

A MICROCOMPUTER COMPENSATED SENSOR  
FOR SULPHUR-DIOXIDE

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## ABSTRACT

This thesis begins with some illustrative background material concerning the distribution, behaviour and chemical analysis of  $\text{SO}_2$ . The potential advantages offered by sensor systems and remote monitoring when used in conjunction with or instead of conventional laboratory analysis are noted.

A gas sampling system for generating  $\text{SO}_2$  atmospheres was developed using a dispersive infra-red spectrometer as a means to detect  $\text{SO}_2$ . This technique allowed gas samples to be prepared independently of the piezoelectric crystal sensor (PZC). Sorption of  $\text{SO}_2$  on the apparatus surfaces was observed and the kinetics of desorption were investigated using infra-red spectrometry.

A description of the theory underlining the use of PZCs as mass transducers and as gas sensors is included. The behaviour of uncoated PZCs under humid conditions was investigated and the response of coated PZC sensors to humidity is discussed. A temperature compensation technique was developed to improve the performance of PZC sensors for the detection of  $\text{SO}_2$ .

The apparatus used includes a gas cell to house the PZC, a PZC oscillator and a temperature monitor. The data acquisition system used was a purpose-built interface rack operating under microcomputer control. The data was stored on floppy disc. The advantages that such a sensor gives over existing methods, with particular reference to microcomputer control and the output of data, are presented. As an illustration of the technique, another

microcomputer was used to represent the measured response with respect to temperature of an uncoated PZC by a Fourier series equation and to compensate the PZC for this temperature response.

Procedures for coating the PZCs with N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine (Quadrol), in order to adsorb SO<sub>2</sub> specifically, are discussed. Calibrations of the response of a PZC sensor to an injection of a small sample containing SO<sub>2</sub> into a flowing gas stream were carried out. The behaviour of coated and uncoated PZCs to temperature was investigated prior to the automatic compensation of measurements of SO<sub>2</sub> concentration with respect to temperature.

The nature of the calibration and the result of temperature correcting the PZC sensor suggest that the SO<sub>2</sub> on quadrol adsorption process follows the Freundlich isotherm. General suggestions are made about the implementation of multi-parameter, run-time corrections for sensors. More specific recommendations are made concerning the further development of PZC sensors particularly their correction for temperature, humidity and chemical interference.

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**DEDICATION**

**TO GRANDPA**

**CHAPTER 1**  
**INTRODUCTION**

In recent decades there has been growing concern over the potential hazards of all substances. This has occurred within a wider appreciation of the need to consider industrial health and safety, the environment, land management, national health programs and international aid. Most chemicals have been found to be toxic given a sufficiently high concentration and it is now recognised that even trace amounts of some have an adverse effect on ecosystems and the environment. The problem of analysing these chemicals is compounded by the continual massive growth in the number of known chemicals, all of which are potentially harmful.

Within industry the need to maintain competitiveness has resulted in an increase in the monitoring and control of process stream environments by selective chemical analyses. This has allowed better regulation of stream composition and hence more economic operation.

These initiatives have generated a need for better analytical methods, methods that are more accurate, sensitive and selective as well as being faster, free from interferences and from error. The older 'wet' chemical methods are being replaced by new instrumental methods which are more economic and can detect new compounds. There is also a need for sensors for remote and personal monitoring.

## 1.1 SULPHUR DIOXIDE

### Production and Uses

Sulphur dioxide gas ( $\text{SO}_2$ ) is widespread in industrial use, it is produced by oxidising sulphur containing minerals. The most important use of  $\text{SO}_2$  is as an intermediate in the production of sulphuric acid. It is also an intermediate in the production of sulphites, thiosulphates, carbon disulphide and sulphur containing organic compounds.  $\text{SO}_2$  is used as a reducing agent in the sugar, leather, paper and glue industries.  $\text{SO}_2$  is used as a fungicide and a bactericide and at low concentrations is a widely used preservative for foods. It is more toxic to undesirable micro-organisms than to desirable ones and so is used extensively in the brewing industry.

Dry liquid  $\text{SO}_2$  is not a reducing agent but is a refrigerant and a useful non-aqueous solvent for oil refining, preparative reactions and nuclear magnetic resonance spectroscopy. Other industrial processes that use  $\text{SO}_2$  are starch production, non-ferrous metal refining and leaching ores.

### Pollution

$\text{SO}_2$  is an abundant atmospheric pollutant. In certain areas this is largely due to combustion, primarily of the fossil fuels but also of wood, tobacco, and other biomass. Thus the sulphur which is essential to life is converted into a hazardous species.

Other atmospheric pollution consists of the fumes extracted from

and the effluents discharged by all activities which either use or produce  $\text{SO}_2$ . In some of the processes such as oil refining and the combustion of fossil fuels a proportion of waste  $\text{SO}_2$  can be recovered by flue gas desulphurisation.

Considerable quantities of  $\text{SO}_2$  are released into the workplace environment during these processes. In all of them there is potential for on-line  $\text{SO}_2$  monitoring and monitoring of the industrial environment.

The remainder of the atmospheric  $\text{SO}_2$  burden comes from natural sources of which there are three main types: biogenic, volcanic and marine. These sources mainly produce reduced sulphur species:  $\text{H}_2\text{S}$ ,  $\text{COS}$ ,  $\text{CS}_2$ , dimethyl sulphide and dimethyl disulphide.  $\text{SO}_2$  results from their air oxidation.

$\text{SO}_2$  is rapidly oxidised in the upper atmosphere to  $\text{SO}_3$  which combines with atmospheric moisture to form dilute sulphuric acid mist that further reacts to form sulphate particles or falls back to earth as acid rain.

This characteristic oxidation and variable meteorological conditions causes a wide range of sub-ppm  $\text{SO}_2$  concentrations to be observed over urban areas. Wherever  $\text{SO}_2$  pollution is a problem, visibility may be expected to decrease as relative humidity increases due to scattering by aerosols.

#### Damage to Property

The release of  $\text{SO}_2$  into the atmosphere accelerates the weathering

of materials such as steel, stone and bronze. Carbonaceous materials used in buildings and sculptures are particularly at risk. In the presence of moisture  $\text{CaCO}_3$  is changed to  $\text{CaSO}_4$ , the volume of which is almost twice that of the original carbonate. Cracking and disintegration of the surface layers results. This process disfigures marble, limestone, carbonated statuary and ancient murals painted on lime mortar, which becomes carbonated by the action of air.

#### Toxicity

$\text{SO}_2$  is an irritant gas particularly of the respiratory tract and its effect is due to the formation of sulphurous and sulphuric acids on contact with moisture. Acute poisoning is characterised by intense irritation and difficulty with breathing. Chronic  $\text{SO}_2$  poisoning causes and aggravates respiratory complaints [1.1].

#### Effect on Vegetation

Chronic damage by  $\text{SO}_2$  is being inflicted on agricultural, forest and ornamental vegetation with a resultant economic loss. The plants most sensitive to  $\text{SO}_2$  are alfalfa, the grains, cotton and others that have a high rate of physiological activity in their leaves with a correspondingly high rate of gaseous exchange. Plants are more susceptible in spring and early summer when under favorable growth conditions the stomata are open for longer periods as the toxicity of  $\text{SO}_2$  is a function of the rate at it is absorbed.

## 1.2 EXISTING METHODS FOR SULPHUR DIOXIDE DETERMINATION

This is an overview of  $\text{SO}_2$  determinations that are of interest in four respects. Firstly, as the existing methods used by industry upon which sensors will have to enhance and improve. Secondly, as methods which can be used for absolute calibration of sensors in different environments. Thirdly, to show the reactions and side reactions which may interfere with the  $\text{SO}_2$  determination under certain conditions and, finally, as chemistries of  $\text{SO}_2$  towards which novel coating materials and interactions of sensors could possibly be tailored.

Most chemical methods for  $\text{SO}_2$  determination rely on one of three principles. Namely, acid-base, redox or spectrometric determination. There are also a number of instrumental methods.

In most cases gas phase  $\text{SO}_2$  must first be absorbed into solution and this takes considerable time, in some cases up to 48 hours [1.2] depending on the concentration. Other disadvantages are that these methods give only an average concentration over the sampling time and during adsorption a number of side reactions can occur leading to errors. Most absorption procedures are either specific to, or have only been used with, particular determination methods and these are described in context. There is however one absorption procedure that has been used with many determinations and will, therefore, be described first.

$\text{SO}_2$  can be absorbed from a sample by passing the gas through water via a bubbler. A novel conductrimetric sensor has been described in which a gas-porous membrane separates the gas from

de-ionised water [1.3]. More usually dilute alkali solution is used, but as  $\text{SO}_2$  is absorbed the pH falls and this could affect the absorption efficiency. It is better, therefore, to absorb in a buffer solution [1.4]. However, sulphite solutions formed when  $\text{SO}_2$  is absorbed in water or alkali are unstable and during the sampling process a substantial amount is oxidised by air [1.5].

This oxidation can be overcome by absorbing in formaldehyde solution [1.6] which gives rise to the stable hydroxymethylsulphonate ion. However low sampling rates must then be used to avoid frothing and foaming.

Not only is this a general purpose absorption procedure but in addition equivalent standard solutions can be prepared easily in the laboratory using sodium metabisulphite or sodium hydroxymethylsulphonate.

#### Acid Base Methods

The alkali method has been widely used in air pollution studies. Air is passed through standard dilute alkali and the excess alkali is determined by titration. Although rapid, the method is subject to considerable error in certain environments because all acidic components such as hydrogen chloride and hydrogen fluoride interfere positively and ammonia negatively. An alternative is to measure the sulphite directly using ion chromatography [1.6]. A gas sensor has been developed in which  $\text{SO}_2$  diffuses through a permeable silicone-rubber membrane into a thin film of electrolyte containing bisulphite ions. The subsequent increase

in pH is sensed by an internal electrode [1.7].

As an alternative to eliminating oxidation one can promote it!  $\text{SO}_2$  reacted with dilute hydrogen peroxide is oxidized under neutral or acidic conditions to sulphuric acid, under alkali conditions to sulphate. For example a passive monitoring badge has been used in which  $\text{SO}_2$  is absorbed in de-ionised water and then reacted with peroxide [1.4]. The sulphate solution can then be determined by a number of methods: ion chromatography, titrimetry, gravimetry or conductrimetry.

Unfortunately, any acid or alkaline gas interferes in most cases. A prefilter can remove soluble salts and sulphuric acid mist from gas phase samples, however, many filter materials also remove most of the  $\text{SO}_2$  [1.8] and if it is permitted to collect any quantity of material, the resulting filter cake may remove  $\text{SO}_2$  as well. Since  $\text{NO}_2$  is only slowly soluble in water there is more chance of its interference with more efficient gas collectors. For example the addition of a second identical stage capable of absorbing 85.8% of the incoming  $\text{SO}_2$  and 28.6% of the incoming  $\text{NO}_2$  will increase the overall collection efficiencies to 98.0% and 49.0% respectively and decrease the ratio of  $\text{SO}_2$  to  $\text{NO}_2$  from 3 : 1 to 2 : 1. The same argument applies to lowering the rate of sampling.

Measurement of changes in conductivity have been employed chiefly in auto-analysers for the measurement of low concentrations of  $\text{SO}_2$  in air. The gas commonly passes over a countercurrent of sulphuric acid/hydrogen peroxide absorber which passes to a

small volume flow conductivity cell to give a rapid measurement [1.9]. Alternatively, air is blown in a fine jet over the surface of a small volume conductivity cell which is replenished periodically [1.10].

Conductrimetry is interfered with by anything which can dissolve in water or weak acid to yield ions. Because of this lack of specificity a knowledge of the levels of other contaminants is necessary to judge the  $\text{SO}_2$  level. Many of these problems can be overcome by using ion chromatography [1.4].

An International Standard has been described in which hydrogen peroxide solution is used as the absorbent in the determination of  $\text{SO}_2$  with the resulting sulphuric acid being determined by titrimetry using either an indicator or a potentiometric end-point detection [1.11]. The titrimetric method, when combined with a number of distillation procedures [1.6, 1.12, 1.13, 1.14, 1.15] has become a standard method for the determination of free and bound  $\text{SO}_2$  in foodstuffs.

The gravimetric determination of  $\text{SO}_2$  using absorption in alkaline hydrogen peroxide has also been used for foodstuffs [1.14]. Barium sulphate is precipitated by the addition of barium chloranilate. However interference from particulate sulphate and  $\text{SO}_3$  as well as time consuming drying have limited the use of this determination although it is preferred in the presence of oxides of nitrogen. An alternative method in which the sulphate ions are precipitated by barium perchlorate and the excess ions are determined by the thorin spectrophotometric method has been

published as a British Standard [1.2].

### Redox Methods

In the iodine oxidation technique, iodine solution functions as both oxidant and absorbent. The  $\text{SO}_2$  is commonly trapped in an excess of iodine solution and the remaining iodine is then back-titrated with standard sodium thiosulphate using starch indicator [1.13]. Other iodimetric titrations involve adding iodine to a starch-iodine collecting solution to match the original colour [1.15] and drawing the air sample through a starch-iodine solution until the blue colour is just removed.

There are several disadvantages to using iodine as absorber. Some iodine is invariably lost by evaporation into the passing air stream, therefore a blank is necessary which is somewhat dependent on temperature. Alternatively, about 25% potassium iodide is added to stabilize the absorber but then some of this iodide can be air oxidized to iodine.

Alternatively, absorption takes place in alkali, which is then acidified and the liberated sulphurous acid determined with standard iodine solution. The iodine titration to a starch end-point has been used directly analyse  $\text{SO}_2$  in wine, but, a more accurate end-point has been obtained potentiometrically [1.13].

An alkali absorbed  $\text{SO}_2$  solution or wine can be run into acidified iodine solution and titrated with thiosulphate or acidified with hydrochloric acid and the aqueous  $\text{SO}_2$  titrated with iodate. The

advantage of these methods is the stability of the standard solution compared with an iodine solution that must be standardised daily.

Dilute permanganate solution has been used to absorb and oxidise  $\text{SO}_2$ , acidified potassium dichromate solution also quantitatively oxidises  $\text{SO}_2$  and can be used for its determination.

These redox methods suffer positive interference from other reducing substances in the atmosphere (hydrogen sulphide, organics etc) and negative interference from oxidising agents (eg free halogens,  $\text{NO}_2$ , organic peroxides and ozone). The interference of  $\text{NO}_2$  will again depend on the collection efficiency. The method is perhaps preferable in the presence of  $\text{SO}_3$ .

$\text{SO}_2$  has also been determined electrochemically, which is free from many interferences affecting other redox methods, for example amperometrically by differential pulse polarography [1.16].  $\text{SO}_2$  has been determined by flow injection analysis using both potentiometric determination by an ion-selective electrode [1.17] and amperometric detection [1.18]. In the latter method the  $\text{SO}_2$  was oxidised with a glassy-carbon electrode in the wall-jet configuration and determined in wines. A diffusion cell pulse-damped a substantial background noise and eliminated most interferences increasing the detection limit. However, the electrode was only stable for one day at a time.

### Colorimetry and Spectrometry

Measuring the absorption coefficient of a coloured sulphonate in the range 560-580 nm is the only inherently specific method for determining  $\text{SO}_2$ . However, interferences can still occur because of side reactions.

One such method uses the Schiff reaction which has been developed into the most sensitive 'wet chemical' method for the determination of  $\text{SO}_2$  free from the interference of  $\text{SO}_3$  and  $\text{H}_2\text{S}$ . Urone and Boggs [1.19] describe the colorimetric method, the reagent is fuchsin bleached with acid and having formaldehyde added.  $\text{SO}_2$  is absorbed in alkali and on adding the reagent gives a red-violet colour. However, anionic wetting agents interfere in the reaction; their presence may be detected because they react slowly with the fuchsin reagent and do not depend on the presence of formaldehyde. Thiols also interfere. The problem of protecting the collected sulphite from air oxidation long enough to permit the final reaction is a disadvantage and was investigated.

It had been suggested that the sulphite complex with sodium tetrachloromercurate(II) was highly resistant to oxidation. West and Gaeke [1.20] absorbed  $\text{SO}_2$  in this solution as a stable non-volatile complex, which was initially thought to be disulphito-mercurate(II), but subsequently proved to be dichlorosulphito-mercurate(II). However, the sulphite complex is broken down on addition of the colour developing reagent showing that the coloured sulphonate is more stable. Thus  $\text{SO}_2$  is still able to participate in the Schiff reaction. The advantage of this

collection method is that the sampling rate may be as high as 5 l/min, with no loss due to decreased efficiency of absorption. They also found that hydrogen sulphide precipitates mercuric sulphide, which must be removed by filtration or centrifugation.

Para-rosaniline hydrochloride was found by West and Gaeke to form a more sensitive and more stable colour developing reagent than basic fuchsin, which is an impure mixture of rosaniline and para-rosaniline hydrochlorides. Nitrogen dioxide interferes if its concentration exceeds 2 ppm and colour development is prevented completely if more than 8 ppm is present. Ozone also interferes as do certain particulates, notably iron, which can be removed by filtering the incoming air, but this produces the same problem of caking as above. These principles have been used as the basis for automatic analysers for the continuous analysis of atmospheric SO<sub>2</sub>. Numerous modifications in the colorimetric reagent have been made subsequently. The addition of N,N-dimethyl formamide makes the colour more intense [1.21]. It was shown that the interference of nitrogen dioxide could be reduced by treatment with a number of substances, but that the best results appeared to be achieved with sulphamic acid [1.22].

A passive monitoring badge has been developed using this procedure in which the gas permeates through a silicone membrane into the absorbing solution [1.4]. The captured SO<sub>2</sub> was later determined by the West-Gaeke procedure. A number of flow colorimeters have been developed using simplified reaction schemes. The method has recently been applied to the direct determination of SO<sub>2</sub> in foodstuffs by flow injection analysis

[1.7]. An International Standard specifying this method for the determination of  $\text{SO}_2$  in ambient air is in preparation [1.23].

In related studies,  $\text{SO}_2$  was determined by chemiluminescence during oxidation with potassium permanganate, after absorption in sodium tetrachloromercurate solution [1.24]. It was thus shown that the ozone interference arising in the West-Gaeke method was due to the inhibition of dye development and not the fixation of  $\text{SO}_2$  as disulphitomercurate. The substitution of 1-naphthyl-ammonium chloride for para-rosaniline hydrochloride produced a fluorometric version (excitation 342 nm, emission 442 nm) of the Schiff reagent [1.25]. The sensitivity is two orders of magnitude better than the colormetric method.

These West-Gaeke based methods use toxic mercury compounds. This has recently been overcome by absorbing in morpholine solution and then measuring the absorption at 560 nm spectrophotometrically [1.26].

In another recent method  $\text{SO}_2$  was absorbed in a pH 7 phosphate buffer and was then determined with 5,5'-dithiobis (2-nitrobenzoic acid) at 412 nm [1.27].

There are several granular gels that change colour when exposed to small amounts of  $\text{SO}_2$ , for example ammonium vanadate on silica gel. The concentration is estimated by colour comparison. Impregnated filter papers may also be used for the detection of  $\text{SO}_2$ . For example a starch, potassium iodide, potassium iodate and glycerol reagent, which is stained purple by  $\text{SO}_2$ .

Another commercial passive monitor for  $\text{SO}_2$  contains a strip of phenolsulphonephthalein impregnated paper. The colour changes from red-purple to yellow on reaction to  $\text{SO}_2$  and a direct reading of the length of stain in millimetres is related to the concentration [1.4].

These direct reading methods are not sensitive enough to measure  $\text{SO}_2$  in ambient clean air so absorption is still necessary. However, they are useful for detecting and roughly determining  $\text{SO}_2$  in field tests.

#### Other Instrumental Methods

A conventional double beam UV spectrometer can operate at 213.8 nm where  $\text{SO}_2$  absorbs strongly [1.28]. A direct reading fluorometric approach to sulphur dioxide measurement has also been reported [1.29].

$\text{SO}_2$  can be determined by a number of other laboratory instrumental techniques. A chemiluminescence method in which  $\text{SO}_2$  enhances the luminol/ $\text{NO}_2$  reaction has been described [1.30] but is interfered with by  $\text{H}_2\text{S}$ , ethyl mercaptan and ozone. Chemiluminescence during the permanganate oxidation of  $\text{SO}_2$  has also been used in conjunction with flow injection analysis [1.31].  $\text{SO}_2$  in air has been determined in real-time by a hydrogen-rich flame photometric method, which uses separation on a GC column [1.32], but the response is not linear.

A gas chromatographic method has been developed to

measure the gas in food headspaces. The column separated  $\text{CO}_2$ ,  $\text{SO}_2$  and water which were then determined by an electrolytic conductivity detector [1.33].

### Conclusion

A variety of methods have been suggested and developed for  $\text{SO}_2$  because the determination is of widespread application. It must also be noted that for specific applications the interferences with a method may be of minor or of no importance. These reactions form the basis of future possibilities for sensors for  $\text{SO}_2$ . For instance, the formation of a stable mercury complex may form the basis of a device where  $\text{SO}_2$  replaces a larger ligand giving a mass amplification of the kind reported for HCN [1.34]. The mercury(II) complex has already been used as a specific piezoelectric crystal coating for  $\text{SO}_2$  [1.35] but a sensor containing toxic mercury(II) compounds may be unacceptable in many circumstances.

### 1.3 SCOPE OF THIS WORK

This thesis describes work carried out at the Trace Analysis Laboratory, Chemistry Department, Imperial College, London, SW7 2AY *between October 1981 and November 1984.*

It was shown earlier that  $\text{SO}_2$  is a useful industrial chemical but must be monitored as a hazardous pollutant. Some procedures for determining  $\text{SO}_2$  were described. The disadvantages of these methods are sampling and collection, which make them inappropriate for rapid monitoring. Although the speed and accuracy of analyses may be improved by using automation and instrumentation, the sampling problems are not overcome. This point is discussed in Chapter 3 with reference to the analysis of cigarette smoke. The measurement of  $\text{SO}_2$  by an infra-red instrument is then demonstrated.

Automated systems allow multiple determinations to be carried out but they are expensive and analyses have to be sequential giving rise to long total analysis times. An alternative approach would be to use small, cheap, sensors allocated to individual channels. Microcomputer control of such sensors, operating in the on-line real-time mode, normally allows signals to be acquired from each sensor in a time resolved manner. Investigating multichannel detection is outside the scope of this work, the aim being to develop a single sensor for  $\text{SO}_2$  which can be combined easily with other similar sensors into a multichannel system.

In Chapter 2 the phenomenon of piezo-electricity is explained and the use of piezo-electric crystals (PZCs) as chemical sensors is

described mathematically. To summarise, when mass is coupled to the electrode surface of a PZC a proportional decrease in frequency occurs. For the crystals used in this work the mass sensitivity is predicted to be 1100 Hz per  $\mu\text{g}$ . Selectivity towards a specific gas is achieved by coating the crystal with a substance that preferentially adsorbs the species of interest. The absorption laws on which quantitative spectroscopy is based are also stated.

Instrumental dispersive infra-red spectrometry was employed in Chapter 3 to validate gas dilution procedures for the production of standard  $\text{SO}_2$  atmospheres and to investigate the gas rig capabilities for dynamic sampling. The phenomenon of sorption and desorption of  $\text{SO}_2$  from polymer materials was investigated. Then the gas rig was used to prepare  $\text{SO}_2$  concentrations for calibrating PZC sensors.

Chemically modified PZC mass transducers could be used in an on-line sensing application. They have been shown to be highly sensitive in particular circumstances. However, they are not yet available in a form well suited to routine industrial use. They are not intrinsically selective towards specific gas molecules, this is achieved by a chemical modification and these processes need further development to improve selectivity and long term performance.

However, for this to be achieved, the short and long term behaviour of the PZCs in response to humidity at particular temperatures must first be understood, so that water vapour and

temperature limits can be set for their preparation, storage and analytical environments. This will ensure that reproducible behaviour is obtained from uncoated PZCs which will yield meaningful results when modified.

In Chapter 4 a microcomputer controlled system that measures the frequency and the temperature of a PZC is described and in Chapter 5 it is used to demonstrate and investigate the humidity and temperature effects on uncoated crystals. Strategies are also developed to limit these effects and guidelines for acceptable humidity and associated temperature limits are given to ensure that these parameters do not affect the long term reproducibility of the sensors.

Water vapour commonly interferes when monitoring with a coated crystal sensor and the base frequency of a PZC is a function of temperature. It is, therefore, desirable to correct for changes in humidity in the analytical environment. Such corrections can only realistically be applied in real-time by using a dedicated in-line microcomputer as demonstrated by Fielden, McCallum, Stanios and Alder [1.36].

In that work the effects of water vapour on a PZC detector for toluene di-isocyanate were corrected with an in-line microcomputer controlled instrument that measured the frequency of two differently coated crystals. The correction procedure assumed that the responses were linear and additive, however, empirical calibration was employed as predictions based on laboratory measurements failed. Such limitations could be overcome by using

more sophisticated data handling procedures and multi-parameter correction algorithms.

In parallel, the effect of temperature on particular PZC sensors has been investigated as a precursor to implementing the latter correction. It is shown that a non-linear temperature correction of a PZC sensor for  $\text{SO}_2$  is feasible by the novel approach of combining an in-line microcomputer controlled data acquisition system with on-line data processing and correction.

At the end of Chapter 5, it is demonstrated that with microcomputer technology it is possible to determine the thermal response over the entire experimental range very easily. In Chapter 6 a data analysis procedure is described and demonstrated. The procedure uses a Fourier series and produces an equation for the thermal response as a 21 term series for use in the correction process. The practical implementation of these procedures and corrections is also considered.

In Chapter 7, sensitivity and partial selectivity for  $\text{SO}_2$  is achieved by a chemical modification which involves coating the crystal with N,N,N',N' tetrakis 2-hydroxypropyl ethylene diamine which preferentially adsorbs  $\text{SO}_2$ . A number of coating methods are described. Log-linear plots were obtained for dynamic calibrations and it is suggested that this indicates a particular adsorption process. Using the Fourier series description of a PZC temperature response, a temperature corrected static determination of  $\text{SO}_2$  is obtained.

It is concluded in Chapter 8 that by incorporating a micro-computer into a PZC sensor system, sophisticated data handling procedures for the deconvolution of the frequency changes due to temperature from those due to  $\text{SO}_2$  concentration have been implemented providing a considerable advantage over existing instrumentation. The fact remains that the  $\text{SO}_2$  concentration continues to vary with temperature, it is believed that this is due to the absorption process. Methods to make the data processing in-line are discussed along with suggestions as to the implementation of a multi-parameter non-linear correction for sensors. The long term aim being to obtain real-time results in the real world.

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## CHAPTER 2

### THEORY

In this chapter the theoretical basis of piezoelectric crystal sensing is considered. The effect of piezoelectricity is described as are the materials that exhibit piezoelectric properties and the reasons why they do so. The piezoelectric crystals (PZCs) used in this work are described with their methods of preparation. The use of PZCs as frequency determining components of oscillators and their use as mass sensors is explained. The Sauerbrey equation is derived in a form which describes theoretically the relationship between frequency and deposited mass when using PZCs to determine the concentration of gas phase species.

The basis of infra-red (IR) absorption is briefly stated. Beer's relationship between concentration and absorbance, which must be proven for an IR system to be used quantitatively, is derived and is modified for the case where concentration varies with optical path length.

## 2.1 THEORY OF PIEZOELECTRIC CRYSTAL SENSORS

Piezoelectricity was first positively identified by Pierre and Jaques Curie in 1880 [2.1, 2.2]. They discovered that when single crystals of certain crystalline substances were deformed in particular directions electric charges appeared on their surfaces with this charge disappearing when the pressure was removed. They later showed that these crystals become strained when subjected to electric fields.

### Piezoelectricity

Piezoelectricity is the electric polarity resulting from the application of mechanical pressure to a dielectric crystal. The resulting distortion of the crystal structure (fig. 2.1) separates the charge centres of oppositely charged ions giving rise to a dipolar crystal (fig. 2.2). The electric polarisation produced is proportional to the applied stress.

The crystal is obtained as a slab or bar with electrode material applied to two particular opposite faces. If mechanical pressure is applied to an isolated PZC the polarisation gives rise to a voltage difference across the electrodes, and if the electrodes are short circuited a pulse of charge can be observed during loading. This is the principle of electronic gas lighters where the short circuit occurs after ionisation of the gas by the (high) voltage difference. If the force is reversed, so is the polarisation. Conversely, application of a voltage difference across the electrodes, resulting in an applied electric field,

produces a distortion in certain directions in the crystal, where the strain is directly proportional to the field and changes sign as the sign of the field is reversed; fig. 2.3 shows this schematically with some exaggeration for ease of illustrating the concept. This reciprocal relationship is referred to as the piezoelectric effect. The generation of polarisation under mechanical stress is known as the direct piezoelectric effect, and the production of mechanical strain by an electric field is called the converse piezoelectric effect. It is the converse piezoelectric effect that is used in this work.

#### Piezoelectric Materials

Crystalline quartz is the principal piezoelectric material used commercially. Quartz has the important qualities of being a completely oxidised compound, insoluble in water and stable at temperatures over 100°C. For all practical purposes, therefore, it is chemically stable. Quartz is cheap, hard and mechanically rugged, has low internal losses when used as a vibrator and expands little with heat. Rochelle salt (sodium potassium tartrate) has a large piezoelectric effect, but is sensitive to changes in temperature; it decomposes at 55°C. It also requires protection against moisture and is electrically unstable. Barium titanate provides lower sensitivity, but greater immunity to temperature and humidity effects. Other crystals that have been used for piezoelectric devices include tourmaline and synthetic crystals such as ammonium dihydrogen phosphate, dipotassium tartrate, lithium niobate and ethylenediamine tartrate, which is

used in frequency-modulated oscillators and selective band-pass filters because of the wide gap between its resonant and anti-resonant frequencies.

#### Necessary Condition

There are 20 crystal classes which are piezoelectric. In order to exhibit piezoelectricity it is necessary for a crystal structure, of which there are 32 classes, to lack a centre of symmetry and to generate an electric polarisation under stress. For a given crystal, the axis of polarisation depends on the direction of the stress. In the crystal classes of lowest symmetry, the application of stress in any direction generates an electric polarisation, whereas in crystals of higher symmetry only the application of stress in particular directions can produce an electric polarisation. These effects of crystal symmetry also apply to the converse piezoelectric effect when an external electric field, applied to the crystal, results in a small strain.

#### Matrix Formulation

For either the direct or converse piezoelectric effect, the complexity of the relationship between the mechanical and electrical vectors in a crystal depends on crystal symmetry. The relationship can be described mathematically using matrices. A quartz crystal having a three-fold axis of rotation and three two-fold axes perpendicular to the three-fold axis has only two coefficients describing the relationship.

### Electromechanical Coupling

The direct piezoelectric effect makes a crystal a generator and the converse effect makes it a motor. Consequently, the electric properties depend on the mechanical load and the mechanical properties depend on the electric boundary conditions.

The square of the electromechanical coupling factor,  $k$ , is defined as the ratio of the stored electrical energy to the corresponding mechanical form to which it can be converted. In quartz the coupling is about 10 per cent.

### Construction

Only the purest crystals of white translucent quartz are suitable; Brazil is the major supplier. A thin wafer, cut from this quartz, vibrates only at its resonant frequency which is determined by the way it was cut and by its dimensions. For each type of cut the natural frequency is mainly determined by the thickness; the thinner the crystal the higher the frequency. A 10 MHz crystal is about 0.2 mm thick. The raw plates are carefully ground, by lapping and etching, and an evaporated metal film is deposited on each side to act as electrodes. The electrode metal is normally silver or aluminium but can be gold.

The directions labelled  $x_1$ ,  $x_2$  and  $x_3$  in fig. 2.4 are the piezoelectric or polar axes of a hexagonal quartz crystal. There are three such directions due to symmetry, with three respective y-axes, although for clarity only one y-axis is shown. The single z-axis is normal to all x and y-axes and is the axis of

optical symmetry; it is not polar.

A plate cut with its faces perpendicular to one of the x-directions is an X cut and is shown hatched in fig. 2.4, while one cut with its faces parallel to one of the lateral faces is Y cut. However, both X cut and Y cut quartz plates are subject to changes in frequency with temperature due to changes of elastic modulus.

Fig. 2.5 shows a mounted AT cut crystal. Such crystals are used most commonly in piezoelectric microbalances, they are cut from a single right handed quartz crystal parallel to the x-axis and at an angle of  $35^{\circ}15'$  to the z-axis (fig. 2.6). This type of crystal vibrates in the thickness-shear mode, which has no nodal points on the face of the crystal (fig. 2.7). Hence, the frequency of vibration is independent of the elastic properties of thin films, such as electrodes and coatings, added to the crystal surface. In addition they are nearly free from the temperature effect, which is discussed and investigated in Chapter 5.

### Oscillation

If alternately stretched and squeezed, a crystal slice becomes a source of an alternating voltage. Conversely, if an alternating potential difference is applied to the electrodes on a PZC an oscillating electric field will occur, which will cause the crystal to vibrate mechanically. If the driving frequency is close to the natural resonant frequency (or an overtone) of a particular crystal mode of vibration in the direction of the

applied field, then resonance will occur. When the crystal is incorporated as the frequency controlling component of the oscillator generating this alternating voltage and all mechanical and electrical losses are overcome, the vibrations will sustain themselves and generate electrical oscillations of constant frequency. The exact harmonic depends on the other components in the circuit and the mass loading of the crystal. In the oscillator used in this work ca. 10 MHz crystals vibrate at the fundamental frequency under normal mass loadings.

The operation of a PZC in the frequency domain has an advantage over purely analogue sensors such as electrochemical ones in that variations in the output voltage have no effect on the measured signal. Therefore, transmission losses are prevented and the effect of noise pickup is significantly reduced.

#### Frequency Dependence on Mass

The theoretical basis of the piezoelectric crystal microbalance for evaporated metal films was developed by Sauerbrey in 1959 [2.3]. His results for film deposition should, in principle, be directly applicable to thin films of any material adhering to the crystal.

The resonant frequency,  $F$ , of an AT cut crystal vibrating in the fundamental thickness-shear mode is:

$$F = \frac{N}{a} \quad (2.7)$$

$N$  = Frequency constant for AT cut quartz, 0.1679 MHz cm, which

equals half of the velocity of propagation of a transverse wave in the plane of the crystal.

$a$  = thickness of the crystal which may be expressed as:

$$a = \frac{M}{A\rho} \quad (2.8)$$

$M$  = Mass of the crystal

$A$  = Area of the crystal

$\rho$  = Mass density of the quartz crystal,  $2.654 \text{ g cm}^{-3}$ .

Therefore:

$$M = \frac{\rho NA}{F} \quad (2.9)$$

For quartz  $\rho$  and  $N$  are constant, differentiating for constant area:

$$\frac{dM}{dF} = - \frac{\rho NA}{F^2} \quad (2.10)$$

From this equation the resonant frequency shift caused by a single incremental change in mass of the crystal (and hence thickness) from  $M$  to  $M+\Delta M$  can be calculated:

$$\int_F^{F+\Delta F} \frac{-1}{F^2} dF = \frac{1}{\rho NA} \int_M^{M+\Delta M} dM \quad (2.11)$$

$$\left( \frac{1}{F} \right)_F^{F+\Delta F} = \frac{1}{\rho NA} \left( M \right)_M^{M+\Delta M} \quad (2.12)$$

$$\left( \frac{1}{F+\Delta F} \right) - \left( \frac{1}{F} \right) = \frac{1}{\rho NA} ([M+\Delta M] - [M]) \quad (2.13)$$

$$\frac{-\Delta F}{F^2 + F\Delta F} = \frac{\Delta M}{\rho NA} \quad (2.14)$$

$$\Delta F = - \frac{F^2 + F\Delta F}{\rho NA} \Delta M \quad (2.15)$$

For  $\Delta F \ll F$ :

$$\Delta F = - \frac{F^2}{\rho NA} \Delta M \quad (2.16)$$

At this point the fundamental assumption of Sauerbrey is made: The frequency shift caused by the change in mass of the crystal,  $\Delta M$ , will also be caused by the addition of an identical foreign mass,  $\Delta M_T$ , to the crystal surface, eg a metallic film. This assumption has been borne out experimentally. It is a logical assumption because surface depositions on an AT cut quartz crystal vibrating in the thickness-shear mode act strictly as dead weight (they have negligible contribution to the elastic properties of the vibrating crystal). However, if the total deposition becomes too thick it will become strained in oscillation and this assumption will no longer be valid.

The application of electrodes to the surface of the crystal causes a decrease in resonant frequency, but, because of the difference in mass, the wavelength corresponding to the resonant frequency of the electroded region (fig. 2.5) is longer than that of the periphery. If the mass of the electrodes is sufficient, the resonant frequency difference between the two regions will be great enough for vibrations generated in the electroded region not to propagate beyond it. Since only the electroded region is energised, the vibrational energy is said to be trapped [2.4], and the crystal behaves as if its area were that of the electrode,  $A_a \text{ cm}^2$ .

Now eqn. 2.16 becomes:

$$\Delta F = - \frac{F^2}{\rho N A_a} \Delta M_T \quad (2.17)$$

Eqn. 2.17 states that the resonant frequency decreases linearly with the addition of foreign mass.

For thin films, the mass sensitivity per unit area is a constant for a specific crystal. For type AT cut quartz it equals  $2.24 \times F^2 \text{ MHz}^{-1} \text{ cm}^2 \text{ g}^{-1}$ . Hence it is desirable to use high frequency crystals for film-deposition work as the mass sensitivity is proportional to the frequency selected.

Eqn. 2.16 can thus be written in the common form:

$$\Delta F = - 2.24 F^2 \frac{\Delta M_s}{A_a} \quad (2.18)$$

where  $F$  is expressed in MHz,  $\Delta M_s$  in g and  $A_a$  in  $\text{cm}^2$ .

In a piezoelectric crystal gas sensor, the electrode is itself coated with a chemical absorbent which selectively absorbs the gas component of interest producing a sensor specific to that species. In Chapter 7 the techniques used to produce selective sensors are described along with the range of possible materials and their degree of selectivity. This chapter is more concerned with the theoretical aspects of the piezoelectric effect than its applications.

In accordance with most researchers in the area of piezoelectric mass measurement, it is assumed that the active area for mass measurement is conterminous with the area of the electrode. This is valid if the coating completely covers the electrode. Therefore, eqn. 2.18 applies when sorbent, sorbate and electrode, together act as foreign mass totalling  $\Delta M_s$ . However, sorbent adhering to the crystal outside the active area has a negligible effect on the vibration of the active area.

The Sauerbrey equation only applies to subsequent mass additions

after the first if, and only if,  $F$  is the frequency of the crystal loaded with all previous mass additions to the current one.

Since the PZC resonant frequency is invariably measured after the electrodes have been deposited, it is proper to ignore the contribution to  $\Delta M_t$  from the electrode mass and the associated decrease in crystal frequency. The contribution of the electrode to the total deposition becoming too thick must not be ignored. Eqn. 2.18 now becomes:

$$\Delta F = - 2.24 F^2 \frac{\Delta M}{A} \quad (2.19)$$

where,  $F$  is the frequency of the crystal loaded only with the electrode,  $\Delta M$  refers to the sorbent and sorbate and  $A$  is the active area which is equated to the area of the electrode.

Because of the assumption made in deriving eqn. 2.16, the effective mass sensitivity decreases slightly as the deposited mass increases. If  $\Delta F$  is less than 0.5% of  $F$ , the non-linearity will be less than one per cent. For large mass additions the response is non-linear and the following equation can be used, which has the same form as eqn. 2.15 but for which the terms described under eqn. 2.19 apply:

$$\Delta F = - \frac{F^2 + F\Delta F}{\rho NA} \Delta M \quad (2.20)$$

Although the Sauerbrey equation predicts a linear relationship between absorbed mass and frequency change this does not imply a linear relationship between gas phase concentration and frequency change. The absorption process relating the gas phase

concentration to the absorbed mass has not been considered and may well be a non-linear process, especially when the concentration varies dynamically. This is the case for the discrete measurements described in Chapter 7 where the calibration is shown to be non-linear.

The mass sensitivity of a typical crystal oscillating at 10 MHz is  $0.9 \text{ ng Hz}^{-1}$ . The exact value depends on crystal frequency, dimensions and geometry.

## 2.2 THEORETICAL ASPECTS OF INFRA-RED SPECTROMETRY

### Absorption of Electromagnetic Radiation

This is the process whereby the intensity of a beam of electromagnetic radiation is attenuated in passing through a material or medium. The factors on which absorption depends and which are relevant to quantitative spectroscopy are the nature of the absorbing species, the wavelength of the radiation, the thickness of the absorbing medium and the concentration of the absorbing species.

