Cricket platform This allows complex sensors and actuators to be integrated into the Cricket system The addition of bus devices greatly enhances the use of the Crickets as a learning and development tool Examples of such sensors, produced by MIT researchers, in order to measure stimuli for which there are no simpler sensors available include

- Heart rate monitor
- Optical distance sensor
- Clap sensor
- Reflectance sensor

A microcontroller is embedded onto these sensors in order to measure their responses and to communicate this information to the Cricket These sensors are also known as bus devices, signalling the need for a communication bus in order to transfer measurements and information back and forth Other devices that have been developed for use under this system include

- Hex display
- LCD display
- RF communication board

The bus devices are interfaced to the cricket through a three-core wire, from the Cricket's bus port to the devices One wire is held at +5 volts, another at ground (0 volts) and the third is connected directly from the pin RB0 on the Cricket's microcontroller to the corresponding pin on the bus device's microcontroller

Each bus device has its own identification, since many bus devices can be daisy-chained to the Cricket A master-slave method is implemented when using such bus devices The Cricket acts as the master, and the sensors as slaves, waiting until a command is sent from the Cricket before implementing an instruction [2]

Figure 2 4 shows a graphic representation of the bus protocol The bus line is held in the high state, with the pins dedicated to communication from each device connected together A transmission consists of a 100 microsecond pre-start pulse, where the bus line is driven low, followed by a start bit, 8 data bits and a 9^{th} bit to indicate whether the bitstream was data or a command A 'one' signifies a command, while a 'zero' indicates data A low 10^{th} bit follows to signify the end of the transmission

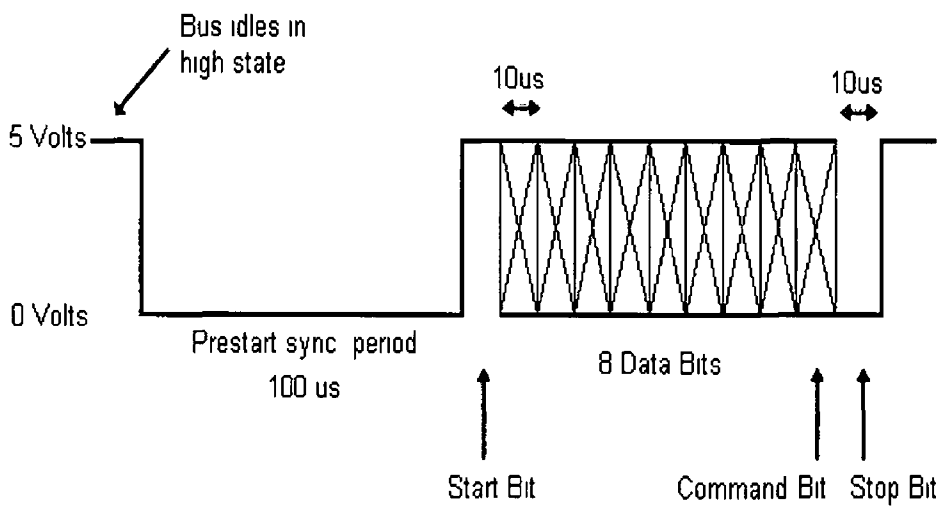

Figure 2 4 Bus protocol signal

The pre-start synchronization pulse allows all connected bus devices to prepare to capture and process the proceeding bus data Every device connected to the communication bus should be ready to receive data before the synchronization pulse ends Since every bus device has its own identification address, only the device with which the Cricket is selected to communicate, will dedicate its time to the Cricket after processing the bus data The rest of the bus devices connected will return to their previous state, either collecting data, or waiting for their address to be called

It is possible to communicate directly with a bus device using the Command Centre window present in the Cricket Logo software (Figure 2 2) If, for example, one wished to find the value being recorded at an instant by a bus device, typing 'send bsr $150' would tell the bus device with address '50' to relay its current reading back to the Cricket, where the '1' signifies this is a command and not data The Cricket in turn would send the value back to the PC, and this would appear in the monitor window of the software

An RF transceiver (Radiometrix RF TRX v1 2, Lemos Int , USA) has already been developed as a bus device for the Cricket platform This can be used to relay information from one Cricket to another, or to and from the PC via the interface used to communicate with the Crickets This enables remote sensing where line of sight is restricted, and the infra-red communication abilities of the platform are compromised

2 4 RCX Brick Overview

LEGO have produced many Mindstorms construction kits that are readily available on the retail market Although these kits differ in size, content and project capabilities, they all consist of the following core components

- RCX brick
- Motors and various sensors
- LEGO bricks, including axles, gear wheels and other mechanical components

The RCX brick (Figure 2.5) is at the centre of any project built from these kits. It is based upon the same principles of operation as the Cricket, although it is housed in a more robust package. However, it does lack the feature of a bus line, and therefore the developmental attributes of the RCX are not as wide-ranging as those of the Cricket. Essentially, the RCX is a miniature computer with an LCD screen, and contains the circuitry required to drive motors and collect and store data using a collection of miniaturized sensors.

There are three input sockets allowing the RCX to collect data from up to three resistive sensors simultaneously. Three output sockets allow the RCX to drive miniature motors in both directions for any stated length of time. There is also the option of driving the motors at any one of seven operational speeds.

Figure 2.5 RCX Brick

Any project built around the RCX brick can be almost completely autonomous. Like the Cricket, the RCX converses with the desktop by infra-red means, through an IR 'tower'. This is directional, however, and the IR transceivers of both the brick and the tower must be lined up to allow communication.

2 5 RCX Programmıng Envıronment

The programmıng envıronment, RCX Code, ıs used wıth the RCX bnck It ıs essentıally the same as the Logo Blocks software that has already been dıscussed for use wıth the Cncket Programmes are "wntten" by pıecıng together the vanous shaped ıcons, each of whıch has a specıfic command assıgned to ıt Thıs sımplıfies the task of wntıng programmes and also makes ıt more appealıng to chıldren, sınce the software ıs graphıc-based and programmes do not have to be manually typed

Other programmıng software, that has been developed by LEGO Mındstorms enthusıasts, ıs also avaılable These programmıng envıronments are more suıtable for people who want to develop new sensors and transducers for use wıth the RCX platform One of these software packages (NQC) [3] has been used ın the development of the colour sensor outlıned ın chapter 4, and ıs dıscussed ın more detaıl ın sectıon 4 3

2 6 Conclusıon

Two dıfferent sensor platforms have been ıntroduced and theır applıcatıon to pnmary level educatıon dıscussed A sımple and accessıble method of programmıng the RCX and Cncket that allows chıldren to control the respectıve platforms has been descnbed The method of communıcatıon wıth basıc resıstıve sensors has been ıntroduced along wıth the ıncorporatıon of such sensors ınto the Cncket platform The way ın whıch more complex sensors can be created and the communıcatıon protocol that allows data exchange between the sensor and Cncket has also been dıscussed

The method by which simple sensors are linked to the RCX has been addressed, and the capabilities of the system discussed The incorporation of a more complex sensor, (colour) and the programming of the RCX in order to interface the developed sensor is discussed in chapter 4

The differences in capability between the two platforms are evident and the considerations when developing sensors for use with either have been addressed It is also apparent that the Cricket is of more benefit to the researcher because of the presence of a bus line to allow more complex sensors be attached The LEGO RCX is more suitable for use with children, as it was developed to be The programming language, although sufficient to programme the RCX, is not very beneficial to the researcher, therefore prompting some to develop their own programming environments in order to use the RCX at its full potential

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3 NQC download websıte http //www cs uu nl/people/markov/lego/

Chapter 3

Oxygen and Carbon Dioxide Sensors

3 1 Introduction

Oxygen sensors have been developed for a wide range of applications Such uses include the measurement of dissolved oxygen in water [1], monitoring of exhaust gases in cars [2] and the measurement of oxygen concentration in enclosed environments such as in food packaging applications [3] Likewise, carbon dioxide sensors are used in many industrial applications [3] and for the monitoring of indoor air quality [4]

The development of sensors for both analytes for educational purposes is outlined in this chapter The detection methods employed, their performance and data logged in the case of both sensors are discussed

The primary objective here was to develop simple sensors to be used in experiments designed to demonstrate physical facts In experiments where only one gas was being sensed, e g 'candle in a jar' which demonstrates that oxygen is required for combustion, only the oxygen sensor was used Other experiments demanded the use of both sensors simultaneously, e g photosynthesis, where the concentration of one gas increased as the concentration of the other decreased

It was not imperative for the developed sensors to be extremely accurate The ability to detect changes in oxygen concentration of around two percent was deemed acceptable for the purposes required The emphasis was placed on making a robust sensor that would perform repeatably It was also necessary for the sensors to have a fast response to the,changing analytes so that any changes could be measured in close to real-time The method by which these attributes were obtained is discussed in this chapter

3 2 Oxygen Sensing

The operation of the oxygen sensor described in this chapter is based on the quenching of fluorescence in the presence of oxygen Luminescent transition metal complexes such as ruthenium polypridyl complexes are quenched by oxygen There are many ruthenium complexes suitable for oxygen sensing The particular fluorescent ruthenium complex, $[Ru(Ph_2phen)_3]Cl_2$ is used in this application to quantify the concentration of oxygen, where (Ph_2phen = 4, 7-diphenyl-1, 1—phenanthroline) [5] This compound has a high absorption in the blue-green region of the spectrum and is excited using a blue LED A large Stokes-shift is associated with the compound and it emits in the red spectral region

The oxygen quenching process is described by the Stern – Volmer equation [6],

$$I_0/I = 1 + K_{SV}p[O_2]$$

$$K_{SV} = k\tau_0$$

where I and I_0 are respectively the fluorescence intensity in the presence and absence of oxygen K_{SV} is the Stern-Volmer constant, and $p[O_2]$ is the oxygen gas partial pressure τ_0 is the excited-state lifetime of the fluorophore in the absence of oxygen, and k is the bimolecular quenching constant These equations lead to a calibration plot associated with oxygen sensors of I_0/I verses the oxygen partial pressure

3 3 Oxygen Sensor

The oxygen sensor developed employed the method of quenchıng of fluorescence ıntensıty The reasons for doıng thıs were

1 It ıs a relatıvely easy detectıon method to realıse

2 The requıred cırcuıtry ıs mınımal

The dısadvantages of usıng thıs method are

1 Each sensor must be ındıvıdually calıbrated

2 The LED ıntensıty, and therefore the output sıgnal, may fluctuate

3 The posıtıon of the LED and photodıode relatıve to the sensıng film must remaın constant

The sensıng film was prepared by ıncorporatıng the ruthenıum complex ın a sol-gel sılıca film In partıcular 17mg of the oxygen-sensıtıve complex, $[Ru(Ph_2phen)_3]Cl_2$, was dıssolved ın 5 248ml of ethanol and mıxed wıth 1 313ml of pH1 HCl whılst stırrıng The requıred amount, 2 870ml, of methyltrıethoxysılane (MTEOS), the sol-gel precursor, was then added drop-wıse whılst stırrıng and the mıxture was stırred for a further 4 hours at room temperature The film was then deposıted onto PMMA slıdes by stamp-prıntıng and then cured at 70°C for 18 hours

The sensor configuratıon was based on a patent for effıcıent fluorescence capture [7] A sensıng film was deposıted on top of a waveguıde Thıs was ıllumınated dırectly usıng a blue excıtatıon LED (I_{max} = 470nm, NSPB 500 Nıchıa, Germany) The fluorescence from the sensıng film was coupled ınto the waveguıde and guıded through ıts length to be detected at the end-face by the photodıode The fluorescence from the sensor film ıs not coupled ısotropıcally ınto the waveguıde At a certaın angle the fluorescence intensity is a maximum. The photodiode is positioned at this angle with respect to the end-face for efficient detection [8]. It was observed that for this sensing configuration, the angle at which the intensity was greatest was 30°.

Figure 3.1a shows an outline diagram of the flow-cell used to house the slide and also to retain the electronic components at the correct distances and angles with respect to the coated slide.

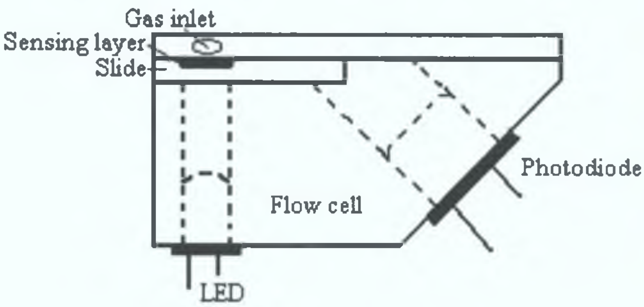

Figure 3.1a Sensor Flow Cell

Figure 3.1b Cell on PCB

The cell was machined from aluminium, and was mounted directly onto the printed circuit board (Figure 3.1b) that also incorporated the necessary circuitry. It was only 15mm high and did not add significantly to the size of the sensor. The top of the cell was made detachable so that the slide could be easily replaced. The gas inlet port was positioned directly above the sensing layers position so that the gas mixture could flow freely across the sensing film's surface.

3.4 Sensor Outline

Figure 3.2 shows a block diagram of the electronic components used in the fabrication of the oxygen sensor. Since the sensor works on the basis of measuring light intensity, it could be adversely affected by ambient light The flow cell eliminates most of the ambient light falling directly onto the photodiode However, to overcome this problem fully, the excitation light source must be modulated and lock-in detection used A reference signal of the same frequency as the modulation signal (666Hz) is required so that the detection circuitry, which includes a lock-in chip (AD630), can effectively extract the emitted signal from the sensing film

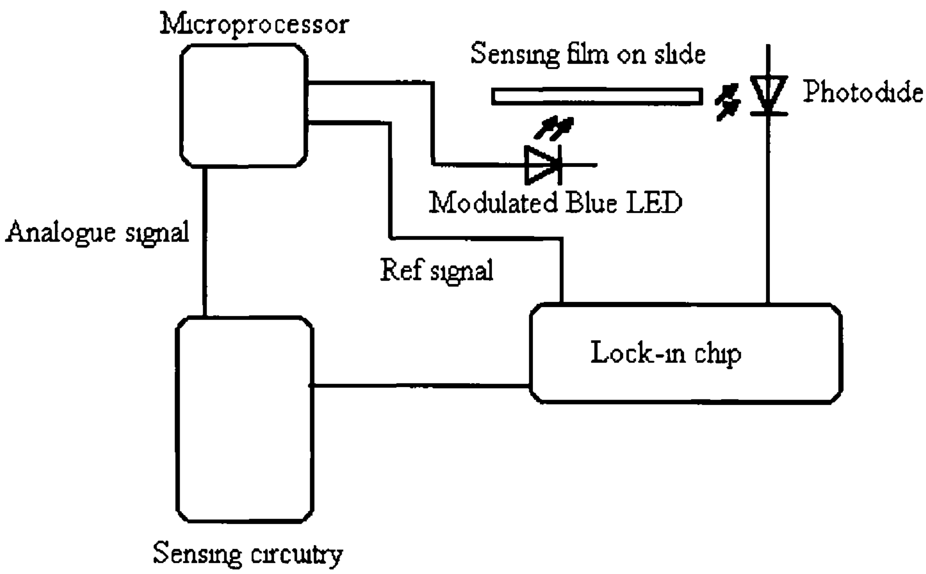

Figure 3 2 Sensor Block Diagram

A microprocessor controller (PIC16f872) was used in order to control the circuit This microprocessor was chosen because of its analogue to digital capability This allowed the raw sensor reading to be fed directly into one of the input pins on the microprocessor, where it was changed to a digital format that could be communicated to the sensor platform to which the sensor was connected Another feature of this microprocessor is that it has a large onboard programme memory (2K), making it suitable for storing the necessary programme code and also the required look-up tables

Figure 3 3 is a circuit diagram of the sensing circuitry used in order to determine the oxygen concentration using the flow cell and coated PMMA slide outlined in the previous section The circuit is based around the lock-in chip, AD630, which receives a modulated signal, from the photodiode, which is proportional to the intensity of the emitted light from the sensing film

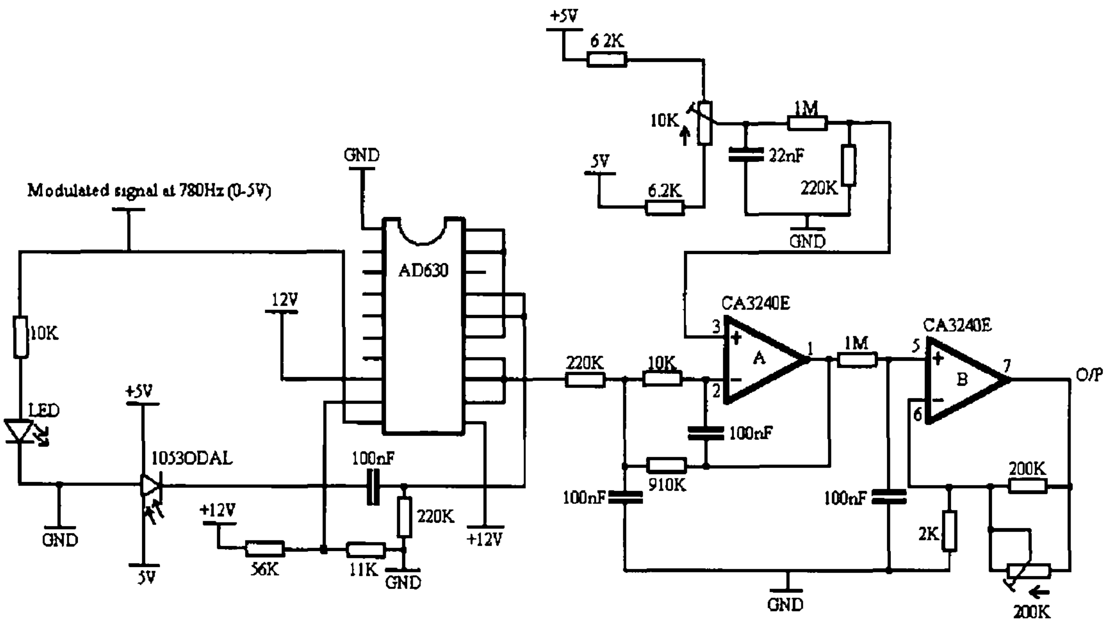

Figure 3 3 Oxygen sensor circuit diagram

An integrated photodiode amplifier (IPL 10530 DAL, IPL Inc, Dorset, UK) was used to detect the emitted light This photodiode was chosen because it has a fast response and is therefore capable of detecting the signal from the film at the frequency at which the LED is modulated The integral amplifier cancels the need for a preamplification stage before the signal is received by the AD630 This has the effect of minimizing the number of components needed, and therefore reducing the overall size of the sensor

To reduce the size of the sensor circuit further, the microprocessor was used to modulate the excitation light source, instead of using a dedicated frequency generating circuit This resulted in stable square-wave frequency modulation (< 5 Hz distortion) of the LED used to illuminate the ruthenium complex, due to the fact that a crystal oscillator was used for the timing of the microprocessor The modulated signal ranged from 0 to 5 volts The modulated signal was driven from two of the output pins of the microprocessor One of these pins was channeled directly to the reference port on the lock-in amplifier chip, while the other was connected to the LED through a current-limiting resistor in order to provide the excitation light for the sensing film This results in a very clean and stable excitation light output

Since the sensor was designed for remote applications, it was necessary to use a battery as the power source This required a reduction in the power consumption of the circuit Because the AD630 and the op-amp used (CA3240E) needed a positive and negative supply to function properly, two nine-volt batteries were used to provide the required power After the modulated signal is extracted from the noise by the AD630, it is demodulated and turned into a dc signal This is then amplified once more before being fed into one of the analog ports on the microprocessor

The final gain stage of the sensor is variable, so that changes in the quantity of the oxygen sensitive film from sensor to sensor i e variations in sensitivity, can be accommodated There is also an internal offset, which can be adjusted so that the sensing range of the film can be centered on the oxygen concentrations being measured

The circuit used with the RCX needed miniaturization so that it could be incorporated into a wide range of applications where size was a limiting factor Figure 3 4 shows a circuit diagram of the miniaturized circuit based on the circuit in Figure 3 3 This circuit was produced by Whistonbrook Technologies Limited, (Luton, UK) The circuit is powered by two AAA batteries The flow cell and the size of the LED and photodiode are the limiting factors in the size of this sensor However, even with these limitations, the sensor still has a footprint of only 55 by 25mm

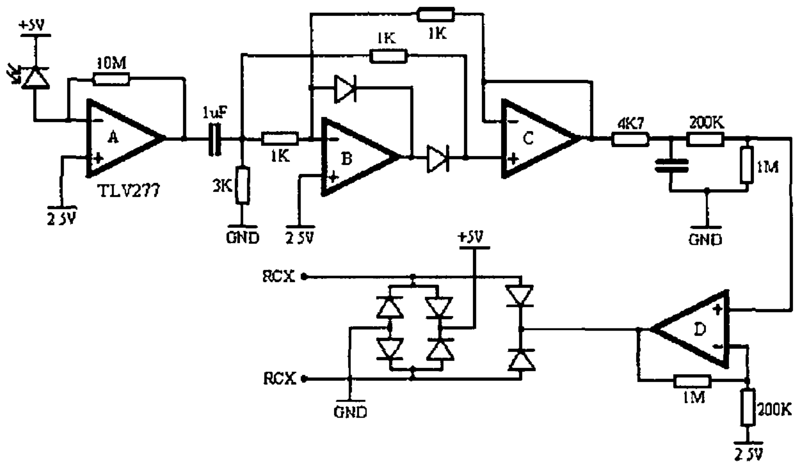

Figure 3 4 Miniaturized Oxygen Sensor Circuit

3 5 Interfacing Oxygen Sensor with RCX and Cricket Platforms

The circuit diagram, which is shown in Figure 3 3, is common to both sensors designed for the particular sensing platforms In both cases, a PIC microprocessor is used to modulate the excitation LED, and also provide the reference signal that is used in the AD630 in order to extract the sensor signal from noise

As explained in chapter 2, Figure 2 4, the Cricket platform uses a bus protocol in order to extract data from sensors whose output is in a form other than a changing resistance In order for the Cricket to communicate with the oxygen sensor, a microcontroller was embedded in the sensor in order to convert the analog output signal of the sensor into a digital signal, which then could be relayed to the Cricket using the bus line

A PIC16F872 was used in order to control the sensor and to communicate with the microprocessor on the Cricket It was chosen because of the fact that it has onboard analogue to digital capability, and also a large memory bank (2K) This allows calibration information of the sensor to be stored in the memory and therefore an actual concentration reading can be sent to the Cricket, as opposed to an arbitrary number between 0 and 256

The configuration of the additional circuitry needed in order to interface the sensor with the Cricket is shown in Figure 3 5 Two separate I/O pins were used to modulate the LED and provide a reference signal for the AD630 As a power saving consideration, the sensor could also be programmed so that it was continuously in stand-by mode Upon receiving the appropriate signal from the Cricket, the microprocessor would turn on the detection circuitry needed to determine the oxygen concentration, turn on the LED, take in the analogue signal and return the oxygen concentration to the Cricket in digital form After the information was sent, the microprocessor then shuts off the power to the rest of the circuit while it continuously tests for a new command from the Cricket

The I/O pin, RB0, was used as the communications channel between the oxygen sensor and the Cricket platform This is because previous sensors designed for use with the Cricket use this pin as the communication channel This simplifies the programming, so that the part of the code used for taking readings from the respective sensors need not be changed in any way

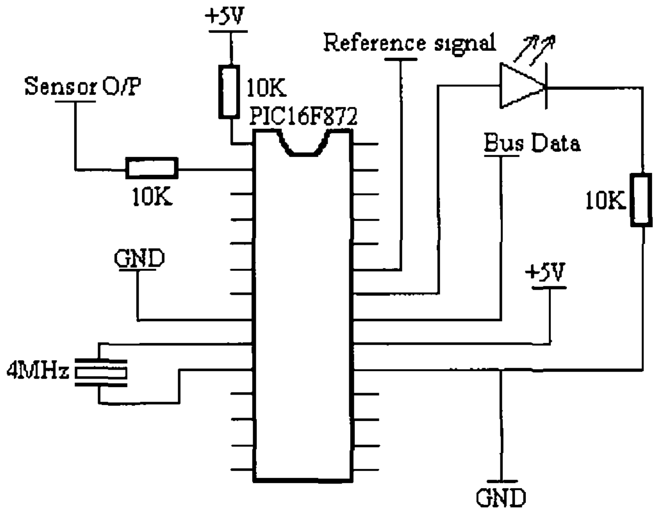

Figure 3 5 Microcontroller circuit on oxygen sensor

When interfacing the sensor with the RCX Brick, a different approach was needed The Brick had no facilities to allow a bus protocol communications line to be implemented in order to communicate directly with an external sensor Instead, the RCX determines the sensor value by measuring the resistance of the sensor output Because the oxygen sensor uses a photodiode in order to measure the fluorescence of the oxygen sensitive dye, the output of the sensor is nominally a changing voltage In order to connect the sensor to the RCX, the output voltage of the sensor needed to be changed to a resistance Figure 3 6 shows the circuit used to accomplish this

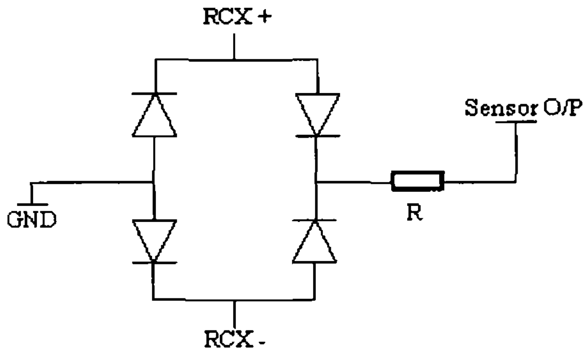

Fıgure 3 6 Oxygen sensor/RCX ınterface cırcuıt

All dıodes used ın the cırcuıt were 1N4148 dıodes The sensor output was connected to the dıode brıdge through the resıstor R The value of thıs resıstor determıned the lınearıty of the output resıstance wıth respect to the output voltage of the sensor Fıgure 3 7 shows the effect of usıng dıfferent resıstors ın the posıtıon of resıstor R It ıs evıdent from thıs graph that as the resıstance value R ıs ıncreased, the lınearıty of the sensor output also ıncreases over the sensıng range However, thıs also led to a reductıon ın the sensıtıvıty of the sensor Thıs can be seen from the slope of the ındıvıdual resıstance plots ın Fıgure 3 7 Wıthout a serıes resıstance, the R value was 0 99849, usıng a resıstance of 1kΩ gave an R value of 0 99827 and a resıstance value of 10kΩ gave an R value of 0 99939 The output from the RCX ıs a 10 bıt A/D conversıon of the voltage across the sensor

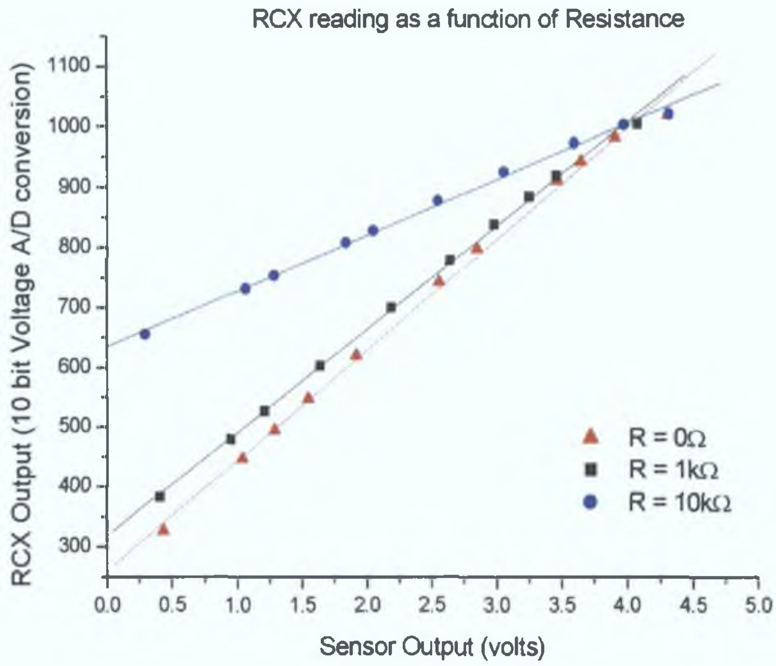

Figure 3.7 Effect of changing Resistance value

A value of 1kohm was used in the circuit developed for use with the RCX platform. This gave a linear response over a wide range and also allowed for a good resolution of the sensor output. The oxygen sensor was continuously on when used with the RCX platform.