### Beer-Lambert Law of Absorption

In a homogeneous medium the fraction of incident radiative energy absorbed is proportional to the thickness of the absorbing substance. In terms of a beam of photons travelling through the substance, the rate of photon absorption with distance travelled is proportional to the power of the photon beam. In the absorption of electromagnetic radiation by gases, liquids and solutions. Each light absorbing molecule absorbs the same fraction of radiation incident upon it, whether the molecules are closely packed at high pressure or highly dispersed at low pressure.

The relation between the intensity of a parallel monochromatic beam, which emerges from a plane parallel layer of absorbant of constant thickness, and its thickness has the following form:

$$\frac{dI}{dx} = -k c I \quad (2.21)$$

$I$  = intensity or radiant power of unabsorbed radiation at a distance  $x$  cm into the substance

$k$  = a constant for the medium at the wavelength and temperature being considered (absorption coefficient)

$c$  = the concentration which is uniform and independent of path length.

The following expression is obtained by integrating eqn. 2.21 over a finite thickness of the substance equal to a total path length of  $x$  cm:

$$\ln \frac{I_0}{I} = k c x \quad (2.22)$$

$I_0$  = intensity or radiant power of a monochromatic parallel beam of radiation incident at the surface of the medium

$I_0$  must be corrected for reflection from the incident surface and window absorption. This is most easily done by defining it as the power passing through a blank in the same sample container.

Eqn. 2.22 above is more usually written as

$$\log \frac{I_0}{I} = \xi c x \quad (2.23)$$

where,  $\xi = k/2.303$  is known as the (specific) absorption coefficient for the absorbing substance at constant temperature and wavelength. When  $c$  is the molar concentration,  $\xi$  is called the molar absorption coefficient. Equation 2.23 is the fundamental equation of quantitative absorptimetry.  $\xi$  depends on the nature of the absorbing species, but not its concentration, and on the wavelength of the radiation. To a

lesser extent  $\epsilon$  changes with the nature of the solvent and the temperature of the absorbing species.

If the Beer-Lambert law is true for a particular system, a plot of absorbance,  $A = \log (I_0/I)$ , against the concentration for different concentrations will yield a straight line, the slope of which is equal to  $\epsilon$ . In other words; if the Beer-Lambert law can be shown to apply, absorbance can be used as a quantitative measure of concentration. In most systems the radiation is not monochromatic and so deviations occur. For gaseous absorption  $c$  can be replaced by the partial pressure of the absorbant.

In Chapter 3 it will be seen that the normal derivation of the Beer-Lambert law (eqn. 2.23) is valid for static gas measurements.

#### Spatial Variation of Concentration

In some circumstances the concentration of the absorbing species may not be constant, for instance when a flow through gas cell is used the concentration varies both spatially and with time. The spatial variation is outside the scope of eqn. 2.23.

However, the Beer-Lambert law will still apply if the concentration is uniform over a plane parallel layer of absorbing species of limiting thickness,  $dx$ , even though a visible concentration gradient may exist in the  $x$  direction but not normal to it. The Beer-Lambert law then takes the following mathematical form:

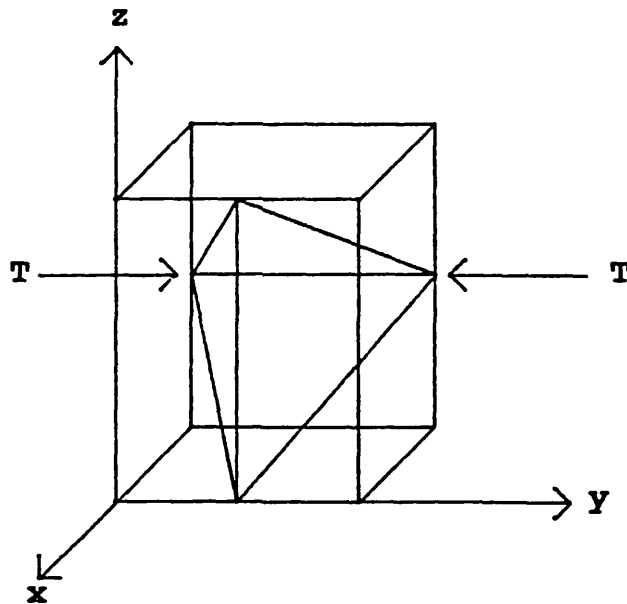
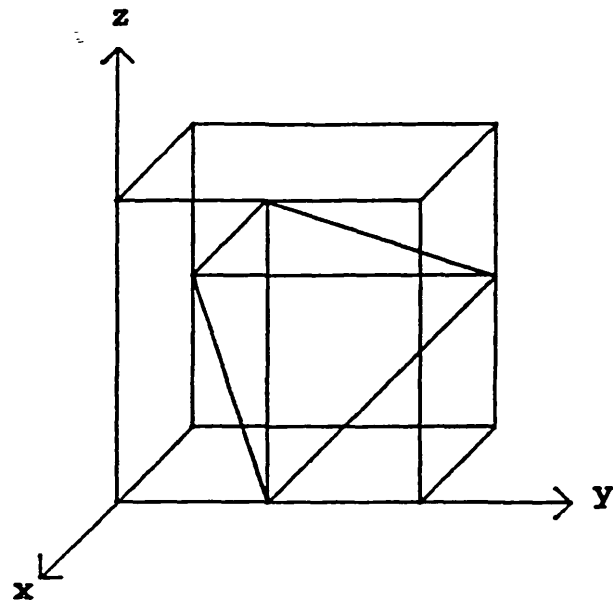
$$\frac{dI}{dx} = -2.303 \epsilon c(x) I \quad (2.24)$$

Integration over the total path length of  $x$  cm gives:

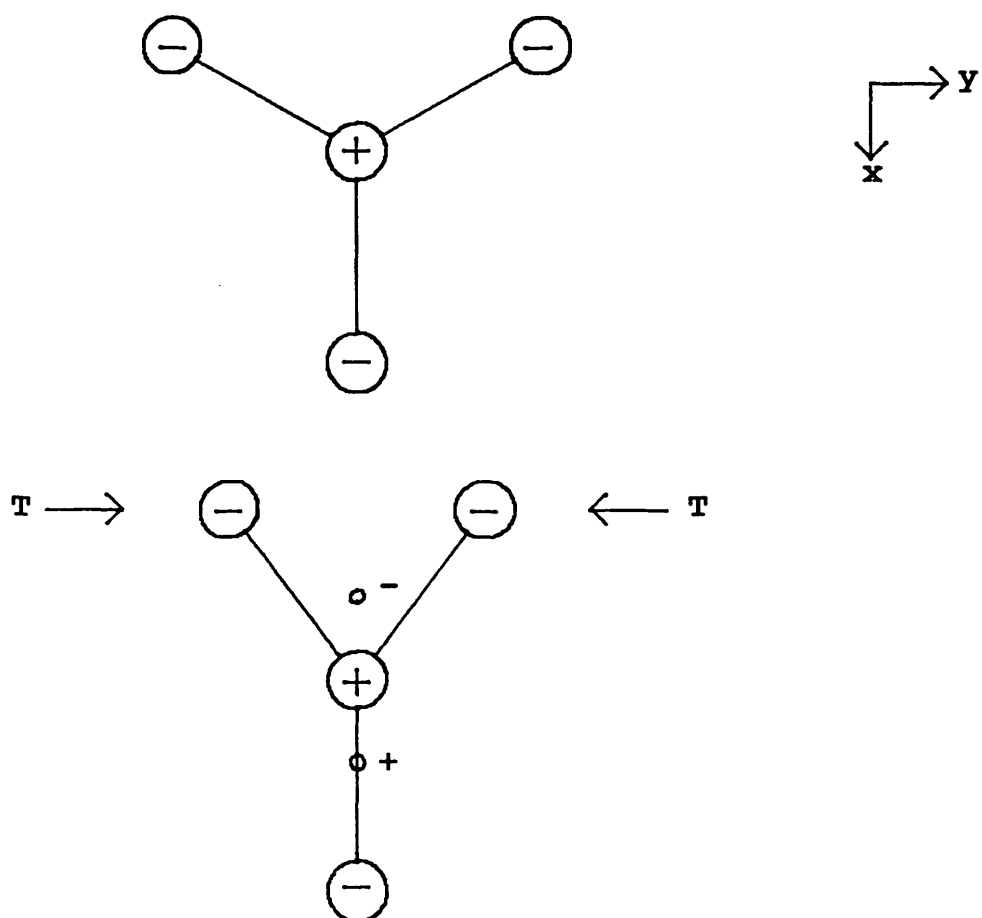
$$\log \frac{I_0}{I} = \epsilon \int_0^x c(x) dx \quad (2.25)$$

This general expression is of use in situations where the concentration is constant normal to the incident radiation i.e. uniform cross-sectional distribution but varies with path length.

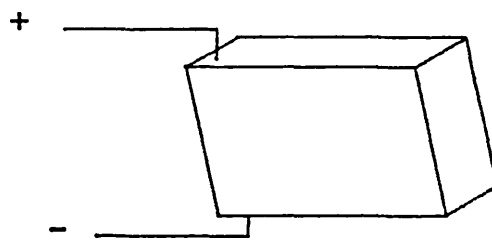
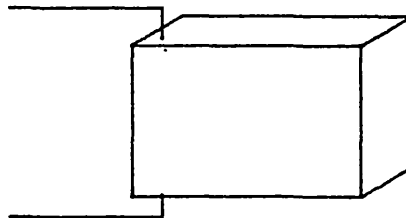
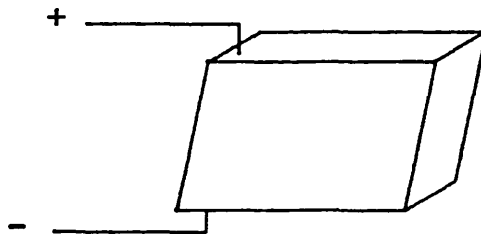
## 2.3 FIGURES



**Figure 2.1** The distortion of a quartz silicate tetrahedron by a stress applied in the y-direction which, because of crystal symmetry, results in a net dipole along the x-axis.



**Figure 2.2** The x-y projection of a quartz silicate tetrahedron and the effect of a stress applied in the y-direction. The charge directed along the x-axis is the resultant of two charges in the x-z plane which are not moved by the stress in the y-direction.



**Figure 2.3** The strain produced by an electric field on a piezoelectric crystal and the effect of reversing the field.

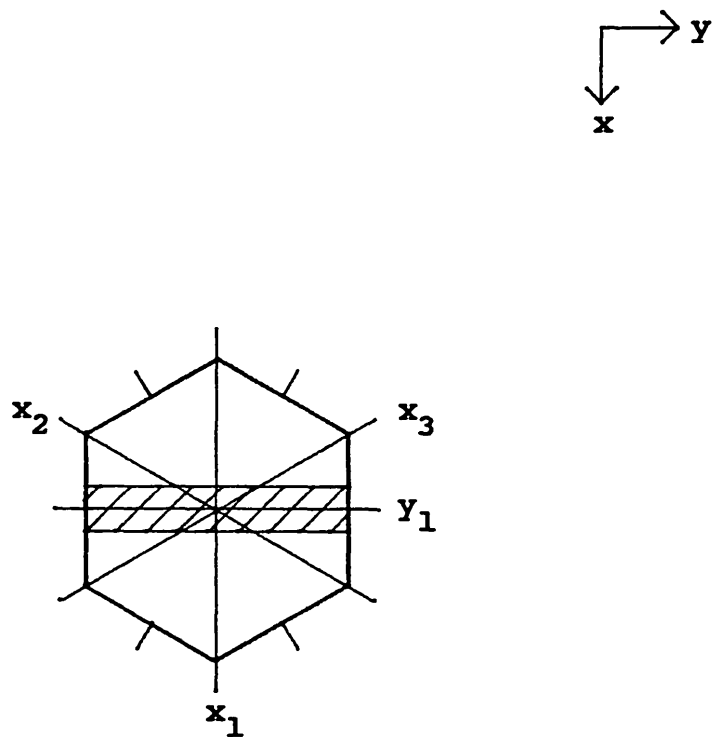
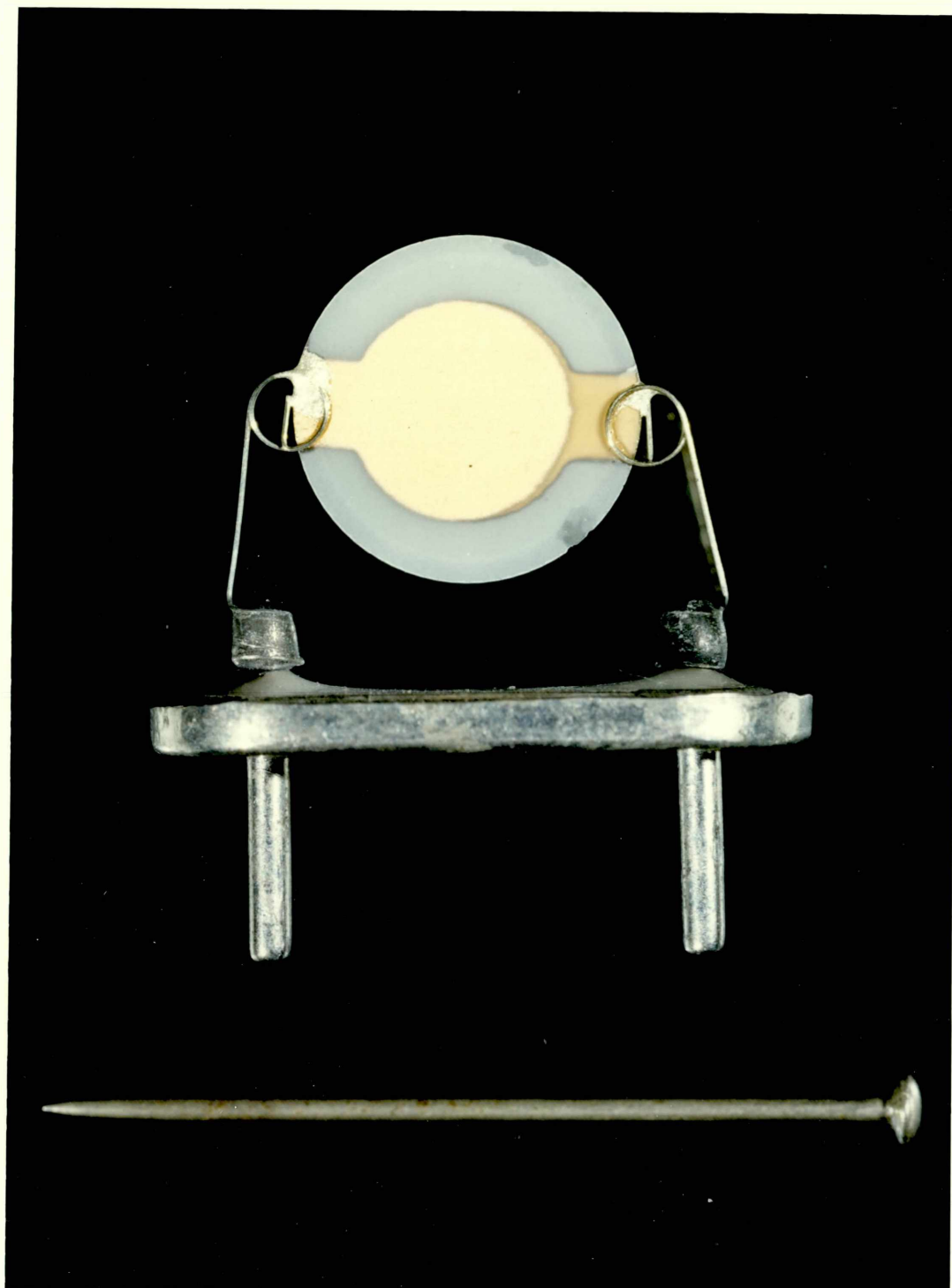


Figure 2.4 A hexagonal quartz crystal showing the  $x$  and  $y$ -axes and an X-cut.

Figure 2.5 (Next page) Plate showing a 10 MHz crystal with gold electrodes mounted in an HC6/U holder. A dressmaking pin is also shown.



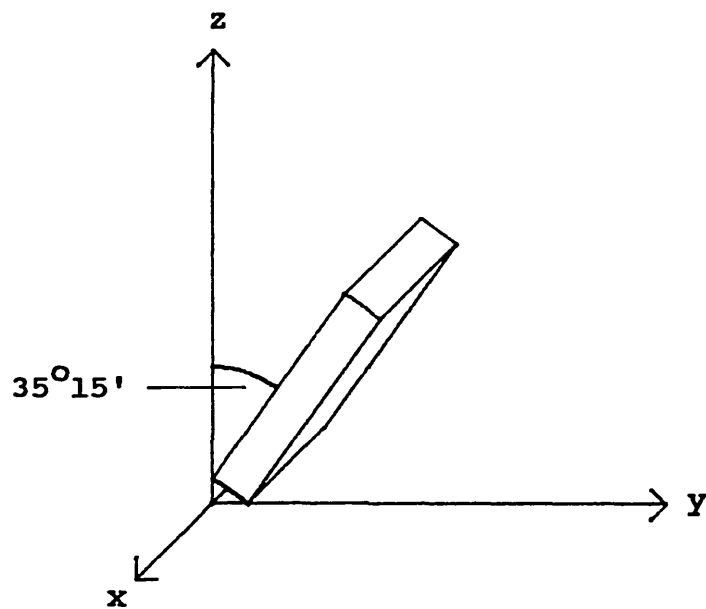
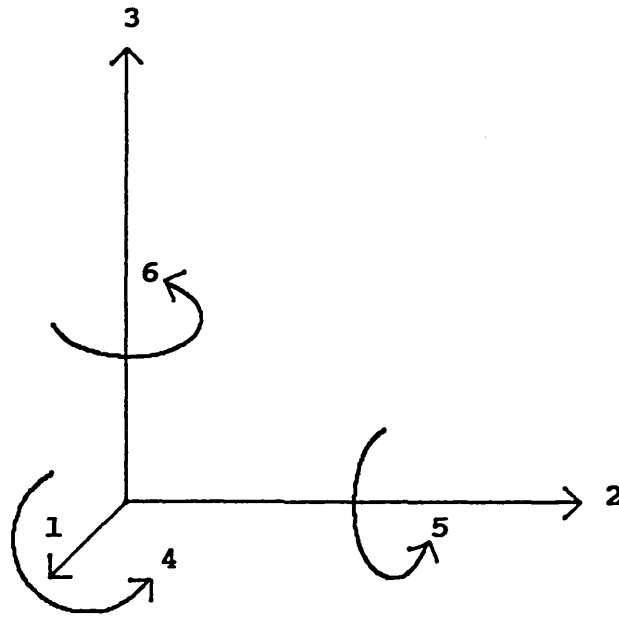
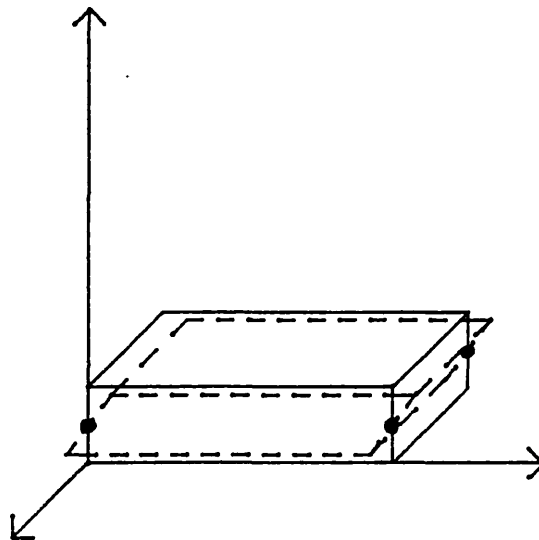


Figure 2.6 The orientation of the AT-cut with respect to the axes of a quartz crystal.



**Figure 2.7** The Thickness Shear mode of vibration, which has no nodes on the surface (nodes are shown).

## 2.4 REFERENCES

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CHAPTER 3

PRELIMINARY INVESTIGATIONS OF ATMOSPHERES CONTAINING

SO<sub>2</sub> USING INFRA-RED SPECTROMETRY

Spectroscopic methods have been extensively applied to the analysis of gases, making particular use of the specificity of an absorption technique. On behalf of the Department of Health, the Laboratory of the Government Chemist (LGC) has regularly determined yields of tar, nicotine and carbon monoxide (CO) in up to 150 major selling brands of cigarettes. The cigarettes are smoked by machine to provide a consistent comparison between brands. Ten 30 ml puffs are taken from each cigarette, the aerosol is filtered and the total vapour phase from each cigarette is collected in a PVC bag for analysis of total CO using an infra-red spectrometer.

Many other constituents of cigarette smoke are also thought to be harmful and the development of methods to determine these presents a considerable challenge to the analytical chemist. One of these constituents is  $\text{SO}_2$ . The determination of  $\text{SO}_2$  by a similar infra-red spectrometric method was investigated. The aims were to assess whether  $\text{SO}_2$  could be analysed quantitatively in an apparatus similar to the LGC smoking engine and to consider potential methods for the multi-channel determination of  $\text{SO}_2$  in real-time.

### 3.1 INSTRUMENTAL

#### Description of the Spectrometer

The optical system that was used for all the infra-red work, described here, consisted of a Perkin Elmer 157 sodium chloride spectrometer that was specially modified for the purpose of this work. Fig. 3.1 shows the optical layout of the instrument which measures infra-red absorption by the double beam principle. Infra-red radiation from a Nernst glower source is split into two collimated beams. The sample is placed in one beam while the other is used for reference purposes. A semicircular silvered rotating chopper (Ch) allows the sample beam to pass directly into the monochromator. However, when turned through  $180^\circ$  it reflects the reference beam into the prism monochromator which allows a small range of wavelengths to fall onto the thermocouple detector (Tc).

Due to the difference between the intensities of the beams, the output of the detector is a direct current with an alternating component superposed on it. The alternating current is selectively amplified and fed to a servomotor that moves a comb shaped attenuator (Atn) into the reference beam until the two beams have equal intensity. A pen is driven from the attenuator by a chain and pulley coupling to give a graphical output displaying the ratio of the intensities as a percentage.

An electrical output signal is derived from a displacement potentiometer. The magnitude of the readout voltage is indicative of the attenuator position: the maximum output is 10 mV and is

equivalent to full scale deflection of the pen. For signal recovery from the spectrometer during most analyses a Bryans 27000 chart recorder was used. This has a floating input with an impedance of greater than 10 k $\Omega$ .

Excessive gain causes oscillations in the output due to positive feedback. Adjustment of the gain control varies the amplitude of the signal applied to the servomotor; the control is set to obtain a rapid non-ringing mechanical response with the servo slightly underdamped. Damping is provided by a velocity feedback circuit that stabilises the servo, along with friction and inertia.

The balance control is adjusted so that when there is no energy both beams the drive remains stationary. Therefore, a zero signal is applied to the feedback system when the two beams have equal intensity.

Turning the 100% control moves a second attenuator out of the sample beam to compensate for absorption by the sample cell. Thus the blank is set at 100% transmission.

The source does not emit the same amount of energy at all wavelengths. To compensate for this, the slit widths are programmed to maintain the energy falling on the detector at an approximately constant level throughout the instrumental range, thus keeping the output response and signal-to-noise ratio constant.

### Modification of the Spectrometer Output

The built-in pen recorder was initially useful in obtaining spectral information. However, the chart recorder's electrical facilities for scaling and backing off and the use of simpler paper were more suitable for the quantitative analyses that followed.

Moreover, the response of the spectrometer's mechanical system was found to be poor and the servo amplifier stage was noisy especially at high gain, which posed further problems for quantitative work. Improved performance was achieved by unlinking the coupling from the attenuator to the internal chart recorder pen. The reduced frictional losses and inertial load on the feedback circuit allowed the gain to be reduced, resulting in an increase in the signal-to-noise ratio.

Since the pen holder no longer moved to show the 100% and 0% positions of the moving attenuator, these had to be redefined as the positions adjacent to the respective end stop microswitches. Should the instrument go off scale, the drive is cut by these switches.

For dynamic sampling analyses a Research Machines 3802 microcomputer was added to the spectrometer via a purpose built interface. Looking at the raw data, an apparent increase in noise was observed due to the fact that the chart recorder had been acting as a passive filter. The microcomputer samples the output signal of the spectrometer at a rate of 1000 samples per second. The mains pick-up component of the noise is eliminated by

averaging over 20 consecutive measurements.

The averaged data are then stored on magnetic disc (50 samples per second) for future analysis. This consists of peak location, calculating absorbance and pressure correction (see page 72). The rate at which analysis can be carried out is far greater than using manual methods such as reading off a chart roll. Other advantages are that the data are portable, accessible and can easily be copied. The results may be compared by superposition of graphs. Hard copy of graphs can be obtained using a Bryans 29000 A4 X-Y plotter. Should the method of analysis be altered then a new set of results can be obtained from the original data without interference from construction lines or traces from the previous analytical process, as may be the case with paper.

#### Gas Cells

The gas cells were obtained from Specac Ltd. The cell body consists of a tube of perspex with an internal diameter of 2 cm and a path length of 10 cm. Both ends are externally threaded to take Teflon end caps which hold the NaCl windows in position, as shown in fig. 3.2. Washers provide a gas tight seal. Two smaller perspex tubes lead off the body. Taps and B10 sockets were joined to these to allow the cell to be connected to a vacuum line and to be removed under gas tight conditions for insertion into the spectrometer. Since there are two tubes the same cell can be used for flow through work. This mode of operation will be described later.

Since the radiation is collimated, the cell volume that is available for irradiation (31.4 ml) depends only on the window area and the cell length. A holder was obtained from Specac that slotted into the cell adaptor and supported the cell in the sample compartment of the spectrometer so that the sample beam passed along it.

However, the gas cell, with end caps, was found to be too long to fit into the available space. In order to place the cell into the sample beam the protective stainless steel tray had to be removed from the sample compartment and the lugs that support the cell adaptor had to be shortened. The gas cell then just fitted, touching the entrance slit. This brought the cell close to the source which, unfortunately, resulted in a heating problem, but this problem was solved by a simple modification, see pages 71 and 78.

The gas cell attenuated the sample beam by about 65%. Specac also supplied a comb shaped attenuator which was placed in the reference beam. The beam intensity was reduced with this device as a coarse adjustment prior to balancing the two beams with the 100% control. Alternatively a second, identical, gas cell was used to attenuate the reference beam.

#### Gas Lines

A vacuum line capable of producing pressures of  $\text{SO}_2$  in the range 0.5 torr to 40 torr was constructed (fig. 3.3) in order to fill the gas cell with static samples of  $\text{SO}_2$ . Pressure measurements in

the range 0.01 torr to 10.0 torr were made using an Edwards vacustat. Above this range a glass manometer was used. Technical grade liquified  $\text{SO}_2$  was obtained from BDH chemicals in a cannister pressurised to 4.5 atm. High purity argon was obtained from BOC.

The apparatus was later modified as shown in fig. 3.4 so that  $\text{SO}_2$  could be sampled dynamically. The gas handling apparatus consisted of two distinct parts: a reservoir and a line for continuously flowing gas. The vacuum line was used to fill the glass reservoir bulb with some partial pressure of  $\text{SO}_2$ , the total pressure was then made up to atmospheric pressure with argon. The routine lowest pressure was  $5 \times 10^{-2}$  torr. Using a gas tight syringe a gas sample was taken from the reservoir and injected through a septum into an argon carrier gas stream, the gases then flowed to the gas cell.

### 3.2 EXPERIMENTAL PROCEDURES

The spectral range of the spectrometer is 6.4  $\mu\text{m}$  to 15.4  $\mu\text{m}$ . In fig. 3.5,  $\text{SO}_2$  absorption bands can be seen at 7.3 and 8.7  $\mu\text{m}$  with molar absorption coefficients of 675 and 195  $\text{l mol}^{-1} \text{cm}^{-1}$  respectively. Since the 7.3  $\mu\text{m}$  band has the most intense absorption it was used for analyses.

The amount of  $\text{SO}_2$  is conveniently represented by its partial pressure in a well mixed atmosphere at STP. Table 3.1 shows the equivalent mass of  $\text{SO}_2$  contained in a gas cell of volume 31.4 ml and the corresponding concentration in air (V/V ppm). Volume/volume measurement was used so that the same figures would apply in air as in the inert gas stream.

| Pressure of $\text{SO}_2$<br>(torr) | Weight of $\text{SO}_2$<br>( $\mu\text{g}$ ) | Concentration<br>(V/V ppm) |
|-------------------------------------|----------------------------------------------|----------------------------|
| 20                                  | 2364                                         | 58200                      |
| 10                                  | 1182                                         | 29100                      |
| 5                                   | 591                                          | 14552                      |
| 1                                   | 118                                          | 2910                       |
| 0.5                                 | 59                                           | 1455                       |
| 0.1                                 | 12                                           | 291                        |
| 0.05                                | 6                                            | 145                        |
| 0.01                                | 1                                            | 29                         |
| 0.005                               | 0.59                                         | 15                         |
| 0.001                               | 0.118                                        | 3                          |
| 0.0005                              | 0.059                                        | 1                          |

Table 3.1 Equivalent partial pressures, masses and concentrations for  $\text{SO}_2$  in the gas cell under complete mixing at STP

### The Measurement of Static Concentrations of SO<sub>2</sub>

Preliminary experiments were carried out with static concentrations of SO<sub>2</sub> in order to produce a usable calibration and to gain expertise in gas dilution procedures.

### Optimisation of the Slit Control

The gas cell was filled with 19.3 torr of SO<sub>2</sub> and a spectrum was recorded at the normal position of the slit control to locate the 7.3  $\mu$ m band. The monochromator was then scanned repeatedly over the absorption band at the various slit control settings. The signal increased with the energy falling onto the detector as the slit control was moved through settings 1 to 6 but the resolution decreased correspondingly. The signal did not increase further for settings 7 and 8.

Since this work is concerned with quantitative analysis and not with spectral resolution, the slit control setting is optimised for the signal-to-noise ratio, whilst resolution is sacrificed. Since the noise was effectively constant during the above series of experiments, it was concluded that the optimum slit control setting was 6.

### The Static Calibration Procedure

The spectrometer was set up using slit control setting 6 and the reference beam attenuated to give zero absorbance at 12.9  $\mu$ m for a cell filled with argon. SO<sub>2</sub> was added using the vacuum line and the gas cell was replaced in the sample beam. Then the

infra-red spectrum around  $7.3 \mu\text{m}$  was measured for various partial pressures of  $\text{SO}_2$  in the range 0.5 - 20 torr. From recorded spectra a calibration of absorbance versus pressure was constructed.

### Dilution Technique

This procedure was used to extend the calibration range of static concentrations of  $\text{SO}_2$ . The initial pressure of  $\text{SO}_2$  in the apparatus shown in fig. 3.3 with taps B, C, D *open* and taps A, E *closed* is measured and has a value of  $P_0$ . Now, consider the two volumes:  $V_a$ , the  $\text{SO}_2$  reservoir (vacuum line section DE) and  $V_b$ , the gas cell and section ABCD. Tap C is closed, section ABCD is vented via tap D and the gas cell is removed so that the spectrum at this pressure can be recorded.

The cell is then replaced and tap C opened. The volume  $V_b$  is now evacuated via tap A. Tap A is then closed and tap D opened allowing the  $\text{SO}_2$  in  $V_a$  to partition between  $V_a$  and  $V_b$ . The new pressure of  $\text{SO}_2$  in the apparatus is,

$$P_1 = \alpha P_0 \quad (3.1)$$

where the dilution fraction is:

$$\alpha = \frac{V_a}{V_a + V_b} \quad (3.2)$$

Again tap C is closed, section ABCD vented via tap D and the gas cell is removed so that the spectrum at this pressure can be recorded. The new pressure of  $\text{SO}_2$  in the apparatus is:

$$P_2 = \alpha P_1 = \alpha^2 P_0 \quad (3.3)$$

This process of dilution can be repeated. It follows that for  $n$

dilutions:

$$P_n = P_0 \alpha^n \quad (3.4)$$

#### Dynamic Sampling Procedure

The apparatus shown in fig. 3.4 was intended to model the on-line monitoring of discrete samples such as puffs of cigarette smoke. Argon continuously flowed along PVC tubing through the gas cell at near atmospheric pressure. Into this stream samples (puffs) of  $SO_2$  were injected from the reservoir which was initially at atmospheric pressure. The spectrometer was set up using slit control setting 8 and attenuated, as before, to give zero absorbance for the pure argon stream. The gas cell was cooled by water flowing through copper coils wound around the cell to dissipate the heat of the infra-red source.

The reservoir bulb was filled to atmospheric pressure with  $SO_2$ , the carrier gas flow rate was set by adjustment of taps E and F in fig. 3.4. Various samples were taken by syringe from the reservoir and injected into the constant flow rate carrier gas stream. The data representing the absorption that occurred as the sample travelled through the gas cell were recorded onto floppy disc using a microcomputer. Smaller concentrations could also be prepared by the gas dilution method.

The calculated absorbances were corrected for the small reduction in the  $SO_2$  partial pressure in the reservoir caused by sample removal.

### Pressure Correction Algorithm

Let the reservoir contain a volume,  $V$ , of  $\text{SO}_2$  at a partial pressure of  $P_0$ . When a sample is drawn, via septum C, the total volume that the  $\text{SO}_2$  occupies increases by the syringe volume,  $\delta V_1$ . The partial pressure of  $\text{SO}_2$  therefore falls to  $P_1$ .

As the pressure change is small ( $< 1\%$ ), the temperature remains constant and the ideal gas law is assumed to hold, so:

$$P_1 (V + \delta V_1) = P_0 V \quad (3.5)$$

which can be written as:

$$P_1 = P_0 \frac{V}{(V + \delta V_1)} \quad (3.6)$$

or

$$P_1 = \frac{P_0}{\left[1 + \frac{\delta V_1}{V}\right]} \quad (3.7)$$

The syringe is now removed from the septum leaving the pressure in the reservoir and syringe at  $P_1$  and changing the reservoir volume back to that of the reservoir,  $V$ .  $P_1$  is the pressure of the first sample of volume  $\delta V_1$ . For the second sample:

$$P_2 = \frac{P_1}{\left[1 + \frac{\delta V_2}{V}\right]} \quad (3.8)$$

Substituting from eqn. 3.8:

$$P_2 = \frac{P_0}{\left[1 + \frac{\delta V_1}{V}\right] \left[1 + \frac{\delta V_2}{V}\right]} \quad (3.9)$$

For the  $n^{\text{th}}$  sample:

$$P_n = \frac{P_0}{\prod_{r=1}^n \left[1 + \frac{\delta V_r}{V}\right]} \quad (3.10)$$

The pressure changes are all small, therefore a linear relationship between the absorbance and the partial pressure of  $\text{SO}_2$  can be assumed. So,

$$\frac{A_n}{P_n} = \frac{A'_n}{P_0} \quad (3.11)$$

where  $A_n$  is the experimental absorbance measured at a  $\text{SO}_2$  partial pressure of  $P_n$  and  $A'_n$  is the calculated absorbance that would be observed if the partial pressure was  $P_0$ . Therefore:

$$A'_n = A_n \prod_{r=1}^n \left[ 1 + \frac{\delta V}{V} r \right] \quad (3.12)$$

$V$  was measured and found to be  $291.0 \pm 0.2$  ml.

#### Band Location

A static concentration of  $\text{SO}_2$  was set up in the cell and the wavenumber scanned from  $6.7 \mu\text{m}$  until the peak reached its maximum value at about  $7.3 \mu\text{m}$ . In this way any error due to wavelength calibration of the instrument was eliminated. This was repeated after every hour to prevent wavelength drift occurring.

#### Re-optimisation of the Slit Control

The optimal setting of this control for dynamic samples might have been different from that for the static work. Therefore, the reservoir was filled with  $\text{SO}_2$  at 767.2 torr and the flow rate set at  $6.2 \pm 0.2 \text{ ml min}^{-1}$ . Samples of volume 0.6 ml of  $\text{SO}_2$  were injected at each of the slit control settings of the spectrometer. The results are shown in fig. 3.6. The *signal* was observed to increase with slit control setting corresponding

to increasing energy throughput and bandpass. Once again, line resolution is not important because the wavelength is not being scanned and so position 8 of the slit control, which gives the maximum signal-to-noise ratio was chosen.

#### Investigation of Blanks

At a flow rate of  $12.8 \text{ ml min}^{-1}$ , using an approximately 10% mixture of  $\text{SO}_2$  in argon mixture and standard experimental procedures, a 1 ml sample was injected into the argon stream. As expected, a peak was observed a few seconds later. Next a 1 ml blank of pure carrier gas was injected and no peak was observed. Neither was a peak observed when air was injected. However, when another sample of the mixture containing  $\text{SO}_2$  was injected, a peak equal in height to the original was seen. As the argon blank gave no peak it was concluded that perturbing the carrier gas stream by injecting an additional volume of gas into it has no effect on the output signal. Also as the air blank gave no peak it was concluded that displacing the carrier gas has no effect on the output signal. For convenience, therefore, air can be substituted for argon when making up  $\text{SO}_2$  mixtures.

### 3.3 RESULTS

#### Static Measurements

A calibration was obtained by preparing  $\text{SO}_2$  pressures in the range 0.6 - 18 torr. At each pressure the absorbance was measured on the standard spectrometer around  $7.35\ \mu\text{m}$  under the optimum conditions described in the experimental procedures. The precision of each measurement is  $\pm(0.004 + 2\%)$  in absorbance,  $\pm 0.25$  torr in the pressure range 1.0-10.0 torr and  $\pm 0.5$  torr above 10.0 torr. A plot of absorbance at  $7.35\ \mu\text{m}$  versus pressure is shown in fig. 3.7. It is linear

in the range 4-13 torr. However, there is a deviation below 4 torr due to desorption as explained later.

#### Further Instrumental Modifications

It was not possible to extend the above calibration to lower pressures as the spectrometer was not able to detect absorbance signals of less than 0.01. This was due to poor mechanical and electrical responses as detailed above (page 64). Therefore, the modification previously described was carried out and with the noise level reduced, the signal was output to the external chart recorder. After backing off to bring the 100% transmission at  $12.9\ \mu\text{m}$  close to the edge of the paper, the chart recorder sensitivity could be increased by a factor of 7. Absorbance signals would then be less than 0.003 at the instrumental detection limit, an enhancement of more than half a decade.

In order to extend the calibration below 1 torr it was necessary

to improve the gas handling procedure. This was done by obtaining lower pressures of  $\text{SO}_2$  using the dilution technique. It can be shown from eqns. 3.4 and 2.23 that a logarithmic plot of absorbance versus the number of dilutions,  $n$ , should be linear with a slope of  $\log \alpha$ , where  $\alpha$  is the dilution fraction. The fractional error in absorbance becomes significant at greater dilutions as can be seen by the scatter from dilution no. 9 onwards. Therefore the earlier measurements are more statistically significant. Hence, when calculating the slope by linear regression, the results must be weighted in proportion to the inverse of the dilution number. By presenting the results in this form <sup>in fig. 3-8</sup> it is shown in fig. 3.9 that the calibration is linear over two full decades. The average dilution factor between successive absorbance ratios compared to that calculated from the corresponding observed pressures (whilst on scale) agrees to within 1%. It is therefore acceptable to convert back by calculation to the format of fig. 3.7, i.e. absorbance versus pressure. The second and subsequent pressures were calculated from the initial measured pressure and the dilution factor. Thus a comparison was obtained (fig. 3.9) in which the effect of the precision of each pressure measurement had been eliminated relative to fig. 3.7. Each pressure now has a fractional error equal to the accuracy in the initial pressure measurement. The non-linearity in fig. 3.7 has also been eliminated by using the dilution technique although it is not clear whether this was due to eliminating the memory effect of the original gas handling procedure or eliminating the reliance on the vacustat

measurements.

In fig. 3.9 the two decades of linearity are shown but it has not been possible to show the non-linearity shown in fig. 3.8 by the extended range of the log format.

#### Desorption of Sulphur Dioxide from Perspex

During the static calibration measurements accidental damage to the cell occurred when chloroform, used for cleaning the windows, was introduced into the cell. This resulted in internal cracking of the plastic along stress planes. Although cracked internally, the cell was able to maintain the vacuum required during dilution and to contain the  $\text{SO}_2$  as the cracks did not extend to the external surface of the cell.

Further experiments with the cell revealed a persistent memory effect thought to be due to sorption and desorption of  $\text{SO}_2$  at sites along and within the cracks. This was verified by evacuating the cell and placing it in the spectrometer. Initially, the absorbance was seen to rise with time as  $\text{SO}_2$  desorbed into the vacuum as illustrated in fig. 3.10.

The following day further absorbances of the contents of this cell were measured and these began lower than the final absorbance of the first day but higher than the initial absorbance. The implication of this is that the some but not all of the  $\text{SO}_2$  had been re-sorbed overnight. Monitoring was continued for 5 days, the results are shown in fig. 3.10.