The software used in order to display the oxygen concentrations measured by the sensor connected to the Cricket is the graphing function of the Cricket Logo software. Figure 3.8 shows the real time graph of the changing oxygen concentrations using this software. The oxygen concentration was stepped from 25% to 5% in steps of 5%.

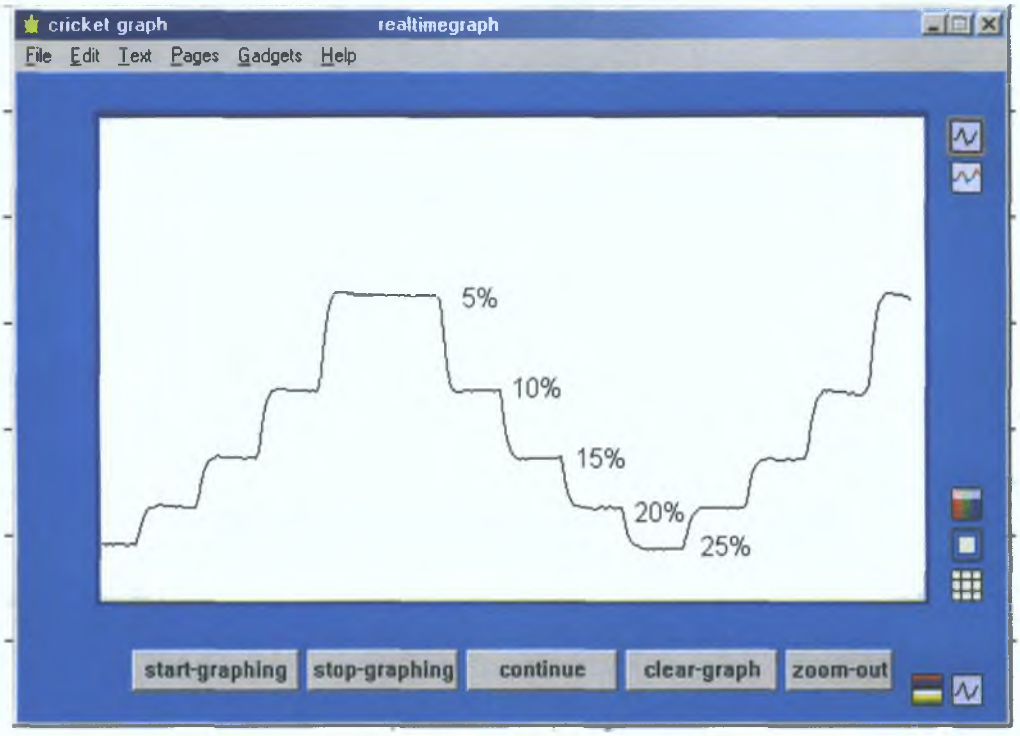

Figure 3.8 Cricket Software interface

3.6 Sensor Calibration

To calibrate the oxygen sensors, different concentrations of oxygen were flowed over the sensing film while the sensor output was being recorded by the platform for which the sensor was designed. The method by which the oxygen concentration was regulated is as follows. A Labview programme was used in order to control two mass flow controllers (MFCs). One MFC controlled the flow of oxygen, while the other controlled the flow of nitrogen gas. Figure 3.9 is a schematic representation of the calibration set-up.

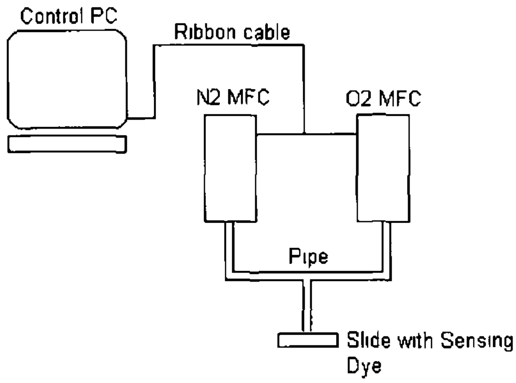

Figure 3 9 Gas Calibration System

The outputs from the two MFC's were then mixed together and the resultant gas mixture flowed over the oxygen sensitive film The sensor output in volts can be recorded by various means

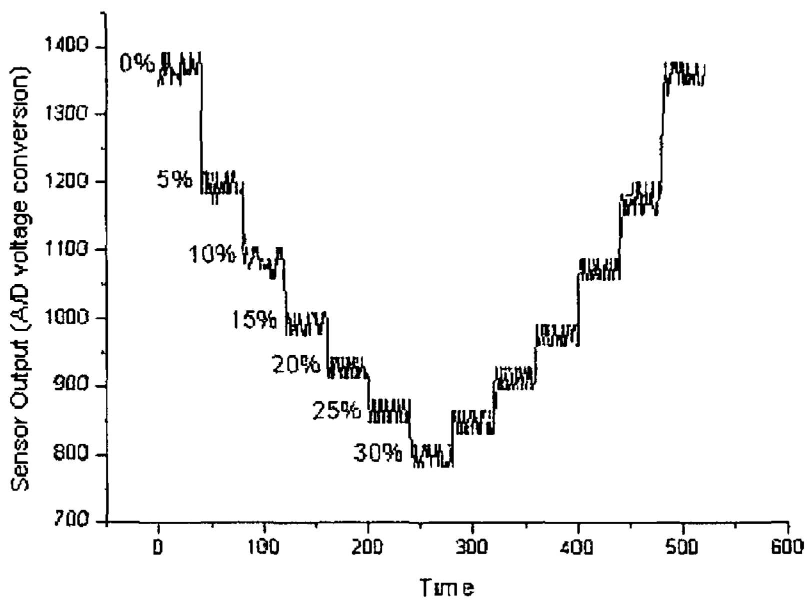

Figure 3 10 Sensor output for different oxygen concentrations

One method is to digitise the signal and load it into a PC This is carried out by using a Bytronics card (MPIBM multifunction I/O), which takes the analogue voltage sıgnal from the sensor and transforms ıt ınto a dıgıtal sıgnal that the PC may store A plot of these data from an MTEOS R=4 oxygen sensıtıve film ıs shown ın Fıgure 3 10 Usıng the Stern-Volmer equatıons outlıned ın sectıon 3 2, a Stern-Volmer plot of the data for thıs slıde was plotted Thıs ıs shown ın Fıgure 3 11 Thıs graph can then be used as a calıbratıon plot for the partıcular film

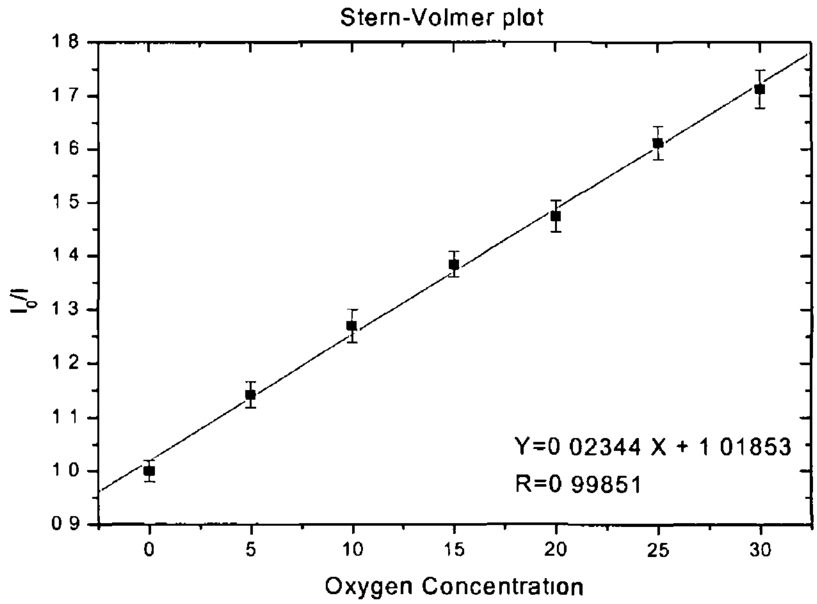

Fıgure 3 11 Stern-Volmer plot

The software ınterface ın Fıgure 3 8 was used ın order to dısplay the oxygen concentratıon Each ındıvıdual sensor had to be calıbrated ındependently, sınce the method of ıntensıty measurement was employed ın the sensors

The same process of obtaınıng calıbratıon data was employed for both the RCX and Crıcket platforms A typıcal graph of the raw data readıng dısplayed on the RCX brıck whıle calıbratıng a sensor ıs shown ın Fıgure 3 12 The equatıon of the graphed lıne was calculated and was then used ın the vısual basıc code so that the oxygen concentratıon could be plotted ın real tıme from that partıcular sensor

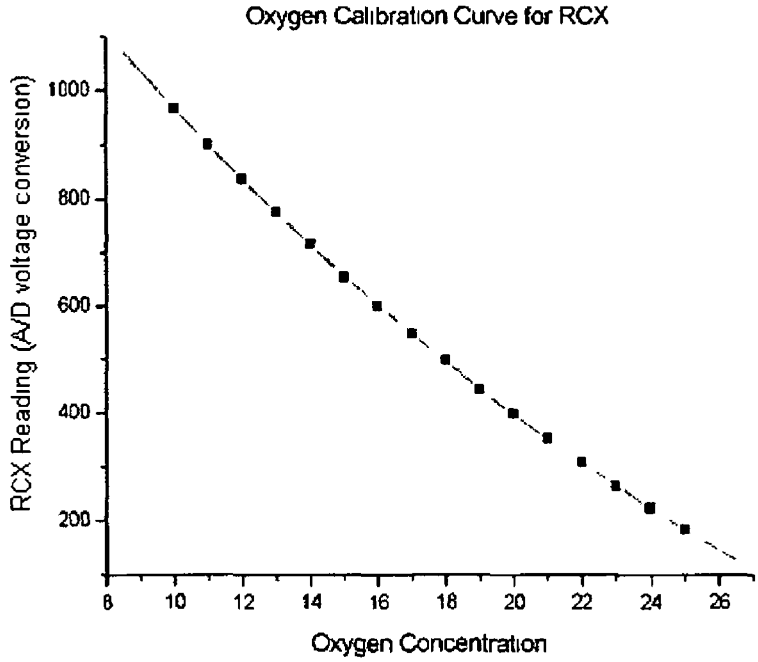

Fıgure 3 12 Calıbratıon curve of RCX oxygen sensor

The above method was used both for the ınıtıal ıntensıty measurement cırcuıt shown ın Fıgure 3 3, usıng lock-ın detectıon, and the mınıaturızed cırcuıt, whıch ıs outlıned ın Fıgure 3 4

To calıbrate the sensor for use wıth the Crıcket, a sımılar approach was employed However, durıng the calıbratıon, the Crıcket Logo software ınterface was used ın order to determıne the sensor output value, whıch was an arbıtrary number between 0 and 255 The values correspondıng to a set of oxygen concentratıons were recorded, and a table drawn up such as that ın Fıgure 3 13

A look-up table was then built corresponding to that particular sensing film and this was then stored in the memory of the on-board microprocessor This enabled the sensor to send out the real oxygen concentration to the Cricket software, or to calculate and store the concentrations over a period of time

Oxygen	Sensor O/P	Oxygen conc	Sensor O/P
0	175	15	48
5	128	16	44
6	120	17	40
7	111	18	35
8	102	19	32
9	92	20	27
10	85	21	23
11	77	22	19
12	71	23	15
13	65	24	12
14	59	25	9

Figure 3 13 Look-up table for Cricket oxygen sensor

The calibration curve relevant to this sensing film is shown in Figure 3 14

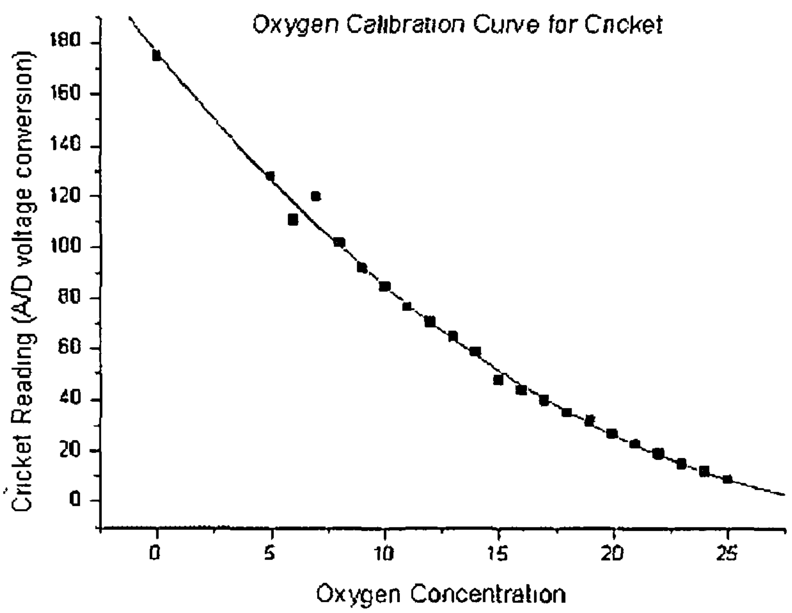

Figure 3 14 Calibration curve of Cricket oxygen sensor

The non-linearity of the sensor response to changing oxygen concentration is intrinsically linked to the fundamental non-linearity suggested by the Stern-Volmer equation (page 21)

3 7 Oxygen Sensor Conclusion

The underlying theory of sol-gel based oxygen sensors has been outlined An oxygen sensitive film has been constructed and the Stern-Volmer equation introduced to characterise the film Oxygen sensors fabricated for use with both the Cricket and RCX platforms have been explained in detail, as have the methods by which they are interfaced with either platform The calibration method used has been outlined and graphs of the calibrations plotted and analysed The detection range of the sensors has been optimised for oxygen concentrations relevant to their applications in educational experiments i e from 0% to 25%

3 8 Carbon Dioxide Sensing

The development of an intensity based carbon dioxide sensor was undertaken to complement the oxygen sensor The gas-sensing component was again sol-gel based This section outlines the construction of the carbon dioxide sensitive material The pH sensitive fluorescent dye, 1-hydroxypyrene-3,6,8-tri-sulfonate (HPTS) was used as the indicator for carbon dioxide concentration determination This dye has an absorption band in the blue spectral region (440nm) and an emission band in the green (515nm) When gaseous carbon dioxide is dissolved in water, carbonic acid is formed This acid reacts with the deprotonated dye and causes a reduction in the green fluorescence [9]

3 9 Carbon Dioxide Sensor

The electronic circuit used to determine the carbon dioxide concentration data using the pH sensitive film was the same as that used for the oxygen sensor shown in Figure 3 3, the only difference being that the LED used to excite the dye has a spectral peak at 450nm, (Roithner LaserTechnix, LED450-01U, Austria) The pH sensitive fluorescent dye discussed in the previous section was stamp-coated onto a PMMA slide The same flow cell that was used in the oxygen sensor, Figure 3 1, was again employed in this role

3 10 Sensor Calibration

The calibration of the carbon dioxide sensor was carried out in the same manner as for the oxygen sensor Using two MFCs, one for carbon dioxide and another for nitrogen, controlled by a Labview programme, different concentrations of carbon dioxide gas were flowed through the cell containing the sensing film Again, the output of the sensor was monitored and recorded using a Bytronics card (MPIBM3 multifunction I/O) to digitise the analogue signal from the sensor circuit, and a PC was used to store and display the data

The main difference in the calibration procedure was that the gases needed to be humidified This was necessary so that water was present with which carbon dioxide could form carbonic acid This leads to a change in the pH and causes a change in fluorescence intensity To achieve this, the gases were flowed through glass wash bottles filled with de-ionised water, whereupon a humidity of 100% was maintained Concentrations in carbon dioxide of between 0% and 100% were used and a graph of the sensor output obtained and is shown in Figure 3 15

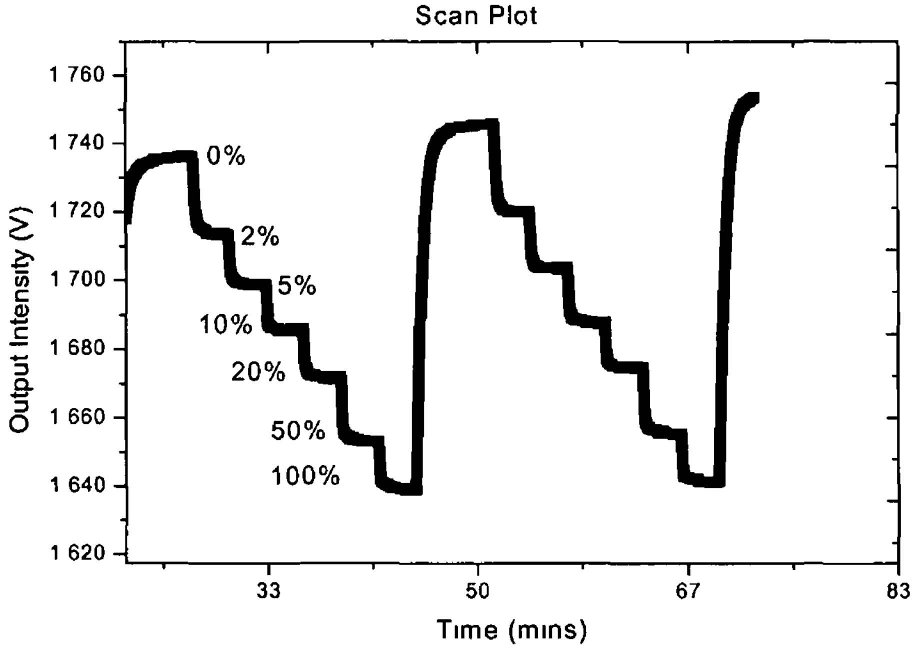

Figure 3 15 Sensor output for various concentrations in CO_2

In a classroom experiment, this sensor could be used to detect CO_2 concentrations in exhaled air The sensing film is sensitive enough to distinguish the small CO_2 difference between inhaled and exhaled breath These data were used to create a calibration curve for the particular film used The calibration curve employed in carbon dioxide sensing plots $(I_0 - I)/I$, where I_0 is the intensity of the fluorescence when the carbon dioxide concentration is zero, and I is the fluorescence intensity at a particular concentration, against the carbon dioxide concentration [10] The calibration plot obtained using the data in Figure 3 15 is shown in Figure 3 16

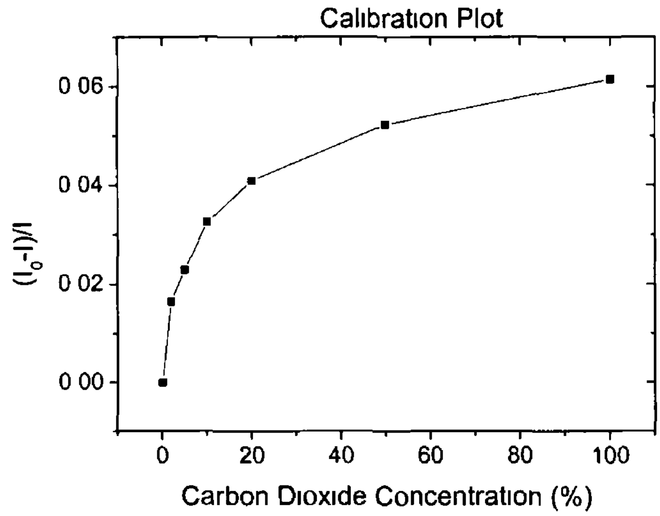

Figure 3 16 Calibration plot for Carbon Dioxide sensor

3 11 Carbon Dioxide Sensor Conclusion

A carbon dioxide sensor has been developed based on fluorescence intensity measurements using a pH sensitive indicator dye The electronic configuration used in this sensor is identical to that of the oxygen sensor The same excitation light source can be used, but would lead to a smaller spectral separation between the excitation and emitted light This sensor has been shown capable of detecting the full range of carbon dioxide concentrations (0 to 100%)

3 12 Sensor Demonstration

The oxygen sensor developed in this work has undergone pilot tests in a classroom environment Figure 3 17 shows primary school children using this sensor to determine the effect of exercise on the amount of oxygen consumed by the body. Further work will be required to fully validate the robustness of the sensors.

Figure 3.17 Children using Oxygen Sensor with RCX in Realtime

3.13 Conclusion

Compact, portable and robust sensing circuitry for fluorescence based sensors using intensity measurements has been developed. This technology has been applied to both oxygen and carbon dioxide sensing applications. The oxygen sensor has been interfaced with both the RCX Brick and Cricket sensor platforms. The performance of the oxygen sensor as an educational resource has been demonstrated in a classroom environment. The oxygen sensor has been used to quantify the difference in the amount of oxygen consumed when carrying out different levels of exercise. Future work could involve the incorporation of the CO_2 sensor into these platforms in a similar way

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Chapter 4

Colour sensor

4 1 Introduction

The sense of vision plays a great role in human life, especially the recognition of different colours Colour is used in everyday life to indicate warnings, signals or as a process control measurement, for example [1] The eye can easily distinguish not only between different colours, but also between colours of the same hue and different shade To duplicate this sensory adaptation accurately using an electronic system is difficult to achieve In order to develop such a system for use as an educational tool, a simple system using basic optoelectronic components was created

4 2 Colour Sensor

A colour sensor was developed for use with the RCX brick platform in this project This allows children to "teach" the RCX to recognise a set of colours The sensor consisted of a light generation system to illuminate the object to be sensed, and a light receiving system to read the diffuse light reflected from the object The illumination system consists of a multicolour LED (RS DN7559787) that has three different spectral components Each component, red, green and blue, can be turned on individually by biasing the pin specific to the required colour

A PIC microcontroller (PIC16F84) is used to produce various colours in sequence upon receiving a string of pulses from the RCX The sensing element consists of a light dependent resistor (RS DN4442286) in a voltage divider configuration, the resistance of which changes in accordance with the intensity of the light reflected onto it This resistive reading is then recorded and processed by the RCX

4 3 Colour Sensor Circuit and Calibration

The circuit used to enable the RCX to identify a range of pre-determined colours is shown in Figure 4 1 This enables the colour sensor to be linked to the RCX using only one of the sensor inputs present on the RCX To operate this circuit, the RCX sends out an initial pulse This makes the PIC microcontroller turn on the first output, thereby enabling the multicolour-LED to emit in the red region

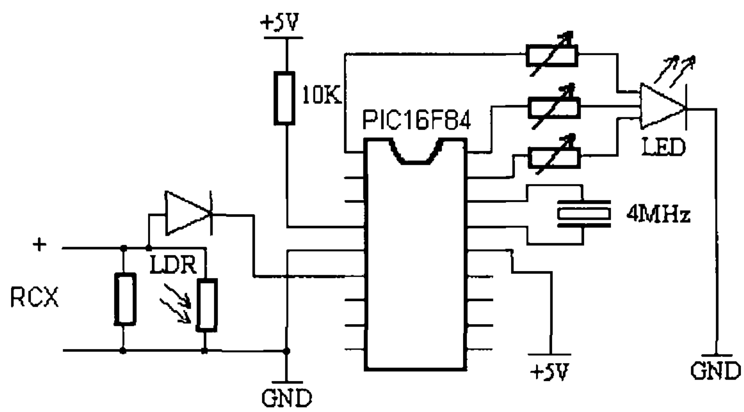

Figure 4 1 Colour Sensor Circuit

The RCX then switches to passive sensor mode and reads the value of the LDR A second pulse is sent out to the microcontroller by the RCX, thus prompting the emission of the green component of the multicolour-LED This value is recorded and the blue component is then illuminated and the LDR's resistive value recorded in the RCX

The process of colour identification takes place by loading each of the three values into an array This array of numbers is accessed by an algorithm, that is pre-recorded in the RCXs memory The output result of the RCX is compared to a predetermined set of values for a range of colours that were investigated during the calibration of the sensor

Each LED component is connected in series with a 10K potentiometer, the value of which determines the intensity of each spectral component The relative reflected light intensity could then be varied so that the sensor could be calibrated To do so, the sensor was placed on the white square of a colour rendition chart (T37-756, Edmund Optics Ltd) and the potentiometers adjusted until the voltage reading across the LDR was the same irrespective of the spectral component being illuminated

The light reflected from a surface is given by

$$R = \frac{I_r}{I_0}$$

where, R is the fraction of incident light that is reflected from the surface under illumination, I_r is the reflected light intensity and I_0 is the intensity of the incident light [2] The resistance of the LDR increases as the intensity of the incident light decreases Therefore the reflectance can also be described as

$$R = \frac{r_r}{r_0}$$

where, r_r is the resistance of the LDR while the coloured surface is illuminated and r_0 is the resistance measured using the reference white surface

Since the voltage across the LDR is the same for each LED component after calibration using a white surface, the r_0 value is the same for each Therefore the reflectance, R, is dependent only on the r_r term The ratios of the reflected components could then be used to recognise a set of colours

The limitations of this approach are such that any colour to be identified must first be "taught" to the RCX by placing the sensor head on the coloured surface and recording the values of the LDR under illumination of each spectral component in turn Using the above method, only very similar colours to those predetermined could be recognised, so an error margin is written into the programme

The LED and LDR are placed together at an angle of forty-five degrees in a black LEGO brick Care is taken so that no light from the LED is shone directly onto the LDR, but is reflected diffusely from the surface under investigation Figure 4 2 shows how the LED and LDR are placed with respect to each other

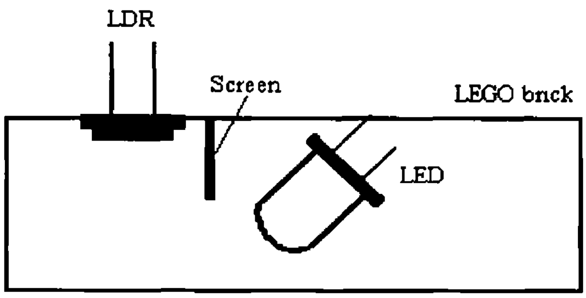

Figure 4 2 LED and LDR positioned in LEGO brick

Figure 4 3 shows the relative intensities of the three components of the multicolour LED using an 'Ocean Optics' spectrometer In each case, a current-limiting resistor of 200Ω is used. It is clear from this figure that the blue part of the LED gives the greatest emission intesity.