Unfortunately these observations include both kinetic effects (the dependence of the rates of desorption and sorption on surface and gas concentrations and on temperature) and thermodynamic factors (the temperature dependence of the equilibrium between the surface and gas concentrations of  $\text{SO}_2$ ). As a result fig. 3.10 is rather elegant but difficult to interpret.

The temperature within the cell varied because it was very close to the IR source. Heating occurred by convection, conduction and radiation during the day and cooling occurred at night after the instrument had been turned off.

In order to obtain meaningful kinetic and/or thermodynamic information, the temperature of the cell had to be kept near constant to  $\pm 1^\circ\text{C}$ . Cooling water was continuously passed through copper coils wound around the cell to attempt to stabilise the temperature. The cell was left in the sample compartment of the spectrometer which remained on overnight. Under these conditions the law of mass action relates the equilibrium constant of the process to the ratio of rate constants for sorption and desorption. Fig. 3.11 shows a plot of absorbance after the cell was exposed to 1 atm. of  $\text{SO}_2$ . At constant temperature the system approaches equilibrium in about 3.5 hrs. For the earlier results the temperature was not constant but increased slowly and so no equilibrium state was reached in 12 hours.

### Kinetics of Desorption

For a first order process the rate of desorption depends on the number of sorbed molecules. That is,

$$-\frac{dn}{dt} = kn \quad (3.13)$$

where  $n$  is the number of sorbed molecules,  $k$  is the rate constant for desorption at constant temperature and  $t$  is the elapsed time.

The integral of eqn. 3.15 is,

$$n = n_0 e^{-kt} \quad (3.14)$$

where  $n_0$  is the number of molecules initially sorbed.

Therefore, assuming that the rate of re-sorption is negligible, the number of desorbed molecules is:

$$n_d = n_0 - n = n_0 (1 - e^{-kt}) \quad (3.15)$$

Now, from the Beer-Lambert law of absorbance (2.23):

$$A \propto c \propto n_d$$

Substituting for  $n_d$ ,

$$A = K (1 - e^{-kt}) \quad (3.16)$$

where  $K$  is a constant. At equilibrium  $t$  is large and so:

$$A_{\infty} = K$$

$$\text{ie} \quad A = A_{\infty} (1 - e^{-kt}) \quad (3.17)$$

rearranging gives:

$$\ln \left[ 1 - \frac{A}{A_{\infty}} \right] = -kt \quad (3.18)$$

Therefore  $\ln(1-A/A_{\infty})$  was plotted against  $t$  (fig. 3.12) and the near linearity of the plot shows that first order kinetics are obeyed with a rate constant of  $(2.6 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ . There is a slight deviation from linearity at small temperature and this

change in kinetics is attributed to the cell heating up to thermal equilibrium.

A new cell was obtained and exposed to 4 atm of  $\text{SO}_2$  for 30 min. The resulting absorbance plot (fig. 3.13) shows, however, that less  $\text{SO}_2$  was sorbed than in the cracked cell. This implies that the cracks have a relatively large surface area. As can be seen from fig. 3.14, the desorption process is also first order for the new cell.

These results suggest that the data points at the low pressure end of figs. 3.7 and 3.9 have a higher than expected absorbance because of desorption. Fig. 3.7 shows this effect more markedly because, in the method used to prepare these  $\text{SO}_2$  atmospheres, the cell was exposed to 20 torr between each reading. Therefore, the effect remained about constant but only significant at lower  $\text{SO}_2$  pressures. However, in fig. 3.9 the dilution technique was used in which the  $\text{SO}_2$  pressure always decreased and so the memory also decreased accordingly.

At this stage it would be appropriate to demonstrate sorption of  $\text{SO}_2$  by the gas cell and calculate the rate constant. On consideration, it was concluded that it was not possible to measure the rate constant for sorption using infra-red absorption spectroscopy. This was because this would involve measuring a small increase in the large background level of unsorbed  $\text{SO}_2$ . Referring to the Beer-Lambert law (eqn. 2.23) it can be seen that the combination of ratio and log terms mean that no change in absorption could be seen for small sorptions.

### Dynamic Sampling

The microcomputer system, which is described in detail in Chapter 4, was used for data acquisition, storage, analysis and correction (according to eqn. 3.12). A typical result of a dynamic sampling experiment is shown in fig. 3.15. After a small lead time an absorbance peak is obtained from a dynamic sample. The steep attack of the peak shows that the leading edge of the sample did not diffuse nor mix to a significant degree as it flowed in the tubing to the gas cell.

The effective concentration seen by the instrument remains approximately constant for 0.5 s and then the intensity gradually decays to zero. The decay has a time constant just under 1 s corresponding to the sample being swept from the gas cell.

### Demonstration of the Sorption of SO<sub>2</sub> by PVC Tubing

During the early development of procedures and apparatus, sorption of SO<sub>2</sub> was observed when filling the reservoir. A simple manometer was used to indicate the pressure in the SO<sub>2</sub> reservoir. It consisted of a loop of PVC tubing, with one side connected to the reservoir and the other open to the atmosphere. When the mercury levels in the two loops were equal the reservoir had been filled to atmospheric pressure. With the reservoir filled with SO<sub>2</sub>, isolated from the rest of the apparatus via taps B and C and connected to the manometer via tap C, the mercury rose on the connected side of the manometer, showing that gas was being sorbed. When sorption was followed by evacuation of the manometer

via tap A, bubbles were observed in the mercury column but only on the side that had been exposed to  $\text{SO}_2$ , showing that the gas was being desorbed. In later work this effect was eliminated by changing to a glass manometer for which no sorption nor desorption of  $\text{SO}_2$  was observed.

#### Investigation of the Carrier Gas Flow Rate

The reservoir was filled with an approximately 10% mixture of  $\text{SO}_2$  in argon to a pressure of 767.4 torr. 1 ml samples from this mixture were then injected into the carrier gas stream at different flow rates. The standard experimental procedures were followed in all other respects.

Peak heights were measured, corrected and averaged over five samples. The background under each peak was estimated by interpolation from the background transmittance before and after each peak. The absorbances were then calculated and plotted against corresponding carrier gas flow rates (fig. 3.16), decreasing with increasing flow rate.

The samples were injected over a constant time interval. An initial explanation of fig. 3.16 is, therefore, that at higher flow rates the sample is being diluted in a greater volume of carrier gas. Calculation shows, however, that the diluent volume at a flow rate of 14 ml/min is only 0.1 ml which is less than the 1 ml sample volume. Therefore, dilution by carrier gas on injection does not explain why the signal at 14 ml/min dropped to less than half of its value at 3 ml/min, where the diluent volume

is negligible.

It will therefore be necessary to look at the behaviour of the system during detection not injection to explain the results in fig. 3.16. It will be seen that at higher flow rates, although the signal is reduced, the advantage of a more linear calibration is gained. Further advantages are that more results can be obtained in a given period as the time taken for the sample to travel along the tubing and the time to sweep the sample from the cell decrease in proportion to the flow rate.

#### Dynamic Calibration

In fig. 3.17 the peak absorbance has been plotted against various sample volumes of up to 0.5 ml, at a flow rate of 15 ml/min. In the figure a linear relationship between absorbance and sample volume holds from 0.1 to 0.5 ml such that increasing the sample volume directly increases the absorbance. Sorption by the apparatus and retention by the syringe displaces the calibration slope from the origin such that the sensitivity is reduced significantly below 0.1 ml.

Referring to the Beer-Lambert law modified for variation in concentration with optical path length (eqn. 2.25), it can be seen that absorbance is proportional to the integral of concentration. From fig. 3.17, therefore, the detected integral of concentration is proportional to the injected sample volume under the above experimental conditions.

Setting this argument aside, calculation shows that the conditions for laminar flow in the gas cell are not met as the Reynolds number  $N_{Re} \ll 2300$ . The condition for laminar flow being  $N_{Re} > 2300$ . In other words turbulent flow exists in the gas cell and, associated with it, mixing. The following mechanism is proposed to explain the increase in signal at lower flow rates in fig. 3.16. As the flow rate is decreased the amount of mixing decreases and the sample slug remains more intact. The slug travels via the centre of the gas cell in the fastest flow but this is also where viewing occurs and so an increased signal due to a more intact sample is seen.

On entering the gas cell at higher flow rates the sample slug is mixed by turbulence with carrier gas to a greater extent and its volume increases. The concentration decreases and lower signals are seen. Since eqn. 2.25 applies to fig. 3.17 (and only for uniform visible cross-sectional concentration) each visible section of the gas cell has an uniform distribution of sample in it due to mixing at 15 ml/min. The volume increase described must include a factor of increase in cross-sectional area since increase in length alone (sample stretching) has no effect on the concentration integral in eqn 2.25.

Results that obey the Beer-Lambert law would not be observed at lower flow rates where in any section of the gas cell the slug area was less than the visible area due to insufficient mixing. This would manifest itself as a reduction in the slope of the calibration curve at high sample volumes.

The results showed a deviation from linearity, of this nature, with decreasing flow rates. The reproducibility of the results, be the calibration linear or non-linear, is also reduced for decreasing flow rates due to variable effects of insufficient mixing.

However, as the flow rate is increased, a state is asymptotically approached corresponding to a homogenous cross-sectional distribution of gas throughout the cell for which linear calibrations can always be obtained. Fig. 3.17 is linear and reproducible and so the above state exists for that particular experiment.

Clearly, fig. 3.16 shows this asymptotic behaviour and it, therefore, also indicates the flow rates for which linear, reproducible calibrations can be expected.

### 3.4 CONCLUSIONS AND DISCUSSION OF FURTHER WORK

In this chapter a dispersive infra-red spectrometer has been used to determine  $\text{SO}_2$  quantitatively for investigative work. Signal processing deficiencies in the spectrometer were found to limit the detection limit under static conditions to 0.03% (27  $\mu\text{g}$ ). Modifications were made to the spectrometer signal processing chain and an improved performance was obtained giving a detection limit of 0.01% (9  $\mu\text{g}$ ).

Subsequently, the experimental procedure was changed from static to dynamic sampling which gave better background correction and microcomputer data acquisition was added to improve detector performance and data handling. A detection limit equivalent to injecting 1.5  $\mu\text{g}$  of  $\text{SO}_2$  was achieved. The amount of  $\text{SO}_2$  detected at the gas cell is estimated to be less than 0.002% assuming that there are no sorption losses in the apparatus and that complete mixing occurs on entering the gas cell. Neither assumption is entirely true but the assumptions have opposing effects on the estimated concentration at the detection limit.

As the above detection limit is an order of magnitude outside the range expected by LGC for analysis of a cigarette (50-500 ng) it can be concluded that LGC's existing instrumentation for CO analysis can not be used to determine  $\text{SO}_2$ . In addition difficulties would occur with their apparatus due to adsorption by PVC.

In infra-red spectrometry the measurement is invariably detector limited and so the detector's ability to "see" a small change in

a large signal will always be the fundamental restriction on detection limits for absorbance measurements. In this case it approached 1 part in 2000.

The development of techniques for the specific application of multi-channel real-time determination of  $\text{SO}_2$  in cigarette smoke at the nanogram level will now be considered. A dynamic investigation is of interest to LGC because the combustion products may vary with time. Understanding this variation could lead to recommendations about filter efficiencies and/or desirable stub length.

To use a laboratory instrument like the IR spectrometer with the smoking engine it is necessary to tailor the sampling method to the instrument, in this case by taking the sample to it in a gas stream, i.e. remote sampling. Errors may arise by sorption on the sampling apparatus. Sequential multi-channel analysis cannot be carried out in real-time as analyte must be stored in the sampling apparatus. Not only is valuable time resolved information lost but considerable time is also taken up between measurements. With chemical sensors placed close to the sites of combustion these limitations could be avoided and therefore this work now considers on-line detection using chemical sensors.

Automatic multiplexed data logging is necessary to record the large amount of data produced by real-time multi-channel analysis. The same microcomputer as used with the IR instrument was also applied to real-time microcomputer control of the multi-channel technique.

IR instrumentation is readily available, rapid to set up, selective, straight forward to use, reliable, and easy to maintain. This work involved improving gas handling procedures to prepare SO<sub>2</sub> atmospheres at the ppm level. This was achieved using the dilution technique. In the development process it was shown that SO<sub>2</sub> is sorbed reversibly by certain plastics under high pressure.

This chapter provides a foundation, for the investigation of the multi-channel real-time detection of SO<sub>2</sub> which requires the development of new instrumentation.

Piezoelectric crystal (PZC) sensors detect the mass change that occurs as a substrate absorbs gas phase species and are therefore not background limited. The correct choice of substrate gives both high sensitivity and selectivity. The investigation of the use of PZC sensors is described in the next five chapters. As this is a new technique it would be prudent to remain with a known analyte. The SO<sub>2</sub> preparation and sampling techniques and hence the PZC SO<sub>2</sub> calibrations that follow have been validated using an accepted, tried and proven method. The PZC technique will be applied in order to determine SO<sub>2</sub> at nanogram levels.

To make a sensor output compatible with a microcomputer requires some interfacing. In the laboratory application this is best done with a flexible interface system dedicated to the microcomputer that can be tailored to many sensors' requirements. The same microcomputer system was later used for signal processing with PZC detection as described in the next chapter.

3.5 FIGURES

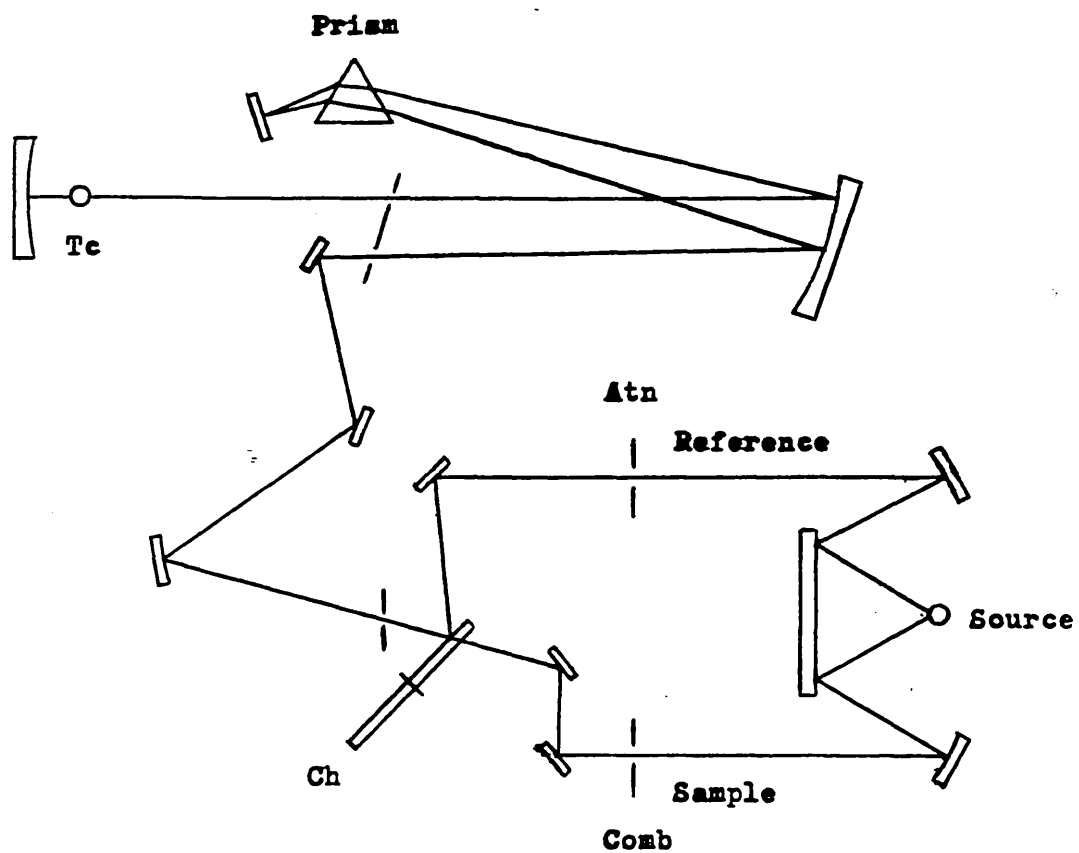


Figure 3.1 The optical layout of the infrared spectrometer.

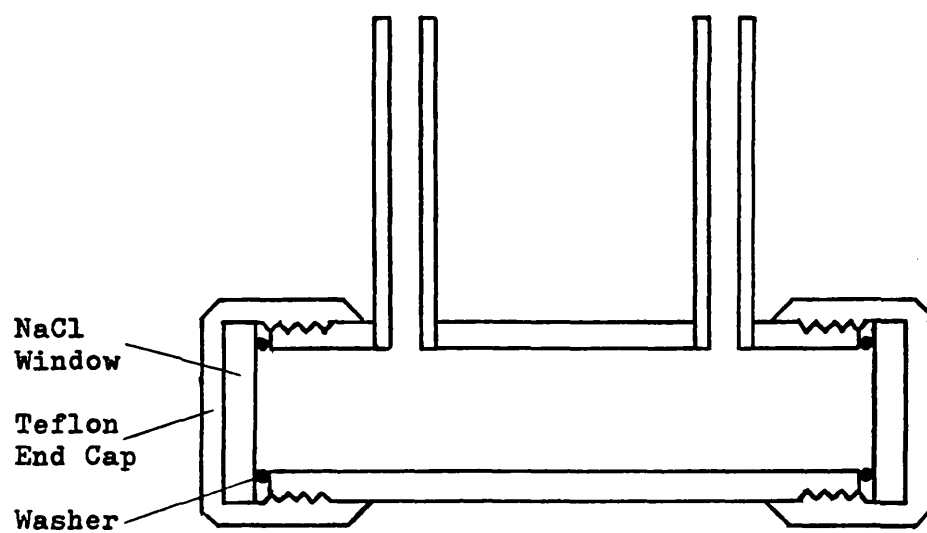


Figure 3.2 The infrared gas cell.

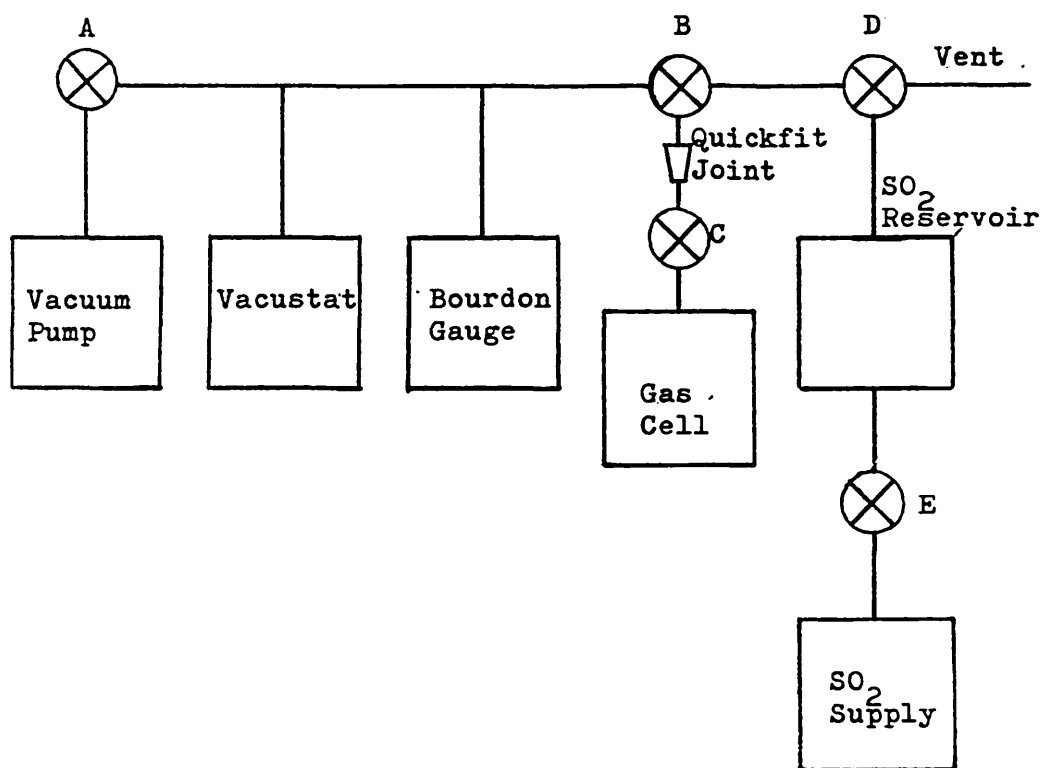


Figure 3.3 Schematic diagram of the vacuum line used to prepare gas atmospheres.

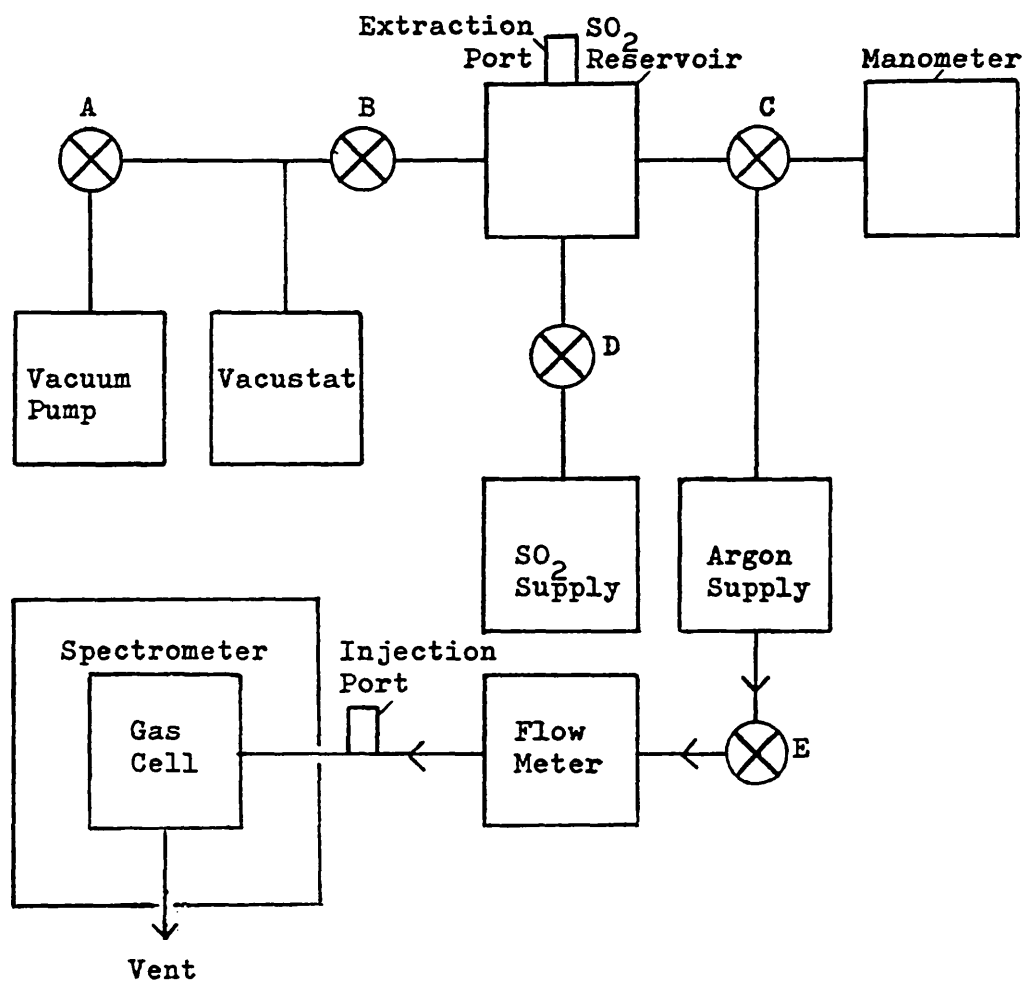


Figure 3.4 Schematic diagram of the gas line used to investigate the behaviour of  $\text{SO}_2$  in a dynamic gas stream.

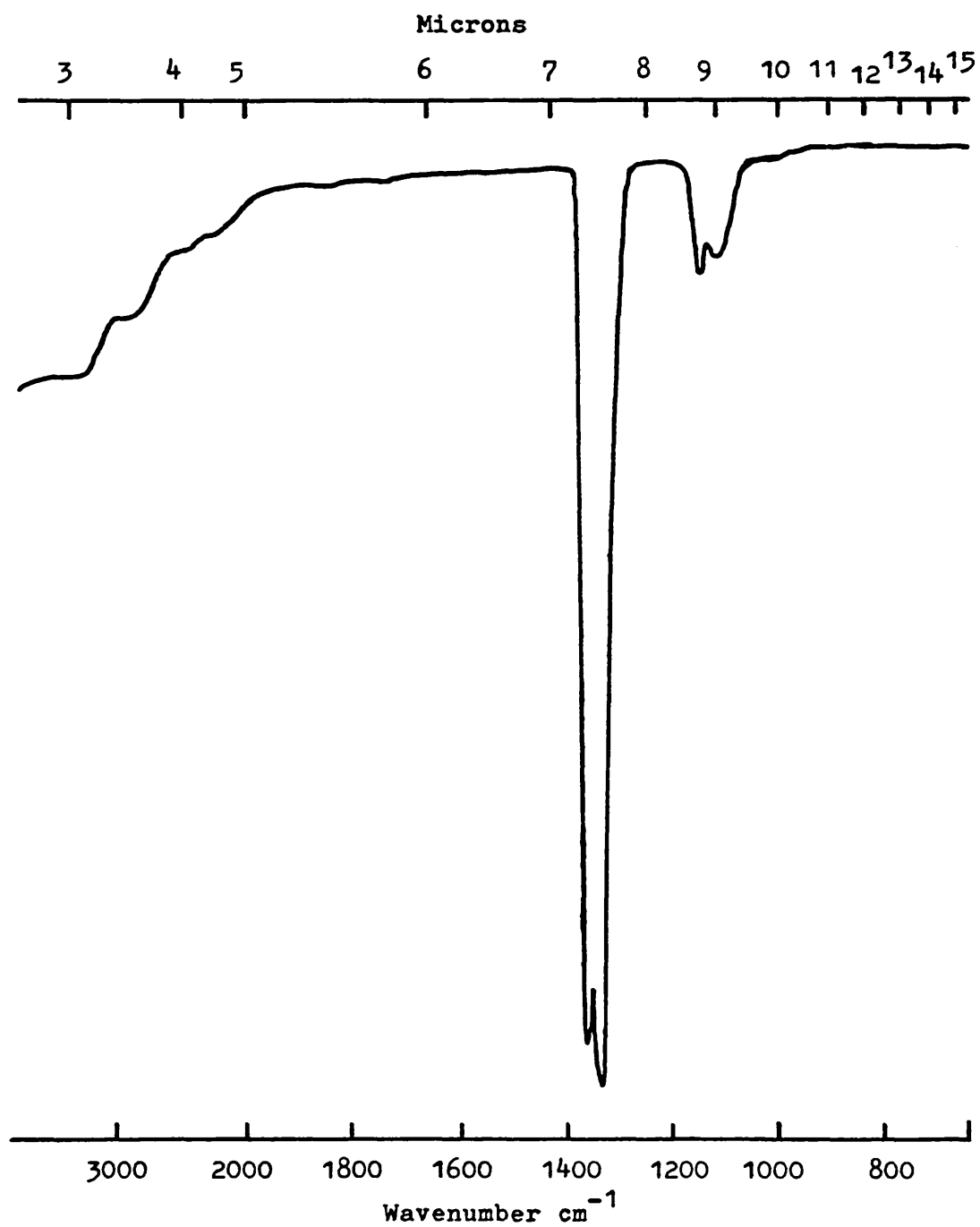


Figure 3.5 The infra-red spectrum of SO<sub>2</sub> from 2.5 to 15  $\mu\text{m}$ .

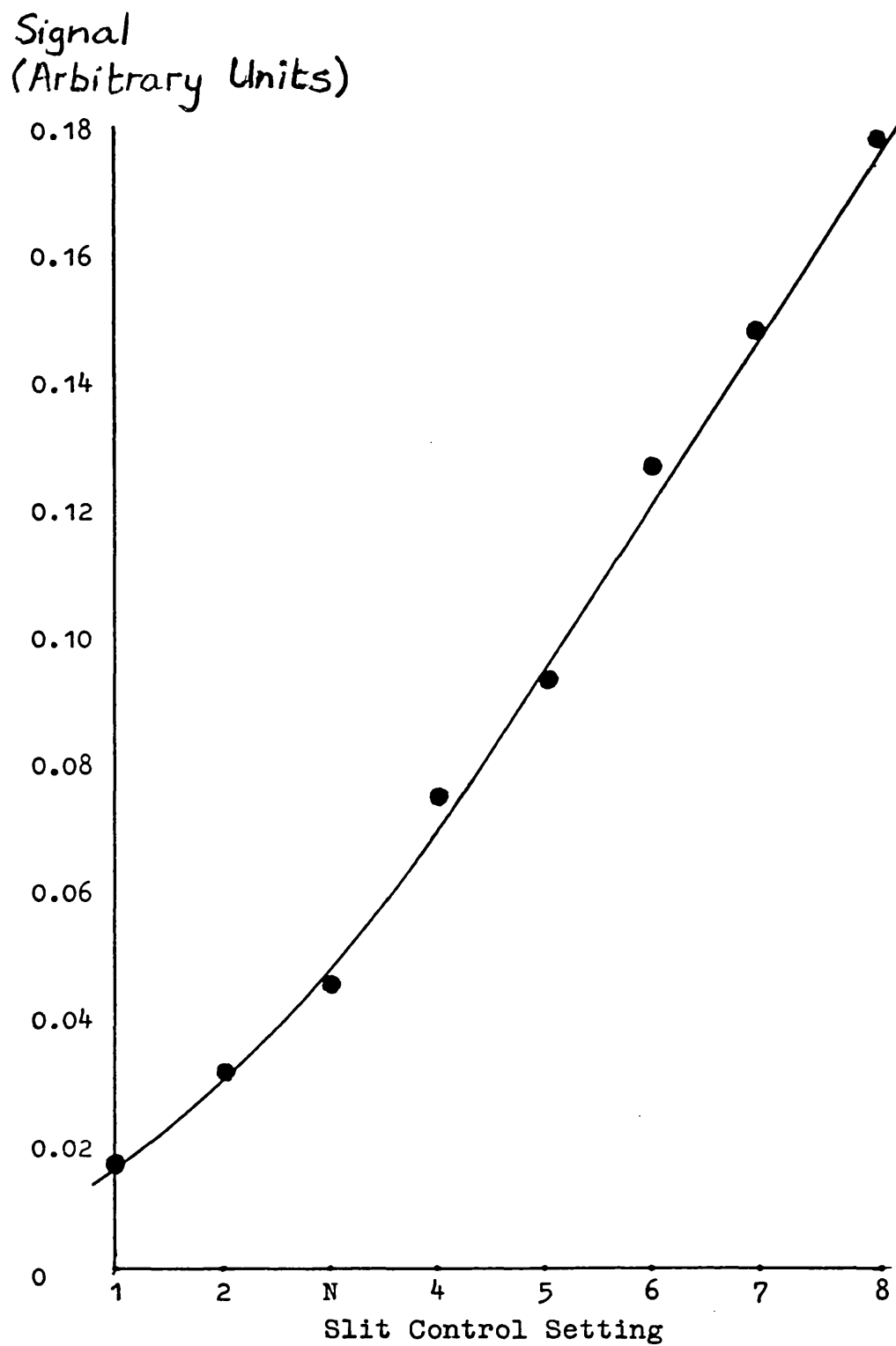


Figure 3.6 The *Signal* variation with slit control setting for dynamic samples.

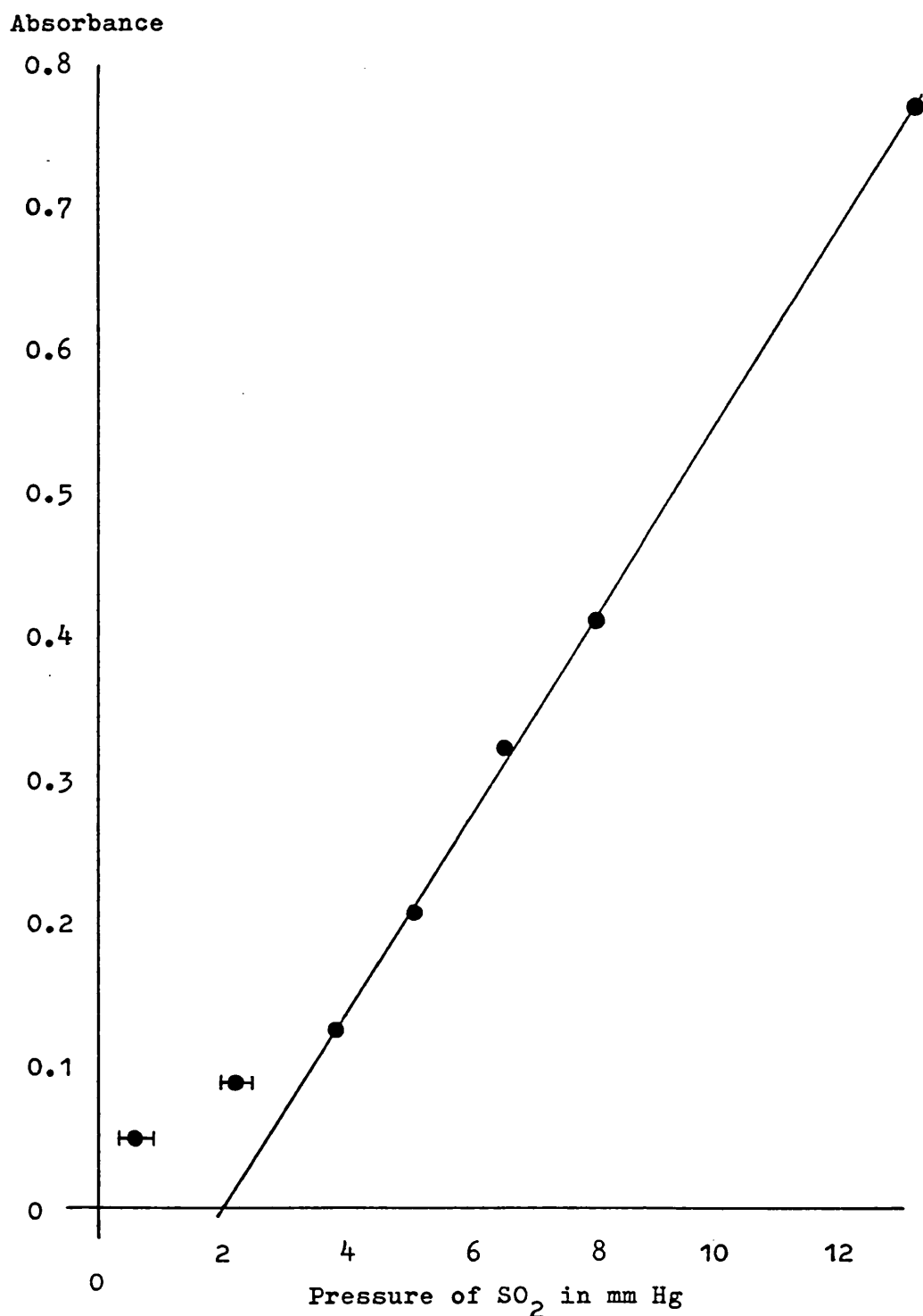


Figure 3.7 Calibration of absorbance at 7.35  $\mu\text{m}$  against measured  $\text{SO}_2$  pressure.

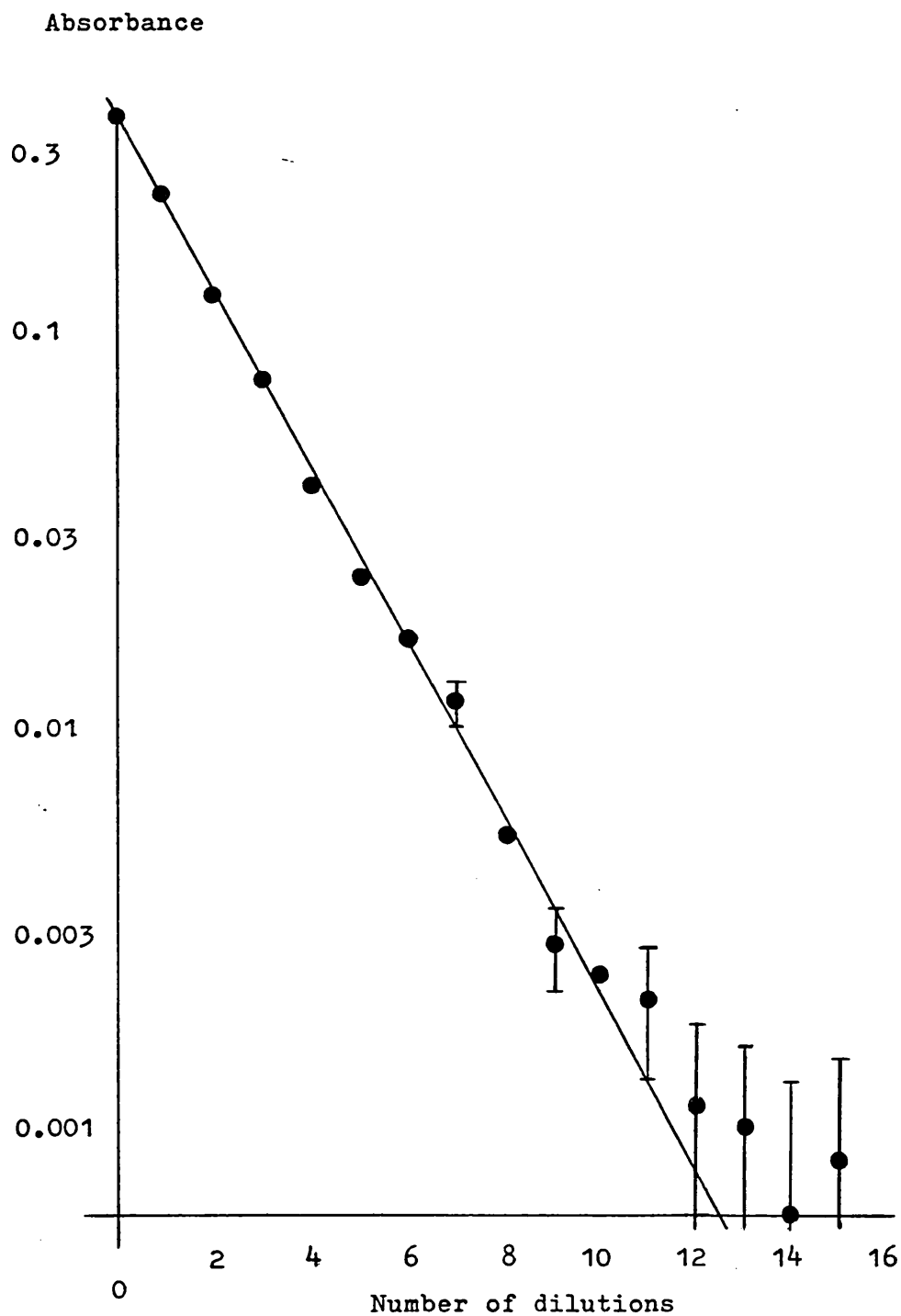


Figure 3.8 A wider calibration that was obtained by successively diluting  $\text{SO}_2$  in the gas cell.