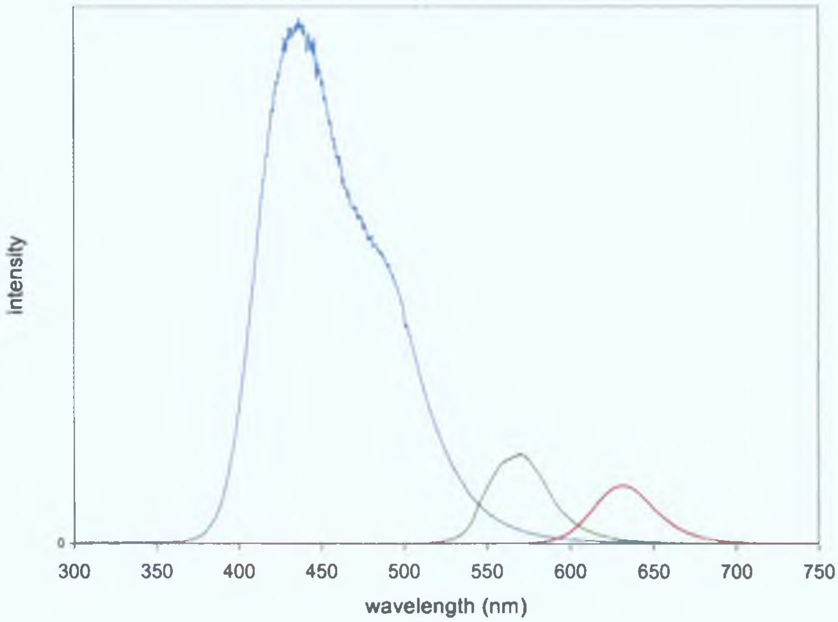

Figure 4.3 Spectral Emission of Multicolour LED

The above method of adjusting the current through each LED component enables the user to ensure that the individual components emit light at the same intensity. It also reduces the need to use the software on the RCX to compensate for the intensity differences and cancels the necessity for scaling factors to be written into the programme.

Figure 4.4 shows the LDR output when the sensor is placed on different colours of the rendition chart under illumination of each of the three spectral components of the tricolour LED. Initially the sensor head was placed on the white square of the rendition chart and the current flowing through each of the LED's components adjusted accordingly so that the light intensity from each one falling on the LDR was equal.

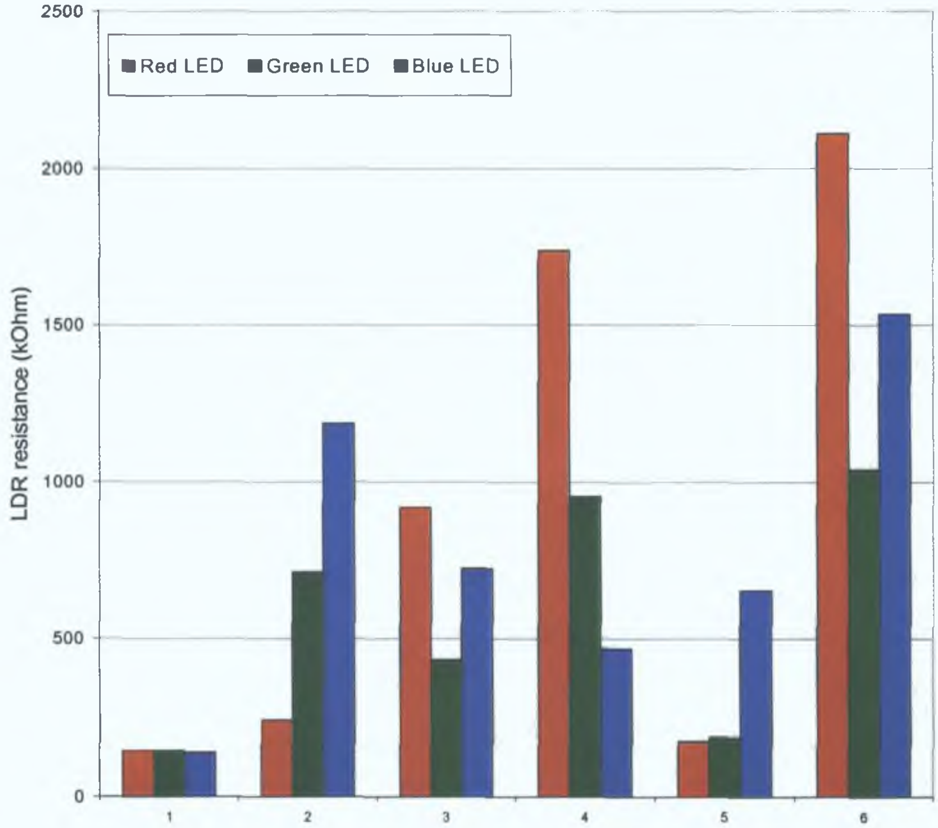

Figure 4.4 LDR readings for White (1), Red (2), Green (3), Blue (4), Yellow (5) and Black (6) cards

The readings shown in Figure 4.4 show that as the spectrum under investigation is traversed from higher to lower wavelengths, the relative intensity of reflected red light decreases, while the intensity of reflected blue light increases.

4.4 Programming

Although the commercially available programming software can be used when prototyping any new sensor developed for the RCX brick, there is also a freeware programme called "Bricx" which is available for download [3]. Figure 4.5 is a screen capture of this particular programming environment.

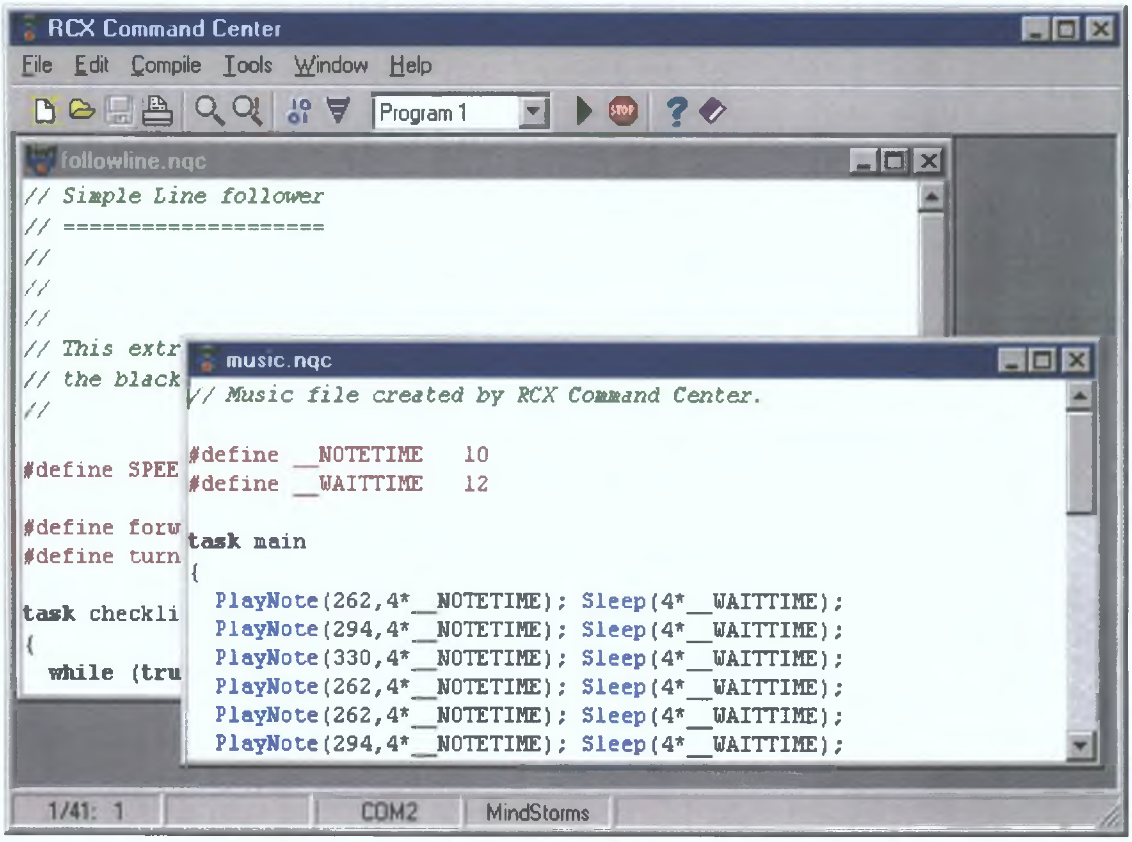

Figure 4.5 Bricx Programming Environment

This software allows a higher level of programming to be used when developing new sensors. The code used in order to write programmes using the Bricx command centre is known as NQC (Not Quite C). It is similar to C in most respects, but has additional commands relevant to common tasks performed by the RCX. It is not especially suitable for children to use but is very effective when used in a developmental capacity

The finished programme is downloaded to the RCX in the usual manner by way of the IR tower The code written in order to integrate the colour sensor with the RCX is given in Appendix C In this example the colour sensor has been 'taught' to recognise five different colours

4 5 Colour Sensor for the Cricket

A colour sensor for use with the Cricket was also developed Because the Cricket is very limited in its data processing abilities, this particular sensor was very basic A microprocessor (PIC16F872) was incorporated into the sensor to enable communication with the Cricket and also to control the sensor The multicolour LED described in the section 4 2 was also employed in this sensor Figure 4 6 is a circuit diagram of this sensor

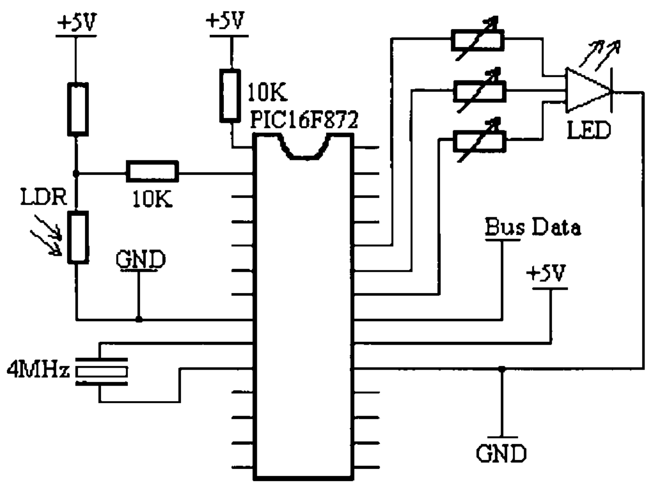

Figure 4 6 Colour Sensor for use with Cricket

The sensor is able to recognise the three primary colours In order to determine others, more programming capability is required The sensor operates by reading the voltage difference across the LDR while the target surface is illuminated with each component of the LED in turn as in the sensor for the RCX The LED and LDR were both housed in a black LEGO block as in Figure 4 2

The microprocessor can then evaluate the colour being sensed by using the recorded voltages This was simply done by determining which spectral component produced the largest reflected light intensity The sensor was calibrated using the red, green and blue segments of the colour rendition chart and adjusting the variable resistors so that the red spectral component gave the greatest reading on the red segment and so forth A predetermined value is then relayed back to the Cricket depending on the determined colour

4 6 White LED

Initially the possibility of using a white LED (Farnell 352-6860) in order to make the detector smaller was examined It was decided to use a white LED in conjunction with a tri-colour photodiode (Hamamatsu S7505) This photodiode consisted of three separate detector sections coated respectively with different optical filters (red, green and blue) Hence the three different colour components of the reflected light from the surface of the item being interrogated could be measured simultaneously

The spectral output of the LED investigated (shown in Figure 4 7) was determined using an Ocean Optics spectrometer Although the output of the LED appears white, it is clear from the graph that there is a high peak in the blue region of the spectrum

This led to a very large reading from the blue filtered photodiode component regardless of the colour being investigated

If the above components were to be used in a colour sensor, the three components of the photodiode would need to be amplified individually before the voltages being processed by the microprocessor This would involve the integration of a series of amplification stages therefore enlarging the overall circuit By using a single photodiode and a tri-colour LED, the same effect is achieved by employing three variable resistors

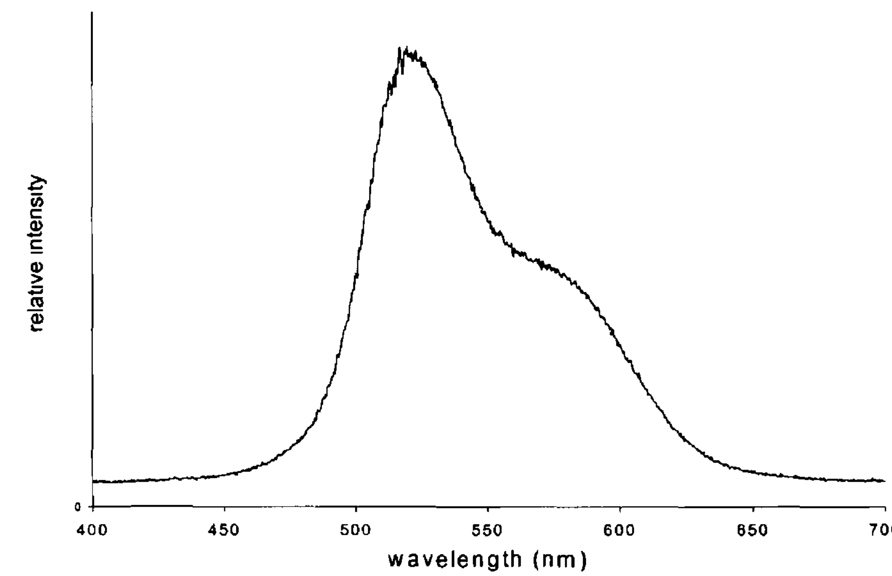

Figure 4 7 Spectral output of White LED

The need for a more complex circuit and the large intensity difference across the spectrum of the white LED determined that a tri-colour LED be used in conjunction with a single photodiode in this role This approach is applicable only if the complexity of the of the detection circuit can be justified i e in detecting smaller colour changes as in the case of chemical reactions

4 7 Conclusion

This chapter has detailed the construction of a simple colour sensor This sensor was used with the RCX to recognise a pre-determined set of colours The method of programming the sensor has been outlined This sensor could be used with the LEGO Mindstorms kit to follow coloured lines on differently coloured backgrounds, or to use different colours to initiate a response from the RCX The sensor was developed further to detect analytes, such as pH and nickel sulphate, using colour based measurements These processes are detailed in chapter 5

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2 Matıas, F A , Vıla, M , et al "**A sımple devıce for quantıtatıve colorımetrıc dıffuse reflectance measurements** " Sensors and Actuators B, **88** 60-66, 2003

3 http //vısl technıon ac ıl/projects/2002s07/docs/Brıcxcc%203 3/brıcxcc htm

Chapter 5

Colour Sensing Applications

5 1 Introduction

The colour sensing technique discussed in chapter 4 was applied to the development of a pH sensor The development of a novel pH sensor for educational purposes as an introduction to the concept of pH and its performance is described The applications of such a sensor in a learning environment could include pH determination of different beverages and of household products such as cleaning agents etc The pH measurement of condiments, such as vinegar, baking soda, salt and sugar solutions, could also be safely carried out by children using this sensor

As a proof of principle in an environmental application, a nickel sulphate sensor based on colour measurement was also developed The presence of nickel sulphate in water poses a health risk to aquatic life and, in the case of drinking water, a hazard to humans Nickel sulphate is a known carcinogen [1][2] The detection of nickel sulphate in water solutions using the colour sensor was investigated The detection and measurement of nickel sulphate concentrations involves the use of an analytical reagent, dimethylglyoxime (DMG) [3] It is obvious that the chemicals employed in the detection of nickel sulphate make this an unsuitable demonstration in a primary level educational environment, but it could be used in a controlled laboratory setting

5 2 pH Sensor

The construction of a simple sol-gel based pH sensor was undertaken as an application of the colour sensor This sensor could be used in a classroom environment to demonstrate pH measurements using such simple household materials as vinegar and baking soda Two LED's were used to illuminate the sensing film in turn, and a photodiode was employed to measure the reflected light intensity from the film This section discusses the fabrication of a pH sensor for use in an educational context

5 3 pH Sensitive Sol-gel Preparation

A pH sensing film was prepared in the following manner 29 4mg of bromocresol purple (BCP) was weighed into a glass vial and 4g of ethanol (C_2H_5OH) added This was stirred for 10 minutes 2g of pH1 HCl was added drop-wise whilst stirring and the contents left for a further 10 minutes 5 4g of tetraethoxysilane (TEOS) and 0 54g of methyltriethoxysilane (MTEOS) were also added drop-wise The contents of the vial were left mixing for 1 hour The resultant solution was left to age at room temperature overnight [4]

Glass slides were prepared by immersion in a sodium hydroxide (NaOH) solution for 1 hour They were then washed with de-ionised water and dried using compressed dry air The slides were dip coated in the pH sensitive solution by withdrawal at a rate of 1 5 mm/s They were then dried at $70^{O}C$ for 17 hours The coated slides were then immersed in a $2x10^{5}$ molar solution of NaOH for 48 hours This process reduces the reaction time of the films to changing pH by reducing the population of silanol groups within the sensor matrix, therefore allowing them to react rapidly with protons in the analyte solution [5]. Figure 5.1 is a graph representing the absorbance of the pH sensitive film after immersion in different pH solutions for a period of 10 minutes at a time. The spectra were obtained using a UV-vis spectrometer.

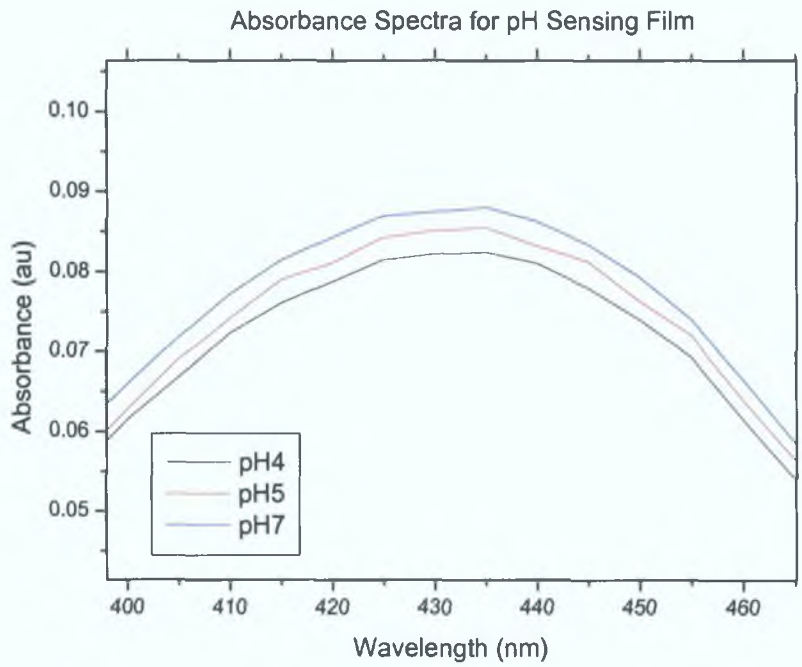

Figure 5.1 Absorbance spectra for pH sensing film

The absorbance of the film for pH solutions from pH4 to pH7 was approximately constant in the near infra-red region of the spectrum. This is shown in Figure 5.2.

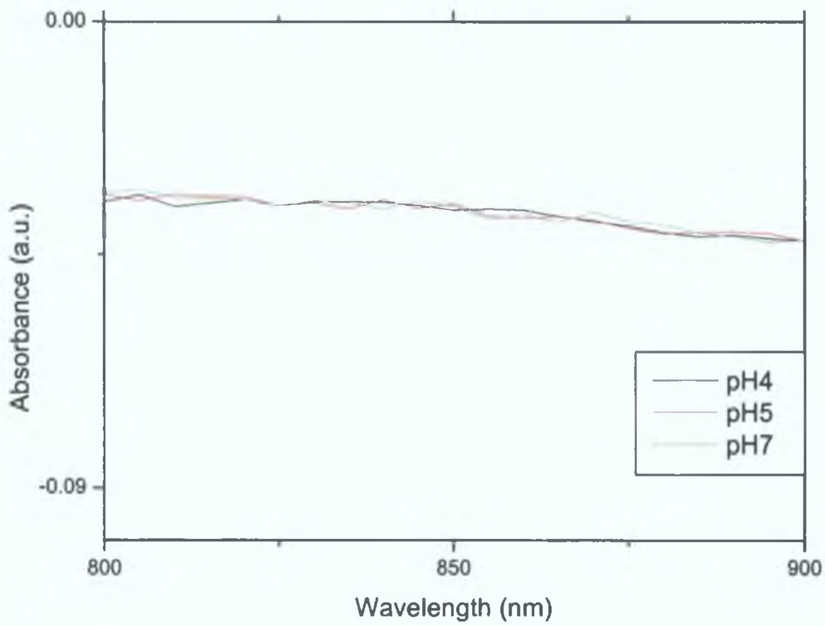

Figure 5.2 Absorbance spectra in IR range

5.4 pH Sensor Outline

Buffer solutions at pH integer values between pH4 and pH8 inclusive were prepared to test the films. The cell shown in Figure 5.3 was used to house the sensing film and the optoelectronic components. The buffer solutions were flowed in turn across the bottom of the slide and voltage readings taken corresponding to the reflected light intensity from the sensing layer in each case under illumination of the blue LED and then the IR LED.

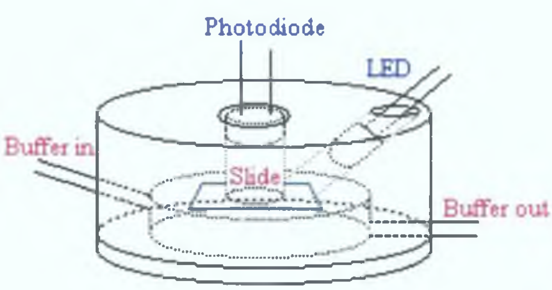

Figure 5.3 pH sensor cell

The IR LED was chosen so that its output spectrum coincided with the region in which the absorbance of the pH sensing film was approximately constant over the range of pH values for which the film was tested.

The blue LED used was the blue component of the tricolour LED that was described in section 4.3 and whose spectral peak coincided with the absorbance peak of the sensor film. This LED was used because the absorbance of the film at the wavelengths emitted by the LED was dependent on the pH of the solution.

Each buffer was left in contact with the film for 10 minutes before the voltage readings were recorded to ensure a complete colour change in the dye. Figure 5.4 is a graph showing the circuit output as a function of pH solution using both blue and IR LEDs.

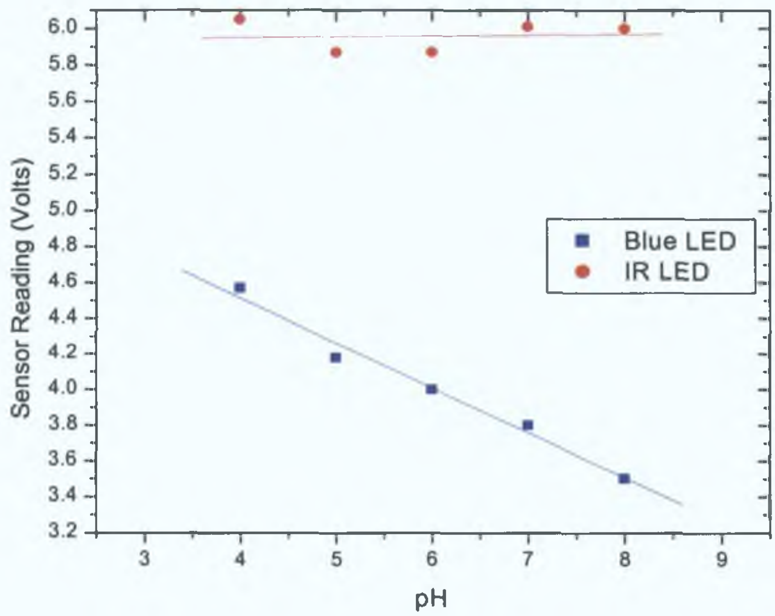

Figure 5.4 Sensor Output (V) v pH

Because the voltage reading over the range of pH solutions does not significantly change under illumination of the IR LED, these readings could be used as a reference As the pH increases, the absorbance of the film increases in the blue visible wavelength range, hence the reflected blue light intensity decreases [6] By comparing the ratio of the two signals, the pH of the solution in contact with the sensing film could be determined

5 5 pH Conclusion

A simple optical arrangement has been implemented to illuminate a pH sensitive film and record the reflected light intensity An NIR and blue visible LED were used, one as a reference and the other to determine film absorbance, which is dependent on pH The reflected intensity from the film decreases as the pH increases, thereby enabling determination of pH of the solution The response time of the sensing film was of the order of minutes This could be controlled by changing the length of time that the films were treated in the NaOH solution, or by changing the molarity of same [5]

5 6 Kubelka-Munk Reflectance Theory

The theory of reflectance devised by P Kubelka and F Munk [7] was initially developed as a method of investigation of paint films The calibration of nickel sulphate sensors described in the following section, is governed by this relation The assumption is made that the particles making up a surface are much smaller than the thickness of the layer being investigated It is also assumed that both scattering and absorbing particles are distributed uniformly throughout the layer In the case of using this method in the analysis of liquid solutions, the solution being scrutinised should be homogeneous Illumination of the solution should ideally employ diffuse monochromatic light and the reflected light should be viewed from an angle such that the specular reflections from the solution or surface should be minimal

When a light beam passes through a liquid solution, the attenuation of the light is expressed by the Beer-Lambert law given by

$$T = \frac{I_t}{I_0} = \exp(-\varepsilon l C)$$

where, T is the transmittance, I_0 is the intensity of the incident light, I_t is the intensity of the transmitted light, ε, the molar absorptivity, C is the concentration of the analyte and l, the thickness

Using reflectance analysis, the reflectance of the diffuse light incident on a surface, where the distribution of the scattering and absorbing particles is uniform, can be expressed by

$$R = \frac{I_r}{I_0}$$

where, R is the fraction of incident light that is reflected from the surface under illumination, I_r is the reflected light intensity and I_0 is the intensity of the incident light

An LED is used in this case to illuminate the solution and a photodiode is employed to measure the reflected diffuse light When light falls on a photodiode, configured in photovoltaic mode, a voltage, V, is produced that is proportional to the intensity of the incident light, i e V = kI, where k is a constant The voltage increases with ıncreasıng lıght ıntensıty In reflectance analysıs, the optıcal densıty, A, of the reflected measurement ıs gıven by

$$A = -\log R$$

and therefore

$$A = -\log\left(\frac{V_0}{V}\right)$$

where V_0 ıs the voltage regıstered from the reflected lıght off a reference whıte surface, or ın thıs case where the concentratıon of the analyte ıs zero

The Kubelka-Munk relatıon used to determıne the concentratıon, C, of an analyte relatıve to the dıffuse reflectance, R, ıs gıven by

$$f(R) = \left[\frac{(1-R)^2}{2R}\right] = \frac{\varepsilon C}{S}$$

where S ıs the scatterıng coeffıcıent of the solutıon [8] A plot of f(R) versus the concentratıon of the analyte therefore should yıeld a straıght lıne graph

5 7 Preparatıon and Measurement of Nıckel Sulphate Solutıons

The preparatıon of the varıous nıckel sulphate solutıons whose concentratıons were to be measured usıng a dıffuse reflectance method ıs outlıned as follows A quantıty of $NiSO_4$ was drıed ın an oven at 150°C for 6 hours Thıs was then ground to a fine powder and drıed at the same temperature for a further 12 hours Thıs ensured that any water present ın the $NiSO_4$ had been evaporated A 1% alcoholıc solutıon (w/v) of Dımethylglyoxıme (DMG) was arranged by dıssolvıng 1g of DMG ın Ethanol

Concentrations of $NiSO_4$ between 100ppm and 800ppm were prepared by adding the respective masses of $NiSO_4$ to a number of 10ml vials. 2ml of Nitric Acid (HNO_3), was added to each vial and the mixture heated to 70°C whilst stirring for approximately 12 hours until dissolution. The contents of each vial were then transferred to 100ml volumetric flasks and the volume in each completed with distilled water [3].