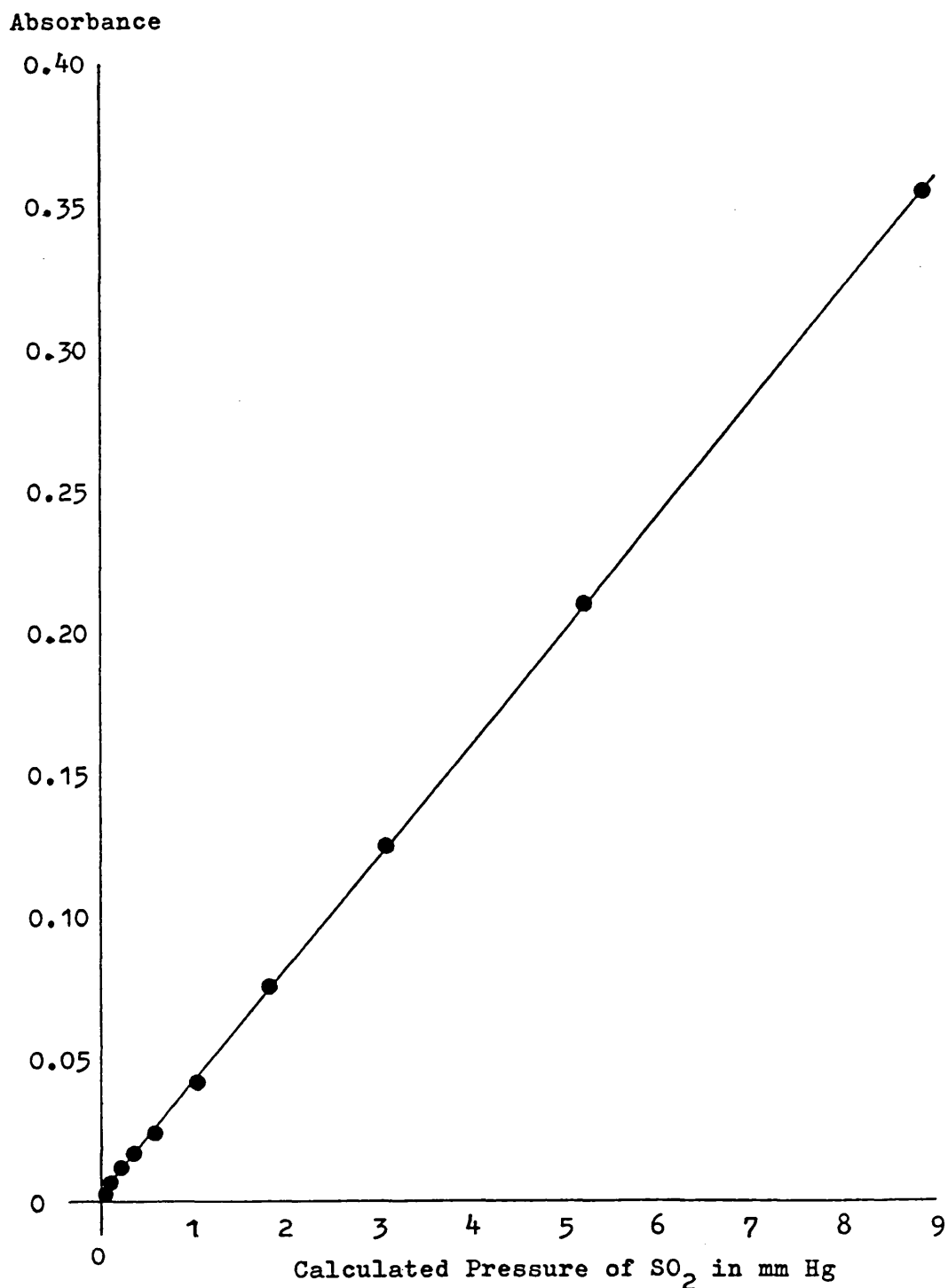


Figure 3.9 A wider calibration of absorbance at 7.35  $\mu\text{m}$  against calculated pressure of SO<sub>2</sub> using the gas dilution technique.

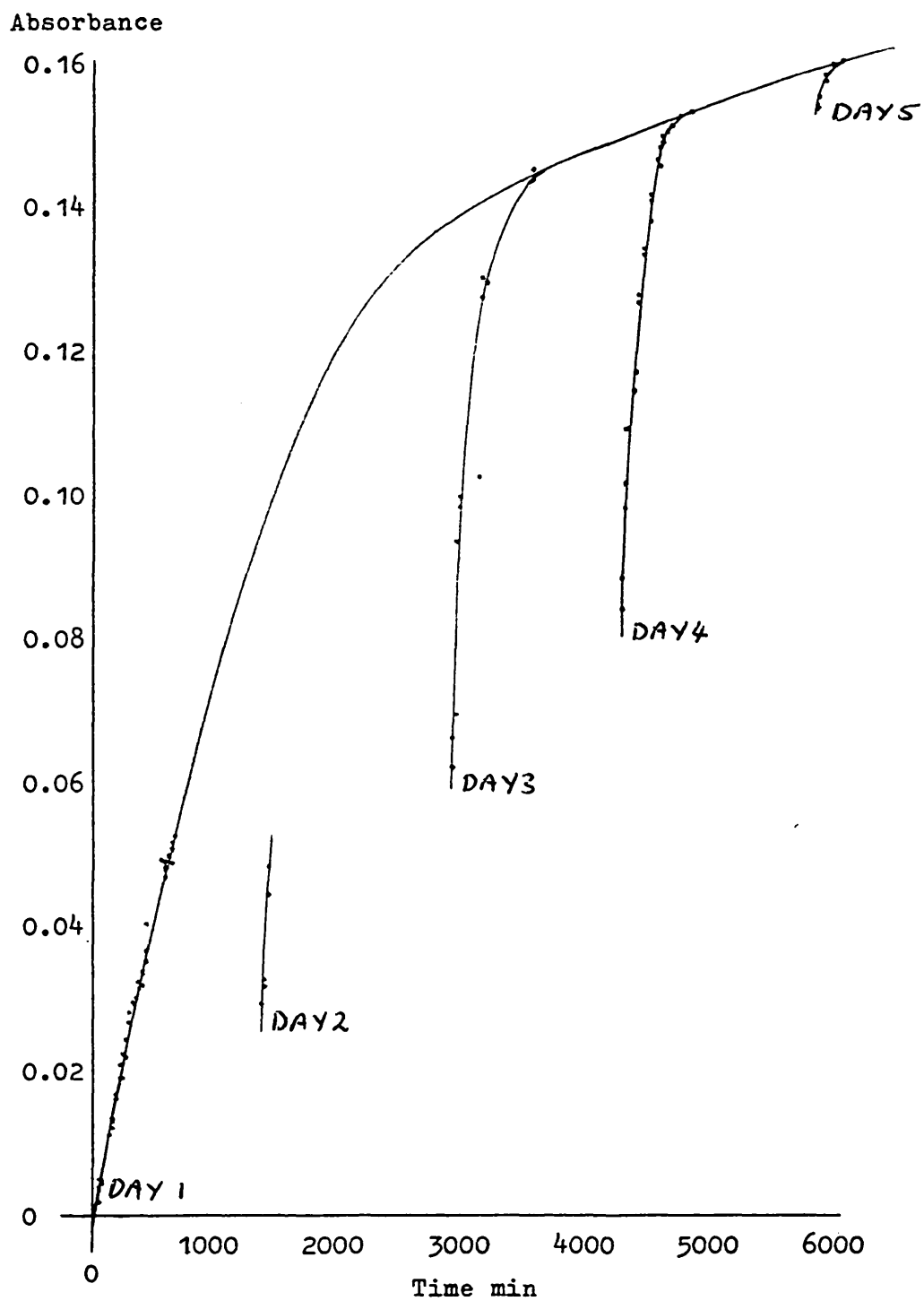


Figure 3.10 The adsorption and desorption of  $\text{SO}_2$  from the gas cell with variation in temperature.

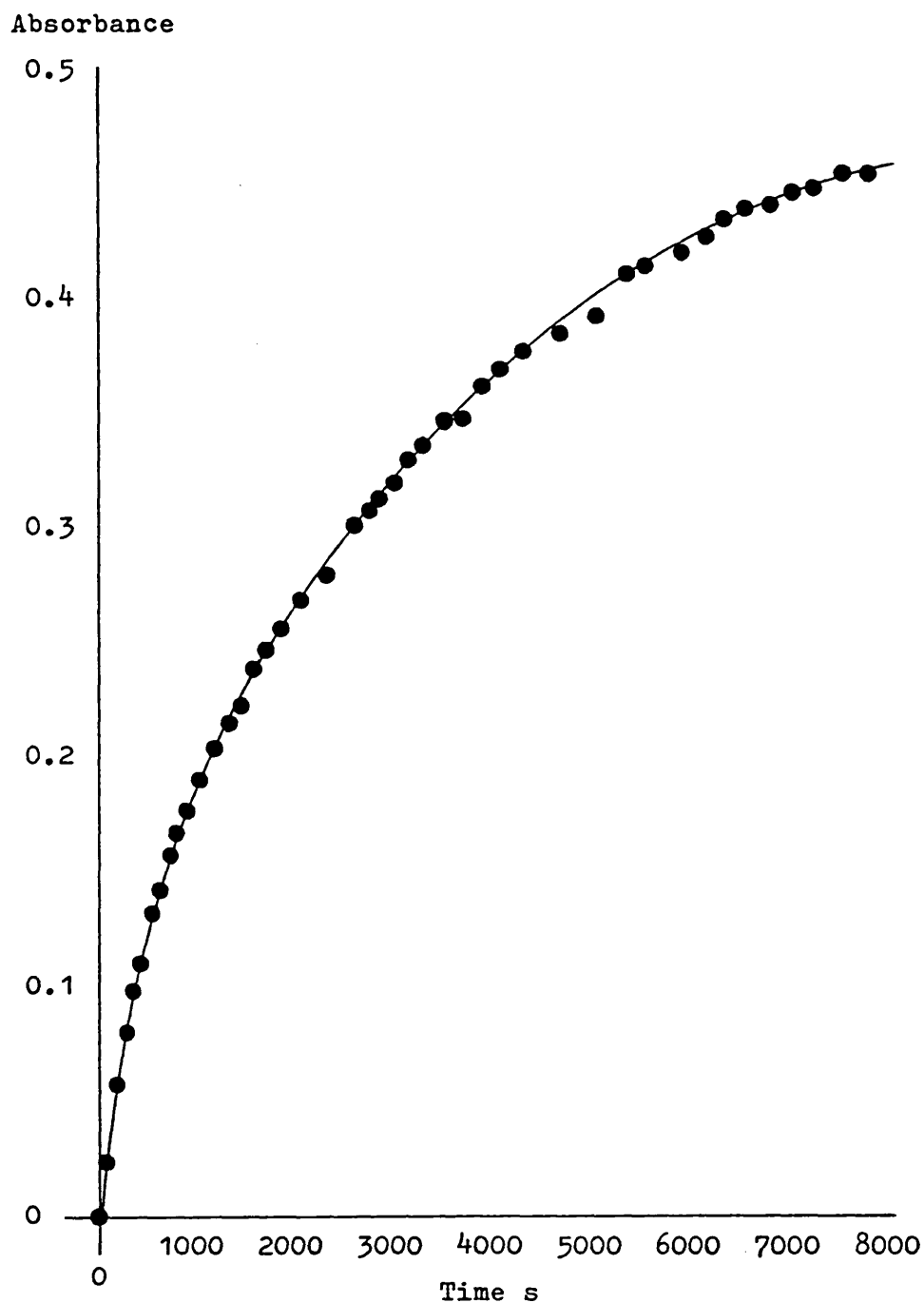


Figure 3.11 The desorption of  $\text{SO}_2$  from the walls of a gas cell exposed to 1 atm. of  $\text{SO}_2$  for 10 min.

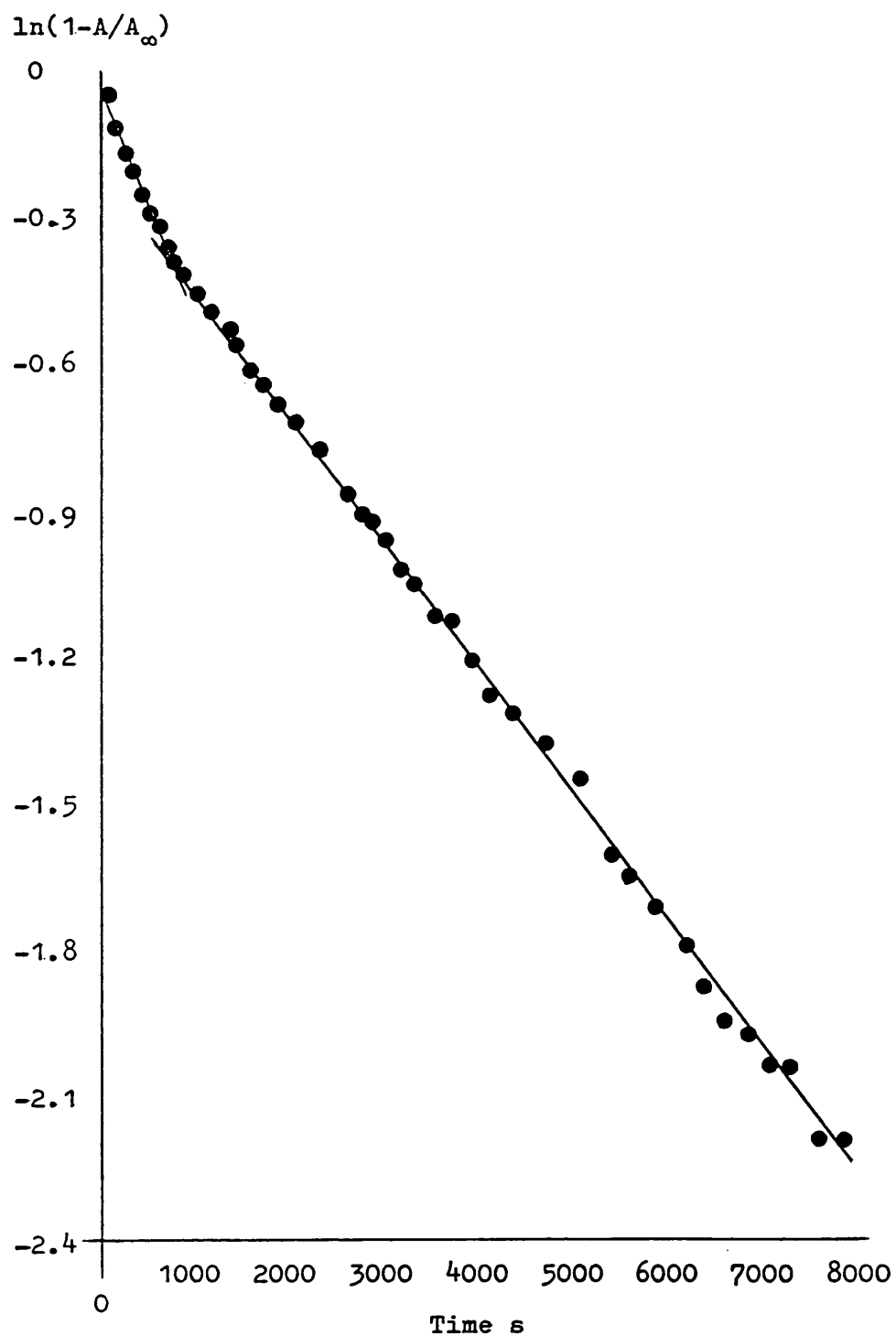


Figure 3.12 Kinetic plot of  $\text{SO}_2$  desorption from the walls of a gas cell exposed to 1 atm. of  $\text{SO}_2$  for 10 min.

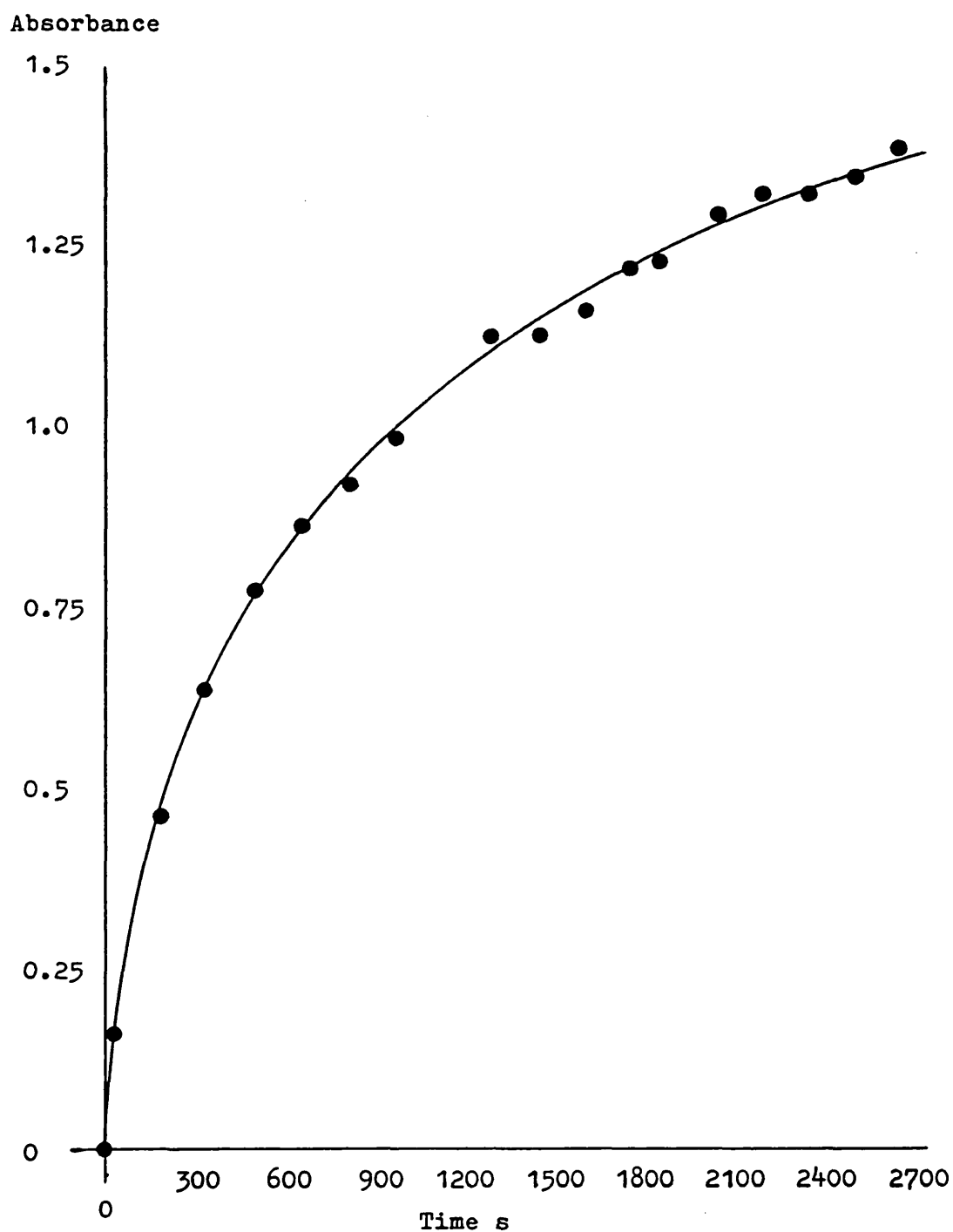


Figure 3.13 The desorption of  $\text{SO}_2$  from the walls of an uncracked gas cell exposed to 4 atm. of  $\text{SO}_2$  for 30 min.

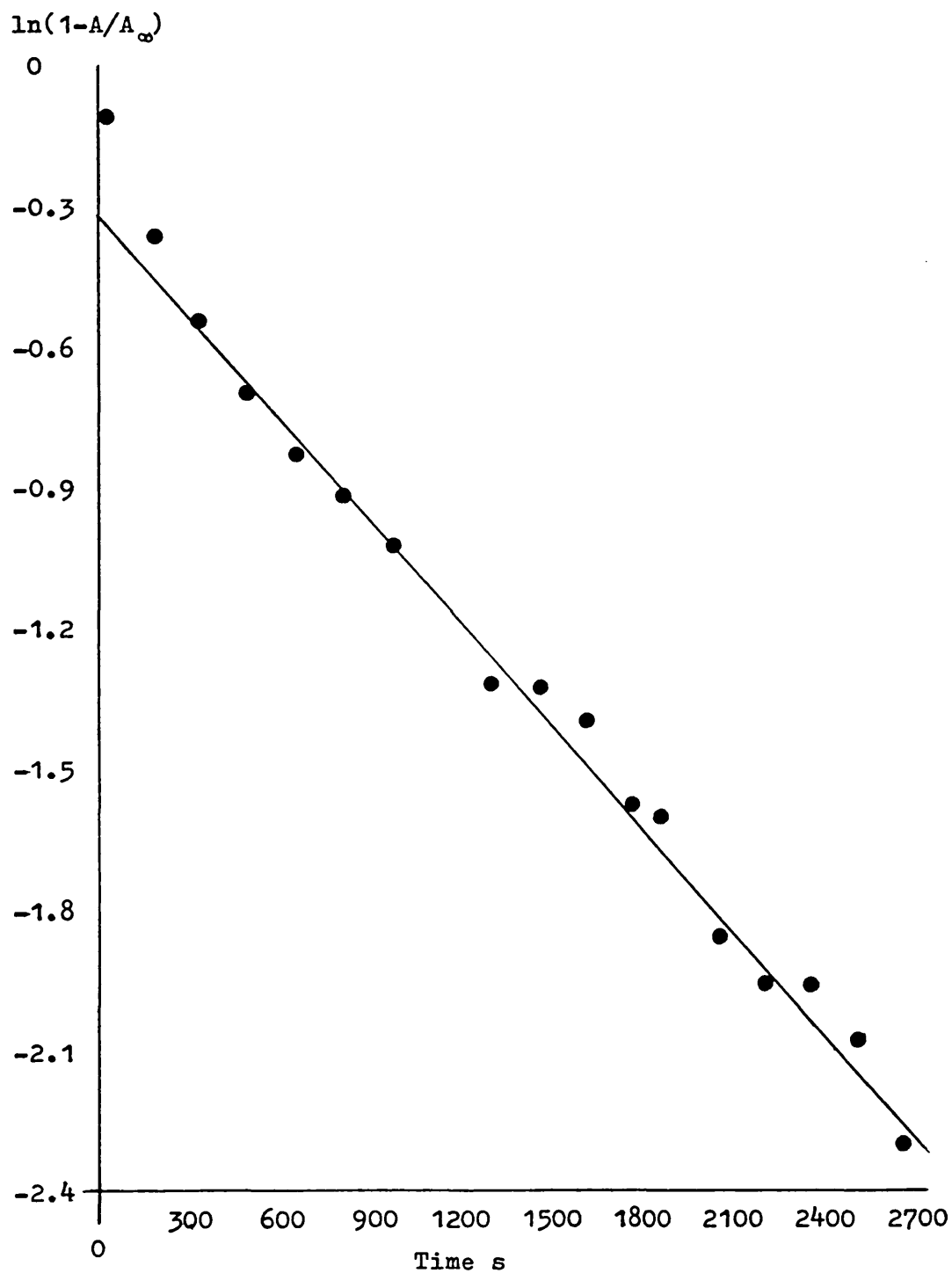


Figure 3.14 Kinetic plot of  $\text{SO}_2$  desorption from the walls of a second gas cell exposed to 4 atm. for 10 min.

Peak Height (arbitrary units)

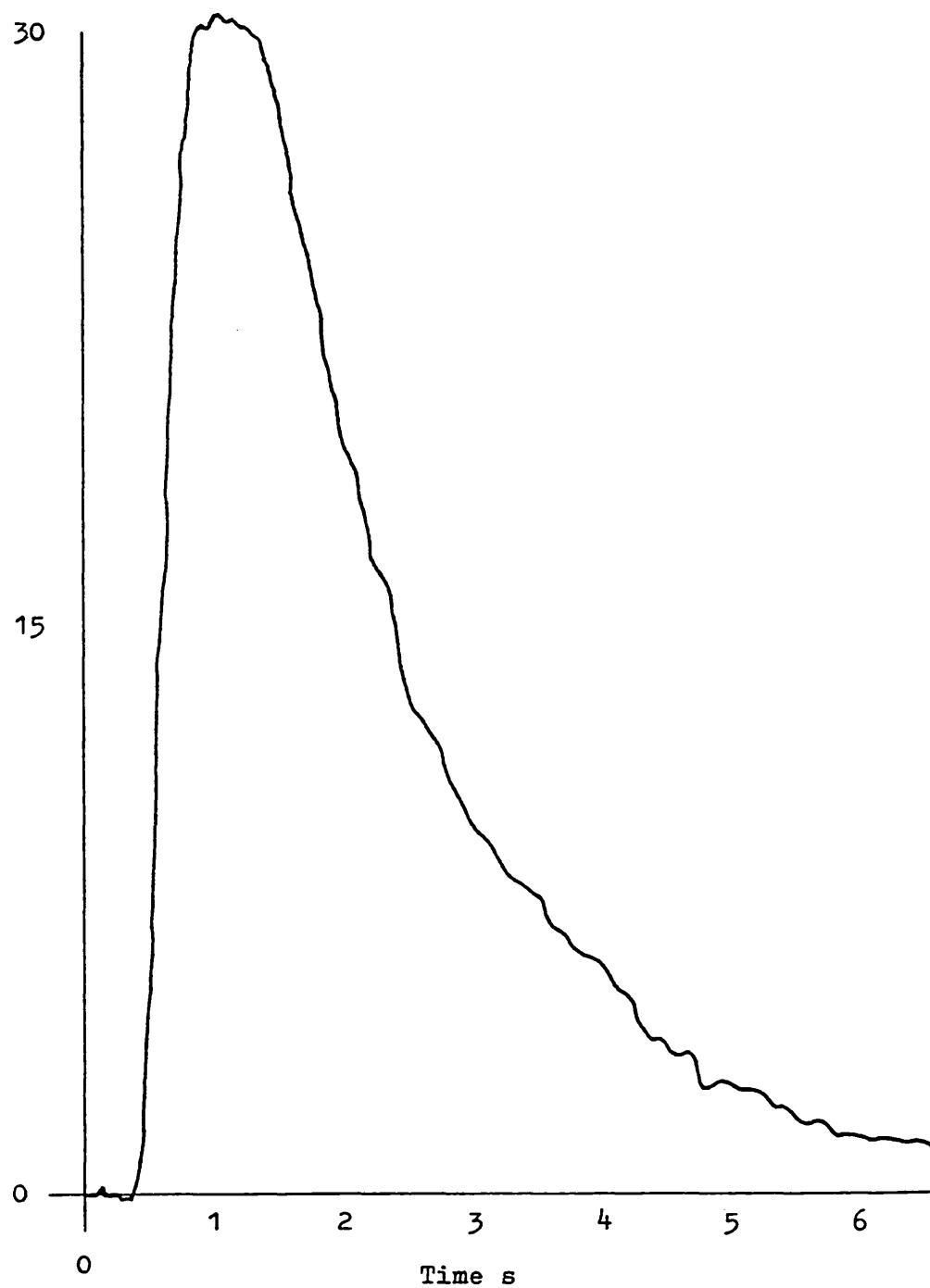


Figure 3.15 A typical absorbance peak obtained from a dynamic  $\text{SO}_2$  sample.

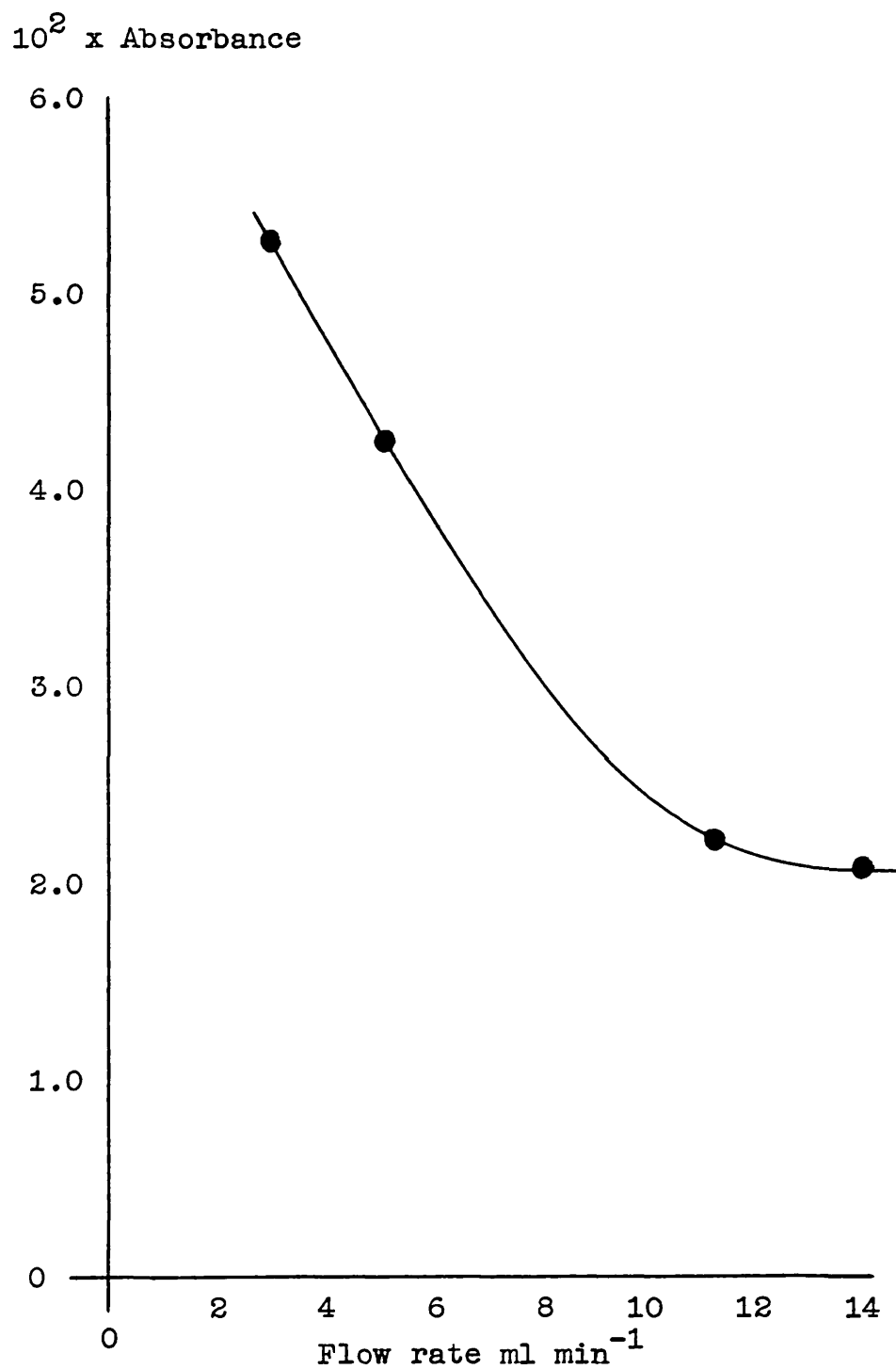


Figure 3.16 Variation of absorbance with the flow rate because of dispersion of  $\text{SO}_2$  on entering the gas cell.

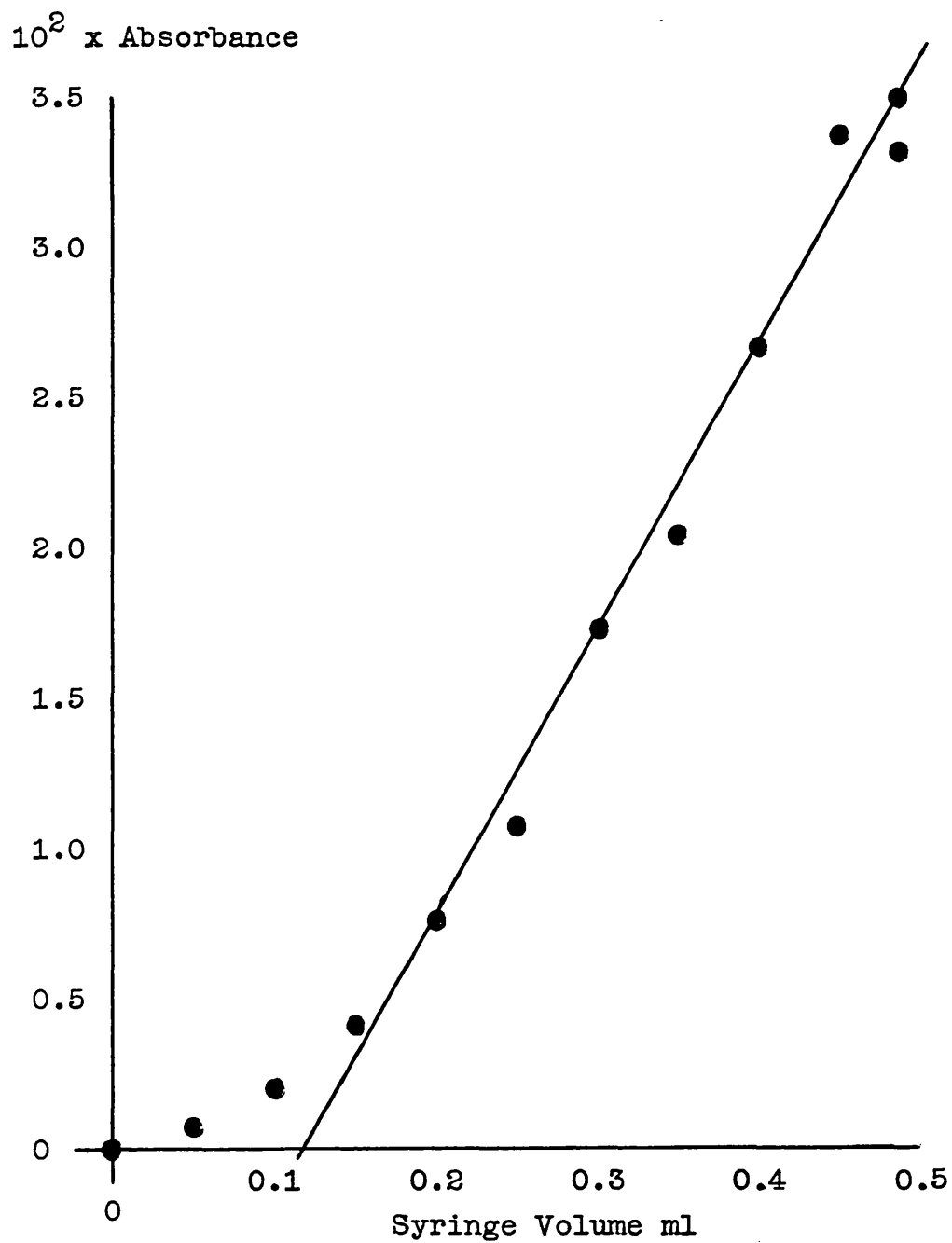


Figure 3.17 The linear relationship of absorbance versus injected SO<sub>2</sub> sample volume at constant concentration, showing that the sample is dispersed on entering the gas cell.

**CHAPTER 4**  
**PIEZOELECTRIC CRYSTAL INSTRUMENTATION**

### Uses of Piezoelectric Crystals

The most basic use of PZCs is in electronic lighters where compressive forces on PZCs generate voltages large enough to produce ignition sparks. By virtue of their sharp electro-mechanical resonance piezoelectric crystals (PZCs) are widely exploited in commercial and military communications. Quartz crystals are used for accurate frequency control of oscillators in radio, telegraph and television radio-frequency transmitters. Circuits with very high stabilities of 1 part in  $10^9$  or greater are used in everyday objects like digital clocks, watches and computers. Ovened oscillators have extremely high stabilities and are used in frequency counters. Low frequency crystals, de-tuned to produce many harmonics, act as multiple frequency standards. Selective band-pass filters with low losses can be built by incorporating PZCs as circuit elements.

Highly efficient sonic and ultrasonic transducers can be made with PZCs, the mechanical impedances of which closely match those of liquids and solids. They may also be used in the gas phase to good effect, even though matching is poor. Because of their small size and cost, PZCs are commonly found in crystal microphones and loudspeakers.

PZCs are used in mass and thickness monitoring as small, cheap sensors. The basic principles of mass monitoring were explained in Chapter 2. Thickness monitoring uses the same principles but it is also assumed that the bulk density of a coating material is equivalent to that of a thin layer on the PZC.

The related but less well known use of PZCs as chemical sensors in analytical chemistry and their use for the detection of micro-concentrations of substances is the subject of this work.

### Instrumental

The PZC instrumentation that was used in this work is described in this chapter. This includes a gas cell and oscillators to drive two crystals. These were developed from designs described in the literature. Although the PZC is an electrical component within the oscillator it is physically separate and is located in a gas cell where it is exposed to the analyte gas. The electrical connection of the PZC is thus long and complex. The performance of the oscillator and, therefore, of the sensor is shown to be critically dependent on this connection.

A Research Machines Ltd (RML) 3802 microcomputer and a temperature monitor were added to this conventional PZC instrumentation. The apparatus and the method by which the microcomputer controls the measurement of frequency and of temperature are described in this chapter. The interface between the micro, the PZC oscillators and the temperature sensors is a self-contained modular rack in which a multiplexed frequency and a corresponding temperature are measured almost simultaneously.

By eliminating the user from direct measurement, computer data acquisition considerably reduces the time required to obtain each datum. This increases the amount of data that can be measured in a set period which improves the statistical significance of the

results. For PZC work, the maximum data acquisition rate is set almost exclusively by the pulse counting procedure for frequency measurement, that is:

$$\text{measurement time} = \frac{1}{\text{resolution}} \quad (4.1)$$

Mass selectivity is achieved by coating the crystal with a substance that preferentially adsorbs the species of interest. However there remain additional, unwanted frequency changes as a result of changes in temperature and humidity. The apparatus enabled these effects to be investigated and the investigation indicates their significance in ambient monitoring applications and the degree of control that is necessary to maintain a constant frequency under laboratory conditions.

Furthermore, in Chapter 5 it is shown that the humidity response is itself affected by temperature. In Chapter 6 the microcomputer control approach to data acquisition for determining the detailed frequency responses of PZCs with respect to temperature is described. In Chapter 7 the apparatus is used to perform temperature compensation of a  $\text{SO}_2$  measurement and, with the unwanted frequency changes removed, to investigate coating behaviour.

#### 4.1 GAS LINES

The experimental set-up for testing PZC sensors is shown schematically in fig. 4.1. This apparatus allows the environment of the crystal in terms of gas composition and temperature to be varied rapidly. The apparatus can be modified to vary the water composition of the gas stream.

The analyte carrier gas stream is argon supplied from a regulator at pressures in the range 5-30 PSI. By passing it through a critical orifice (E), flow rates in the range 12-119 ml/min can be obtained. High purity argon from BOC is used which has an initial water content of less than 3 vppm. The argon is dried over silica gel and anhydrous calcium chloride contained in Dreschel bottles sitting in a water bath. By passing in close proximity to the drying agents and to heat exchanging coils in the water bath, the gas stream is brought to the temperature of the water bath which is controlled to within  $\pm 1^{\circ}\text{C}$  of a temperature in the range 4-60 $^{\circ}\text{C}$  by a Conair Churchill Thermoflow recirculating thermostatted water heating pump. A septum for injecting  $\text{SO}_2$  samples comes next in the flow line. The septum is as close as possible to the detector cell within which the analyte gas stream is directed by jets on to the oscillating PZC. The gas flow then passes over a temperature sensor and out of the detector cell. Finally, the flow rate is measured using a bubble flow-meter, the most suitable for the range of flow rates used, and then the gas goes to waste. The remaining apparatus was used (as described in Chapter 3) to prepare  $\text{SO}_2$  samples by gas dilution and to inject them using the dynamic sampling

procedure. A Hamilton Bonaduz 1001 TLL microliter syringe was used for this. Since  $\text{SO}_2$  is absorbed by plastics, the critical areas of the apparatus were constructed from Pyrex glass.

## 4.2 PIEZOELECTRIC CRYSTAL CIRCUITRY

### Piezoelectric Crystals

The PZCs used in this work are AT cut, operated at the fundamental mode resonant frequency of 10 MHz. Those with silver electrodes were obtained from Senator Crystals and those with gold from the Quartz Crystal Company. The crystals to be used as sensors were obtained in unsealed HC6/U holders. A few PZCs were obtained hermaetically sealed in HC6/U holders for testing the circuitry and for use as reference crystals.

In order to protect the surface finish of the silver electrodes of uncoated crystals from tarnishing they were kept in an evacuated dessicator.

### Frequency Measuring

The PZC work was initially started with a Racal SA 535 1.2 MHz Universal Counter-Timer which can function as a six digit frequency meter. However, frequencies of about 10 MHz are beyond the range of this device.

The driving circuit design, therefore, incorporates two quartz crystal oscillators and a frequency mixer/output buffer giving the difference in frequency. This beat frequency is typically 5 kHz and can be measured with the SA 535 meter to a resolution of 0.1 Hz. One crystal oscillator is used for the sampling PZC, the second crystal oscillator for a reference PZC.

The circuit is shown in fig. 4.2(b) and (c) and is contained in a diecast aluminium case with its own power supply. The power supplies to the FET oscillators are individually decoupled via R14. For the detector oscillator, active load Z2, see fig. 4.4(a), consists of: load capacitors C9, C10 and C11, an HC6/U socket protruding through the walls of the case, an HC6/U plug, a 0.5 m parallel twin cable, the HC6/U socket in the detector cell and the crystal. There are slight differences in the reference crystal oscillator which does not need C9 as shown in fig. 4.4(c).

A dual gate FET (Q1) serves as the frequency mixer and a monostable (IC1) as an output buffer providing a pulse of duration 10 ns at the difference frequency,  $f_1 - f_2$ . The oscillators are tuned to have different base frequencies so that any particular crystal oscillates 6120 Hz higher in the second oscillator compared to the first. This ensures that  $f_1 - f_2$  never goes to zero and hence is always measurable for any experimentally obtainable frequency change. Because of the minus sign, this frequency increases with increasing mass loading.

#### Improved Driver

After the microcomputer system had been installed it was possible to measure frequencies of 10MHz directly. The previous driving circuit had the limitation that the oscillation frequency of each crystal could not be measured. It was only possible to measure the difference between them. This was rectified by taking outputs directly from both the oscillators. The frequency mixer was

retained because it allowed a reference crystal to be used for compensation purposes as in earlier work [4.1-4.5]. The direct outputs then act as a check on matching.