To investigate the prepared samples, a quantity of 2ml was taken from the prepared solution and transferred to the cell, B, shown in Figure 5.5. To this was added 0.15ml of ammonium hydroxide (28%) and then 0.1ml of DMG in ethanol. On addition of the DMG the solution turned a pink colour. The cell containing this solution was covered with the LED and photodiode housing, A, as shown in Figure 5.5, and the voltage reading recorded while the solution was being illuminated by a red LED and then by a green LED. This was repeated for all the prepared nickel sulphate solutions. The cell, A, was fabricated from white nylon, whilst the housing, B, was made from black plastic to exclude as much ambient light as possible.

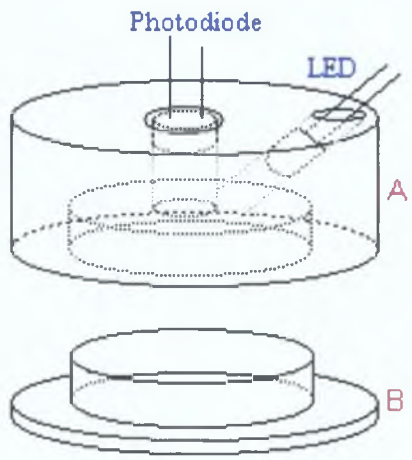

Figure 5.5 Cell used for diffuse reflectance measurements

The circuit used to detect the signal is based on an amplified and filtered current to voltage converter as shown in Figure 5 6

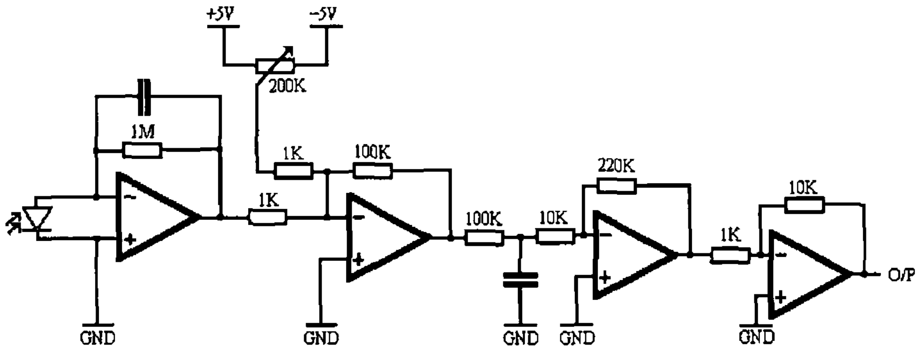

Figure 5 6 Light intensity detection circuit

The LED used to illuminate the various samples was the tricolour LED introduced in the previous chapter Figure 5 7 shows the voltage readings for the samples investigated under illumination of both the green and red spectral components of the LED The voltage decreases with increasing nickel sulphate concentration, indicating that the reflected light intensity is inversely proportional to the analyte concentration

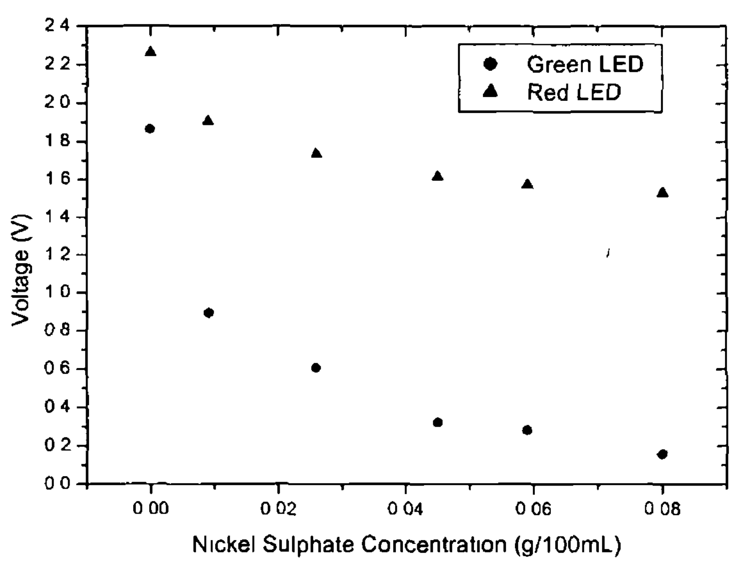

Figure 5 7 Relationship between sensor output and $NiSO_4$ concentration

Using the voltage readings taken while illuminating the samples with the red spectral component of the LED, a graph of the Kubelka-Munk relation, f(R), was plotted against the nickel sulphate concentration [3] A straight line graph was observed for low concentrations of between 0 and 0 08g/100ml, as shown in Figure 5 8 An R value of 0 99256, from a linear fit of the data, confirms that there exists a linear relationship between the reflectance and $NiSO_4$ concentration This indicates that the procedure discussed can be used as a reliable method in the measurement of $NiSO_4$ concentrations in a water solution, using the relation

$$R = \frac{I_r}{I_0} = R_W \exp(-kC)$$

where, R_W is the reflectance from a reference white surface and k is a proportionality constant

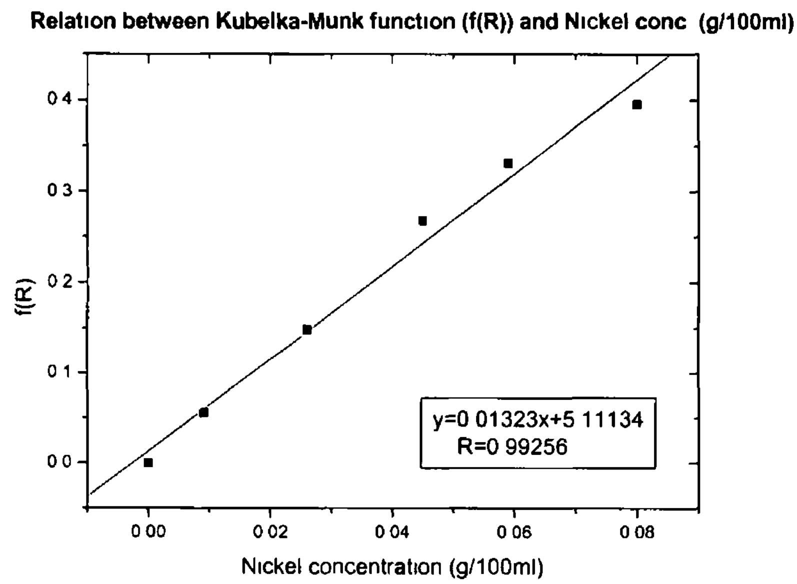

Figure 5 8 Relation between Kubelka-Munk function and $NiSO_4$ concentration

5.8 Summary of Nickel Sulphate Work

A simple method of measuring $NiSO_4$ concentrations has been established using diffuse reflectance measurements and low cost electronic components and circuitry. A suitable reaction cell has been made. Initially, the determination of nickel sulphate concentration was to be undertaken using the same principles as those employed in the pH sensor. This involved determining a region in the absorbance spectrum where the absorbance was constant for changing analyte concentration. Figure 5.9 shows the transmission spectra for different concentrations of nickel sulphate in solution.

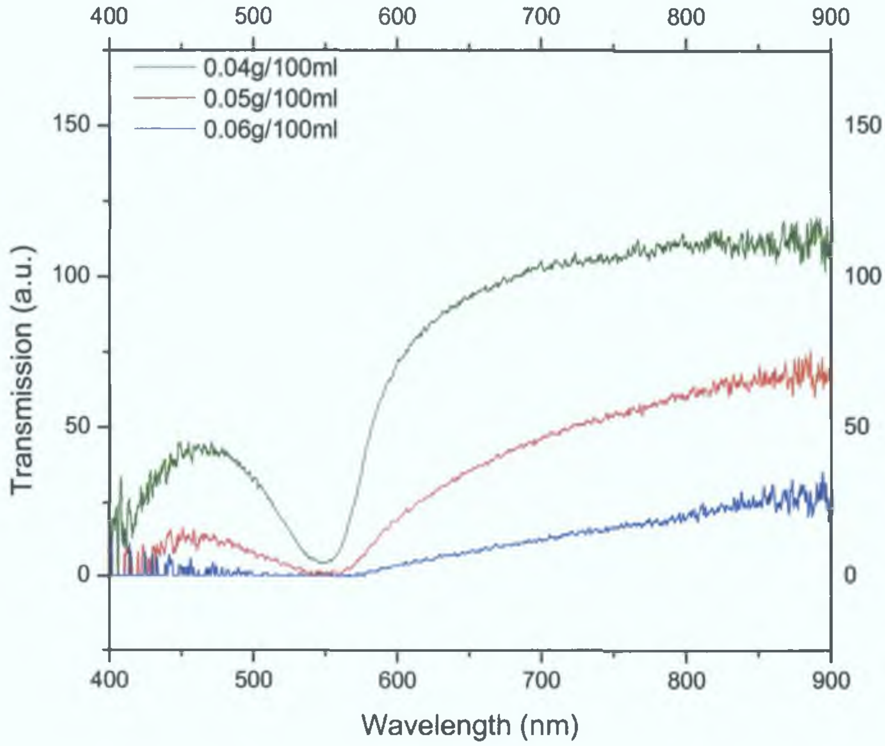

Figure 5.9 Transmission Spectra for $NiSO_4$ solutions

The results observed show that there is no region where the transmission, and therefore the absorbance, is the same for different concentrations This proves that the method of referencing employed in pH sensing cannot be applied in this case Hence, only simple, non-referenced colorimetric analysis methods can be used to determine the concentration of $NiSO_4$ in this example

5 9 Conclusion

The colour sensor outlined in the previous chapter has been applied in the role of pH sensing and the colour monitoring of solutions (as a surrogate for environmental monitoring) It has been shown that the method employed in the determination of the pH of different solutions was not suitable in the sensing of nickel sulphate These sensors could be used as a demonstration of curriculum related phenomena in the classroom or as tools in educational projects

As in any optical sensor, parameters such as temperature and ambient light may have an adverse effect on accurate measurement When using an LED, the intensity and spectral distribution may vary with temperature To overcome these effects, a circuit employing a temperature compensation module could be developed Ambient light effects on the sensor output could be negated by using lock-in techniques

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Chapter 6

Conclusions

The work presented in this thesis described the development of various optical sensors and their incorporation into sensing systems that could be used in an educational role The hardware and software issues of the two sensing platforms have been discussed and their attributes outlined

The oxygen sensor has been demonstrated in a classroom environment At the time of writing, the carbon dioxide sensor had not been interfaced with either sensing platform, although there is no reason why this cannot be achieved in the future A colour sensor was also fabricated for use with the RCX This was achieved using basic low cost optoelectronic components and circuitry

An absorption based pH sensor capable of detecting pH in the range from pH4 to pH8 has been demonstrated By using two spectrally different LED's, i e one visible and one NIR, the sensor has an in-built reference To make the pH sensor suitable as an educational tool, the sensing layer must be housed in a light proof casing that is permeable to liquid, so that the solution whose pH is being determined may contact the sensing layer This configuration would allow the ingress of the solution whose pH was being investigated, whilst excluding ambient light Again, lock-in circuitry could be employed to nullify the need for the above arrangement

The process by which the concentration of an analyte in solution could be determined by diffuse reflectance was also investigated In particular, nickel sulphate was used as a proof of principle It was found that this process was an unsuitable application for the colour sensor because there was no suitable region in the absorbance spectrum where a reference measurement could be obtained The chemistry involved in preparing the solution for interrogation makes this sensor inappropriate as a classroom based experiment, although this could be demonstrated in a controlled laboratory setting

Future work could involve the incorporation of the carbon dioxide sensor into classroom experiments The employment of this sensor in conjunction with the oxygen sensor has uses in experiments that demonstrate photosynthesis and respiration To take this project further, the integration of the developed colour based sensors into classrooms could be undertaken