Now, the frequency from one of the above three sources is selected by a purpose-built multiplexer and measured by a board in the interface rack.

The active load of each oscillator, which includes the crystal, connections, leads and load capacitors, affects the frequency, stability, amplitude and waveform of the output. The output loading of the oscillator circuit also affects these parameters. Optimisation of these parameters by use of load capacitors C9, C10 and C11 was carried out when the oscillators were first built. However, the sample channel was altered by the addition of the cable and second HC6/U plug socket combination. This gave rise to an unstable frequency exhibiting drift, wild fluctuations, random noise and periodic instability, see fig. 4.3(a) and (b). It was, however, still possible to carry out experiments because these instabilities occurred only occasionally.

The original HC6/U socket in the sample channel also gave problems. Its purpose in connecting a PZC directly to the detector oscillator was superfluous and in operation the socket, having no locking action, often worked loose with the associated capacitance change affecting the frequency. It was therefore replaced by a miniature BNC socket and the HC6/U plug on the cable was replaced with the corresponding miniature BNC plug.

This gave a more mechanically sound connection.

In order to take outputs directly from each oscillator, buffers (IC2) were added to both channels so that the change in load that occurs when the multiplexer switches could not degrade the frequency stability. The amplitude and waveform of each oscillator were re-optimised by replacing the load capacitors with C5. The modified circuit is shown in fig. 4.2(a); fig. 4.4(b) shows the modified active load.

The outputs of these buffers are low noise, sine waveforms of approximately 10 MHz at TTL levels. Square waves are not observed because their period is similar to the switching time of the integrated circuits. After making these improvements the measured frequency was found to be extremely stable showing digitisation noise only as in fig. 4.3(c).

#### Frequency Multiplexer

The multiplexer (fig. 4.5) was built to switch between the three frequencies output by of the driving circuit (two oscillators and the difference output). It was designed to be controlled by a single timer board within the interface rack and to operate at frequencies of ca. 10MHz. 74 series TTL integrated circuits (ICs) were used in its design.

The counter (IC1) on the multiplexer board has one of four states (0-3) and is incremented on each clock pulse from the controlling timer board which is also connected to the carry

signal. The count is decoded by the 2 to 4 line multiplexer (IC2) to give the desired output frequency i.e.  $f_1$ ,  $f_2$  or  $f_1-f_2$ . This switching does not result in a loss of amplitude because the circuit is digital, nor does it cause an alteration in the frequency because each pulse coming from the currently chosen input must be reflected at the output.

Light emitting diodes D1-D3 are incorporated as a diagnostic tool for the controlling software, to show whether any hardware faults occur and to display the currently selected output channel.

### 4.3 TEMPERATURE SENSING

#### Temperature Sensors

Temperature measurements are accomplished by AD590 kH integrated circuit temperature sensors for which the output current is proportional to the absolute temperature ( $1 \mu\text{A/K}$ ). Since the AD590 kH is a current sourcing device it is ideally suited for this remote sensing application where the transmission of the output does not produce degradation due to line resistance, connector resistance or noise.

#### Circuits

In the apparatus, a temperature sensor is located in the detector cell in close proximity to the PZC. The output current is transmitted over a twisted pair line to the interface rack where it flows through a  $1 \text{ k}\Omega$  load resistor which produces a voltage proportional to the absolute temperature. The other temperature sensors are used similarly to monitor the temperature of the reference crystal and the frequency measuring board. The circuit required to do this is very simple and is shown in fig. 4.6. The three output voltages then pass to an analogue multiplexer board which selects one of them. The offset and gain of the multiplexer are used to signal condition the output voltage so that it lies between  $+10$  and  $-10\text{V}$  over the temperature range  $0$  to  $80^\circ\text{C}$ .

The signal then passes to a 12-bit ADC board where it is measured with a resolution of  $0.02$  degrees per bit. In the one second interval it takes to obtain one frequency measurement, 50

corresponding temperature measurements are obtained with a noise level corresponding to  $\pm 0.03^{\circ}\text{C}$  which is the same as the ADC resolution. Calibration by adjusting the 100  $\Omega$  resistors is only necessary at one temperature because of the linear output of the temperature sensors.

#### 4.4 DETECTOR CELL

In the detector cell (fig. 4.7), which is similar to one previously described [4.6], the sample gas is split into two streams which impinge simultaneously on the opposite faces of the crystal. For improved sensitivity the two streams are brought by jets very close to the centre of the crystal, which is the most mass sensitive region. Karmarkar and Guilbault [4.6] reported that this type of cell gave a three fold improvement in sensitivity over a cell with a non-directed inlet.

The main body of the cell is built around a B24 socket. The crystal holder plugs into an HC6/U socket attached with studding to an aluminium block which is bonded with epoxy resin into the end of a B24 cone. The connections pass through the block and join the parallel twin cable, which runs to the oscillator. The crystal is, thus, situated in the flattened portion of the cell but is easily removed for inspection, cleaning, coating and storing. An additional feature is the temperature sensor which is installed in the enclosure in close proximity to the crystal.

#### 4.5 REFERENCE CELL

The reference crystal is located in a glass bulb and is immersed in a water bath which is maintained at  $25 \pm 1^\circ\text{C}$ . When the electronic mixer is used for output, this crystal provides the constant frequency,  $f_1$ , from which the variable frequency,  $f_2$ , is subtracted to give the beat frequency.

#### 4.6 WATER VAPOUR GENERATION APPARATUS

A method for generating defined quantities of water vapour has already been developed in this laboratory [4.7]. Argon is passed at a fixed flow rate of 1.0 l/min over a constant surface area of water contained in a Dreschel bottle. The temperature is controlled between 5 and 50°C by placing the Dreschel bottle in a water bath with a thermostatic control.

An experimental calibration is carried out to determine the amount of water vapour carried (mg/l argon). To do this, a calcium chloride drying tube is connected to the outlet of the apparatus and the amount of water vapour carried per litre of argon is determined gravimetrically. The calibration graph is shown in fig. 4.8.

For normal use the device is attached to the apparatus shown in fig 4.1 in parallel to and bypassing the drying tubes so that dry argon can still be passed over the crystal when water vapour is not required. Using this system the crystal temperature thermostat must always be set greater or equal to the humidity one in order to prevent condensation of excess water.

#### 4.7 MICROCOMPUTER SYSTEM

The signal processing interface was a 6U Eurorack system designed and built by the Imperial College Chemistry Microprocessor Unit. The interface formed part of the microcomputer data acquisition system as illustrated in fig. 4.9. The interface rack holds 16 function boards on double Eurocard PCBs. On each board an eight-bit number is available to the microprocessor which identifies the type of board e.g. ADC, DAC, timer or multiplexer. A software controlled method of addressing the individual boards allowed the user to access the boards without having to know their exact position in the rack. This method is called "type/number" addressing, in which each board is addressed by its identifier number and by the number of boards of that type, which is counted up from the left most slot position.

The procedure whereby one of three frequencies is selected by the digital multiplexer was described earlier. This occurs under microcomputer control via a timer board operating in single shot mode. This frequency is measured by a purpose built board which has a range of 0 to 20 MHz and a resolution of 1 Hz. The internal reference is a RS 307-430 10 MHz crystal oscillator module. The cost of a frequency meter of equivalent range with microcomputer compatibility, such as the RS232 serial or GPIB parallel interface, would be prohibitive.

After selection and conditioning by a 16 channel analogue multiplexer board, the temperature signal then passes to a 12 bit ADC board. Analogue to digital conversion is initiated every

20 ms by a pulse from a second free running timer board. At the end of each conversion, which takes about 10 ms, the computer then reads the conversion value from it with a resolution of 0.02 degrees per bit.

A BASIC program was written on the RML 3802 to acquire experimental data from the sensors via the interface rack. The program calls standard subroutine modules, most of which were included in the software used in Chapter 3. It is these modules which allow the 3802 to control the boards in the interface rack. They were written, assembled and linked to produce a modified RML BASIC interpreter.

The software allows for calibration of the temperature sensors at one temperature and averages 50 temperature measurements for each frequency measurement. Frequency and temperature data are stored every second on floppy magnetic discs. Under menu selection, the results can be presented in any combination of the following ways: numerically on the VDU and the printer, graphically on the VDU and on the chart recorder (frequency versus time) or the X-Y plotter (frequency versus temperature). Presentation can occur either during acquisition or after the experiment has been completed using further software. The output to the chart recorder or X-Y plotter is via a graphics board, which is a modified digital to analogue converter board.

Additional software was produced for conversion of data to text format for transfer to a BBC B microcomputer (BBCB) via an RS232 interface. A program was produced for the BBCB which Fourier

transforms frequency change with respect to temperature data and gives 21 term Fourier series representing temperature calibrations. This will be explained in more detail in Chapter 6.

# 4.8 FIGURES

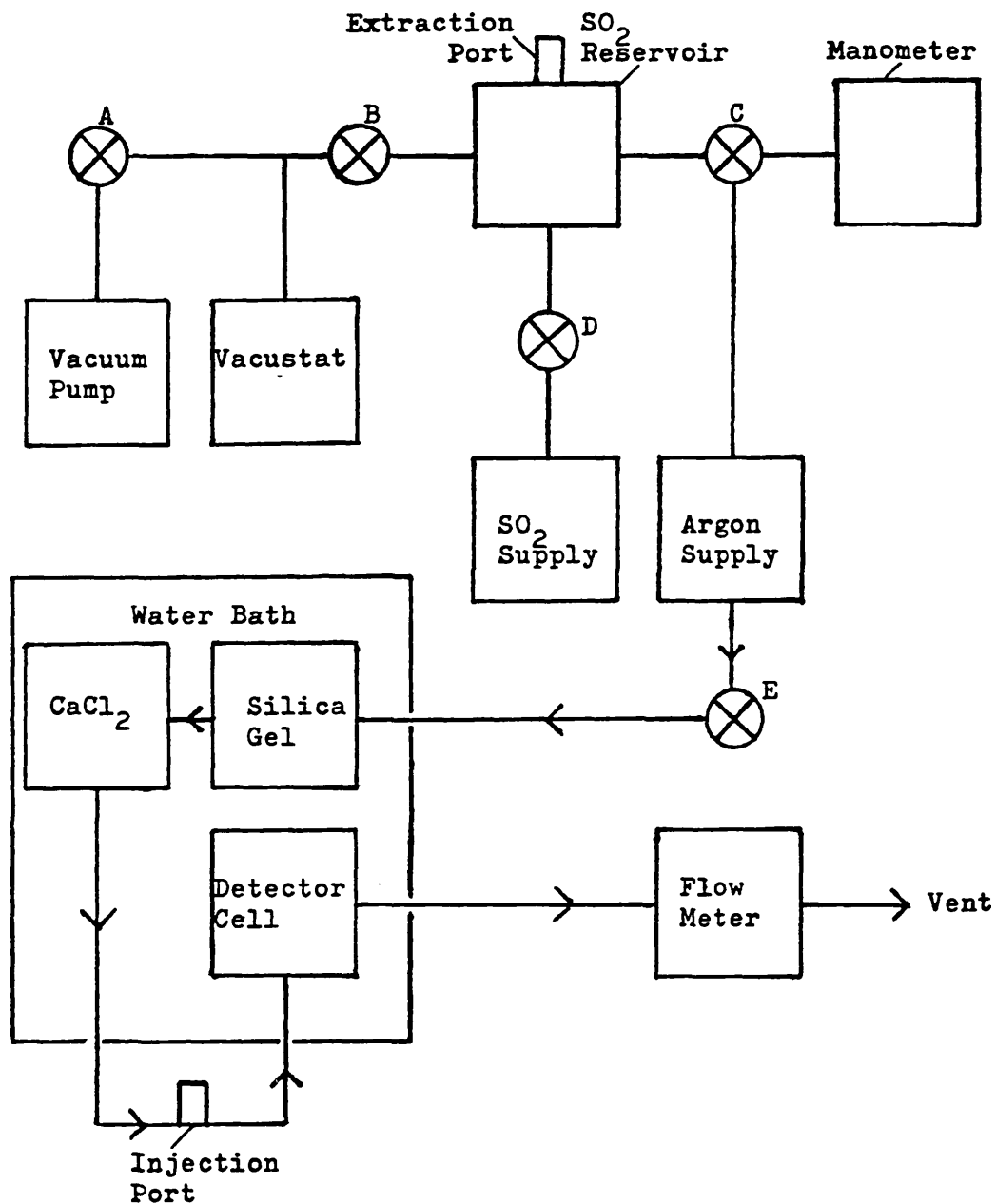
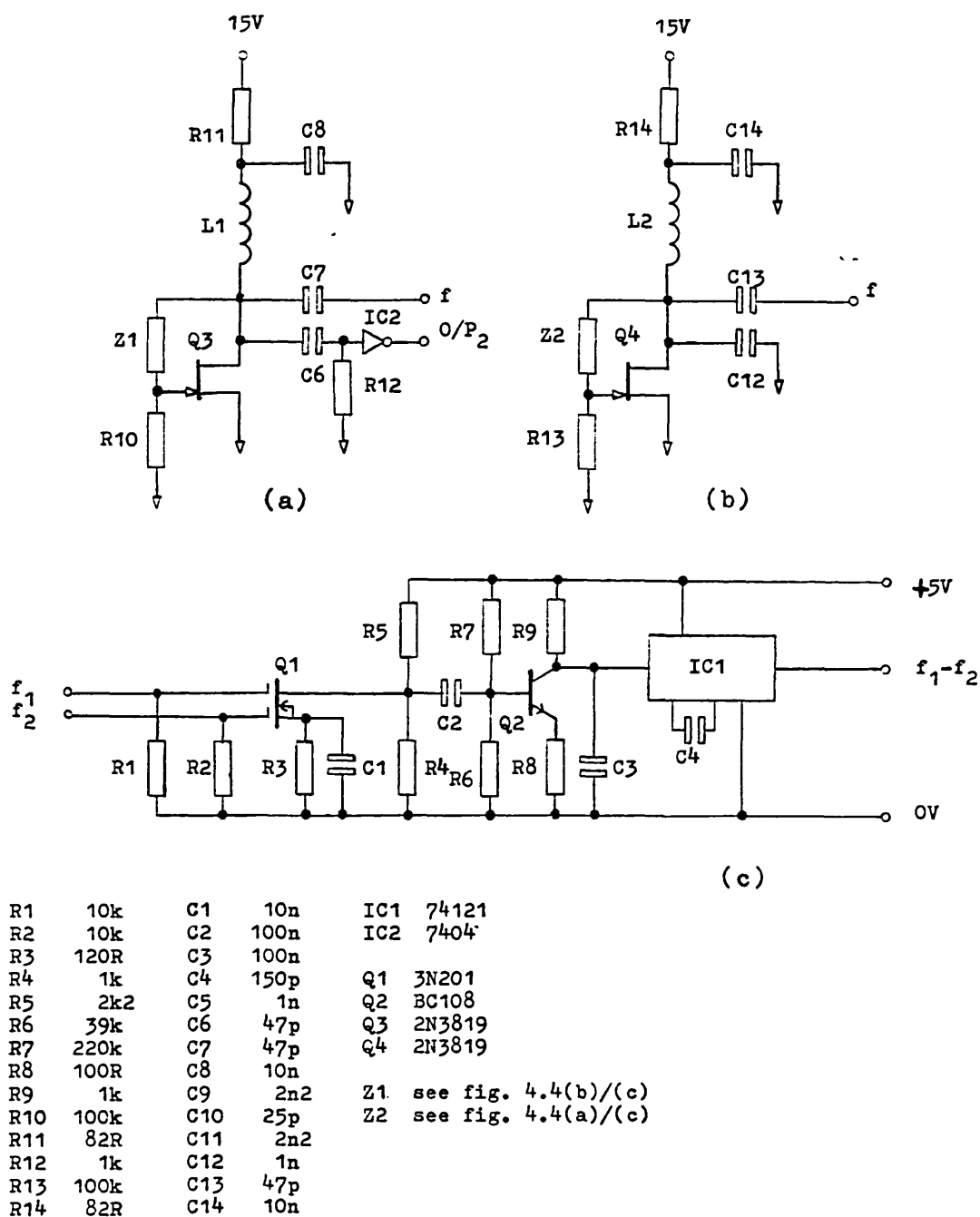


Figure 4.1 Schematic diagram of the gas line used to investigate the thermal response of piezoelectric crystal sensors and to calibrate them for sulphur dioxide.



**Figure 4.2** Circuit diagrams of (a) a Pierce type piezo-electric crystal oscillator with a buffered output, (b) oscillator with non-buffered output and (c) a frequency mixer with high impedance input and buffered output.

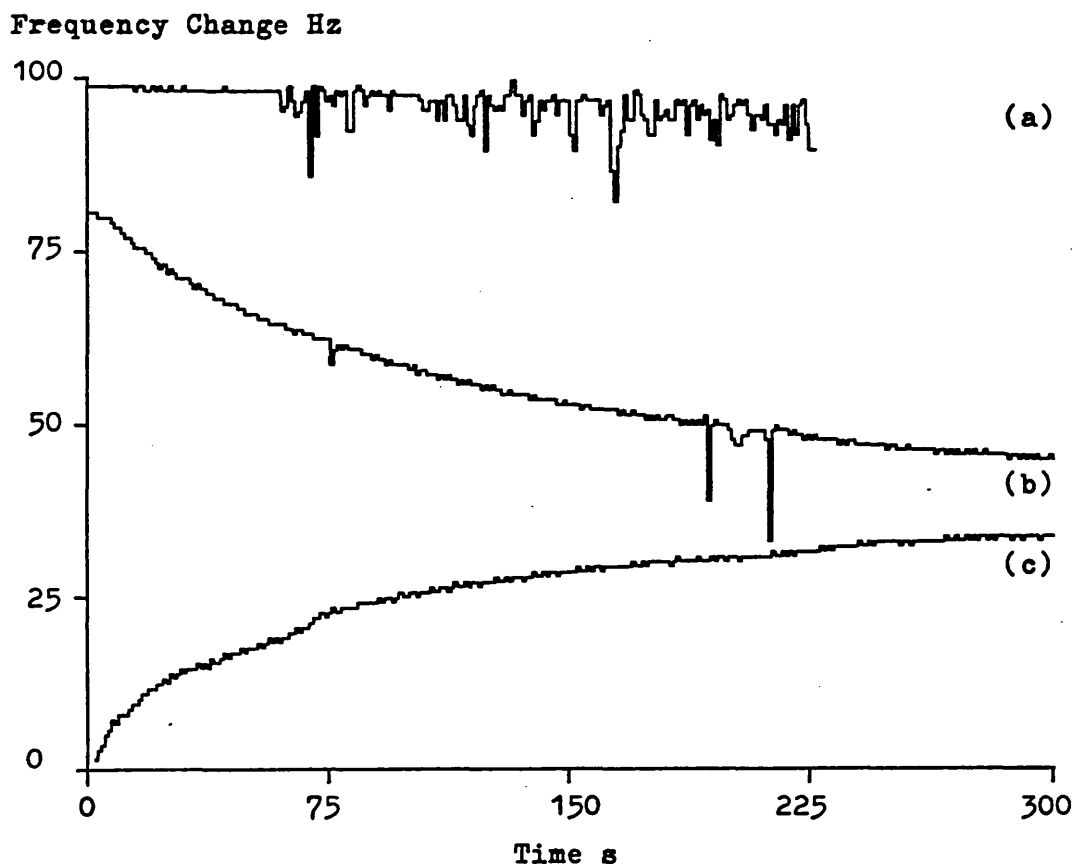


Figure 4.3 The sample oscillator performance. Typical data obtained from the original oscillator: (a) when totally unstable and (b) when usable but occasionally unstable. (c) Totally stable performance obtained after optimisation.

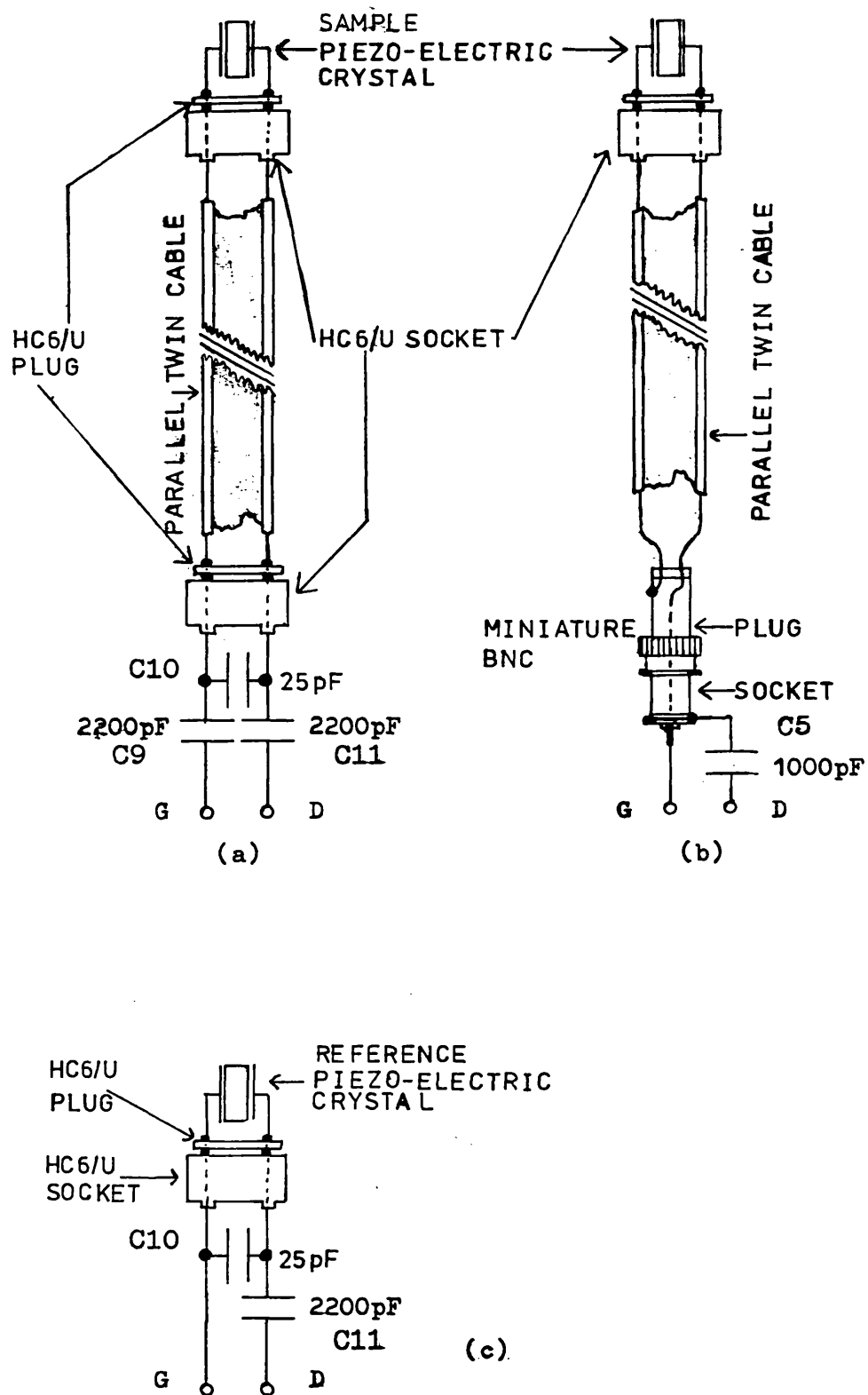


Figure 4.4 The electrical connections between the piezo-electric crystals and the oscillators of (a) the original, (b) the modified and (c) the reference driving circuits.

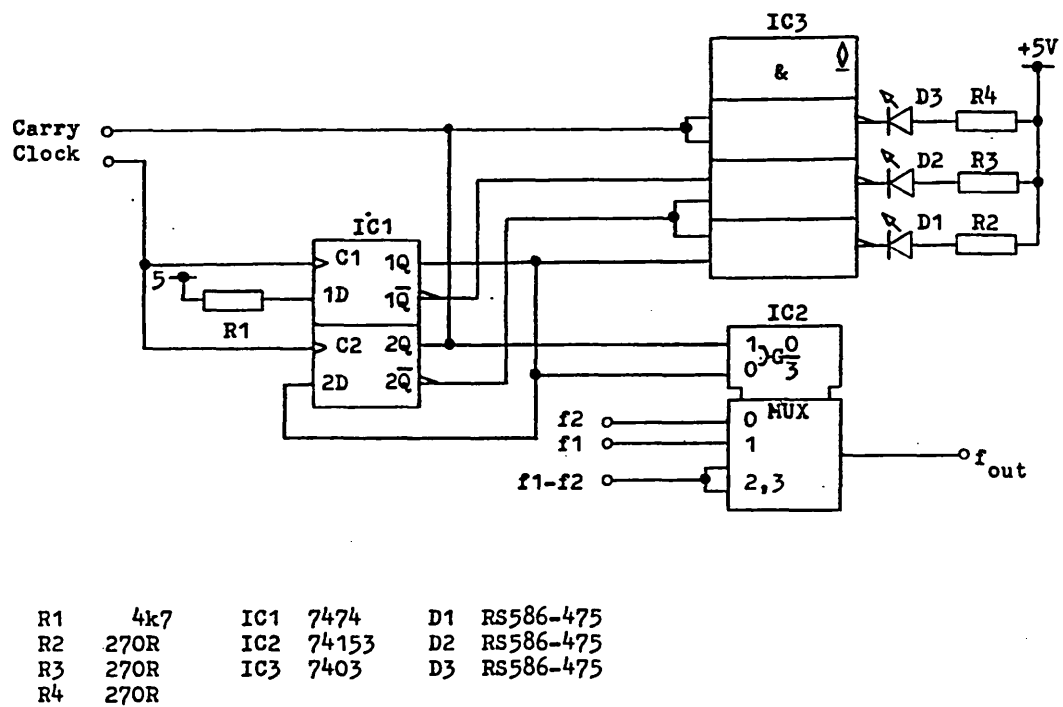


Figure 4.5 Frequency Multiplexer.

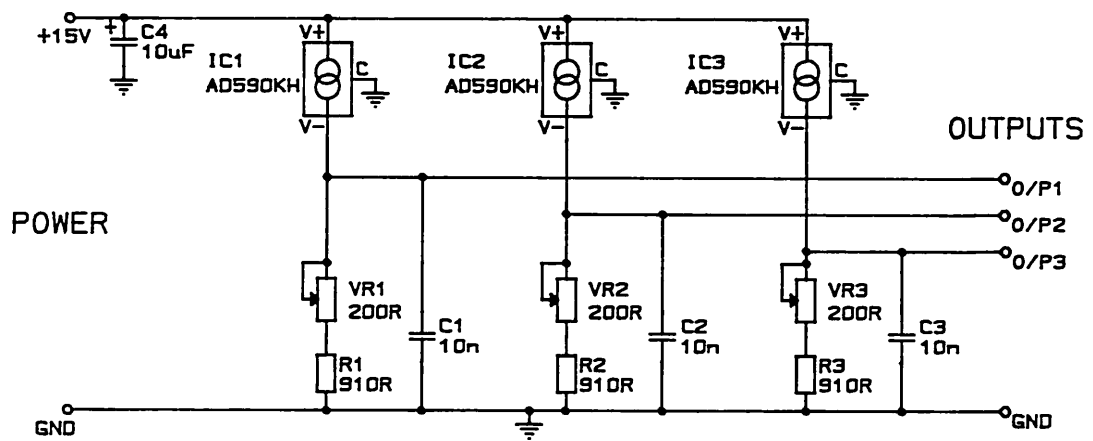


Figure 4.6 The temperature sensor array.

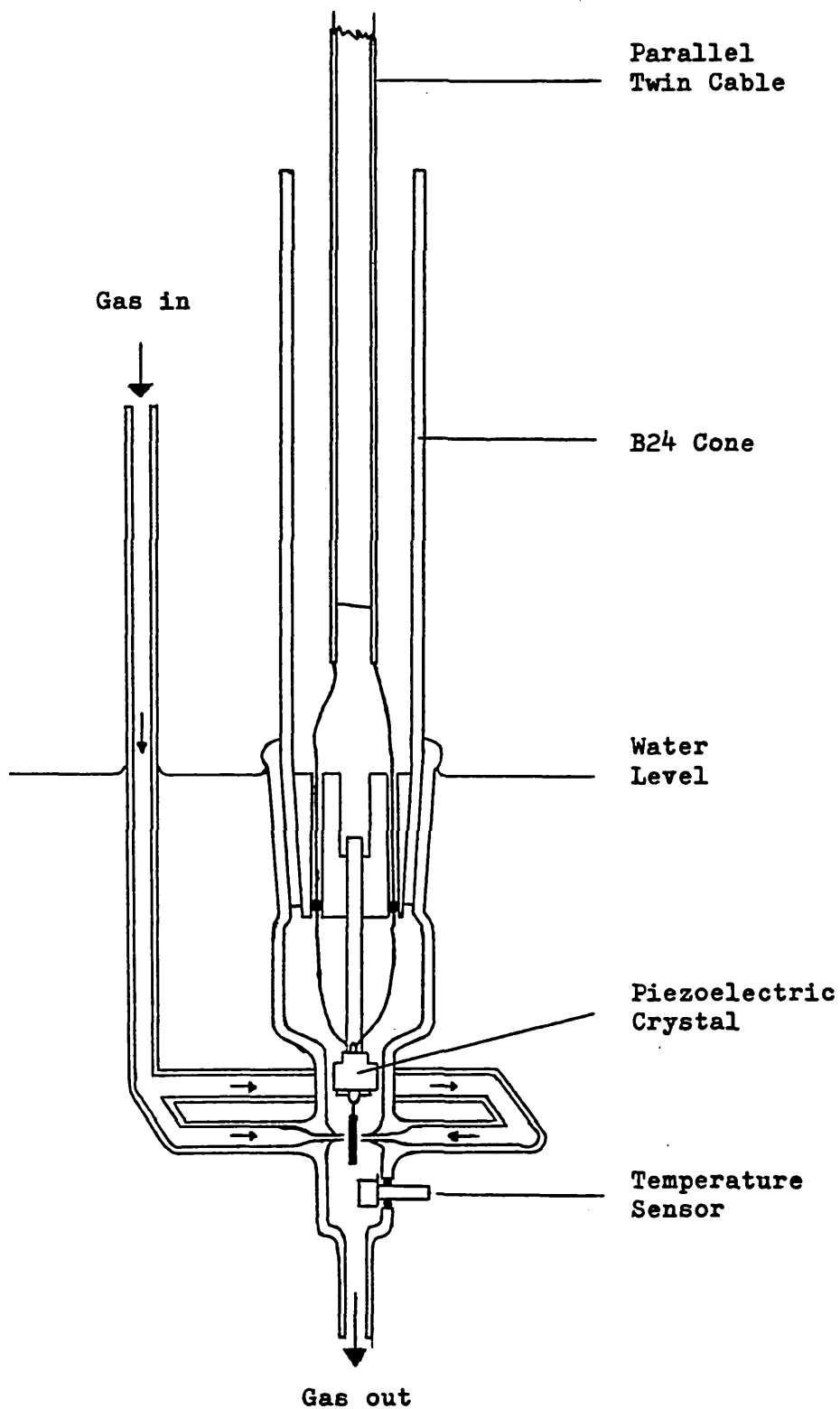


Figure 4.7 The detector cell assembly.

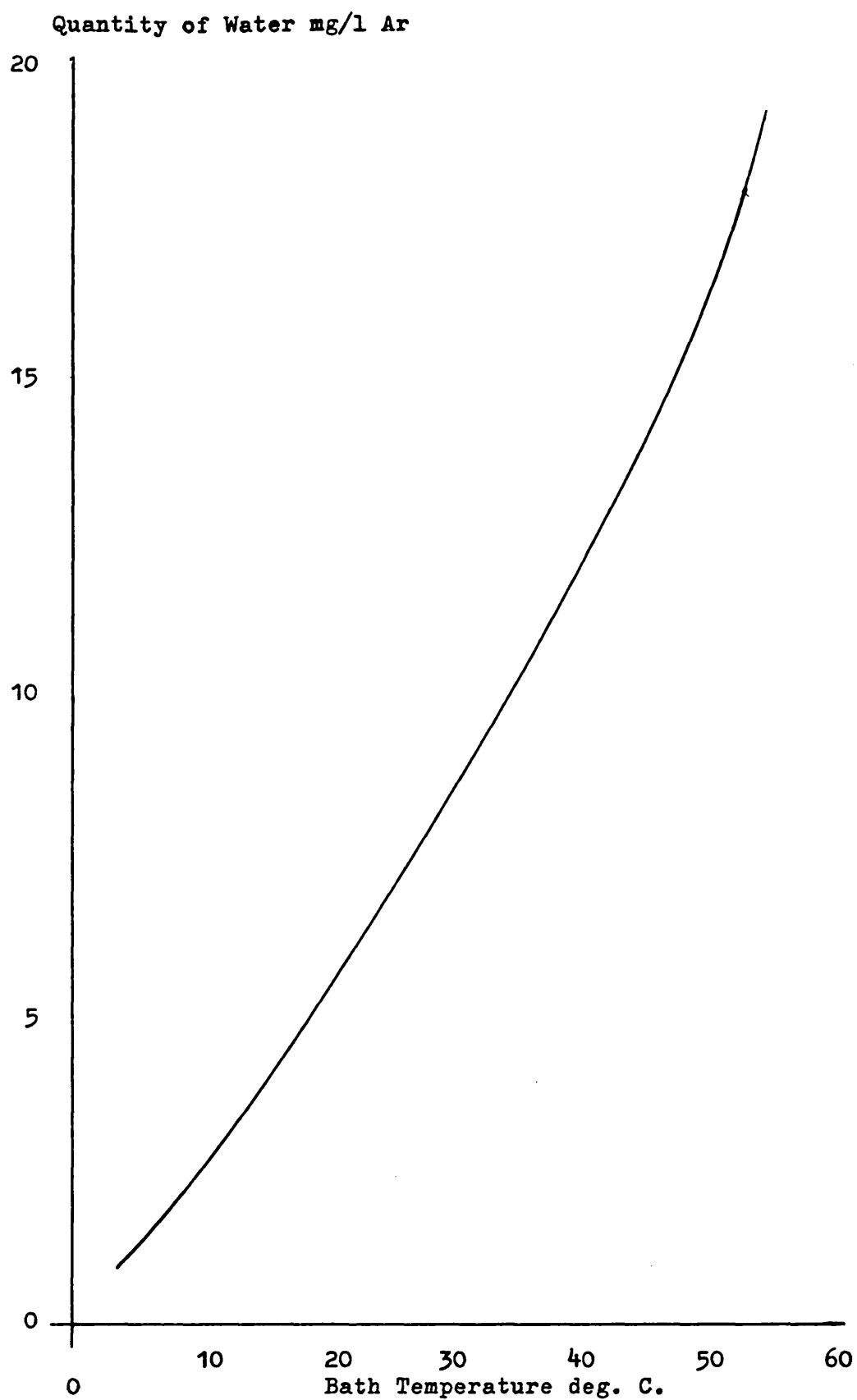


Figure 4.8 The calibration of the water vapour generation apparatus at a fixed gas flow rate of 1l/min.

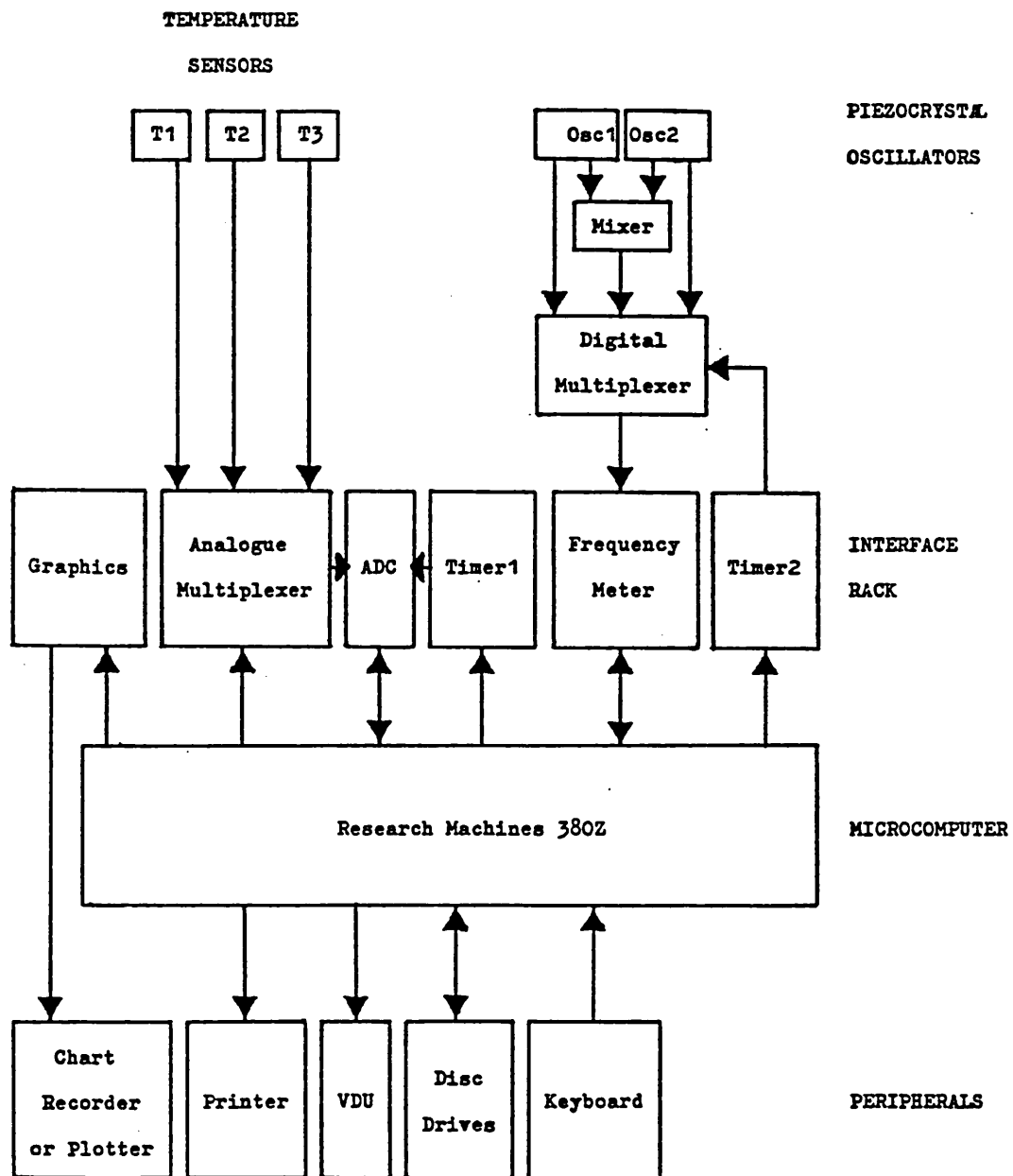


Figure 4.9 Block diagram of the microcomputer and interface system.

#### 4.9 REFERENCES

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#### 4.10 APPENDIX - OUTLINE OF DATA ACQUISITION PROGRAM

##### Main Routine

Start

Initialise the variables

Initialise the interface rack

Calibrate the temperature

List the commands on the screen

Print the status of each command on the screen

    Repeatedly get a character from the keyboard

    If the character is a command then perform command  
        list the commands  
        print the new status

    Else if data acquisition is enabled then call the data  
        acquisition subroutine

Until the end command is executed

##### Outline of the Data Acquisition Subroutine

Wait for an interrupt from the frequency board

Read bytes 0 to 3 on the frequency board

Clear the interrupt

Convert binary coded decimal into frequency

Get 50 conversions from the ADC board, using interrupt read and  
clear

Average the 50 conversions

Scale the digital value to temperature

Print and plot the data on the screen

If the disc is enabled then save the data on disc

If the plotter is enabled then plot the data

If the printer is enabled then send the data the printer

Return to the main routine

The possible commands are:

'A' to enable/disable the acquisition of data

'C' to calibrate the temperature

'D' to enable/disable disc output

'E' to end

'G' to enable/disable plotted output

'P' to enable/disable printed output

'S' to select one of the multiplexed frequencies

'T' to select one of the multiplexed temperatures

## **CHAPTER 5**

### **THE PRACTICALITIES OF PIEZOELECTRIC CRYSTAL SENSING: AN INVESTIGATION OF HUMIDITY AND TEMPERATURE EFFECTS**

In Chapter 2 the theory underlining the use of PZC sensors for chemical analysis was described and in Chapter 4 the apparatus used in this work was described. In this section the practical aspects that limit the performance of a PZC under ambient conditions are considered. A number of general problem areas occur, although the applicability of those factors depends on the particular circumstances.

Notable problem areas are: reproducibility, selectivity, lifetime, flow rate dependence, PZC temperature, oscillator stability and baseline drift. Many of these problem areas affect PZC sensors at run time and may therefore be considered as interferences.

Reproducibility between crystals is poor due to variations in the quantity and structure of the coating material applied. This phenomenon has not been reported in the literature. In Chapter 7 ways to minimise these effects are discussed.

For nearly all PZC sensors water vapour causes most of the problems of interference since they are not selective to it. Fielden, Mc Callum, Stanios and Alder [5.1] developed a microcomputer controlled portable detector for toluene diisocyanate (TDI) which used two PZCs with different coatings for humidity correction. They assumed that the responses of the PZCs to TDI and water were linear and additive. The results were encouraging but showed that a more complex correction algorithm is needed. In Chapter 6 a general correction procedure that is applicable to any response is considered.

Sensor lifetime is reduced by physical ageing and poisoning of the coating due to non-reversible reactions with the analyte and other gas phase species. Mass transport of analyte results in flow rate dependence. Irreversibility and mass transport effects are illustrated in Chapter 7.

Oscillator stability, which caused some problems earlier, as described in Chapter 4, and variations in PZC temperature both give rise to baseline drift.

The first objective of this chapter is to investigate the interaction between uncoated PZCs and humidity. This leads to a presentation and discussion of results on the response of PZCs to humidity and, of necessity, to temperature. The direct interaction between uncoated PZCs and temperature is then introduced.

## 5.1 INTRODUCTION TO HUMIDITY EFFECTS

It has been reported that humidity interferes with the PZC determination of  $\text{SO}_2$  using quadrol coatings [5.2, 5.3]. In order to develop a PZC sensor that produces reproducible results, the fundamental interaction between uncoated PZCs and humidity must first be investigated. The reasoning behind this is related to the storage and preparation of PZCs since water adsorbed in a PZCs previous history can interfere with experiments. If a PZC is kept under ambient conditions, where there are always significant levels of water vapour, it will adsorb water from its surroundings. Under such conditions uncoated crystals show large decreases in frequency from their dry state. It is not practical to investigate PZCs in this condition as they exhibit indeterminate frequency changes due to variations in the amount of adsorbed water. During an experiment, adsorbed water will begin to desorb into the inert gas stream and an unacceptably long delay of several hours will be required to establish a stable baseline.

The humidity effect is investigated in this chapter and the mechanism of the adsorption process is deduced from a kinetic treatment of the experimental results. Procedures are developed to reduce the interference. It is concluded that these procedures can be applied with confidence during the development of a PZC sensor.

## 5.2 EXPERIMENTAL DETAILS AND RESULTS FOR HUMIDITY EFFECTS

### Note on Terminology

Relative humidity, a commonly used term in environmental monitoring, is defined [5.4] as the ratio of the quantity of water vapour present in an atmosphere to the quantity which would saturate at the existing temperature (be in equilibrium with solid or liquid). It is also defined as the ratio of the pressure of water vapour present to the saturated vapour pressure at the same temperature. Since vapour pressure is a function of temperature, the relative humidity of a fixed amount of water vapour in a closed system is a function of temperature. Throughout this work, therefore, the term humidity is used in reference to concentration of water vapour i.e.  $\text{mg H}_2\text{O dm}^{-3}$  which is independent of temperature. This terminology allows experiments to be performed at different temperatures, without changing the numerical measure of the quantity of water in the gas phase.

### Investigation and Results

Assuming that the mechanism for the interference from humidity results from water vapour condensing on the PZC surface and being adsorbed, the amount of adsorbed water at equilibrium should depend on the humidity and on the temperature of the PZC. In particular, at a fixed temperature the amount of adsorbed water should increase with increasing humidity. Any increase in mass loading of the PZC gives a corresponding decrease in resonant

frequency which is the interference. The observed process is spontaneous at room temperature and is, therefore, exothermic with a negative entropy of condensation. According to the principle of Le Chatelier and Braun [5.5] it follows that at a fixed humidity the amount of adsorbed water should decrease with increasing temperature. The process is assumed to be:



An equilibrium constant for adsorption (adsorption coefficient) can be written for this process,

$$K = \frac{k_a}{k_d} = \frac{\Delta F}{[\text{H}_2\text{O(g)}]} \quad (5.2)$$

where the concentration of adsorbed water is represented by the frequency change of  $\Delta F$  Hz caused by a corresponding mass change on the PZC surface.

A series of five runs was carried out to determine the humidity response at fixed PZC temperatures (14, 20, 25, 30 and 35°C) using the apparatus described in Chapter 4 with the modification for water vapour production. The vapour was maintained in an unsaturated state thus avoiding droplet formation.

For the first run, the detector cell holding the PZC was held at a fixed temperature of 14°C and dry argon was passed over the PZC at a flow rate of  $1 \text{ dm}^3 \text{ min}^{-1}$ . Once a baseline had been established, a frequency reading was taken. The flow was then diverted through the water vapour generation apparatus and the measured frequency increased. After about six minutes the frequency had stabilised at a higher level and a second reading

was taken. The temperature of the water vapour generation apparatus was also noted. When dry argon was passed over the PZC for a second time, the measured frequency returned to the baseline. This procedure was repeated for various humidities in the range  $2 - 12 \text{ mg H}_2\text{O dm}^{-3}$  (temperatures of the water vapour generation apparatus in the range  $10 - 40^\circ\text{C}$ , see fig. 4.8). This procedure was repeated with the PZC thermostatted at progressively higher temperatures of 20, 25, 30 and  $35^\circ\text{C}$ .

The results are displayed fig. 5.1 which is a plot of frequency change against humidity. At each temperature the interference becomes worse as more water vapour condenses on the crystal at higher humidities. Furthermore, for the conditions and PZC temperature used in this experiment, the frequency change is linear with respect to humidity.

From the Sauerbrey eqn. 2.19 frequency change is proportional to the mass of adsorbed water. It can therefore be concluded that the mass of adsorbed water is directly proportional to the humidity.

The behaviour shown in fig. 5.1 is in agreement with eqn. 5.2 which, therefore, describes the observed behaviour as well as the equilibrium constants for the assumed condensation mechanism. Thus, the slopes of fig. 5.1 at five temperatures give, by linear regression, values for the experimentally determined, adsorption coefficient as shown in table 5.1.

| Temperature<br>°C | K<br>Hz mg <sup>-1</sup> dm <sup>3</sup> |
|-------------------|------------------------------------------|
| 14                | 54.5                                     |
| 20                | 30.3                                     |
| 25                | 15.0                                     |
| 30                | 10.8                                     |
| 35                | 7.8                                      |

Table 5.1 Experimentally determined equilibrium constants  
for water condensation on an uncoated crystal

As these equilibrium constants are measured by a PZC at known humidities they conveniently include Hz and mg in their units as opposed to the more conventional mol. From the Sauerbrey eqn. 2.19 frequency change can be converted into mass of adsorbed water, the mass dimensions then cancel so if required the units of the equilibrium constant can be converted to the SI equivalent (dm<sup>3</sup>). The mass terms can independently be converted to the more conventional mol by dividing by the relative molecular mass of water.

Considering all five runs in fig. 5.1 together, it can be seen that at a fixed humidity a smaller frequency change occurs at higher PZC temperatures corresponding to decreasing equilibrium constants in table 5.1.

The temperature dependence of the equilibrium constant can be described by the van't Hoff equation [5.6]:

$$\frac{d(\ln K)}{d(1/T)} = -\frac{\Delta H^\ominus}{R} \quad (5.3)$$

Thus the data in table 5.1 can be used to obtain equilibrium constants at other temperatures over the experimental temperature range by plotting lnK against 1/T and interpolating. For example

the equilibrium constant is estimated to be  $51 \pm 2 \text{ Hz mg}^{-1} \text{ dm}^3$  at  $15^\circ\text{C}$ .

The decrease with temperature of the experimentally determined, equilibrium constants would give a negative value for  $\Delta H^\ominus$  which corresponds with the observed process being exothermic. According to the equation,

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus \quad (5.4)$$

it is therefore possible for the enthalpy to be negative which corresponds to a gas to liquid phase transition. Thus the assumption of a condensation mechanism for the process, described by eqn. 5.1, is justified.

It was thought useful to directly measure the reduction in adsorbed water with temperature. Therefore, two runs were carried out consecutively in which the water vapour generation apparatus was held at fixed temperatures ( $2.5$  and  $5.5^\circ\text{C}$ ) which gave constant humidities of  $0.5$  and  $1.1 \text{ mg H}_2\text{O dm}^{-3}$  respectively and the PZC temperature was increased in steps from about  $8$  to  $50^\circ\text{C}$ . The PZC was allowed to remain at each temperature until a constant frequency had been established.

These results are shown in fig. 5.2(a) and (b). They do not appear to agree with the earlier results since although the frequency initially decreases, (i.e. water is being driven off) it increases again from  $28^\circ\text{C}$  to a maximum at around  $43^\circ\text{C}$ . Apparently in this range more water is adsorbed at higher temperatures which contradicts the proposed mechanism.

However, things become clearer when the third run, fig. 5.2(c), carried out with dry argon flowing over the crystal, is considered. This curve is independent of humidity and must therefore show a response with respect to temperature inherent to the PZC.

All three curves show the same response at temperatures above 28°C, irrespective of the humidity. However the curves show different responses below 28°C, depending on the humidity, due to the effect of temperature on the water adsorption coefficient for the equilibrium.

If the response seen at 0 mg H<sub>2</sub>O dm<sup>-3</sup> is subtracted from that at 0.5 and 1.1 mg H<sub>2</sub>O dm<sup>-3</sup> more meaningful plots (fig. 5.3) are obtained. These show the effect of temperature on the adsorption process directly. It is particularly important to note that at higher temperatures the response of the PZC to water vapour tends to zero.

From eqn. 5.2 the equilibrium constants can be obtained by dividing the frequency change by the humidity. In table 5.2 the equilibrium constants estimated from single points on the curves of fig. 5.3 are presented. These results follow the same trend as table 5.1 with some variation due to experimental error. There is a small deviation at higher crystal temperatures. However, the zero humidity correction, using fig. 5.2(c) to obtain fig. 5.3, can produce some distortion at the higher temperatures. This distortion may arise from the 'dried crystal' having some residual adsorbed water which is expelled at the higher

temperatures.

| Temperature<br>°C | Equilibrium Constants Hz mg <sup>-1</sup> dm <sup>3</sup> |                  |      |
|-------------------|-----------------------------------------------------------|------------------|------|
|                   | K <sub>1.1</sub>                                          | K <sub>0.5</sub> | K    |
| 14                | 57                                                        | 56               | 55.1 |
| 20                | 24                                                        | 32               | 30.6 |
| 25                | 13                                                        | 16               | 15.0 |
| 30                | 7                                                         | 2                | 11.0 |
| 35                | 2                                                         | 0                | 8.1  |

Table 5.2 Estimated equilibrium constants at 1.1 and 0.5 mg [H<sub>2</sub>O] dm<sup>-3</sup> and the overall equilibrium constant for water condensation on an uncoated crystal

These new results expand the data set towards lower humidities than achieved in the first experiment increasing the statistical significance of the results which justify the condensation mechanism. The final column in table 5.2 gives a revised value for the equilibrium constant at five temperatures calculated, by linear regression, from the combined data in fig. 5.1 and the single points on the curves of fig. 5.3 used in the K<sub>1.1</sub> and K<sub>0.5</sub> estimates.

#### Investigation Under Non-Equilibrium Conditions

Eqn. 5.2 and the linear relationship between frequency change and humidity can also be derived from a kinetic discussion of the condensation and evaporation of water molecules at a surface. The rate of condensation of water molecules on the surface is proportional to the rate at which water molecules strike the surface [5.7], which, at a given temperature and pressure varies directly with the humidity. At a given humidity the rate of

condensation is constant. The rate equation is:

$$\left[ \frac{dx}{dt} \right]_a = k_a [H_2O(g)] \quad (5.5)$$

The next experiment carried out verifies that, for a condensation process at constant temperature, the rate of evaporation of water molecules from the surface of a PZC is proportional to the number of water molecules adsorbed. This is proportional to the equivalent frequency change, so the first order rate equation can be written,

$$\left[ \frac{dx}{dt} \right]_d = - k_d \Delta F \quad (5.6)$$

where  $\Delta F$  is the frequency change due to a mass  $\Delta M$  of adsorbed water representing the concentration of  $H_2O(ads)$  in eqn. 5.1.

A PZC at equilibrium with a humid environment was moved into a dry environment. Fig. 5.4 is a plot of the logarithm of the subsequent frequency change from the equilibrium value against time. From the Sauerbrey eqn. 2.19, mass is proportional to frequency change. It is clear that the number of adsorbed water molecules is directly proportional to the frequency change and therefore, from a kinetic treatment, the fact that fig. 5.4 is linear verifies that a first order decay mechanism applies to the desorption of water from the PZC surface. The rate constant that applies to eqn. 5.6 is therefore  $(4.4 \pm 0.4) \times 10^{-3} \text{ s}^{-1}$  at  $15^\circ\text{C}$ .

Since desorption is taking place in dry conditions the net rate of desorption does not depend on the mechanism of the adsorption process.

Moreover, the above experiment is just a special case of the non-

equilibrium effect of adsorbed water on frequency when a PZC is exposed to any finite change in humidity. In general the time dependency can be written,

$$|f - f_f| = |f_i - f_f| e^{(-k_d t)} \quad (5.7)$$

where  $k_d$  is the rate constant for desorption,  $f$  is the frequency and the subscripts denote initial and final values. The pre-exponential factor depends on the thermodynamics of the process and is equivalent to  $\Delta F$  in eqn. 5.6 and eqn. 5.8.

At equilibrium the rate of condensation equals the rate of evaporation and so the ratio of rate constants, the equilibrium constant can be derived:

$$K = \frac{k_a}{k_d} = \frac{\Delta F}{[H_2O(g)]} \quad (5.8)$$

Eqn. 5.8 has been derived mathematically from a kinetic discussion of condensation and evaporation rates yet it replicates the linear relationship shown both experimentally in fig. 5.1 and according to thermodynamic theory in eqn. 5.2. This verifies that  $k_a$  can be used to describe the condensation process by eqn. 5.5 which further justifies the adsorption process.

Since the adsorption coefficient at 15°C was estimated to be  $51 \pm 2 \text{ Hz mg}^{-1} \text{ dm}^3$  and the rate constant for desorption was found to be  $(4.4 \pm 0.4) \times 10^{-3} \text{ s}^{-1}$  at 15°C, the rate constant for condensation can be calculated from eqn. 5.8 as  $0.22 \pm 0.03 \text{ Hz mol dm}^{-3}$  at 15°C.

From the overall rate eqn. 5.7, the frequency change as a function of exposure time under typical ambient conditions of 35% RH ( $4.5 \text{ mg H}_2\text{O dm}^{-3}$ ) at  $15^\circ\text{C}$  has been calculated and is presented in table 5.3. The corresponding time required for the reading to return to within 5 Hz of its starting value when the PZC is returned to dry argon is also given. An error of  $\pm 10\%$  applies to the values in table 5.3.

| Exposure<br>time s | Frequency<br>Change Hz | Recovery<br>time s |
|--------------------|------------------------|--------------------|
| 10                 | 10                     | 158                |
| 20                 | 20                     | 315                |
| 50                 | 45                     | 499                |
| 100                | 82                     | 636                |
| 200                | 134                    | 747                |
| 300                | 168                    | 799                |
| 500                | 204                    | 843                |
| 1000               | 227                    | 867                |

Table 5.3 The frequency change of a PZC against exposure time to  $4.5 \text{ mg H}_2\text{O dm}^{-3}$  and the recovery time to within 5 Hz of the baseline

Initial adsorption is rapid but in comparison desorption is slow so that if the crystal is exposed for only 19.3 s it takes 5 min to recover whilst if it is exposed for 4 min it requires 13 min to recover. This recovery time is only slightly less than the 15 min for a crystal kept at typical ambient conditions i.e. maximum adsorbed water.

### 5.3 DISCUSSION OF OBSERVED HUMIDITY EFFECTS

The experiments at equilibrium show that considerable amounts of water vapour will condense on a PZC stored under ambient conditions and that the equilibrium level of condensed water vapour changes greatly with temperature. In addition there is a convoluted effect of humidity and temperature on the condensation process.

The non-equilibrium investigation simulates the preparation and transfer of PZCs for experimental use and applies when the exposure time interval is less than that required to come to equilibrium. When comparing the frequency change to the exposure time, condensation is even more significant for short term exposures with the associated kinetic rates of condensation very significant on experimental timescales.

The question then arises as to how is it possible to reduce the effects of water vapour. In the light of figs. 5.1 and 5.3 and as the experimental investigation and analysis suggest a condensation mechanism, it is clear that the effect of humidity can be reduced by operating at higher temperatures. It should, therefore, be possible to expose PZCs to ambient humidity levels at an elevated temperature and obtain less adsorbed water in a given time interval.

#### 5.4 PROCEDURES FOR THE REDUCTION OF HUMIDITY

The procedures used to minimise the interference of water vapour during determinations of temperature and  $\text{SO}_2$  responses are now described. Later the interplay of all these factors will be considered as will methods for temperature and humidity correction.

The most important precaution is to store the crystals in an environment that is as dry as possible and to carry out the experiments under dry conditions. Due to rapid condensation, transfer via ambient conditions must be done rapidly and preferably using a heated crystal.

Even so, the conditions will usually be different between storage and experiment. The crystal must therefore be left under the experimental conditions for at least a 10 min period before making measurements which allows the frequency to stabilise and minimises drift.

It is possible to overcome this effect by storing the crystal within the experimental apparatus and thus under the required conditions. This is easily achieved by setting up the experiment the day before and leaving it on overnight. A further precaution was to leave the argon flowing continuously in the experimental apparatus to maintain the steady state that has been achieved there.

As the drying conditions were imperfect and could vary with time, the baseline could change between experiments and show

temperature dependance and slow kinetics. However, by keeping the drying agents fresh and thus the ambient humidity low, the effects could be minimised.

Without these precautions an initial baseline can be measured for a crystal one day and the frequency may be several 100 Hz different on the following day at the same temperature. Taking these precautions reduced the observed variation to only a few Hertz.

## 5.5 TEMPERATURE EFFECTS AND COMPENSATION

### Introduction

In the above section temperature measurement and correction have been discussed very briefly. Yet the results clearly show that PZC temperature effects must be considered during the development of these sensors.

Previous workers have compensated for temperature effects by subtracting the frequency of a reference crystal using an electronic mixer [5.8 - 5.12]. The resultant frequency should only be affected by changes in the analyte concentration and not by changes in temperature which are the same for both crystals.

It is accepted practice to reduce the dependency of PZC frequency on temperature by using PZC cuts which have low temperature coefficients, particularly the AT cut as described in Chapter 2. Another way to reduce the effect, at least for experimental work in the laboratory, is to include thermostatic control to closely regulate the temperature of the PZC. Thermostating was carried out for the initial experiment in this chapter so that a baseline reading could be measured which then acted as a reference for subsequent frequency changes. Strangely this simple procedure has only been previously reported by one group, Moody, Thomas and co-workers [5.13, 5.14].

For an experiment in the temperature domain, it is not possible to thermostat: a compensation method must be adopted.

For both these approaches understanding of the temperature

response of the PZC and its significance in relation to the desired operating temperature range of the sensor are essential in determining the degree of control or level of compensation that is required.

The generalised form of the AT cut PZC temperature response is a third degree relationship with a rather flat region around normal working temperatures [5.12]. For this cut and these temperatures the crystal elastic moduli are nearly balanced. The point of inflexion is known as the turnover temperature and lies within a region where the average temperature coefficient is zero.

The turnover temperature should ideally be at 25°C but this depends on frequency. In the range 0 to 50°C the frequency tolerance from its value at 25°C will normally be less than  $\pm 50$  ppm and frequency tolerances of  $\pm 20$  ppm can readily be obtained as standard from several manufacturers. The temperature coefficient in the flat region can be as low as  $\pm 0.2$  ppm/°C but is more usually  $\pm 1$  ppm/°C. The temperature coefficient over the whole range should be lower than  $\pm 1$  ppm/°C.

For these reasons AT cut crystals make good frequency standards and are often chosen for PZC sensors. However, when real crystals are studied the situation is more complicated as higher order effects are superposed on this general behaviour.

Looking at the crystal used in section 5.2, the temperature response at zero humidity over the range 8 to 50°C has already been measured and is shown in fig. 5.2(c). Not much variation is

observed when operating below 25°C but between 25 and 42°C the response is about 0.8 ppm/°C. Over the whole range measured the frequency tolerance of largest magnitude is +11 ppm and the temperature coefficient of largest magnitude is -7 ppm/°C at 50°C.

Close inspection of the response shown earlier by Snook and Zaft [5.15] reveals that between 25 and 35°C the response is about 0.6 ppm/°C. Over the whole range measured (10 to 45°C) the frequency tolerance of largest magnitude is +7 ppm and the temperature coefficient of largest magnitude is -2.5 ppm/°C at 40°C.

#### Preliminary Observations of Temperature Effects

In order to investigate this effect for a number of PZCs, a method similar to that used to obtain fig. 5.2 was adopted in which results were noted by the user. Dry argon was passed over the crystal continuously to expel water vapour from the apparatus and remove any that may be entrained during the experiment. Then the PZC was held at a set temperature using the water bath until a stable frequency was established. Then a reading was taken and the temperature altered for another datum. Since water vapour is expelled during the first runs, the experiment was usually repeated until consistent results were obtained, for instance fig. 5.2(c) is a third attempt. Temperature responses for 3 more crystals are shown in figs. 5.5 to 5.7. Their frequency tolerances over the temperature range shown are respectively 19, 5 and 15 ppm and their temperature coefficients

of largest magnitude are -2.1, -1.0 and -2.2 ppm/°C.

The variation in temperature response observed from PZC to PZC and from the ideal is due to the tolerances of mass manufacture. As previously noted an AT cut crystal is cut from a single right handed crystal parallel to the x-axis and at an angle of 35°15' to the z-axis. The temperature coefficient and turnover temperature are functions of the angle of cut. Therefore, a sample of real, nominally AT cut crystals will have a distribution of thermal characteristics as shown in figs. 5.5 to 5.7.

PZCs with lower temperature coefficients can be selected after experimental measurement of temperature responses. However, this method of selection is tedious and subjective and can be avoided, see below.

Bristow found that uncoated reference PZCs with aluminium electrodes are sensitive to humidity [5.16]. This problem is also applicable to silver and gold electrodes because it is caused by condensation. Bristow also showed that a sealed reference crystal overcame the humidity effect. However, it responded more slowly to temperature changes than the sample crystal.

Daley and Lundgren also reported that a reference crystal could not be used for temperature compensation because the local environments of the two PZCs are different [5.17]. Additionally, if thermal gradients are present in either crystal, the temperature coefficient may be greatly altered due to a mismatch

of elastic moduli.

The use of reference crystal compensation is also limited because in practice it is difficult to find a matched pair of temperature responses. Crystals can be obtained from manufacturers with parameters within a specified band but they will not be matched and therefore a variation in response will be found. This problem can be overcome by selecting PZCs with matched responses, but a quick method of determining individual PZC responses is still needed and the difficulties with the available method have already been noted.

In conclusion the best approach to adopt is to purchase PZCs specifying as small a temperature response as required, if necessary selecting those with even lower response (assuming a satisfactory measurement method is found, see next chapter). Finally if at all possible, the temperature variation during use should be reduced.

#### Previous Work on Reference Compensation

Carpenter and Brenchley [5.8] described an aerosol monitor using a sealed reference PZC. The thermal time lag of sealed PZCs means that this type of device would fail to follow temperature change in an acceptable period. Cheney and Homolya [5.9] used an uncoated crystal upstream of the detector but even in the absence of water vapour the separate crystals may have experienced different environments. Although Hamilton and Gedeon [5.12] claimed that a reference PZC minimised temperature effects and

that they were eliminated completely by temperature control, the temperature control and the use of low temperature coefficients (less than 0.3 ppm/°C) were the more important factors. Alder and Issac [5.11] were the only people to measure the dry temperature coefficient around room temperature and they achieved quite a reasonable pairing. The effect of water vapour on the unsealed reference PZC was probably masked by the large water response of PEG400, the toluene di-isocyanate sensitive coating.

Scheide and Warnar [5.10] claimed that their reference crystal, which did not have gold electrodes, cancelled humidity as well as temperature effects. Even, assuming that the local environments of the PZCs were the same, it seems very unlikely that a second differently coated or uncoated crystal could have successfully been used to fully compensate for humidity in this way. In general, two such crystals would have different sensitivities to water vapour and so subtracting their frequencies would not cancel the effect.

On the basis that attempts to employ a reference crystal offered only marginal improvement in compensation, Fielden, Mc Callum, Stanios and Alder [5.1] developed an improved method for humidity correction, which allowed for different sensitivities of the two crystals.

#### Empirical Relationships for Temperature Compensation

Returning to the temperature responses, there is a problem with figs. 5.2, 5.5, 5.6 and 5.7 in the interpretation of the results

determined by measuring the temperature response at just a few temperatures. The choice of response curve was made on a limited data set and is, therefore, not statistically significant.

This was not the case for the humidity responses in fig. 5.1 because these were linear relationships and so least squares regressions could be carried out on a small data set. Non-linear least squares or curve fitting procedures are possible for simple functions e.g. quadratic and cubic but not for the temperature responses which are described by more complicated functions. This kind of function requires an empirical relationship e.g.  $AT + BT^2 + CT^3 + \dots$  for which curve fitting is possible if there are enough parameters. However larger data sets are required to minimise subjectivity as many different curves can be fitted through a small number of data points. The solution adopted in this work is to use microcomputer controlled data acquisition combined with the digital smoothing and curve fitting procedures developed in the next chapter to develop empirical relationships for the temperature response of PZCs.

# 5.6 FIGURES

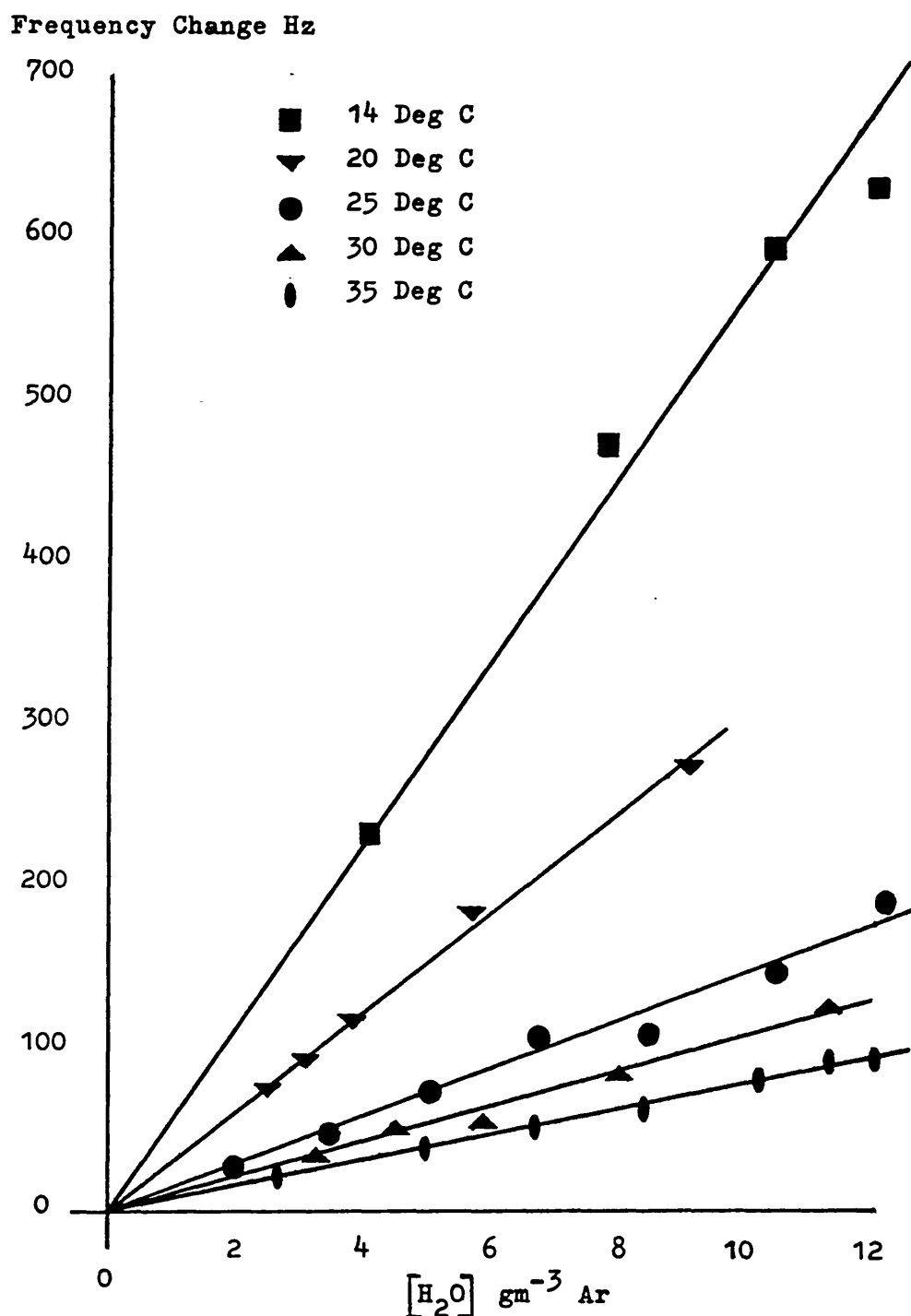


Figure 5.1 The humidity response of a piezoelectric crystal at 14, 20, 25, 30 and 35 Deg C in an argon flow of 1l/min.

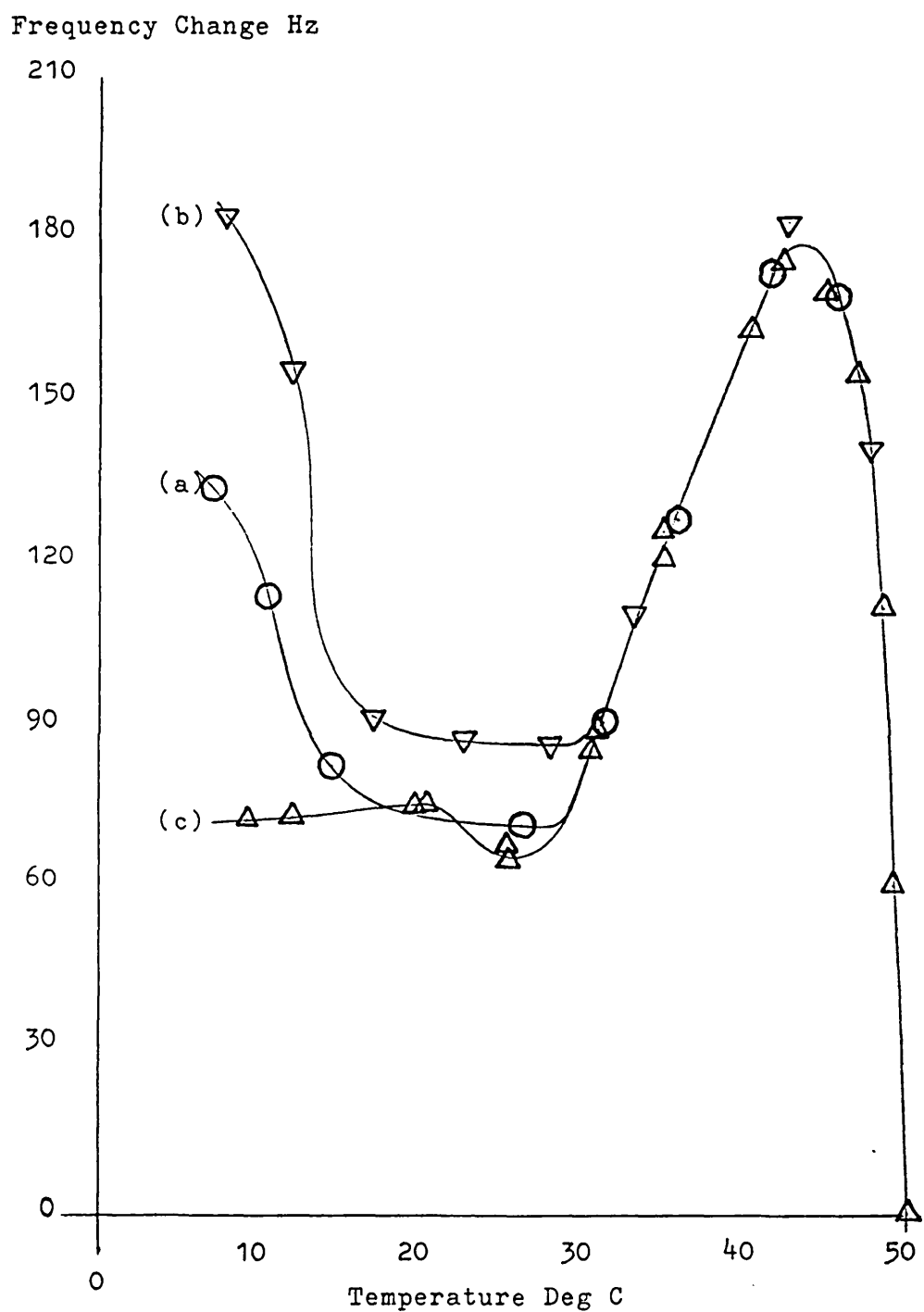


Figure 5.2 The effect of temperature on a piezoelectric crystal with absorbed water vapour: a) at 0.5, b) at 1.1 and c) at 0 mg H<sub>2</sub>O dm<sup>-3</sup>.

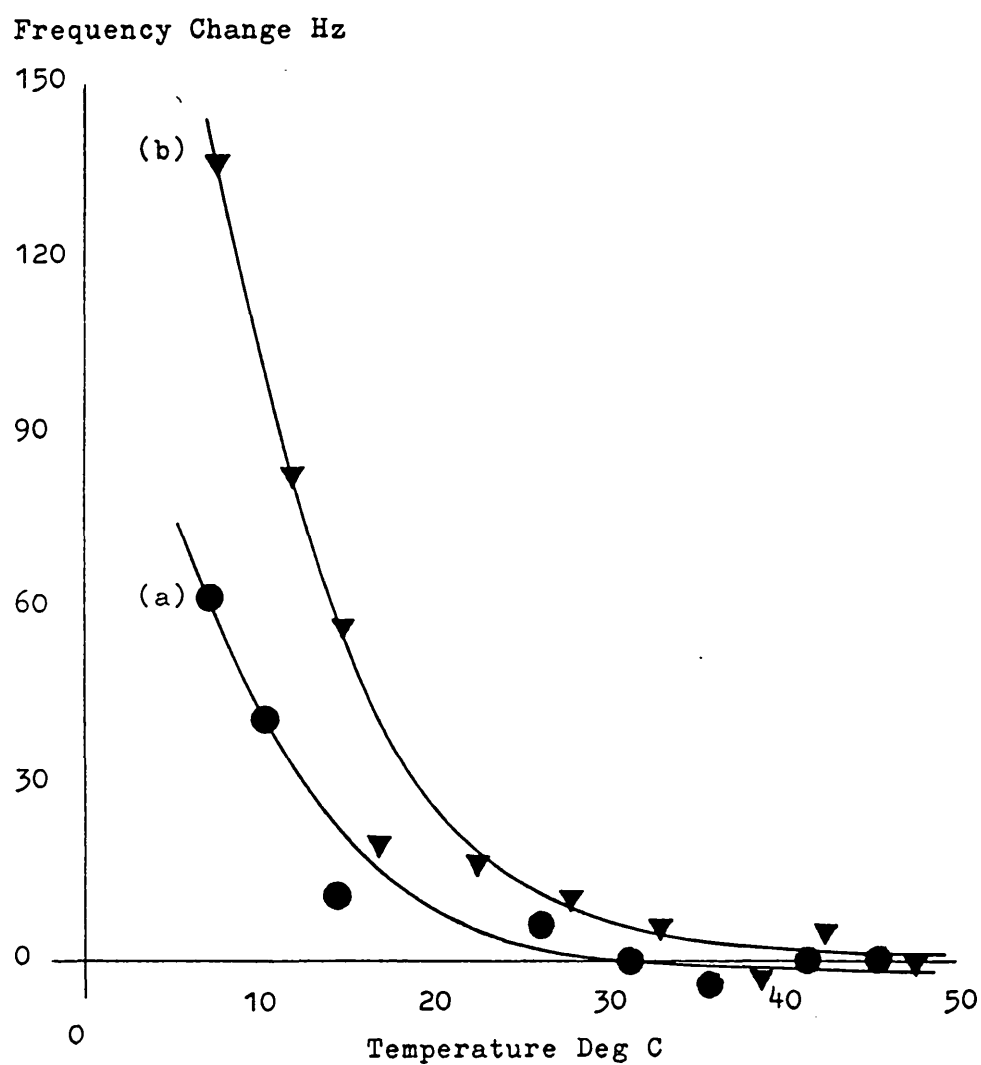


Figure 5.3 The effect of temperature on the water vapour absorbed on a piezoelectric crystal: a) at 0.5, and b) at 1.1 mg  $\text{H}_2\text{O dm}^{-3}$ , corrected using the change at 0 mg  $\text{H}_2\text{O dm}^{-3}$ .

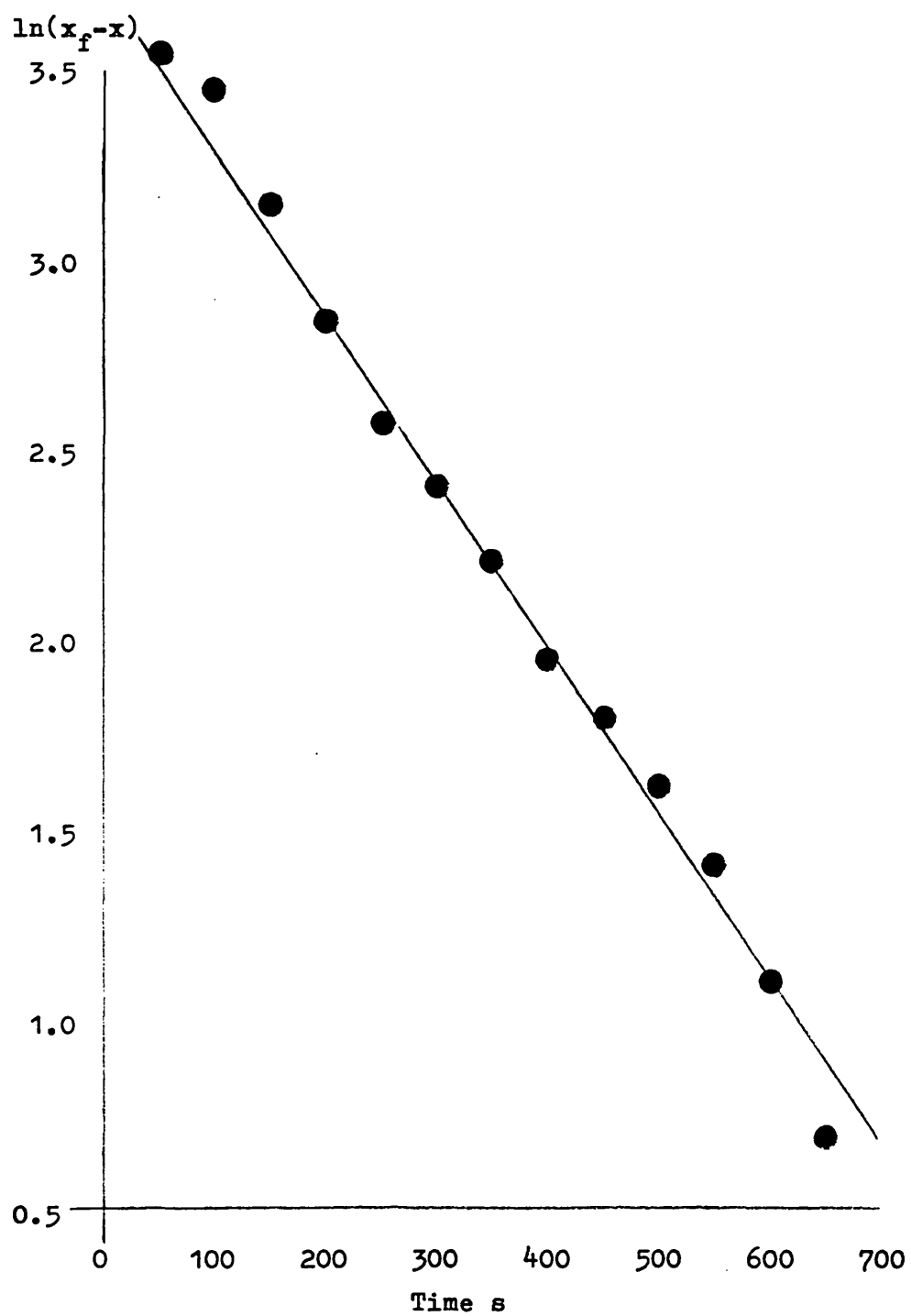


Figure 5.4 Kinetic plot of water desorption from a piezoelectric crystal at 15 Deg C.