Appendix A

Code used for Cricket to communicate with Oxygen Sensor·

```
[const @ 0]
[const timer 1]
[const pcl 2]
[const status 3][const c 0][const z 2][const bank2 5]
[const status1 83]
[const @@ 4]
[const porta 5][const porta-ddr $85]
[const portb 6][const portb-ddr $86]

[const option 1]
[const counter $20]
[const bus-data $21]
[const bus-port portb][const bus 0]
[const bus-port-ddr portb-ddr]
[const temp $22]
[const adcon $1f]
[const adresh $1e}
[const percent $23]
[const adcon1 $9f]
[const adresl $9e]

start
        [bsr io-init]

loop
        [bset 1 portb]
        [bset 2 portb]
        [ldan 5][bsr big-delay]

        [btss bus bus-port]
```

```
        [bsr maın]
        [bset z adcon]
loop1

        [btsc z adcon][bra loop1]
        [bclr 1 portb]
        [bclr 2 portb]
[ldan 5][bsr bıg-delay]
        [btss bus bus-port]
        [bsr maın]
        [bset z adcon]

loop2
        [btsc z adcon][bra loop2]
        [bra loop]

maın
        [bsr btyı20]
        [btss c status][bra loop]
        [lda bus-data]
        [xorn $94]
        [btss z status][bra loop]
        [clra]
        ,[bset bank2 status]

        [clra]
        [lda adresh]
        ,[bclr bank2 status]

        ,BRANCH TO SUBROUTINE 'TABLE' TO GET %AGE O2
        [bsr table]
        [sta percent]
        [sta bus-data]
        [bsr bus-tyo]
```

```
        [bra loop]                       ; and loop!

; the form of a byte is
; 100 usec low time (to allow for interrupt latency)
; start bit(1) + 8 data bits + stop bit (0 for cmnd 1 for data)
; each bit is exactly 10 usec long. The bits should be sampled in the
; middle (this code samples between 4 and 7 usec in)
;
; return a byte in bus data
; also return the inverse of the stop bit in the carry
; commands have a 0 stop bit -> carry set
; data has a 1 stop bit -> carry clear

bus-tyi [btsc bus bus-port]
        [bra bus-tyi]
btyi20  [btss bus bus-port][bra btyi20]          ; wait for sync edge
        [ldan 8][sta counter]
        [bsr an-rts]
btyi30  [nop][nop][nop]
        [ror bus-data]
        [bclr 7 bus-data]
        [btsc bus bus-port]
        [bset 7 bus-data]
        [decsz counter]
        [bra btyi30]
        [bsr an-rts][nop]
        [bset c status]
        [btsc bus bus-port][bclr c status]       ; no stop bit -> carry clear
an-rts
        [rts]

; send a byte down the bus. the "stop" bit is always 0
; of a data byte
; input in bus-data
```

```
bus-tyo [ldan bus-port-ddr][sta @@]
        [bclr bus bus-port][bclr bus @]
        [ldan 24][bsr delay-loop]       , give receiver a chance to sync
        [bset bus bus-port]             , start bit
        [ldan 8][sta counter]
        [bsr an-rts][nop][nop]
btyo50          [ror bus-data]
        , bit -> carry
        [bclr bus bus-port]
        [btsc c status]
        [bset bus bus-port]
        [nop][nop][nop]
        [decsz counter]
        [bra btyo50]
        [nop][nop]
        [bset bus @]
        [rts]
big-delay
        [btss bus bus-port][bsr main]
        [sta temp]
        [ldan 33][bsr delay-loop]
        [btss bus bus-port]
        [bsr main]
        [lda temp]
        [addn -1][btss z status][bra big-delay]
        [rts]

delay-loop
        [addn -1][btss z status][bra delay-loop]
        [rts]
io-init
        [bset bank2 status]
        [bset 0 porta]
```

```
        [bclr 1 portb]
        [bclr 2 portb]
        [ldan $81]
        [sta adcon1]                    ,set adcon1 as 10000001
        [clra]

        [bclr bank2 status]
        [ldan $1]
        [sta adcon]                     ,set up adcon0 as 10000001
        [clra]

        [ldan 60][sta counter]

ıoın20
        [clra]
        [bsr delay-loop]
        [decsz counter][bra ıoın20]
        [rts]

        ,SUBROUTINE TO FIND CORRESPONDING O2 %AGE
        ,load workıng regıster ınto program counter
        ,usıng the command   addwf PCL,F

table
        [ldan 0]
        [andn $0f]
        [lda adresh]
        [addm pcl]
        [rtv 255]       ,0
        [rtv 254] [rtv 253] [rtv 252] [rtv 251]
        [rtv 250]
        [rtv 249]
        [rtv 248]
        [rtv 247]
```

```
[rtv 246]
[rtv 245]       ,10
[rtv 244]
[rtv 243]
[rtv 242]
[rtv 241]
[rtv 240]
[rtv 239]
[rtv 238]
[rtv 237]
[rtv 236]
[rtv 235]       ,20


[rtv 9]
[rtv 8]
[rtv 7]
[rtv 6]
[rtv 5]         ,250
[rtv 4]
[rtv 3]
[rtv 2]
[rtv 1]
[rtv 0]         ,255
```

Code used in RCX Oxygen Sensor

```
,Modulate pin 1 and 2 of port b in 16f872 for
```

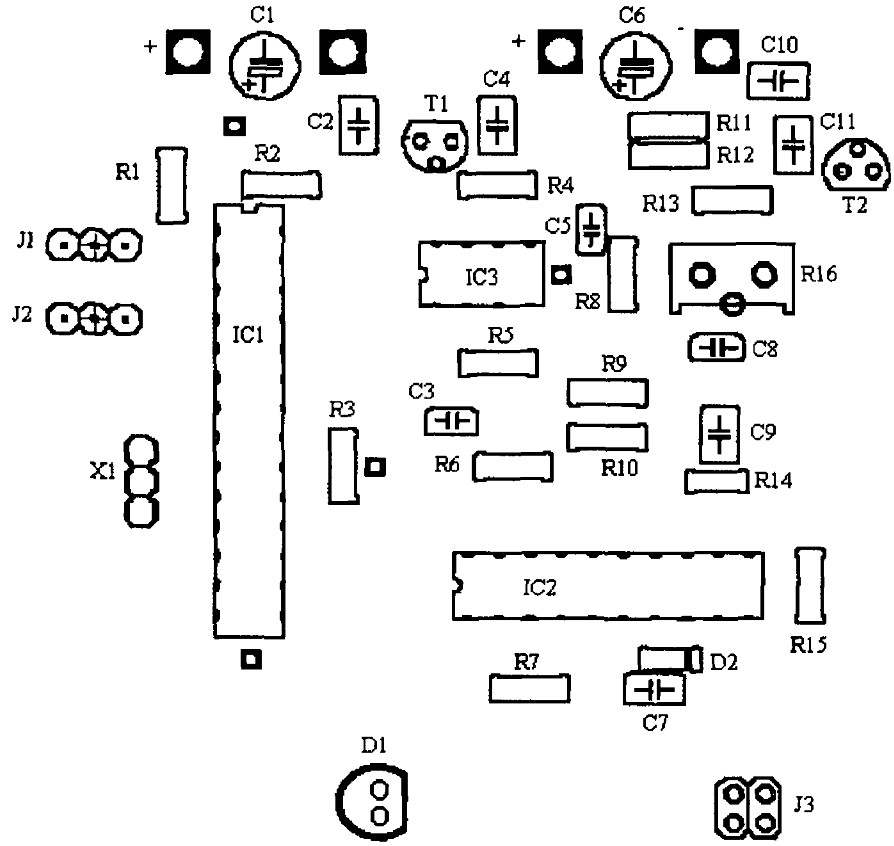
```
,O2 sensor for use with RCX  Freq is 769Hz


        [const @ 0]
        [const timer 1]
        [const pcl 2]
        [const status 3][const c 0][const z 2][const bank2 5]
        [const @@ 4]
        [const porta 5]
        [const portb 6]
[const option 1]
        [const temp $0c]

start   [bset bank2 status]
        [bclr 0 portb]
        [bclr 1 portb]
        [bclr 2 portb]
        [bclr bank2 status]

loop
        [bset 1 portb]
        [bset 2 portb]
        [ldan 1][bsr small-delay]
        [bclr 1 portb]
        [bclr 2 portb]
        [ldan 1][bsr small-delay]

        [bra loop]

small-delay

        [sta temp]
        [ldan 160][bsr delay-loop]              ,26
        [lda temp]
```

```
        [addn -1][btss z status][bra small-delay]
        [rts]

big-delay

        [sta temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [ldan 0][bsr delay-loop2]
        [lda temp]
        [addn -1][btss z status][bra big-delay]
        [rts]

delay-loop

        [addn -1][btss z status][bra delay-loop]
        [rts]

delay-loop2

        [addn -1][btss z status][bra delay-loop]
        [rts]
```

Appendix B

Oxygen Sensor Board Layout

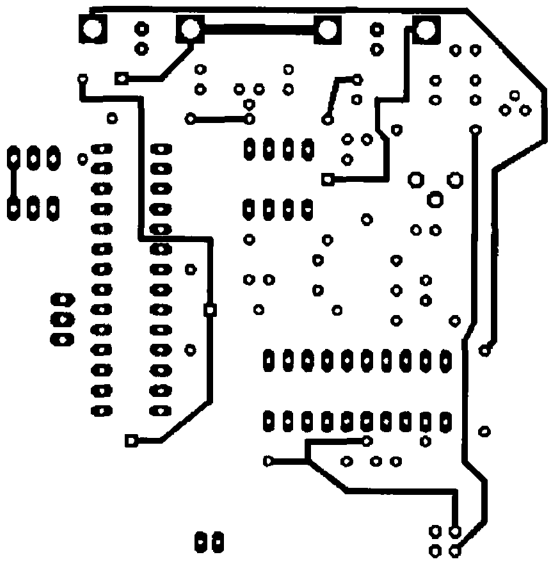
Component Layout



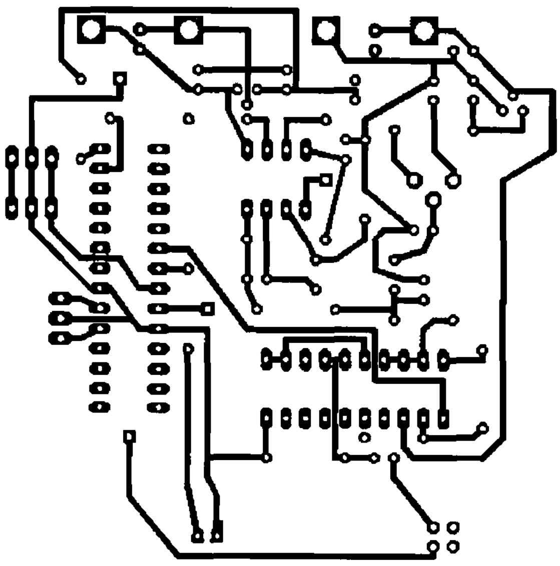
Component Values

Component	Value	Component	Value
IC1	PIC16F872	C2-5,7,9-11	100nF
IC2	AD630	C8	22nF
IC3	CA3240E	R1,3,10	10K
X1	4MHz crystal	R2	1K
J1/J2	3 pin connector	R4,7,8,14	220K
J3	1053odal	R5,9	1M
D1	NSPB500s LED	R6	910K
D2	2 1V zener	R11	2K
T1	78105	R12,13	6 2K
T2	79105	R15	50K
C1/C6	47uF	R16	10K pot

Top layer tracks and pads



Bottom layer tracks and pads



Appendix C

Programme code to recognıse 5 colours

```
#define Color SENSOR_2
#define ScaleFactor 38
#define Offset 1023
#define Threshold 1015

ınt Red, Green, Blue,
ınt RGB, RGB1,
ınt R1, B1,
task maın ()
{

   SetSensor (Color, SENSOR_LIGHT),
   SetSensorMode (Color, SENSOR_MODE_RAW),

   InıtColSensor(),
   //OnFwd(OUT_A),
   //OnFwd(OUT_C),
    SetPower(OUT_A+OUT_C,0),
    OnFwd(OUT_A+OUT_C),
   for (,,)
     {
       //SetOutput(OUT_A + OUT_C, OUT_On),
       //OnFwd(OUT_A+OUT_C),
       //OnFor(OUT_A+OUT_C, 10),  ****
       //OnFor(OUT_C, 10),
        Waıt (10),
       //SetOutput(OUT_A + OUT_C, OUT_Off),
        ReadColor(),
        R1=Red*10,
        B1=Blue/10,
```

```
      RGB=R1/B1,
  if(RGB > 90 && RGB < 110)   //red
  {
     PlayTone(440, 50), // Play 'A' for one half second
  }

  if(RGB > 110 && RGB < 119)  //green
  {
     PlayTone(470, 50), //
  }

  if(RGB > 135 && RGB < 150)   //blue
  {
     PlayTone(490, 50), //
  }

  if(RGB > 125 && RGB < 135)   //purple
  {
     PlayTone(520, 50), //
  }

  if(RGB > 119 && RGB < 125)  //pink
  {
     PlayTone(550, 50), //
  }


      // Motorise(),

 }
}

 void InitColSensor ()
{
```

```
  while (Color < Threshold)
 {
  NextColor (),
 }

}

// Reads all three color components and place them in Red, Green and Blue
variables
sub ReadColor ()
{
   NextColor (),
   Wait (10),
   Red=Color,
   Wait (10),
   NextColor (),
   Wait (10),
   Green=Color,
   Wait (10),
   NextColor (),
   Wait (10),
   Blue=Color,
   Wait (10),
   //Skip Dummy
   NextColor (),
   //if (Color > Threshold)  InitColSensor(),
}


void NextColor ()
{
   SetSensor (Color, SENSOR_LIGHT),
   SetSensorType (Color, SENSOR_TYPE_TOUCH),
   SetSensor (Color, SENSOR_LIGHT),
```

```
  SetSensorMode (Color, SENSOR_MODE_RAW),
}

sub Motorise()
{

 }
```

List of Publications and Conference Presentations:

Oral Presentations:

"Optical Sensing Systems for Primary Level Science Education" **A Markey**, B Tyers, R Shepherd, A K McEvoy, B D MacCraith, B Mikhak, C Strohecker, *Opto-Ireland Conference*, Galway, September 2002

Conference Publications:

"Optical Sensing Systems for Primary Level Science Education" **A Markey**, B Tyers, R Shepherd, A K McEvoy, B D MacCraith, B Mikhak, C Strohecker, *Opto-Ireland Conference,* Galway, September 2002

"Optical Sensing Systems for Primary Level Science Education" **A Markey**, C Smyth, A K McEvoy, E O'Brien, B Tyers, B D MacCraith, B Mikhak, C Strohecker, *SAXII Conference*, Limerick, September 2003

Poster Presentations:

"Optical Sensing Systems for Primary Level Science Education" **A Markey**, C Smyth, A K McEvoy, E O'Brien, B Tyers, B D MacCraith, B Mikhak, C Strohecker, *SAXII Conference*, Limerick, September 2003
(Poster presentation – Awarded Best Exhibited Paper by SFI)

"Optical Sensing Systems for Primary Level Science Education" **A. Markey**, C Smyth, A K McEvoy, E O'Brien, B Tyers, B D MacCraith, B Mikhak, C Strohecker, *BOC Gases Poster Competition, DCU, April 2004*