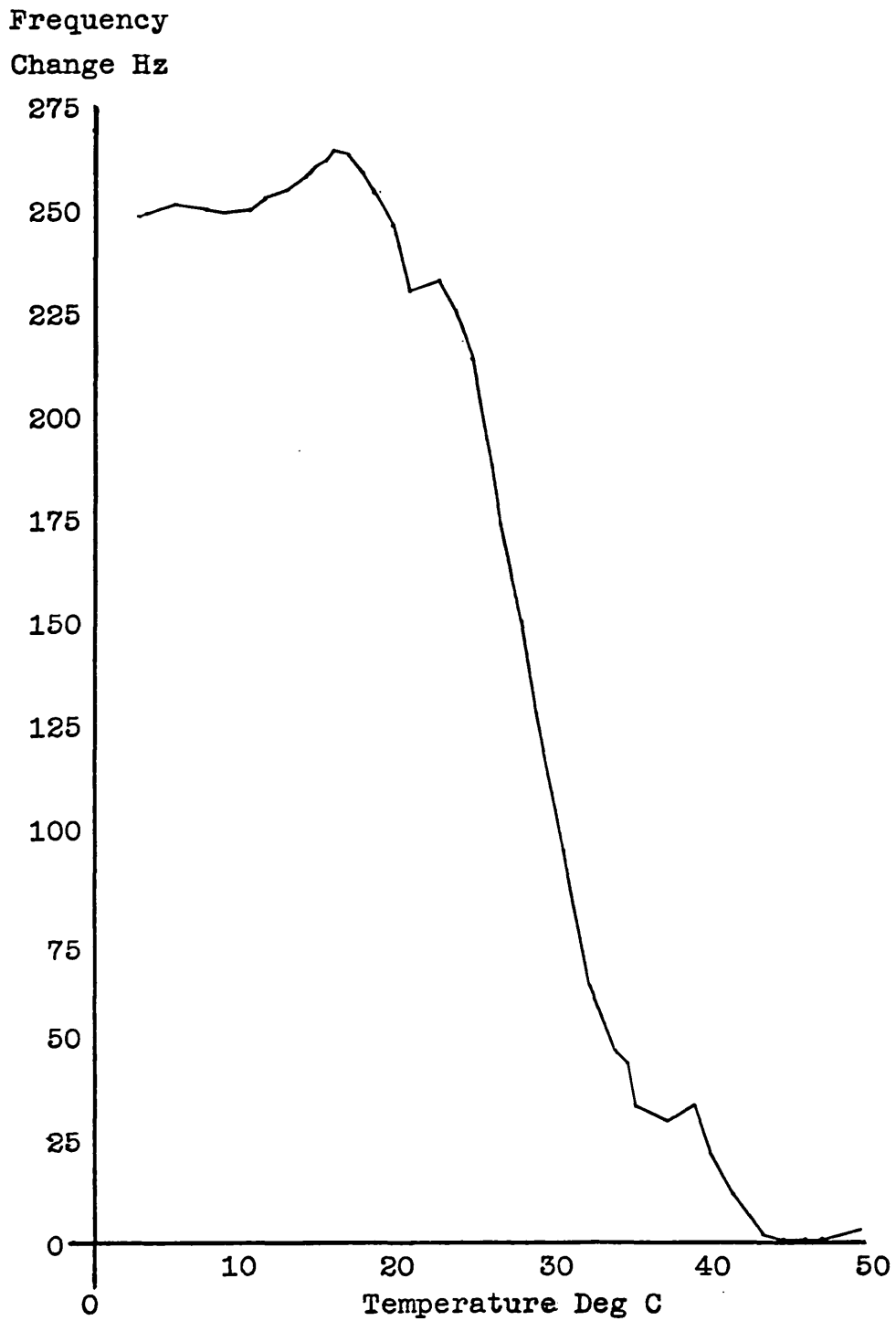


Figure 5.5 The frequency response with respect to temperature of crystal B.

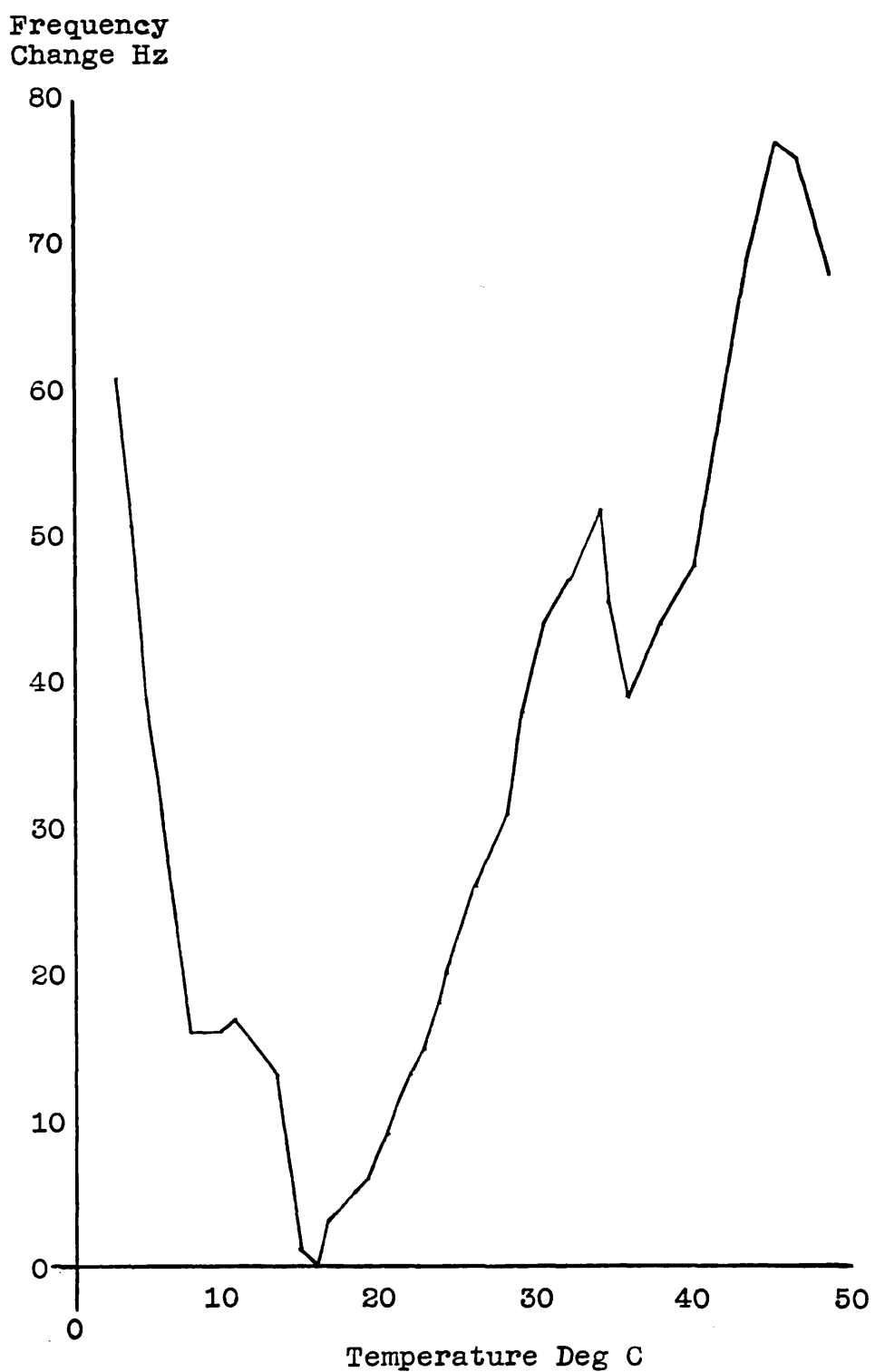


Figure 5.6 The frequency response with respect to temperature of crystal C.

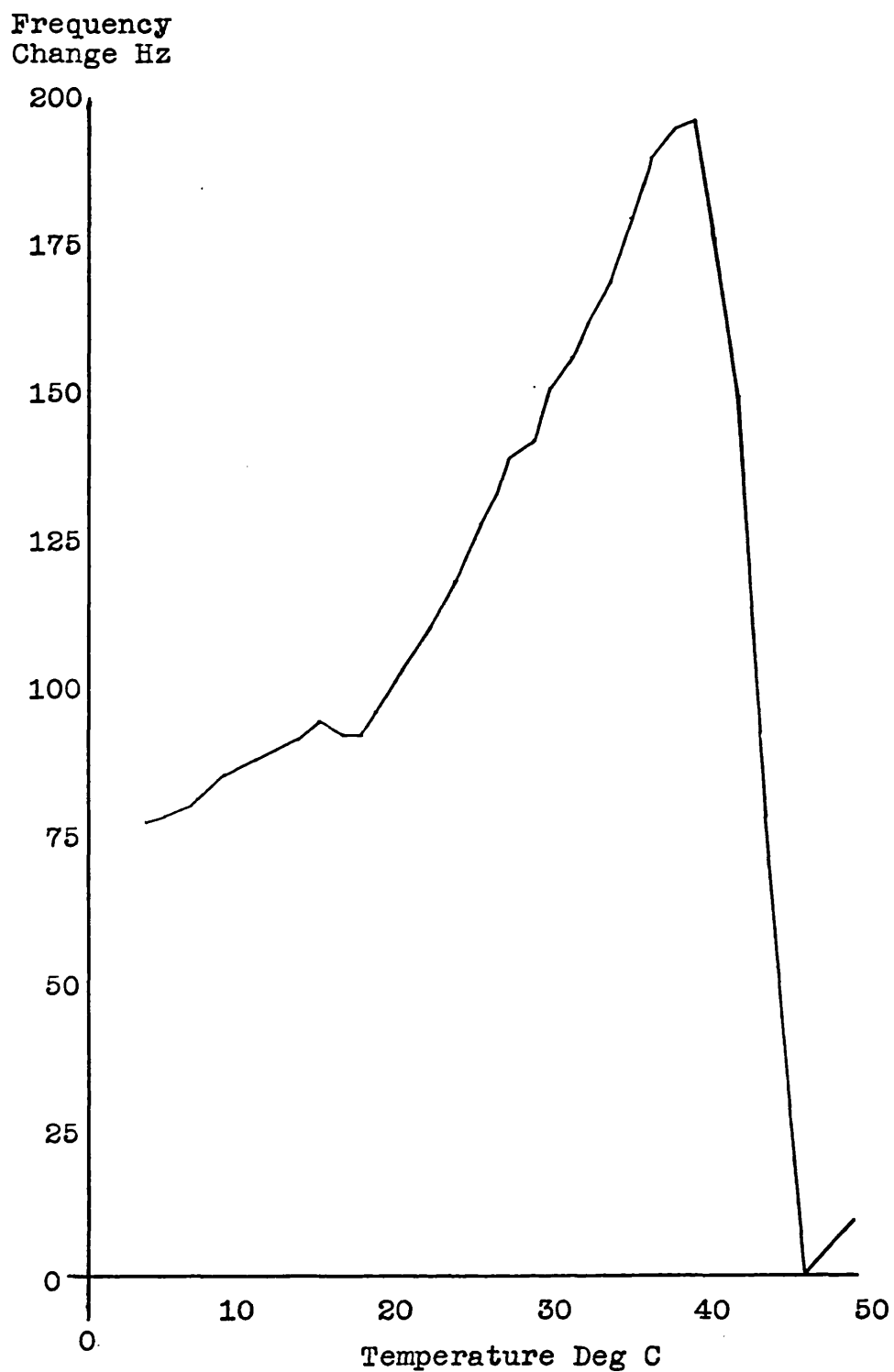


Figure 5.7 The frequency response with respect to temperature of crystal D.

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**CHAPTER 6**  
**A FOURIER ANALYSIS METHOD FOR THE TEMPERATURE COMPENSATION**  
**OF PIEZOELECTRIC CRYSTAL SENSORS**

The determination of mass using a PZC is affected by anything that is absorbed by or condenses on the coating. The choice of coating is made to overcome this effect for example quadrol selectively adsorbs  $\text{SO}_2$  in the presence of  $\text{NO}_2$  and is reported to be 1000 times less sensitive to it [6.1]. However, condensation occurs with water vapour for which the frequency change depends linearly on the mass of condensed water vapour which is assumed to depend on the humidity, temperature and nature of the coating as discussed in Chapter 8. The effect of water vapour on the response can be reduced by placing hydrophobic membrane filters in the gas stream [6.2, 6.3] but the response to  $\text{SO}_2$  also decreases. In their procedure Karmarkar, Webber and Guilbault then subtracted a blank air value to correct for this residual interference.

An improved method for compensation is to use 'smart' sensors that automatically compensate the data as it is acquired to correct for the effect of interferences.

In this chapter a method for processing experimental temperature response data into a form suitable for temperature compensation processes will be described. This method uses a Fourier series to transform data of frequency response with respect to temperature into a trigonometric series [6.4]. Various methods of implementation of such corrections are then considered.

## 6.1 FREQUENCY RESPONSE WITH RESPECT TO TEMPERATURE

The calibration procedure that was used to obtain the frequency response of a PZC with respect to temperature is as follows: The crystal to be calibrated is placed in the detector cell which is then purged with dry argon using the gas line described in Chapter 4. The detector cell assembly is then placed in a drained, recirculating water bath which is filled up with cold water. The temperature dependence of the crystal frequency is recorded continuously by the microcomputer as the temperature is raised from 15.1 to 55.0°C. The data are then transferred via the RS232 serial port to a BBC B microcomputer. The dataset consists of about 300 pairs of data items.

An example of a temperature response between 17 and 52°C as stored and represented by the microcomputer system is shown in fig. 6.1(a). The response curve for this uncoated crystal was obtained over four runs that were reproducible, the deviation being no greater between runs than observed within any one run.

Using this technique it was possible to determine and display the thermal characteristics of PZCs over the whole operating range. PZCs with temperature responses suitable for the appropriate operating temperature range can then be chosen. These will normally have very low temperature coefficients, and compensation can be used to further reduce the effect of temperature. For compensation, knowledge of the frequency expected for a PZC at any particular temperature is required and is obtained from a Fourier series that approximates the measured response data.

## 6.2 DATA CONDITIONING

The raw data are pooled by sorting the data from all runs into ascending temperature. The data are rounded to the nearest tenth of a degree and all frequency or temperature data outside reasonable limits are rejected as glitches. The limits are a step change in frequency of 40 Hz or a temperature change of more than 1°C between adjacent readings. All frequency measurements at a particular temperature are then collected together and averaged. Each averaged data pair is considered valid over a range of 0.1°C.

### 6.3 FOURIER SERIES

The conditioned data can easily be visualised graphically as a histogram of 400 columns. The frequency data is stored in an array with the index,  $i$ , taking values from 0 to 399.  $i$  is related to the temperature datum using the expression given in eqn. 6.1 and always takes integral values. The minimum and maximum indices correspond to the temperatures 15.1 and 55.0°C, respectively.

$$i = 10T_i - 151, \text{ (always an integer)} \quad (6.1)$$

If  $v_i$  represents the frequency datum for the  $i^{\text{th}}$  point, the corresponding temperature  $T_i$  is given by eqn 6.2:

$$T_i = \frac{i + 151}{10}, \quad (i=0, 1, 2, \dots, 399) \quad (6.2)$$

Mathematically, the histogram is a step function,

$$g(x) = v_i, \quad (i=0, 1, 2, \dots, 399) \quad (6.3)$$

where the index,  $i$  is the integral part of  $x$ , an algebraic variable that is defined when  $(0 \leq x < 400)$ .

This function is neither continuous nor differentiable. However, it can be represented by a trigonometric series of the type,

$$f(x) = \frac{1}{2}a_0 + \sum_{r=1}^{\infty} (a_r \cos \pi r x / l + b_r \sin \pi r x / l) \quad (6.4)$$

where,  $r$  takes integral values;  $a_0$ ,  $a_r$  and  $b_r$  are constants and  $l$  is a scaling factor [6.5]. Since eqn. 6.4 is unchanged by replacing  $x$  by  $x+2lk$ , where  $k$  is an integer, it is a periodic function in  $x$  of period  $2l$ . Equating the domain of  $x$  (that is when  $0 \leq x < 400$ ) as the period  $(0 \leq x < 2l)$  gives:

$$l = 200 \quad (6.5)$$

Coefficients  $a_0$ ,  $a_r$  and  $b_r$  can be calculated so that  $f(x)$  tends to  $g(x)$  as  $r$  tends to  $\infty$ , where  $g(x)$  is continuous and differentiable and  $f(x)$  tends to  $g(x-\delta x)+g(x+\delta x)/2$  elsewhere.

The coefficients are defined by:

$$a_r = \frac{1}{l} \int_0^{2l} f(x) \cos \pi r x / l \, dx, \quad (r=0, 1, 2, \dots) \quad (6.6)$$

$$b_r = \frac{1}{l} \int_0^{2l} f(x) \sin \pi r x / l \, dx, \quad (r=1, 2, 3, \dots) \quad (6.7)$$

Substituting in eqn. 6.6 using the identity  $f(x) \equiv g(x)$  and eqn. 6.5 gives:

$$a_r = \frac{1}{l} \int_0^{400} g(x) \cos \pi r x / l \, dx \quad (6.8)$$

Splitting this into 400 integrals,

$$a_r = \frac{1}{l} \sum_{i=0}^{399} v_i \int_i^{i+1} \cos \pi r x / l \, dx \quad (6.9)$$

integrating for  $r > 0$ ,

$$a_r = \frac{1}{\pi r} \sum_{i=0}^{399} v_i [\sin \pi r (i+1) / l - \sin \pi r i / l] \quad (6.10)$$

this is rearranged to give:

$$a_r = \frac{1}{\pi r} \sum_{i=1}^{399} (v_{i-1} - v_i) \sin \pi r i / l, \quad (r=1, 2, 3, \dots) \quad (6.11)$$

Similarly,

$$b_r = \frac{1}{\pi r} (v_0 - v_{399} + \sum_{i=1}^{399} (v_i - v_{i-1}) \cos \pi r i / l, \quad (r=1, 2, 3, \dots) \quad (6.12)$$

and integrating eqn. 6.9 for  $r=0$  gives:

$$a_0 = \frac{1}{l} \sum_{i=0}^{399} (v_i) \quad (6.13)$$

The step-wise approach of eqn. 6.3 in organising the data gives a series of small discontinuities. The inability of the Fourier series to tend to such a step in the data gives rise to localised averaging at each step, which is desirable.

Furthermore, the high frequency terms are eliminated, by limiting  $r$  to 10, which means that a smoothed out representation of the data can be obtained.

This smoothing action would be a disadvantage at one particular step if the whole Fourier range were used for valid data with the first and last data points scaled to 0 and  $399\pi/200$ , respectively. As a result of periodicity, the discontinuity between the frequency values at 0 and  $2\pi$  may be large requiring many high frequency terms to represent it well. Under the limit of  $r=10$ , this discontinuity and the data over a large region around it would not be well represented.

Software has been written to analyse the data contained in the array and calculate the Fourier coefficients up to  $r=10$ . For the integration program to operate efficiently, each array element must contain data. Before calculating the Fourier coefficients, therefore, data is linearly interpolated for empty array elements and extrapolated from  $15.1^{\circ}\text{C}$  to the first data point and from the last data point to  $55.0^{\circ}\text{C}$ .

#### 6.4 DATA BOUNDS

Under angular scaling  $55.0^{\circ}\text{C}$ , is equivalent to  $15.0^{\circ}\text{C}$  and the data must be considered to be periodic. Therefore, the extrapolations are unnecessary and instead a single interpolation is performed to fill in missing data from the last to the first experimental data point using a polynomial function. The valid data is thus nested inside the Fourier range so that the analysis can be performed efficiently on any range of data from  $15.1$  to  $50.0^{\circ}\text{C}$ . It must, however, be noted that the resulting Fourier series is only valid within the limits of the original data. With the data nested within the Fourier range, the undesirable periodic effects described above are avoided by choosing this function to be continuous at  $0$  ( $2\pi$ ).

## 6.5 DISCONTINUITY ELIMINATION AND INTERPOLATION FUNCTION

This function must be continuous and must interpolate values of the frequency with temperature function between the last data point and the first data point. No matter what the values or slopes of the data, it must evaluate to the data at the end points and must also have the same slope as the data at these points. Such a function will ensure a smooth progression of the data values through the fold over region so that no effects due to large discontinuities will spread into the region of real data. A cubic spline is the simplest polynomial expression that meets this requirement.

To simplify the following description and because the range of the cubic must be continuous, variable  $x$  must now be mapped in the region of the end data point (i.e. when  $x$  is close to 400) to be continuous with its value near the start data point. That is:

$$\begin{aligned} \text{if } x > 200 \\ x &\rightarrow x - 400 \end{aligned} \quad (6.14)$$

So for calculations involving the cubic spline all the  $x$  values must be close to zero.

To reduce the effect of noise on the slope, the gradient is approximated at the start and end points of the data  $(x_a, v_a)$  and  $(x_b, v_b)$  by taking the average slope from each of these points to the ten closest points:

$$s(x_a) = \frac{1}{10} \sum_{r=1}^{10} \frac{v(x_a) - v(x_{a+r})}{x_a - x_{a+r}} \quad (6.15)$$

and

$$s(x_b) = \frac{1}{10} \sum_{r=1}^{10} \frac{v(x_b) - v(x_{b+r})}{x_b - x_{b+r}} \quad (6.16)$$

The values of  $x_a$ ,  $x_b$ ,  $v(x_a)$  and  $v(x_b)$  at the end points are then substituted into the equation below to give coefficients for the cubic function:

$$a = m - b \quad (6.17)$$

$$b = c - s(x_b) + 3m \quad (6.18)$$

$$c = s(x_a) \quad (6.19)$$

$$d = v(x_a) \quad (6.20)$$

$$m = v(x_b) - c - d \quad (6.21)$$

The indices of the start and end points  $a$  and  $b$  depend on the range over which the cubic spline is required to interpolate missing data. The interpolation is made by substituting the integer values of  $x$  for which a notional frequency,  $z(x)$ , is required into the equation,

$$z(x) = ay^3 + by^2 + cy + d \quad (6.22)$$

where  $y$  is the normalised variable:

$$y = \frac{x - x_a}{x_b - x_a} \quad (6.23)$$

Now  $z(x)$  for negative values of  $x$  have to be assigned to their correct data point by inverse mapping:

$$\begin{aligned} \text{if } x < 0 \\ x &\rightarrow x + 400 \end{aligned} \quad (6.24)$$

Now all indices from 0 to 399 have true or notional frequency data and the transform calculation as described earlier can be carried out.

## 6.6 RESULTS AND DISCUSSION OF THE APPLICATION OF THE FOURIER SERIES METHOD

The conditioned data for the frequency response of a PZC, with respect to temperature, are shown in fig. 6.1(a). The data has been pooled from four runs, averaged and fitted to a cubic spline. The cubic spline is shown as two regions one below 17°C and one above 52°C. The coefficients of the Fourier series describing the response curve were calculated and are listed in table 6.1. It should be noted that as  $r$  increases the coefficients decrease showing that the high frequency terms are less important.

TABLE 6.1

| $r$ | $a_r$     | $b_r$  |
|-----|-----------|--------|
| 0   | 12144.826 |        |
| 1   | -8.955    | 2.505  |
| 2   | -5.879    | -3.976 |
| 3   | 1.503     | -4.142 |
| 4   | 2.514     | 0.122  |
| 5   | -0.143    | 0.762  |
| 6   | -0.176    | 0.054  |
| 7   | -0.001    | -0.132 |
| 8   | -0.134    | -0.226 |
| 9   | 0.132     | 0.087  |
| 10  | -0.056    | 0.217  |

Figure 6.1(b) shows the reconstructed temperature response obtained by Fourier synthesis using the coefficients given in table 6.1. The synthesised response is a smoothed out representation of the measured response and can thus be used for temperature compensation of the PZC response. All the salient features of the measured response are described without the digitisation and experimental noise inherent in the measurements.

Furthermore, the amount of data to be stored has been reduced to only 21 numbers. The expected frequency response at any chosen or ambient temperature can now be obtained by substitution into the Fourier series, eqn. 6.4, with  $r$  limited to 10 and where:

$$x = 101 - 151 \quad (6.25)$$

This correction has been applied to the uncoated crystal at 0.1°C intervals over the range 17 to 52°C as shown in fig. 6.1(c). The correction is to a temperature of 25°C. Using the correction, it appears that the crystal is temperature independent over this range.

## 6.7 THE IMPLEMENTATION OF COMPENSATION IN A SENSOR

The advantages of using a Fourier series to represent experimental data are (i) smoothing and representation are obtained in a single calculation and (ii) the resulting data is easily transportable. Advantage (ii) arises as the coefficients given in table 6.1 for the 21 term Fourier series can easily be input into another sensor system, manually. Such a procedure would be very tedious for a look-up table of even just 100 points. The coefficients could of course also be transferred by electronic means.

A disadvantage of a Fourier series method is that many sine and cosine calculations are required and these are relatively slow computations in comparison to simple arithmetic operations such as addition, subtraction, multiplication or division. This problem can be overcome for critical real-time applications by using look-up tables. Look-up tables can be implemented in a number of ways as discussed below.

In a dedicated, microprocessor based, 'smart' sensor there are various possibilities for the storage and retrieval of response data.

### 1) Direct Calculation of Temperature Responses from the Fourier Series

In this method 21 sine and 21 cosine calculations are carried out, along with arithmetic operations, in order to calculate the temperature response at a single temperature. Sine and cosine

computations are slow series calculations and so a disadvantage of this method is that the rate of retrieval of a temperature correction value will also be slow.

This method is, however, the most efficient at storing temperature responses as only 21 numbers need be stored for each response.

## 2) Look-Up Table of the Temperature Response

In this method the response is calculated using the Fourier series method at each temperature increment (every  $0.1^{\circ}\text{C}$ ), this is done only once. It is these response values at all temperatures of interest which are stored and the computer merely selects the response indicated by the temperature sensor in real-time.

The retrieval rate is the fastest of all the methods. However, since all possible responses must be stored, it has the greatest storage requirement.

## 3) Look-Up Table of Sines and Cosines

In this method the sine and cosine values corresponding to each temperature increment are calculated and stored along with the 21 coefficients for each response, this is done only once.

A correction value is obtained by using the Fourier series calculation but looking-up the sine and cosine values. Thus only arithmetic operations are carried out which are relatively fast.

The rate of retrieval is therefore far greater than by method 1) although slower than method 2). The great advantage is that once the initial storage overhead of the look-up table is made all the subsequent storage of responses for any number of sensors has the same additional storage requirement as method 1) even though the retrieval rate will be far greater.

The choice of method is a trade off between rate of retrieval and storage requirements, with the choice of trade off dependent on number of data sets to be stored. As an example, the data storage used for each of these implementation methods in BBC BASIC are given in table 6.2. The storage increment is the additional storage requirement for each subsequent data set after the first.

TABLE 6.2  
Typical Storage Requirements

| ! Method !                                          | ! Storage !<br>! (bytes) ! | ! Storage !<br>! increment !<br>! (bytes) ! |
|-----------------------------------------------------|----------------------------|---------------------------------------------|
| ! 1) Direct !<br>! calculation !                    | ! 105 !                    | ! 105 !                                     |
| ! 2) Look up !<br>! table !                         | ! * !<br>! 2000 !          | ! * !<br>! 2000 !                           |
| ! 3) Table of !<br>! sines and !<br>! calculation ! | ! * !<br>! 505 !           | ! 105 !                                     |

The asterisk symbol (\*) indicates dependency of the estimate on the temperature resolution. This has been set at 0.1°C equivalent to a table of 400 points.

Method 1) would only be used where memory is very limited, method 2) for fast retrieval in a one PZC response situation and method 3) where many data sets are needed.

Since the temperature compensations of the response of PZCs were not carried out in real-time in this work, speed of calculation was not an important factor. Therefore, method 1), direct calculation was used throughout this application. The result of applying the temperature compensation procedure to a PZC coated to measure  $\text{SO}_2$  is discussed in the next chapter.

# 6.8 FIGURES

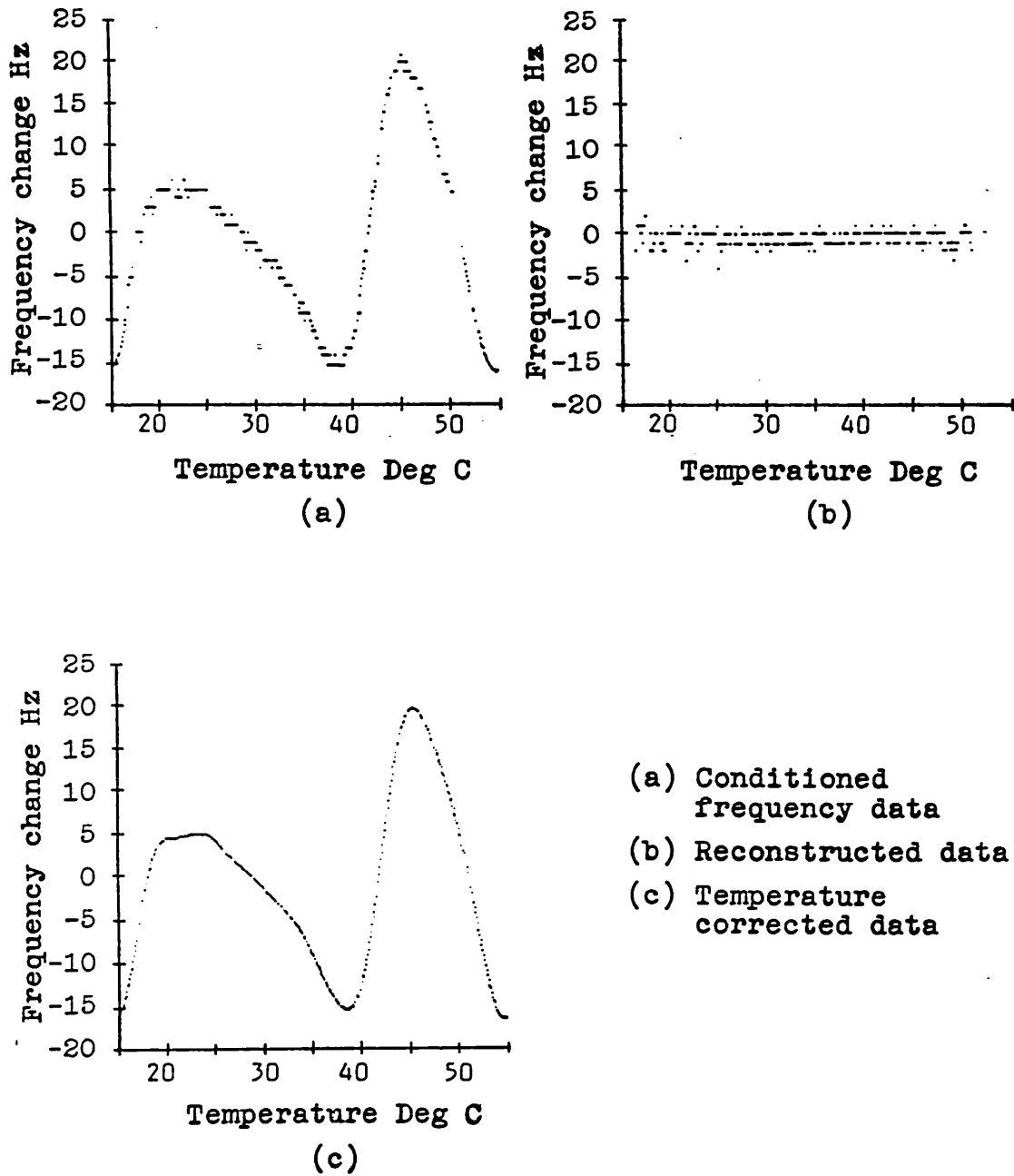


Figure 6.1 Fourier analysis and temperature correction of a piezoelectric crystal sensor.

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CHAPTER 7  
THE ON-LINE MEASUREMENT OF SO<sub>2</sub>

## 7.1 INTRODUCTION

In this chapter the effect of temperature on a coated piezoelectric crystal (PZC) mass sensor used for the detection of sulphur dioxide is investigated. This is possible since a method for the automatic compensation of the PZC element of the sensor with respect to temperature has already been developed in this work. A microcomputer measuring system is therefore used to compensate the frequency changes arising from mass changes, at different temperatures, for the changes arising directly from temperature changes. Information is obtained on the effect of temperature on the behaviour of the coating and on the SO<sub>2</sub> adsorption process. This is an advantage over existing PZC instrumentation where this information is not available.

Initially, the data handling procedure described in Chapter 6 was used to investigate the effect of temperature on the stability of a quadrol coating. Temperature cycling was found to be a useful procedure for monitoring and acceleration of the curing process, which yields a coating stable up to 55°C.

At this point the response of coated PZCs to an injection of a small sample containing SO<sub>2</sub> into a flowing gas stream was determined. This is discussed here in conjunction with the advantages of discrete measurement and the effect on discrete measurement of variation in the flow rate of the carrier gas stream.

Finally, a number of SO<sub>2</sub> measurements were carried out at various temperatures and a temperature correction was applied.

The method involved is more complicated than, although similar to, the correction found in Chapter 6 for an uncoated crystal. The difference is that the effect of temperature on a coated crystal is described by a Fourier series, so that the computer can refer to that data when compensating. The use of this procedure is limited by the effects of curing and stability of the coating.

The effect of temperature on the  $\text{SO}_2$  adsorption is derived from temperature compensated  $\text{SO}_2$  concentration measurements. This effect and particularly the unexpected change in adsorption mechanism above  $35^\circ\text{C}$  are discussed.

## 7.2 COATING

Crystal coatings are of vital importance to PZC sensing. Specificity, sensitivity and durability of sensors will be achieved by the informed choice and subsequent screening and modification of coatings. Inherent non-selectivity is an advantage, if it can be overcome for specific applications, since it will make the PZC hardware standard for different applications.

Specificity and selectivity for a particular application are primarily obtained by the use of sorbent coating materials with a certain degree of selectivity in the target analytical environment. It is not necessary to be selective over components that are not normally present. For instance in soft drinks, with  $\text{SO}_2$  as the target molecule,  $\text{CO}_2$  must be considered as a possible interference but  $\text{NO}_2$  need not. Selectivity is therefore achieved by screening potential coating materials, modifying and improving their sorption of the target species relative to potential interference from the atmosphere under test. Secondly, interference can be reduced by using membranes to filter out unwanted components e.g. water vapour in  $\text{SO}_2$  headspace analysis of beverages.

Selective coatings have been developed for the detection of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{Hg}$ ,  $\text{NH}_3$  and  $\text{SO}_2$  as well as for various organic compounds amines, aromatics, hydrocarbons and organophosphorus compounds [7.1, 7.2, 7.3, 7.4, 7.5, 7.6]. The theoretical basis of PZC sensing has been well reported and was discussed in

## Chapter 2.

The coating of crystals with quadrol, in order to adsorb  $\text{SO}_2$  specifically and the storage conditions for optimal lifetime are discussed. Another factor to be considered in the development of a commercial device is the effect of the environment on the durability of the coating. Irreversibility, coating loss and poisoning all lead to degradation of the sensitivity of the coating and thus reduce the useful lifetime of the sensor.

Quadrol, N,N,N',N'-tetrakis (2-hydroxypropyl) ethylene-diamine, has already been reported as a good coating for piezo-electric crystals in the detection of  $\text{SO}_2$  [7.7, 7.8, 7.9]. It possesses a strong affinity for binding  $\text{SO}_2$  with a marked selectivity over the adsorption of other gases. From the figures given by Karmarkar, Webber and Guilbault it can be calculated that a quadrol coated PZC is 4000 times less sensitive to water vapour than to  $\text{SO}_2$ . However, this hydrophobic nature of quadrol is insufficient to suppress the effect of water vapour at ambient humidity levels.

A thin coating is essential to minimise the tendency of the coating to be volatile which increases with thickness and also to reduce curing and response times by lowering diffusion gradients. The stock of uncoated crystals was kept in an evacuated desiccator because absorbed water compounds the problem of stabilising the coating.

Several methods for coating crystals were investigated: smearing with cotton swabs, dropping from a micro-syringe, application

from a micro-pipette and spraying. Quadrol (minimum 98% by non-aqueous titration) was obtained from Fluka AG Chemicals, it is a highly viscous liquid so in all these methods a solution of the coating in a volatile solvent was applied. Quadrol readily dissolves in many organic solvents (Ethanol, methanol, chloroform, dichloromethane etc).

The concentration of the solution applied to the PZC is critical in obtaining an even distribution of coating. In order to achieve the required quantity and degree of coating at a fixed concentration a change in volume of coating solution is necessary. This cannot always be delivered by the coating process. Since the most mass sensitive portion of a crystal is its centre, it is not necessary to coat the periphery.

Initially a solution of quadrol in ethanol was made up of a concentration such that smearing it onto the electrode on the piezoelectric crystal surface with a cotton swab gave a final frequency change of about 20,000 Hz. This resulted in a thick coating which was very volatile. Diluting the quadrol solution to 0.24 m/V gave a more useful change of about 4000 Hz. However, smearing left drying marks in the form of lines all over the PZC surface. These indicate an uneven distribution of quadrol.

Adding solution dropwise from a micro-syringe was preferred as the centre of the PZC is more evenly coated by this method. However, drying rings occurred around the outside of the electrode. This was not crucial since this area is less sensitive to mass than the electrode which was fully coated. The drop

tended to wander under the influence of gravity. In order to restrict the drying solution to the centre of the PZC, the PZC had to be continually tilted from the near horizontal.

Later dichloromethane was used as the solvent since it is more volatile than ethanol. This shortened the time taken for evaporation making the crystal ready to put aside sooner and reduced the amount of solvent incorporated into the coating, which reduced curing time. However, as dichloromethane is less viscous than ethanol it was harder to restrict the drying drop to the centre of the PZC by tilting.

Applying solution directly to the PZC electrode surface by capillary action using a micro-pipette is more accurate. The pipette can be held in place whilst most of the solvent dries thus allowing the coating to be held at the centre. In addition the volume can easily be controlled at the loading stage and this method is more likely to be reproducible than the previous two methods.

Spraying gave an improved coating quality. The hand held DeVilbiss Sprite Major airbrush was used, supplied with an air flow of 8.2 l/min at 2 bar. The airbrush was adjusted to eliminate splutter and a coating of well defined thickness and structure was obtained.

The curing process is important as measurements made in the presence of solvent evaporation will produce erroneous results in the detection of the target gas.

Quadrol was added, dropwise, by the capillary method in dichloromethane ( $1.7 \times 10^{-4}$  m/V). About 20  $\mu$ l of solution was added. The curing can conveniently be followed by monitoring the frequency according to the Sauerbrey eqn. 2.19 whilst purging the detector cell with dry argon. Fig 7.1 illustrates the process of curing over successive temperature cycles with the same crystal. Curve [i] is the temperature response when the crystal is coated with quadrol and is then heated through the temperature range shown. It can be seen from curve [i] that at temperatures above 35°C there is a progressive loss of mass which is assumed to be evaporation of the solvent and quadrol. When the temperature cycle is repeated the temperature at which mass loss is observed occurs at progressively higher temperatures (curves [ii], [iii], and [iv]) until the coated crystal behaves in the same way as the uncoated crystal.

Repeated temperature cycles of the uncoated sensor are shown in fig. 7.2. Within experimental error (relative standard deviation of 7% in  $\Delta F$  for four consecutive temperature cycles) the response of the sensor with respect to temperature remains the same for each cycle and hence has the same general form as the coated, cured crystal, although the nominal starting frequency ( $\Delta F=0$  Hz) is higher owing to the absence of coating. It can be assumed therefore that the coating is cured after four heating cycles and that the device is now in its prepared state for use as a sensor. At temperatures above 55°C rapid mass loss occurs from the cured, coated crystal corresponding to loss of quadrol itself from the crystal surface.

### 7.3 MEASUREMENTS

Having developed satisfactory methods for coating piezo-electric crystals, the detection of  $\text{SO}_2$  in a flowing argon stream using a PZC can now be demonstrated. A reasonable detection limit of 0.06 vppm is obtained. These experiments were done under dry, thermostatted conditions to find the true response of the PZC to  $\text{SO}_2$  without interference from the effects of temperature and humidity which are both reduced by the choice of conditions.

A  $\text{SO}_2$  mixture of a 380 vppm concentration at atmospheric pressure in argon was prepared in the gas dilution apparatus. The dilution technique was described in Chapter 3. The coated, cured PZC was placed in the measurement apparatus, as described earlier. A Hamilton Bonaduz 1001 TLL 1 ml gas tight syringe was used to take a sample from the silicone rubber septum and 0.9 ml was injected into the gas stream that impinged on the quadrol coated PZC. Subsequent samples were prepared by successive dilutions of the gas in the reservoir with argon. The response of the coated PZC over several orders of magnitude of concentration was rapidly obtained.

Three such runs carried out with the water bath containing the detector cell held at  $40^\circ\text{C}$  and with argon flow rates of about 60 ml/min are shown in figs. 7.3(a), (b) and (c). These are logarithmic plots of the maximum frequency change from the baseline frequency versus  $\text{SO}_2$  concentration. Notice that an order of magnitude change in concentration does not give rise to a corresponding order of magnitude change in change of frequency.

At low concentrations most of the  $\text{SO}_2$  is adsorbed strongly, yet at higher concentrations most of the  $\text{SO}_2$  flows past the PZC without reacting with it. A probable cause of the decrease in sensitivity to  $\text{SO}_2$  with increasing  $\text{SO}_2$  adsorption is the changing nature of the adsorption process as discussed below.

A blank was obtained by injecting pure argon and measuring the frequency change. It was allowed for in fig. 7.3. The value was found to be  $5 \pm 1$  Hz at these flow rates and is due to a perturbation of the gas stream by the injected volume leading to a pressure change, to which the PZC responds.

A quantitative theory of the adsorption process is now described. The heat of adsorption often declines markedly with increasing adsorption. Typical results are shown by Moore [7.10]. This effect obviously indicates a non-uniform substrate with the heat of adsorption being unequal at all the adsorption sites. According to Moore, the lack of uniformity may either pre-exist in different adsorption sites or be caused by repulsive forces between adsorbed molecules making adsorption at some sites less favorable than at others and markedly lowering the heat of adsorption at higher adsorptions. Since the quadrol coating is a liquid all sites are equivalent so any existing non-uniformity can be discounted. However, if the  $\text{SO}_2$  to quadrol bond is partially ionic, as is the case for hydrogen bonding, electrostatic repulsions may become significant. Moreover, as molecular adsorption is basically covalent, repulsion can be large without appreciable separation of charge, i.e. steric, since adsorbed molecules have very restricted geometrical

constraints.

At equilibrium, this behaviour can be described by an empirical adsorption isotherm due to Freundlich [7.10]:

$$\theta = K p^{1/m} \quad (7.1)$$

where,  $\theta$  is the fraction of sites occupied by adsorbed molecules,  $K$  is a constant,  $m$  is a number greater than one and  $p$  is the partial pressure of  $\text{SO}_2$ . An analogous equation:

$$\Delta F = A p^{1/m} \quad (7.2)$$

describes the response seen in figs. 7.1(a), (b) and (c) under non-equilibrium conditions, where the frequency change,  $\Delta F$ , depends linearly on  $\theta$  and where  $A$  is a constant. This similarity probably indicates that the  $\text{SO}_2$  molecule is bonded to the surface by an adsorption process described by the theory leading to eqn. 7.1.

Figs. 7.1(a), (b) and (c) show that 0.06 vppm of  $\text{SO}_2$  can be detected using the methods described here. This detection level can be achieved because a discrete measurement is being taken. Long-term changes in temperature and humidity between measurements and between runs have no effect since a measurement of the baseline frequency (which is a record of these effects) is obtained both before and after each measurement of  $\text{SO}_2$ . The baseline frequency at each discrete  $\text{SO}_2$  measurement being interpolated from the baseline frequencies for the argon gas stream before and after the  $\text{SO}_2$  injection, as part of the peak location procedure. This interpolation allows for short-term variations in baseline frequency during each measurement due to

residual temperature and humidity changes.

When measuring low concentrations of analyte, however, the peak could not be distinguished from the sloping baseline due to variation in the residual humidity. This may also pose a problem if the temperature was to vary significantly.

A possible disadvantage of making a discrete measurement is that a memory effect occurs after the measurement. The desorption kinetics of  $\text{SO}_2$  from the quadrol are slow. Therefore, a continuously sloping baseline between each measurement is observed and is caused by  $\text{SO}_2$  which is still bound to the quadrol from the previous measurement. The memory effect is corrected for using the background correction procedure described above. Although the resulting slope in the baseline contributes to the problems in locating small peaks.

A more significant disadvantage, however, is the effect of argon flow rate on the response. 1 ml samples of 380 vppm of  $\text{SO}_2$  were injected at various argon flow rates. Five readings were taken at each flow rate and plots of the averaged frequency changes, corrected for the gradual decrease in  $\text{SO}_2$  concentration as samples were taken, versus flow rate are shown in fig. 7.4. Several 1 ml samples could be taken before there was any appreciable fall in the concentration.

The following equation has been devised in order to linearise fig. 7.4:

$$\Delta F = \Delta F_{\infty} + \frac{\Delta F_0}{1 + \alpha f_r} \quad (7.3)$$

where  $\Delta F_{\infty}$  is the flow rate independent component of  $\Delta F$ ,  $\Delta F_0$  is

the flow rate dependent component of  $\Delta F$  at zero flow rate,  $\alpha$  is the flow rate susceptibility of the adsorption process and  $f_r$  is the flow rate.

Fig. 7.4 shows that the frequency change doubles as the flow rate is reduced from 100 to 13 ml/min and from it the following values for the terms in eqn. 7.3 are obtained:  $\Delta F_\infty = 37$  Hz,  $\Delta F_0 = 135.3$  Hz and  $\alpha = 0.04753$  ml/min. Sensitivity to  $\text{SO}_2$  can therefore be improved merely by reducing the flow rate but at the cost of longer measurement and recovery times.

In addition some  $\text{SO}_2$  appeared to be irreversibly bound to the coating although most came off within five minutes of the end of the measurement. This binding probably occurs through a rearrangement or an oxidation of the adsorbed  $\text{SO}_2$  molecule.

To reduce atmospheric poisoning and to eliminate any water vapour sorption, coated crystals were kept in an argon filled dessicator and only exposed to ambient conditions for short periods. If left exposed to air, coated crystals lose sensitivity to  $\text{SO}_2$ , probably due irreversible reactions of components in the air with the quadrol coating at binding sites that could be used to bind  $\text{SO}_2$ . Having been coated, PZCs should not be stored under vacuum since the coating evaporates under reduced pressure. Hence the use of inert gas in the dessicator to maintain a reasonable pressure and minimise degradation. Replenishing the argon from the carrier gas supply also ensures that the crystals are exposed to any residual water vapour pressure in the gas line.

Due to this limited exposure to water vapour and irreversible reactions at binding sites, even a well maintained surface will eventually wear out with use. When a coating was worn out the crystal was washed in dichloromethane, dried in vacuo and then re-used.

To study the effect of temperature on  $\text{SO}_2$  determination, the detector cell was initially brought to  $19^\circ\text{C}$  with the sensor under an atmosphere of dry nitrogen ( $<1\%$  RH) and the baseline frequency and temperature were recorded. The cell and sensor were then raised to one of five temperatures in the range  $20$ - $50^\circ\text{C}$  with the sensor under an atmosphere of  $17$  vppm of  $\text{SO}_2$  in dry nitrogen at atmospheric pressure. Frequency and temperature measurements were taken at each of the five temperatures and the temperature correction procedure was applied.

The result of applying the temperature correction procedure is shown in fig. 7.5. The chosen corrected temperature was  $25^\circ\text{C}$  and it can be seen that the correction procedure works well up to about  $32$ - $33^\circ\text{C}$ . There is a mean response of  $48 \pm 3$  Hz for the four corrected data points below  $33^\circ\text{C}$  and none of these points varies significantly from the mean.

However, above  $33^\circ\text{C}$  the corrected  $-\Delta F$  values gradually increase significantly from this mean. Indicating that when  $\text{SO}_2$  is adsorbed onto the coated crystal some process, other than the effect of temperature on the PZC element, is changing the PZC frequency with temperature and that this process only becomes significant at higher temperatures. There are several possible

explanations for the breakdown of the correction procedure which can be postulated after a careful analysis of the data.

Close inspection of the curves presented in fig. 7.5 reveals that the gradient of the tangent to part A of the curve (up to about 32°C) is the same as that for the equivalent part of the curve for the response with respect to temperature of the cured, coated crystal (fig. 7.1), about 0.8 Hz/°C, whereas the gradient of part B of the curve is significantly larger, 1.6 Hz/°C, when compared to the equivalent part of the curve for the cured, coated crystal which remains at 0.8 Hz/°C. Since the temperature correction algorithm is based upon Fourier coefficients obtained from the cured crystal curves shown in fig. 7.1, the method will break down above 35°C. This result is valuable since it reveals that there is a completely different mechanism responsible for the frequency response above 35°C.

A likely cause for the increase in the rate of change of frequency with temperature is desorption of residual water vapour from the PZC cell and its subsequent deposition on the crystal. This increases the total mass adsorbed and hence decreases the frequency of the PZC. This mechanism, however, would also be manifest in the experiments on the frequency response of the cured, coated crystal exposed only to dry nitrogen. No evidence of this kind of behaviour was observed and therefore the possible role of adsorbed residual water vapour can be eliminated. However, it is possible that residual water vapour could combine with the adsorbed SO<sub>2</sub>, which might alter the frequency response.

Another possible mechanism is a change in the adsorption properties of  $\text{SO}_2$  on quadrol with temperature. Intuitively, it would seem likely that the rate of desorption of  $\text{SO}_2$  molecules from the surface would increase with increasing temperature. However, the results presented in fig. 7.5 suggest that mass loading is increased. This apparently anomalous behaviour could be related to the adsorption process already discussed for discrete  $\text{SO}_2$  measurements. For small values of the fraction of sites occupied ( $\theta$ ), there is no interaction between adsorbed molecules. The Freundlich isotherm (eqn. 7.1) can then be written [7.11]:

$$\ln \theta = \frac{kT}{\epsilon_0} \ln p + \text{constant} \quad (7.4)$$

where:  $\epsilon_0$  is the heat of adsorption for small  $\theta$  and  $p$  is the partial pressure, which in this experiment is effectively constant. Thus an increase in temperature may actually increase the number of sites occupied depending on how  $\epsilon_0$  varies with temperature. This is more likely to be true if the nature of the adsorption process changes, e.g. from physical adsorption to chemisorption since the heat of adsorption for the latter is much higher and the rates of sorption for physisorption and chemisorption will be different.

These mechanisms are offered only as tentative explanations of the adsorption processes and the apparent failure of the temperature compensation at temperatures above  $35^\circ\text{C}$ . Nevertheless, the Freundlich isotherm can be used to explain separately the behaviour both at (i) constant flow rate, constant temperature and variable  $\text{SO}_2$  concentration and (ii) at constant

SO<sub>2</sub> concentration, zero flow rate and variable temperature. Further work to study the sorption process and to ascertain validity of the Freundlich isotherm is necessary and is discussed beginning on page 214 of the next chapter.

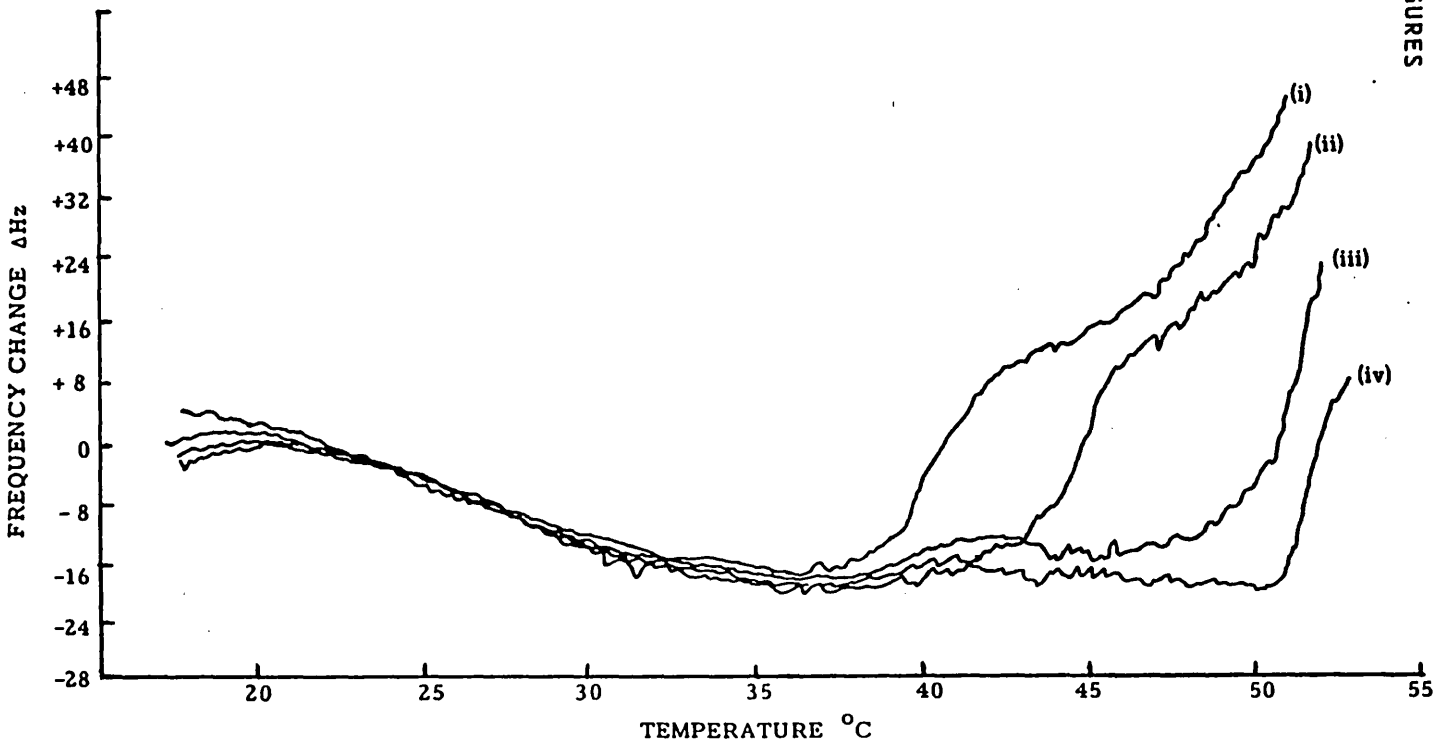


Figure 7.1 The frequency response of a coated crystal during temperature cycling.

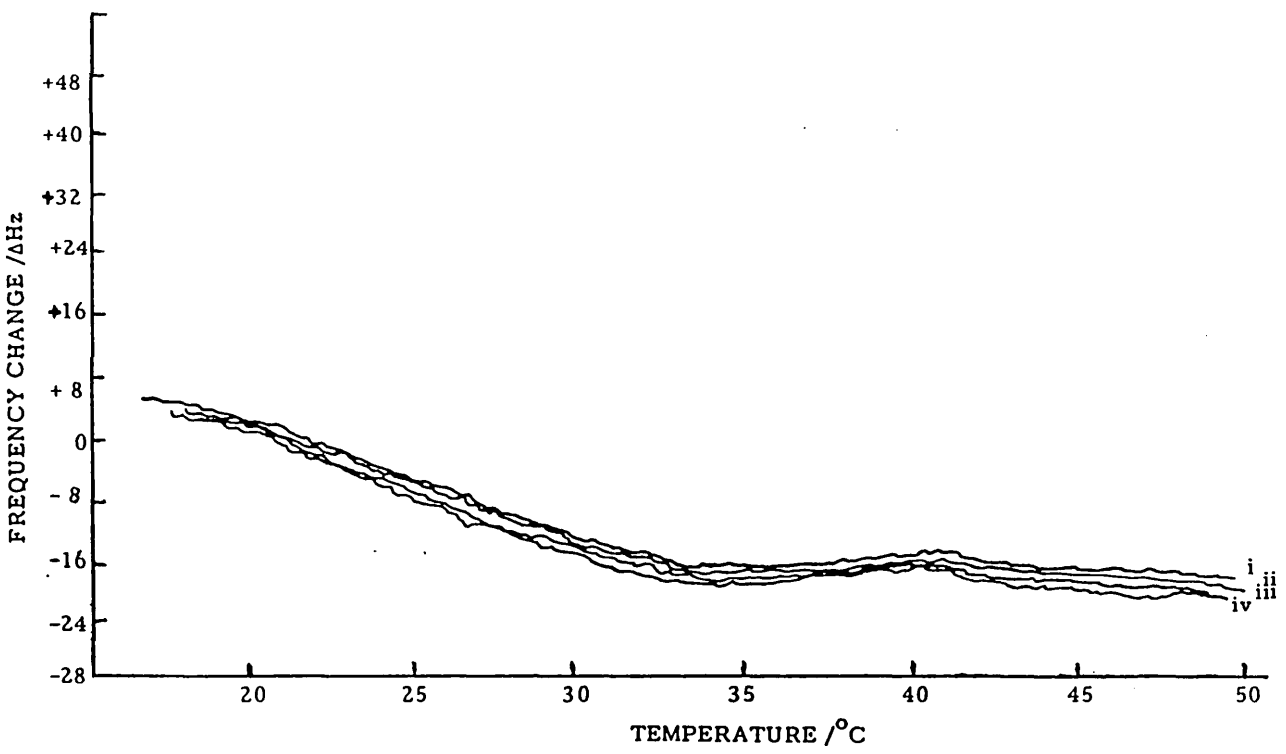


Figure 7.2 The frequency response of an uncoated crystal during temperature cycling.

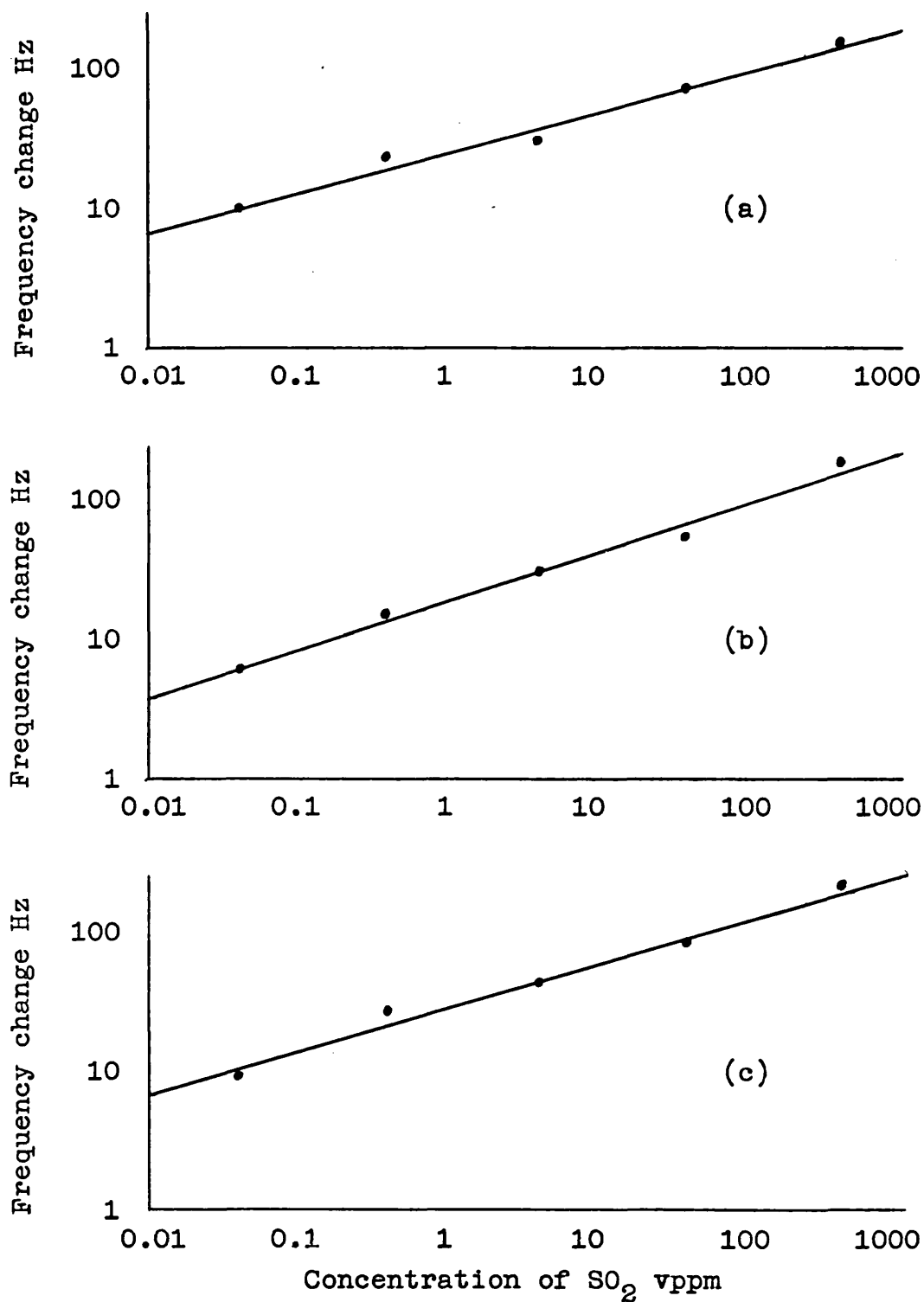


Figure 7.3 Calibrations of crystal frequency with concentration of sulphur dioxide. Flow rate a) 56 ml/min, b) 60 ml/min and c) 62 ml/min; injected volume 0.9 ml.

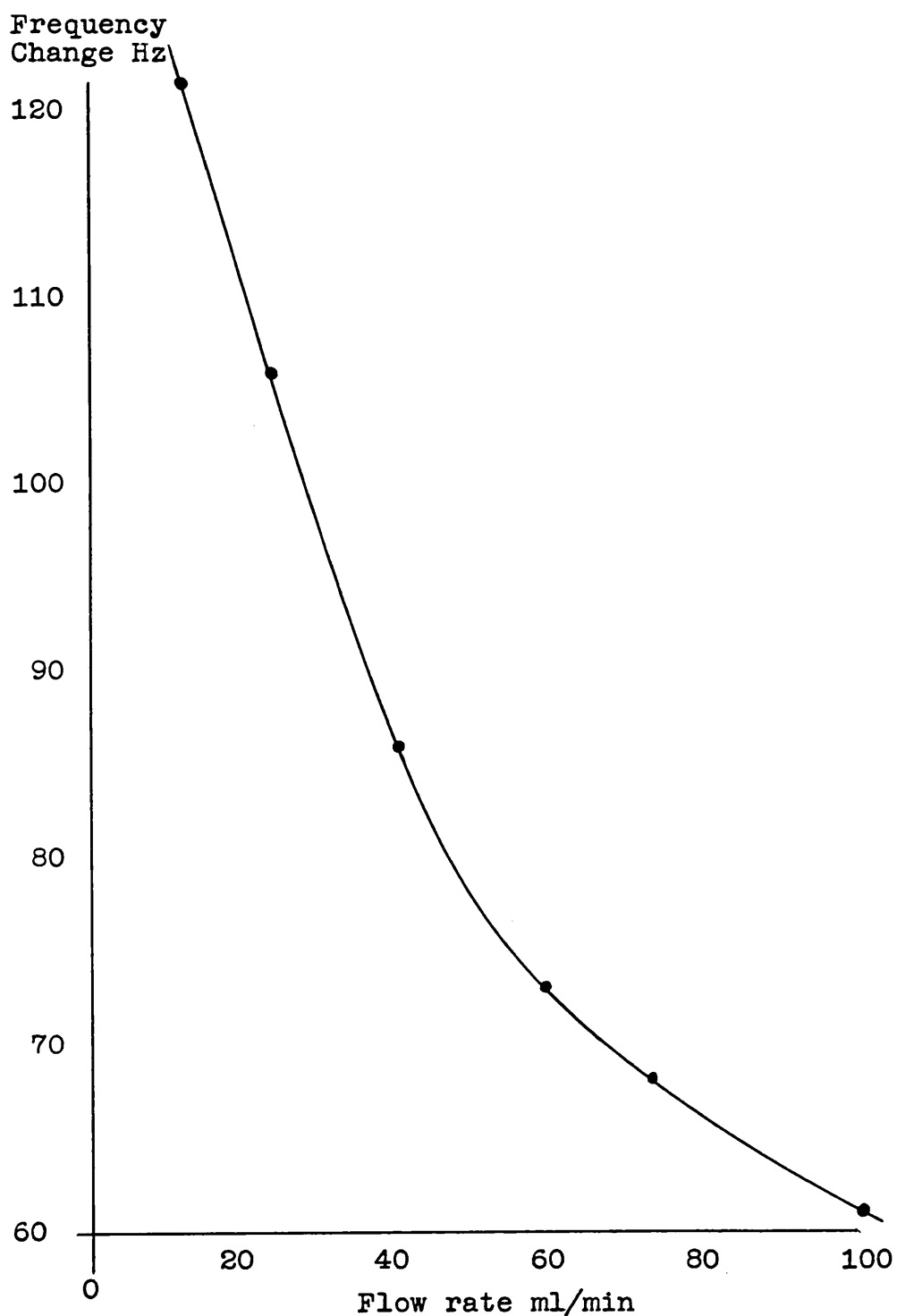


Figure 7.4 The effect of flow rate on the response of a piezoelectric crystal sensor for  $\text{SO}_2$  to a discrete sample.

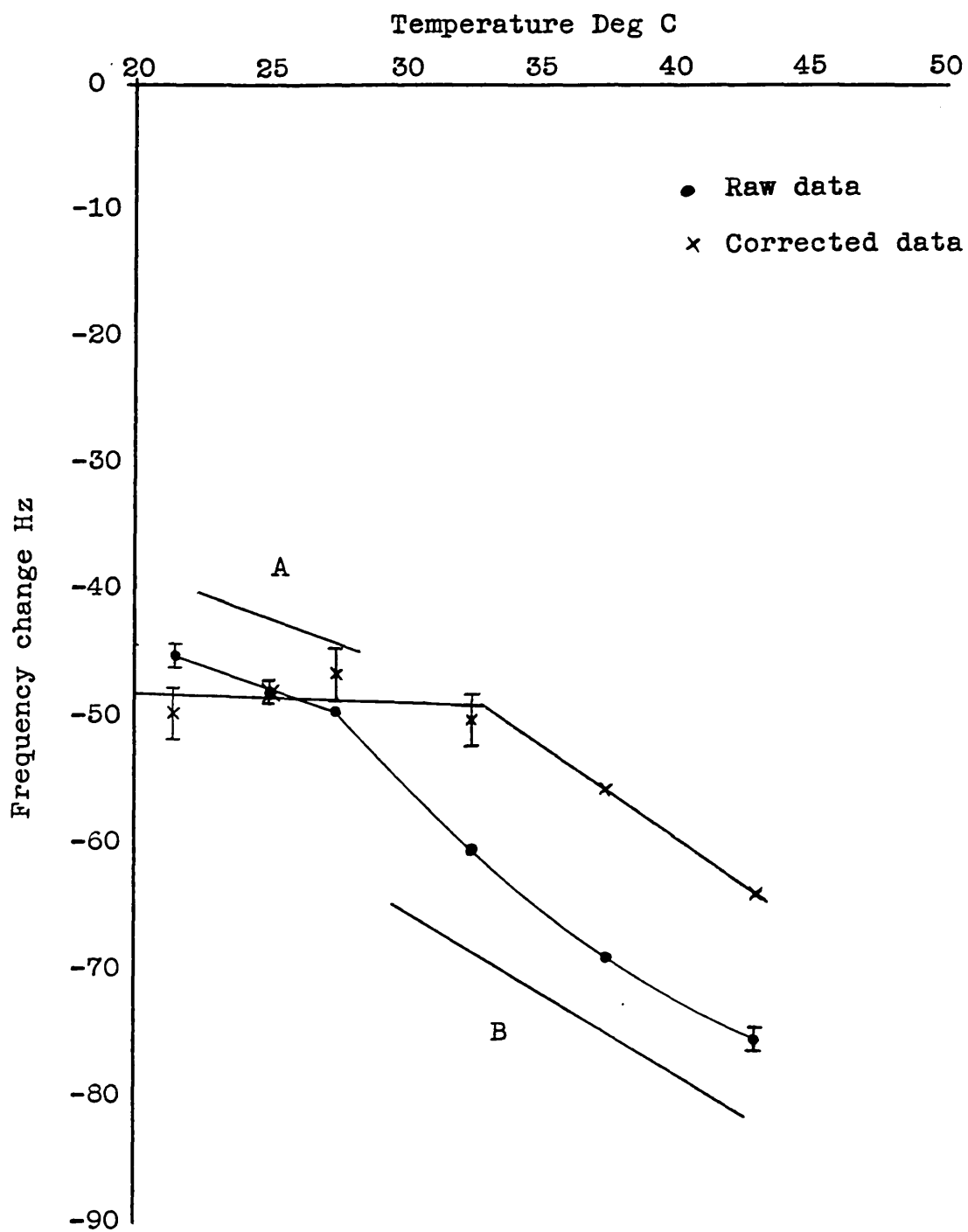


Figure 7.5 Temperature correction of the  $\text{SO}_2$  sensor exposed to 17 ppm of  $\text{SO}_2$ .

## 7.5 REFERENCES

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**CHAPTER 8**  
**CONCLUSIONS**

In this chapter the significance of the effect of temperature to the practical use of piezoelectric crystal (PZC) sensors is discussed. The results obtained by applying microcomputer control to the temperature compensation of a PZC sensor show that there is an effect of temperature on the gas-coating adsorption of  $\text{SO}_2$ . Some further investigations of this effect that could be carried out are therefore suggested.

Humidity was considered to be an interference during this work and procedures were followed to minimise its effect. The interaction of humidity with coated and uncoated PZCs is compared in this chapter as are alternative precautions that could be taken in future work to reduce the interference of humidity on PZC sensor measurements in ambient environments. The possibility of applying a Fourier series based compensation procedure to the humidity problem is discussed. A strategy for reducing the significance of any interference with respect to measurements by a sensor, possibly using Fourier series compensation, is suggested. This leads to a discussion of how compensation could be implemented in multi-parameter systems using arrays of sensors.

The chapter concludes with a discussion of the advantages offered by PZC sensors and suggestions for further work that should be carried out so to make full use of these advantages.

## 8.1 TEMPERATURE

The interference effect of temperature which was demonstrated in Chapter 5 for laboratory work could be considered to be both more of a problem and less of a problem for the practical applications of PZCs. It is more so in the sense that temperature changes cannot be controlled in the real world whereas in the laboratory corrective action can be taken. On the other hand the temperature changes tend to be less drastic in the real world than the deliberate changes made in the laboratory to investigate the effect of temperature.

In Chapter 6 a method which uses Fourier series for the correction of temperature effects was described. The advantages of using Fourier series to represent experimental data are (i) smoothing and representation are obtained in a single calculation and (ii) the coefficients for the resulting 21 term Fourier series can be transferred to another sensor system easily. The microcomputer controlled system, developed in this work, was used to acquire experimental data. The system then used the described Fourier series technique to provide coefficients for temperature compensation. This procedure can be applied to provide an accurate frequency of a PZC for any chosen temperature within its range.

In Chapter 7 the microcomputer controlled system was used to monitor the preparation of a PZC coating and to calibrate a PZC for SO<sub>2</sub> adsorption. Later in Chapter 7 the system was used to compensate a PZC gas sensor that was measuring SO<sub>2</sub> for

temperature effects in the range 15°C to 50°C.

As a result of the apparent failure of the compensation process, useful information about the effect of temperature on the sensing properties of SO<sub>2</sub> sensors can be obtained with the aid of this microcomputer system.

The elucidation of the apparently anomalous sorption behaviour of SO<sub>2</sub> on a quadrol coated crystal at temperatures between 35 and 55°C will require that carefully designed experiments are carried out where vapour concentrations and pressures are strictly controlled during the sorption process. Experiments of this nature are presently being carried out using a more sophisticated test rig and more sensitive surface acoustic wave (SAW) sensors instead of PZCs. The SAW transducers [8.1] are temperature compensated using an integral temperature sensor. Having reviewed the literature, Fox and Alder [8.2] give a critical comparison of SAW devices to PZCs and find that an order of magnitude increase in sensitivity may be expected. This increase is limited by the noise and drift of the SAW sensor system and not by the SAW sensor itself.

It might be helpful to use spectroscopic studies to investigate the SO<sub>2</sub> on quadrol absorption. This could indicate whether the SO<sub>2</sub> is absorbed by the S or the O or both.

Work is also required to unify the separate theories put forward to explain the behaviour of the PZC at (i) constant flow rate, constant temperature and variable SO<sub>2</sub> concentration, (ii) at constant SO<sub>2</sub> concentration, zero flow rate and variable

temperature and (iii) at constant  $\text{SO}_2$  concentration, constant temperature and variable flow rate. This would require experiments to be carried out at many more combinations of the above parameters so that the behaviour of a quadrol coated PZC under any combination of  $\text{SO}_2$  concentration, temperature and flow rate can be predicted. However, the use of empirical theories would simplify this multi-parameter analysis. For example in the general case the flow rate dependence of the PZC behaviour might be described by a more general form of eqn. 7.3.

## 8.2 HUMIDITY

It has been reported in a number of papers that humidity affects uncoated crystals. In his initial experiments Bristow [8.3] attempted to use an uncoated PZC as a reference crystal in order to correct for temperature. However, frequency drift was observed in a flowing air stream and it was suggested that this was caused by water vapour collecting on the electrode. Later Scheide and Warnar [8.4] described the use of a reference crystal that absorbed water vapour from an air sample. Taking these reports into account the humidity response of uncoated PZCs was investigated in order to describe the interaction in a more quantitative way. The results are presented in Chapter 5 and are indicative of a simple condensation mechanism with adsorption proportional to concentration at constant temperature. Since the desorption process shows an exponential decay, the recovery time for short term exposure is not proportional to the exposure time. This can be a major factor in the magnitude of the interference effect of water vapour.

In Chapter 5 the problem of compensating for humidity was also discussed. It was concluded that any humidity effect on coated PZCs could not be corrected for by the use of an uncoated reference crystal. This argument assumes that a coated crystal is unlikely to have the same response to humidity as an uncoated reference crystal. This is reasonable as the coating could either promote the absorption of water vapour or provide a barrier to humidity.

Karmarkar, Webber and Guilbault have reported [8.5, 8.6] that atmospheric moisture physically condenses on quadrol coated crystals giving a strong response of 300 Hz for a 9 MHz crystal. Although the humidity was not measured in this experiment, it appears that interference from humidity at normal ambient levels is a problem as the reported frequency change is comparable to typical sensitivities towards the analyte.

From the work with uncoated crystals in Chapter 5 it is suggested that there may be a further problem in terms of the duration of the humidity effect. However, this will only be confirmed if and when an investigation is carried out to quantify the kinetic aspects of the problem. Karmarkar, Webber and Guilbault offered no evidence to support their suggestion of a physical condensation mechanism. Nevertheless this is acceptable as a initial assumption about the nature of the process and was made in the case of the uncoated PZCs in Chapter 5. Procedures for investigating the effect of humidity on uncoated crystals could be further developed to investigate the effect on coated crystals in order to derive equilibrium and rate constants for the process at various temperatures.

Assuming that the humidity effect is caused by some form of condensation, all similarly coated PZCs are expected to respond to humidity in the same way. The response, however, will depend on the nature of the coating and on the temperature.

As a result of the humidity effects, experimental investigations are complicated by humidity if the PZC is used in ambient

conditions. Following the procedures described in section 5.4, the humidity was therefore reduced to a minimum for the experiments carried out in Chapter 7, which investigated the effect of temperature on PZCs coated for  $\text{SO}_2$  sensing, and those in Chapter 5 which investigated the effect of temperature on uncoated PZCs.

In a practical PZC sensor used for monitoring  $\text{SO}_2$  in ambient air it is possible to reduce the humidity by using filters and membranes in the inlet gas line [8.5, 8.6]. However, this tends to reduce the response to  $\text{SO}_2$ . In future work it may also be appropriate to operate PZC sensors at a higher temperature in order to reduce the effect of humidity as seen in Chapter 5. Unfortunately, this may also drive off the coating or reduce its ability to adsorb analyte as was seen in Chapter 7. It will, therefore, be necessary to carefully consider the temperatures at which future measurements are made.

However, it is not possible to reduce the effect of humidity to an insignificant level by either of these methods without also considerably reducing the sensitivity to  $\text{SO}_2$ . Therefore, it will be necessary to compensate for residual humidity in order to obtain a true  $\text{SO}_2$  measurement.

Further work is, however, necessary in order to develop the temperature compensation method for  $\text{SO}_2$  measurements described here to also be able to correct for the effect of humidity. A correction method could be applied in which another sensor measured the humidity to provide data for a compensation process.

The humidity sensor could be a water vapour sensitive PZC [8.7, 8.8].

### 8.3 REDUCTION OF INTERFERENCES AND THEIR COMPENSATION

In general, future work for eliminating effects caused by humidity, temperature or any other form of interference should be seen as a three stage process: first, a physical reduction in the variability of the interfering parameter, second, a reduction in the response of the sensor to that parameter and, third, elimination of the residual effect by independent measurement of the parameter and deconvolution of the effect.

However, if some of the sensors used to measure the parameters are themselves interfered with then the measurements are not independent and the results could only be obtained by the solution of several simultaneous equations. To carry out these calculations in real-time requires the use of a microcomputer system. A limit on the use of microcomputers for correction is the availability of the appropriate algorithm. For instance, Fielden, McCallum, Stanios and Alder [8.8] have shown in a binary system for the real-time humidity compensation of toluene diisocyanate measurements that considering such equations as linear is an over simplification. A better choice would be Fourier methods which provide a general algorithm to specify non-linear responses.

Where a sensor is interfered with by two parameters, compensation data would have to be measured to define a 3-dimensional surface of sensor response to the two parameters. Separate Fourier series would be calculated to specify the sensor response with respect to one parameter at various values of the other. Then a second

Fourier calculation would be performed to interpolate between the values of the coefficients of the first Fourier series to specify any intermediate section through the 3-dimensional representation of the sensor response. Thus a correction value at any combination of the two parameters could be calculated. Hitherto, the crucial data collection stage would have been difficult but it has been shown that typical data of this nature can be obtained by using the microcomputer system.

#### 8.4 THE FUTURE FOR PIEZOELECTRIC CRYSTAL SENSORS

To overcome difficulties of selectivity in atmospheres with many gaseous components an array of gas sensors could be used, each partially specific to one of the various gaseous species or measuring a physical parameter. A microcomputer would then be used to simultaneously deconvolute the effect of all parameters from all sensors. A large library of data would be involved in these calibrations and the deconvolution algorithm would be complicated, probably using some form of pattern recognition. Therefore, a powerful and efficient microprocessor based system would be required. Hirschfeld has already observed and correlated the response pattern of PZC devices with 13 different GC stationary phase coatings to six organic vapours [8.9, 8.10] but the complicating effects of humidity and temperature have not been considered.

Discrete component oscillators, as described in Chapter 4, would be cumbersome for arrays of PZC sensors and would show a large variation in performance from oscillator to oscillator because of the differing tolerances in individual components.

From the problems with connections from crystal to oscillator encountered in Chapter 4, it is concluded that the PZC to oscillator connection should be as short as possible, preferably with the PZC plugging directly into the oscillator. This could be achieved by miniaturising the electronics so that the oscillator can be fitted onto or into the gas cell.

Integrated circuit oscillators based on inverting logic gates

[8.11, 8.12] are used in microcomputers and have been used for PZC sensors [8.8]. These offer a considerable size reduction and improved ease of construction compared to discrete component oscillators. Nevertheless, passive component values still have to be changed by empirical methods to achieve optimal performance.

Medium scale integrated circuit oscillators such as the 74 Series type 321 and type 626 offer improved performance, functions and inter-oscillator reproducibility stemming from a reduced number of external components. Assuming that the small scale design problem of attaining a gas seal at the PZC combined with a good electrical connection to the oscillator can be overcome, the small size of these integrated circuit oscillators would allow one to be dedicated to each PZC in a close packed array of sensors with each interconnection being short. The type 626 integrated circuit has an oscillator enable input so that oscillators could be run individually. Such precautions would ensure that the oscillators do not interfere with each other.

A method and apparatus for automatically coating a number of PZCs in order to create reproducible coatings of well defined mass, thickness and structure is required. This will enable sensors to be produced to nominal sensitivities and with predicted tolerances. This will facilitate the design of new coating materials for PZCs possibly exploiting some of the properties of  $\text{SO}_2$  demonstrated in Chapter 1 and would be a prerequisite to the investigation of the chemistry of interactions between coating materials and analyte gases. An understanding of this would lead

to the development of improved coatings for particular applications and the commercial exploitation of PZC sensors.

PZC sensors are extremely versatile because the same hardware can be used for differently coated crystals which are sensitive to many different gases. They also have a multicomponent capability in that coatings can be sensitive to a range of compounds of interest. The output is in terms of frequency, interfacing directly with digital electronics which allows easier capture and transfer of data.

The PZC hardware is simple, inexpensive, robust, sensitive, small and rapid in response. The disadvantages of PZC sensors are poor selectivity and interference from humidity and temperature.

Although difficulties exist in using PZC sensors, solutions are worth pursuing because PZC sensors, by virtue of their advantages, could be used on a very wide scale in appropriate applications.

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